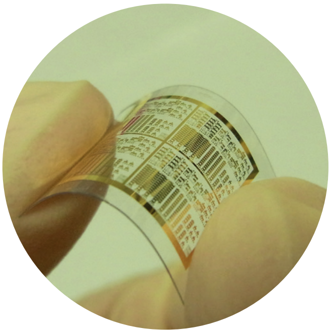


NT13

# Fourteenth International Conference on the *Science and Applications of Nanotubes*

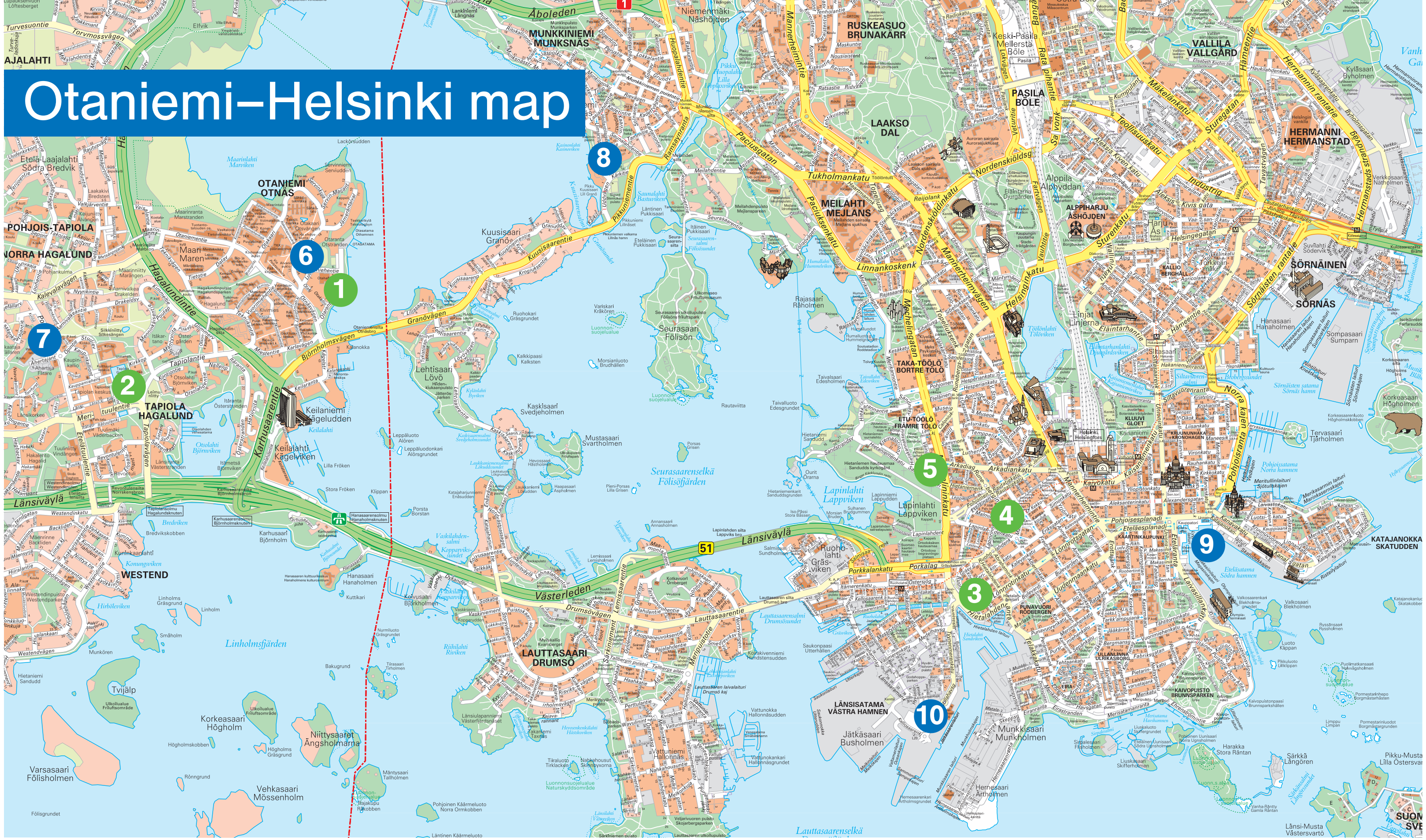
**24–28 June 2013**
**Dipoli Congress Center, Espoo, Finland**
***www.nt13.org***

# Program

| | **Monday 24 June** | **Tuesday 25 June** | **Wednesday 26 June** | **Thursday 27 June** | **Friday 28 June** |
|---|---|---|---|---|---|
| 9:00 | Registration (from 8 am) | K2: S. Hofmann | K3: H. Shinohara | K4: S. Reich | K5: H. Dai |
| 9:15 | | | | | |
| 9:30 | Tutorial A Y.H. Lee | | | | |
| 9:45 | | I3: J. Hart | I7: C. Zhou | I8: L-M. Peng | I12: X. Bao |
| 10:00 | | | | | |
| 10:15 | | C8: D. Krasnikov | C14: T.G. Kim | C21: P. Barbara | C27: M. Borghei |
| 10:30 | Tutorial B C. Bichara | C9: V. Jourdain | C15: W. Kim | C22: A. Catheline | C28: T. Sharifi |
| 10:45 | | Poster+ 1 | Poster+ 3 | Poster+ 4 | C29: P. Ayala |
| 11:00 | | Posters 1 | Posters 3 | Posters 4 | Coffee break |
| 11:15 | | | | | |
| 11:30 | Coffee break | | | | C30: C. Kingston |
| 11:45 | | | | | C31: A. Pakdel |
| 12:00 | Tutorial C A. Ferrari | | | | Summary and poster awards |
| 12:15 | | | | | |
| 12:30 | | | | | NT14 preview |
| 12:45 | | Lunch | Lunch | Lunch | Closing |
| 13:00 | Lunch | | | | Lunch |
| 13:15 | | | | | |
| 13:30 | | | | | |
| 13:45 | | | | | |
| 14:00 | | I4: S.K. Doorn | C16: T. Takenobu | I9: F. Mauri | |
| 14:15 | Opening | | C17: A. Zarbin | | Transport to satellite ferry |
| 14:30 | K1: M.S Dresselhaus | C10: Y. Li | C18: S. Moshkalev | C23: M.J. Green | |
| 14:45 | | C11: J. Zhang | C19: G. Ning | C24: U. Schmidt | |
| 15:00 | | C12: S. Sakurai | C20: B. Archanjo | C25: Y-Q. Xu | |
| 15:15 | I1: A. Porter | Poster+ 2 | Group photo | Poster+ 5 | |
| 15:30 | | Posters 2 | Transport to excursion and free time | Posters 5 | |
| 15:45 | C1: K.E. Moore | | | | |
| 16:00 | C2: J. Terrones | | | | |
| 16:15 | Coffee break | | | | |
| 16:30 | | | | | Satellite ferry departure |
| 16:45 | I2: P.G. Collins | | | | |
| 17:00 | | | Excursion & Banquet | | |
| 17:15 | C3: I. Bondarev | I5: A. Bachtold | | I10: S. Roche | |
| 17:30 | C4: Z. Zhu | | | | |
| 17:45 | C5: Y.C. Choi | I6: H. van der Zant | | I11: Y-W. Son | |
| 18:00 | C6: P. Hubert | | | | |
| 18:15 | C7: A.W. Barnard | C13: S. Hermann | | C26: O. Herranen | |
| 18:30 | Welcome party (Dipoli) | Transport | | | |
| 18:45 | | Espoo City reception | | | |
| 19:00 | | | | | |

| | |
|---|---|
| Keynote talk (45 min) | Tutorial lecture (60 min) |
| Invited talk (30 min) | Poster summary (15 min) |
| Contributed talk (15 min) | Poster session (105 min) |
| Lunch (75 min) | Evening event |

# Otaniemi–Helsinki map

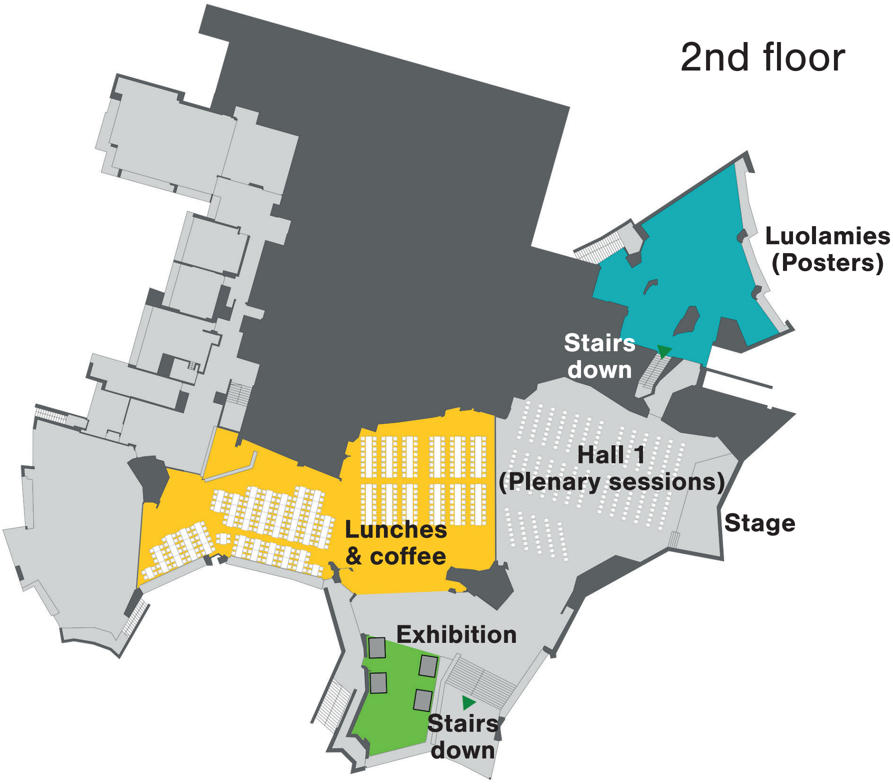


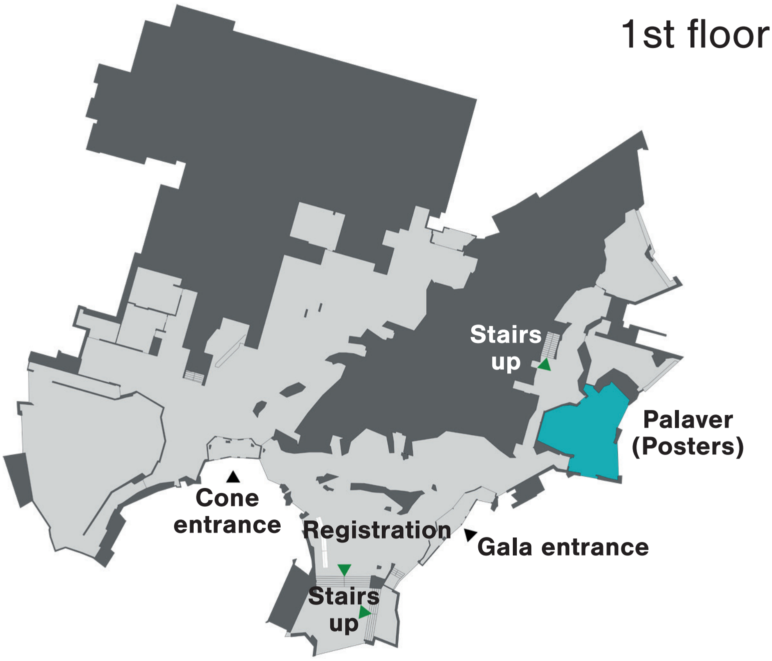
## CONFERENCE HOTELS

① Radisson Blu Espoo (Otaniemi, Espoo)
② Sokos Hotel Tapiola Garden (Tapiola, Espoo)
③ Radisson Blu Seaside (Helsinki center waterfront)
④ Radisson Blu Royal (Helsinki center)
⑤ Academica Hostel (Helsinki center)

⑥ **CONFERENCE VENUE (DIPOLI)**
⑦ **ESPOO CITY RECEPTION (WEEGEE)**
⑧ **CONFERENCE DINNER (KALASTAJATORPPA)**
⑨ **EXCURSION BOATS (KAUPPATORI)**
⑩ **SATELLITES FERRY (LÄNSISATAMA)**

# Dipoli floor map





# NT13 Organizers

Conference hosted by the Aalto University School of Science.

**Aalto University**
**School of Science**

## CONFERENCE CHAIRS

| | |
|---|---|
| Esko Kauppinen | (Aalto University, Finland) |
| Risto Nieminen | (Aalto University, Finland) |
| Pertti Hakonen | (Aalto University, Finland) |

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| David Tomanek | (Michigan State University, USA) |

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## ABSTRACT BOOK

| | |
|---|---|
| Leila Mäkinen | (MojoBox Oy) |
| Toma Susi | (Aalto University) |

## PRINTED MATERIALS

| | |
|---|---|
| Hanna Sario | (Unigrafia Oy) |

## NT13 LOGO

| | |
|---|---|
| Otto Donner | (www.ottodonner.com) |

## WEBSITE

| | |
|---|---|
| Toma Susi | (template by David Tomanek) |

## PHOTOS

Visit Helsinki, Visit Espoo, Aalto University, Dipoli, Yutaka Ohno

# A word of welcome

Aalto University is very proud to host the NT13 conference and to welcome more than 400 participants from all over the world here at the Aalto Campus.

This seminar goes to the core of our Strategy and values. Nanocarbons are important materials for sustainable future technologies. They can not only replace critical materials in e.g. electronics and green energy production, but will also open possibilities to develop completely new type of electronics: We will be able to create flexible and stretchable devices.

Aalto University was created in 2010 by merging three universities: Helsinki University of Technology, Helsinki School of Economics and the University of Art and Design Helsinki. The purpose of creating Aalto University was to strengthen the Finnish innovation system by creating a world-class research university that integrates expertise in science and technology, business and economics as well as art and design.

Carbon nanomaterials have been actively studied at Aalto since late 1990s. It begun with nanotubes, then hybrids and also graphene - theory, modelling, fundamendal properties, synthesis and emerging applications.

On behalf of Aalto University I thank you for coming to Finland and Aalto University, and wish you an inspiring conference!

**Tuula Teeri**

***President***
***Aalto University***

# NT13 International advisory board

**Annick Loiseau**
(CNRS/ONERA, France)
**Richiro Saito**
(Tohoku University, Japan)
**Shigeo Maruyama**
(University of Tokyo, Japan)
**Ying Chen**
(Deakin University, Australia)
**Jin Zhang**
(Peking University, China)
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**Jannik C. Meyer**
(University of Vienna, Austria)
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# Partners and sponsors

The remarkably affordable registration fees of the NT13 Conference – without compromising on the quality of the meeting – have been made possible by generous support from our sponsors and partners.

## SPONSORS

**Gold Sponsor:**
AIXTRON
**Silver Sponsor:**
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**Bronze Sponsor:**
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## FINANCIAL SUPPORT

Aalto University School of Science
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The 13th International Conference on the Science and Application of Nanotubes (NT12)

## EXHIBITORS

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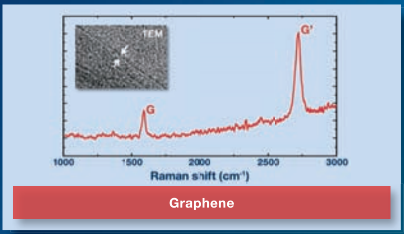
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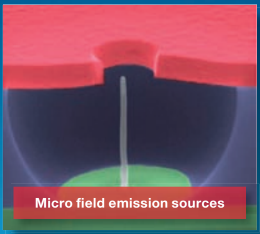

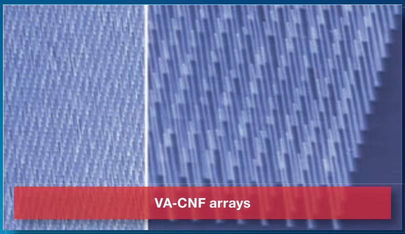

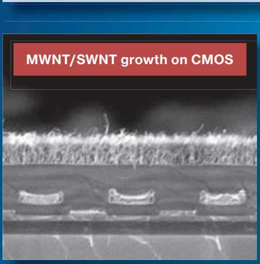

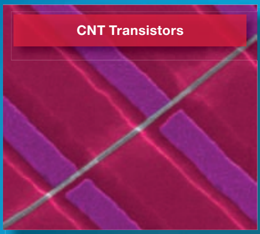

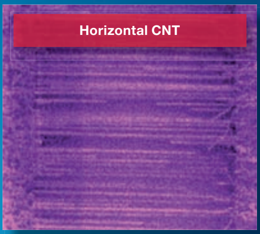

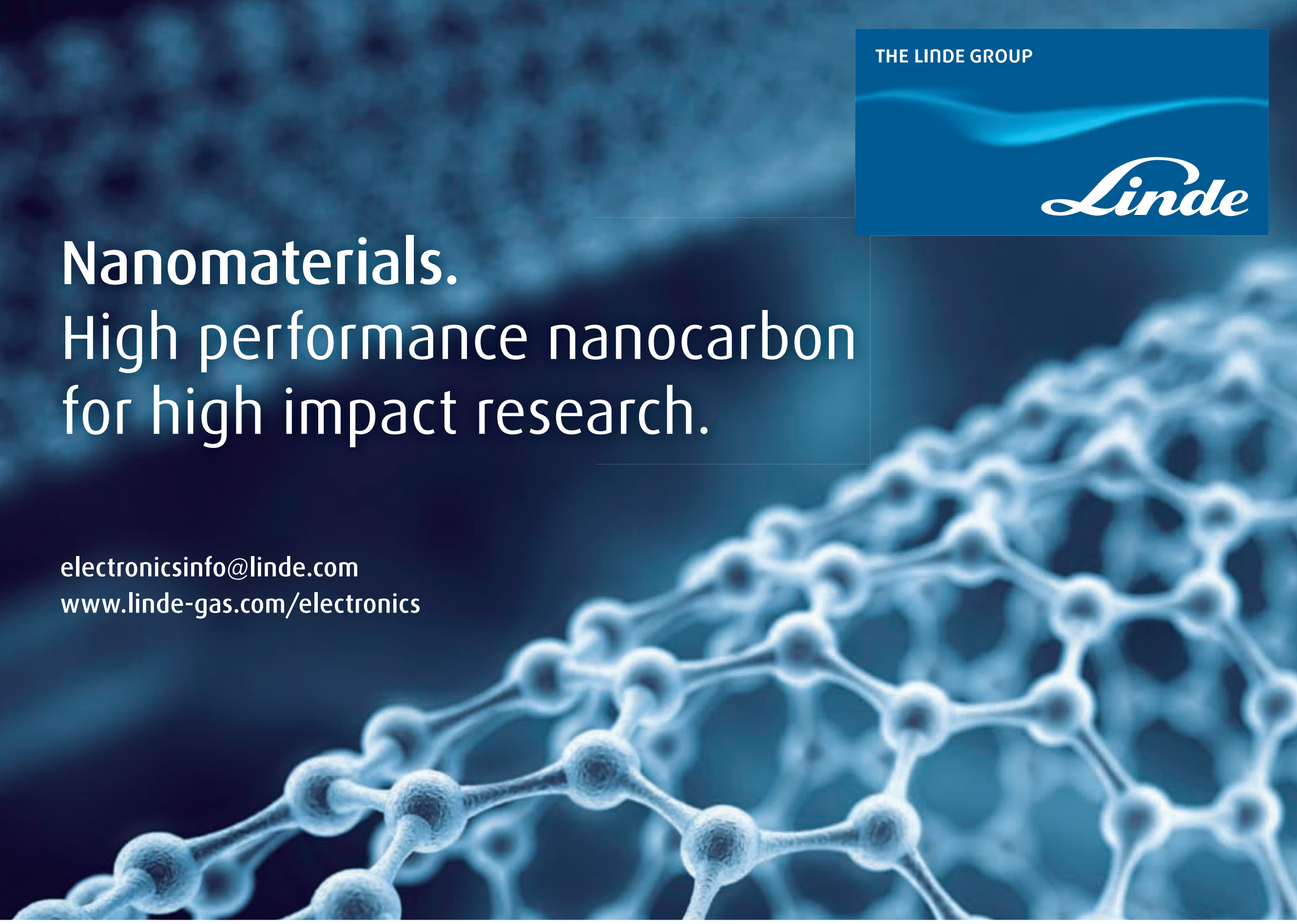

# Charter of the Nanotube (NT) Conference Series

http://nanotube.msu.edu/nt/charter.html

## 1. PURPOSE

The purpose of the NT conference series is to promote scientific progress, to stimulate free exchange of ideas, and to publicize progress in nanotube sciences.

## 2. TARGET ATTENDANCE

2.1 NT conferences are open to all persons interested and active in nanotube research.
2.2 The number of attendees or presentations per attendee may be limited to maintain the informal spirit of communication. Young researchers are treated with higher priority.

## 3. FORMAT

3.1 The organizers will assist in maximizing opportunities for sharing knowledge in an informal atmosphere.
3.2 NT conferences are held in one single plenary session. Parallel sessions are to be avoided.
3.3 Presentations of problems and needs is encouraged as much as presentation of solutions.
3.4 Contributions play a key role at NT conferences. At least half the conference time shall be devoted to contributed presentations.

## 4. CONTRIBUTED PRESENTATIONS

4.1 To provide maximum exposure to contributed results, contributors are invited to summarize their findings in a Poster format. The main purpose of Poster presentations is to facilitate asynchronous scientific discussions related to each specific contribution. It is desirable to have all posters on display during the entire conference.
4.2 The organizers secure adequate time and space for poster sessions. Creative ways to enhance communications, including refreshments, are encouraged.
4.3 Poster+ sessions, consisting of brief 2 minute/2 viewgraph summaries of contributions, may precede Poster sessions, to enhance the exchange of information in a balanced manner. All contributors are encouraged to expose their findings to everyone in this way if Poster+ sessions are offered.
4.4 At large conferences, Poster+ presentations may be substituted by a brief overview of the topic of a focussed poster session, presented by an expert in the field at the beginning of the session. Referring to specific contributions in the session, the Poster Chair should summarize the major progress, the major obstacles, and desirable future directions in the field. Ideally, this should occur in a democratic manner, representing all/most contributions. All contributors are encouraged to communicate their findings to their assigned Poster Chair for presentation well ahead of the conference.

## 5. INVITED PRESENTATIONS

5.1 Invited presentations are selected in a democratic way by members of the advisory board. Presentation of invited talks is reserved for leading, active researchers, not their substitutes. The selection of topics and speakers should reflect the most significant progress and cover the entire active nanotube field. The advisors will resist pressure to select invited talks on other grounds than scientific merit.

5.2 NT conference organizers should generally avoid inviting the same presenter at two consecutive conferences. To avoid conflicts of interest, the organizers should generally avoid inviting contributions of organizers and advisory board members.

## 6. VENUE

6.1 To pay respect to the international character of nanotube research, two consecutive meetings should not be held on the same continent.

6.2 The conference should preferentially be held a location associated with or close to an institution active in nanotube research.

6.3 Convenience of the conference facilities is preferred to luxury. Modest conference accommodations are to be preferred to reduce the conference expenses of participants and to encourage attendance.

## 7. FINANCIAL MATTERS

7.1 NT conferences are organized in a non-profit way. The organizers undertake any reasonable efforts to secure external sponsorship covering local and travel expenses of invited speakers, support student attendance, and reduce the conference fee. Any excess revenue is passed on to organizers of the sequel conference.

## 8. MISCELLANEOUS

8.1 NT organizers promote the spirit of informal communication also by providing name badges to participants. Both first and family names should be spelled out and printed in an easily legible, large font. Academic titles should be avoided.

## 9. REGULATION

All issues related to the organization of Nanotube Conferences are regulated by the Steering Committee of Nanotube Conferences (SCNC).

# Tutorials

**Monday, June 24**
**9:30–10:30**
**TUTORIAL A:** Carbon nanotubes and graphene for electronics
Young Hee Lee (SKKU, Korea)

**10:30–11:30**
**TUTORIAL B:** Nanotube growth mechanisms and chirality control from modeling and experiments
Christophe Bichara (CINaM - CNRS, France)

**12:00–13:00**
**TUTORIAL C:** Raman spectroscopy in graphene, nanotubes and layered materials
Andrea C. Ferrari (University of Cambridge, UK)

# Poster+ presentations

**Tuesday, June 25**
**10:45–11:00**
**POSTER+ 1:** Synthesis and processing
Shigeo Maruyama (University of Tokyo, Japan)

**15:15–15:30**
**POSTER+ 2:** Characterization and properties
Elena Obraztsova (Moscow State University, Russia)

**Wednesday, June 26**
**10:45–11:00**
**POSTER+ 3:** Devices and composites & Energy and environmental applications
Taishi Takenobu (Waseda University, Japan)

**Thursday, June 27**
**10:45–11**
**POSTER+ 4:** Theory and simulation & Non-carbon nanotubes
James Elliott (University of Cambridge, UK)

**15:15**
**POSTER+ 5:** Graphene and nanosheets & Nanotube chemistry and biology
Aravind Vijayaraghavan (University of Manchester, UK)

# Session chairs

| **Day** | **Time** | **Session** | **Chairman** |
|---|---|---|---|
| Mon | 09:30–10:30 | Tutorial A | Alan Windle |
| Mon | 10:30–11:30 | Tutorial B | Yoshikazu Homma |
| Mon | 12:00–13:00 | Tutorial C | Mika Petterson |
| *Mon* | *14:15–14:30* | *Opening* | *Esko Kauppinen* |
| Mon | 14:30–16:15 | Session 1 | Riichiro Saito |
| Mon | 16:45–18:00 | Session 2 | Ado Jorio |
| *Mon* | *18:00–20:00* | *Welcome party* | *Albert Nasibulin* |
| Tue | 09:00–11:00 | Session 3 | Annick Loiseau |
| Tue | 14:00–15:30 | Session 4 | Anna Swan |
| Tue | 17:15–18:30 | Session 5 | Harri Lipsanen |
| *Tue* | *19:00–20:30* | *City reception* | *Pertti Hakonen* |
| Wed | 09:00–11:00 | Session 6 | Rikizo Hatakeyama |
| Wed | 14:00–15:00 | Session 7 | Yuri Svirko |
| *Wed* | *19:30–21:00* | *Conference dinner* | *Risto Nieminen* |
| Thu | 09:00–11:00 | Session 8 | Naotoshi Nakashima |
| Thu | 14:00–15:30 | Session 9 | Kai Nordlund |
| Thu | 17:15–18:30 | Session 10 | Jean-Christophe Charlier |
| Fri | 09:00–11:00 | Session 11 | Toma Susi |
| Fri | 11:30–12:00 | Session 12 | Kim Bolton |
| *Fri* | *12:00–13:00* | *Closing* | *Esko Kauppinen* |

# Monday, June 24

**TUTORIAL A** ***(chair: Alan Windle)***
9:30–10:30 Carbon nanotubes and graphene for electronics (Y.H. Lee) ... p. 36

**TUTORIAL B** ***(chair: Yoshikazu Homma)***
10:30–11:30 Nanotube growth mechanisms and chirality control from modeling and experiments (C. Bichara) ... p. 36

11:30–12:00 **COFFEE BREAK**

**TUTORIAL C** ***(chair: Mika Petterson)***
12:00–13:00 Raman spectroscopy in graphene, nanotubes and layered materials (A.C. Ferrari) ... p. 37

13:00–14:15 **LUNCH**

14:15–14:30 **OPENING** ***(chair: Esko I. Kauppinen)***
Tuula Teeri, President, Aalto University, Finland
Riikka Heikinheimo, Executive Director, Tekes, Finland
David Tomanek, NT founder, Michigan State University, USA

**SESSION 1** ***(chair: Riichiro Saito)***
14:30–15:15 **K1:** Perspectives on carbon nanotube research (M.S. Dresselhaus) ... p. 38
15:15–15:45 **I1:** Imaging the cell-carbon nanomaterial interface at high resolution (A. Porter) ... p. 38
15:45–16:00 **C1:** Vertically aligned double- and single-walled carbon nanotubes for electrochemical surfaces (K.E. Moore) ... p. 39
16:00–16:15 **C2:** Electrical response of carbon nanotube yarns to liquid environments (J. Terrones) ... p. 39

16:15–16:45 **COFFEE BREAK**

**SESSION 2** ***(chair: Ado Jorio)***
16:45–17:15 **I2:** Recording single molecule chemistry with nanotube electronic devices (P.G. Collins) ... p. 40
17:15–17:30 **C3:** Tunable near-field plasmonic effects in individual carbon nanotubes (I. Bondarev) ... p. 40
17:30–17:45 **C4:** Can diamond nanowires form inside carbon nanotubes? (Z. Zhu) ... p. 41
17:45–18:00 **C5:** Development and commercialization of high dispersibility MWCNTs and MWCNT-based conductive composite and ink (Y.C. Choi) ... p. 41
18:00–18:15 **C6:** Quantification of dispersion degree in polymer/carbon nanotube nanocomposites (P. Hubert) ... p. 42
18:15–18:30 **C7:** Carbon nanotubes as semi-flexible polymers: Measuring the entropic spring constant in CNT resonators (A.W. Barnard) ... p. 42

18:30–20:00 **WELCOME PARTY** ***(chair: Albert G. Nasibulin)***

# Tuesday, June 25

**SESSION 3** ***(chair: Annick Loiseau)***

09:00–09:45 **K2:** Towards an understanding of catalytic graphene and carbon nanotube growth (S. Hofmann) ........ p. 44

09:45–10:15 **I3:** Continuous growth and patterning of carbon nanotube forests (J. Hart) ........ p. 44

10:15–10:30 **C8:** Investigation of the active component formation of Fe-Co catalyst during MWCNT growth by means of in situ methods (D. Krasnikov) ........ p. 45

10:30–10:45 **C9:** In situ Raman investigations of the growth of carbon nanotubes (V. Jourdain) ........ p. 45

10:45–11:00 **POSTER+ 1:** Synthesis and processing ***(Shigeo Maruyama)***

11:00–12:45 **POSTERS 1** ........ p. 50

12:45–14:00 **LUNCH**

**SESSION 4** ***(chair: Anna Swan)***

14:00–14:30 **I4:** Raman spectroscopy of chirality-enriched carbon nanotubes (S.K. Doorn) ........ p. 46

14:30–14:45 **C10:** Structure controlled growth of single-walled carbon nanotubes (Y. Li) ........ p. 46

14:45–15:00 **C11:** Lattice-directed growth of single-walled carbon nanotubes on surface: from orientation to chirality control (J. Zhang) ........ p. 47

15:00–15:15 **C12:** Modulating catalyst formation process to control diameter and density of single-wall carbon nanotube forests (S. Sakurai) ........ p. 47

15:15–15:30 **POSTER+ 2:** Characterization and properties ***(Elena Obraztsova)***

15:30–17:15 **POSTERS 2** ........ p. 80

**SESSION 5** ***(chair: Harri Lipsanen)***

17:15–17:45 **I5:** Mechanical resonators based on nanotubes and graphene (A. Bachtold) ........ p. 48

17:45–18:15 **I6:** Carbon-based mechanical resonators (H. van der Zant) ........ p. 48

18:15–18:30 **C13:** Carbon nanotubes for piezoresistive electro-mechanical transducers incorporating a wafer-level technology (S. Hermann) ........ p. 49

18:30–19:00 Transport

19:00–20:30 **ESPOO CITY RECEPTION** ***(chair: Pertti Hakonen)***

# Posters 1

# Posters 2

# Wednesday, June 26

| | | |
|---|---|---|
| | **SESSION 6** ***(chair: Rikizo Hatakeyama)*** | |
| 09:00–09:45 | **K3:** Carbon nanotube-nanowires (H. Shinohara) | p. 114 |
| 09:45–10:15 | **I7:** Chirality-controlled synthesis and electronic applications of single-wall carbon nanotubes (C. Zhou) | p. 114 |
| 10:15–10:30 | **C14:** The study of micro-scale strain on flexible networked single-walled carbon nanotube electronic devices (T.G. Kim) | p. 115 |
| 10:30–10:45 | **C15:** Towards high performance flexible supercapacitors based on carbon nanotubes (W. Kim) | p. 115 |
| 10:45–11:00 | **POSTER+ 3:** Devices and composites & Energy and environmental applications ***(Taishi Takenobu)*** | |
| 11:00–12:45 | **POSTERS 3** | p. 119 |
| 12:45–14:00 | **LUNCH** | |
| | **SESSION 7** ***(chair: Yuri Svirko)*** | |
| 14:00–14:15 | **C16:** Electrolyte gated transistors of aligned carbon-nanotube thin film (T. Takenobu) | p. 116 |
| 14:15–14:30 | **C17:** Liquid-liquid interfaces: a suitable environment to prepare carbon nanostructures-based thin films (A. Zarbin) | p. 116 |
| 14:30–14:45 | **C18:** Electrical and thermal contacts between nanocarbon materials (graphene, nanotubes) and metals: the effects of conventional and localized annealing (S. Moshkalev) | p. 117 |
| 14:45–15:00 | **C19:** Template chemical vapor deposition synthesis of nanomesh graphene and its applications (G. Ning) | p. 117 |
| 15:00–15:15 | **C20:** Reconstruction of graphene layers under electric current (B.S. Archanjo) | p. 118 |
| 15:15–15:30 | **GROUP PHOTO** (Dipoli) | |
| 15:30–17:00 | Transport to excursion and free time | |
| 17:00–19:00 | **EXCURSION** (boat from Kauppatori to Kalastajatorppa) | |
| 19:00–23:00 | **DINNER** ***(Kalastajatorppa, chair: Risto Nieminen)*** | |

# Posters 3

# Thursday, June 27

| | | |
|---|---|---|
| | **SESSION 8** ***(chair: Naotoshi Nakashima)*** | |
| 09:00–09:45 | **K4:** Advanced optical coupling in carbon-based nanosystems (S. Reich) | p. 158 |
| 09:45–10:15 | **I8:** Carbon based high performance nanoelectronic and optoelectronic devices and circuits (L-M. Peng) | p. 159 |
| 10:15–10:30 | **C21:** Carbon nanotube quantum dots as highly sensitive THz spectrometers (P. Barbara) | p. 160 |
| 10:30–10:45 | **C22:** Highly conductive CNT thin films for organic solar cells (A. Catheline) | p. 160 |
| 10:45–11:00 | **POSTER+ 4:** Theory and simulation & Non-carbon nanotubes ***(James Elliott)*** | |
| 11:00–12:45 | **POSTERS 4** | p. 165 |
| 12:45–14:00 | **LUNCH** | |
| | **SESSION 9** ***(chair: Kai Nordlund)*** | |
| 14:00–14:30 | **I9:** How to make graphene superconducting (F. Mauri) | p. 161 |
| 14:30–14:45 | **C23:** Non-covalent functionalization, dispersion, and processing of graphene (M.J. Green) | p. 161 |
| 14:45–15:00 | **C24:** Graphene: a chemical, optical, and topographic characterization with a confocal Raman-AFM-SNOM (U. Schmidt) | p. 162 |
| 15:00–15:15 | **C25:** Enhanced photoresponse in quasi-1D graphene nanostructures (Y-Q. Xu) | p. 162 |
| 15:15–15:30 | **POSTER+ 5:** Graphene and nanosheets & Nanotube chemistry and biology ***(Aravind Vijayaraghavan)*** | |
| 15:30–17:15 | **POSTERS 5** | p. 183 |
| | **SESSION 10** ***(chair: Jean-Christophe Charlier)*** | |
| 17:15–17:45 | **I10:** Transport, magnetism and spin relaxation phenomena in graphene-based materials (S. Roche) | p. 163 |
| 17:45–18:15 | **I11:** Graphene systems with external perturbations (Y-W. Son) | p. 163 |
| 18:15–18:30 | **C26:** Charge noise in multiwalled carbon nanotubes (O. Herranen) | p. 164 |

# Posters 4

# Posters 5

# Friday, June 28

| | | |
|---|---|---|
| | **SESSION 11** ***(chair: Toma Susi)*** | |
| 09:00–09:45 | **K5:** Carbon nanotubes and nanocarbon hybrid materials (H. Dai) | p. 220 |
| 09:45–10:15 | **I12:** The unique chemistry of carbon nanotubes in catalysis (X. Bao) | p. 221 |
| 10:15–10:30 | **C27:** Designing nitrogen functionalities on N-doped few-walled carbon nanotubes for the oxygen reduction reaction (M. Borghei) | p. 222 |
| 10:30–10:45 | **C28:** Formation of active sites for oxygen reduction reactions by transformation of nitrogen functionalities in nitrogen-doped carbon nanotubes (T. Sharifi) | p. 222 |
| 10:45–11:00 | **C29:** Controlled substitutional functionalization in single-walled carbon nanotubes: Is it really possible? (P. Ayala) | p. 223 |
| 11:00–11:30 | **COFFEE BREAK** | |
| | **SESSION 12** ***(chair: Kim Bolton)*** | |
| 11:30–11:45 | **C30:** Large-scale synthesis of few-walled small diameter boron nitride nanotubes (sub. 10 nm) by an induction thermal plasma (C. Kingston) | p. 223 |
| 11:45–12:00 | **C31:** Interface engineering of nanostructured BN surfaces (A. Pakdel) | p. 224 |
| | **CLOSING SESSION** ***(chair: Esko I. Kauppinen)*** | |
| 12:00–12:30 | **SUMMARY AND POSTER AWARDS** (M.S. Dresselhaus) | |
| 12:30–12:45 | **NT14 PREVIEW** (C. Zhou) | |
| 12:45–13:00 | **CLOSING** | |
| 13:00–14:15 | **LUNCH** | |
| 14:15–16:30 | Transport to satellite ferry (Länsisatama) | |
| 16:30 | Satellite ferry departure ***(do not be late!)*** | |

# Monday

TA

# Carbon nanotubes and graphene for electronics

Young Hee Lee

*IBS Center for Integrated Nanostructure Physics, Department of Physics, Department of Energy Science,*
*Sungkyunkwan University, Suwon 440-746, Korea (leeyoung@skku.edu)*

One-dimensional carbon nanotubes (CNTs) show metallic and semiconducting properties depending on the chirality and diameter, while two-dimensional graphene reveals only metallic properties. Although numerous applications have been demonstrated with CNTs due to their versatile properties, the applications to field effect transistors have been often hindered by the metallic properties. On the other hand, graphene have been used for quantum mechanical tunneling devices, while graphene as layered electrodes have been extensively studied. In this talk, I will focus on the applications of CNTs and graphene for transparent electrodes and switching devices. Issues, recent advances, bottleneck technologies, together advantages and drawbacks of these two materials will be extensively discussed. I will also demonstrate several examples of synergistic effect of CNT-graphene hybridized structures. The possibility of realizing transparent, flexible and stretchable devices using all carbon materials will be also discussed.

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TB

# Nanotube growth mechanisms and chirality control from modeling and experiments

Vincent Jourdain[1] and Christophe Bichara[2]

*1 Laboratoire Charles Coulomb – CNRS and Montpellier 2 University, France*
*2 Centre Interdisciplinaire de Nanoscience de Marseille – CINaM*
*CNRS and Aix Marseille University, France (xtof@cinam.univ-mrs.fr)*

In this tutorial, based on a recent review article [1], I will try and summarize our current understanding of the growth of carbon nanotubes in catalytic chemical vapour deposition. This attempt is made rather difficult by the very large number of experimental or theoretical results that often appear quite contradictory. Beyond the well-established background knowledge and results, I will focus on some aspects concerning the relationship between the structure of nanotubes and the synthesis parameters, as it results from a necessarily limited survey of the literature. I will also address some specific open questions (role and state of the catalyst nanoparticles, possibility to control the chiral distribution...) that are of importance for the development of controlled growth techniques required for large scale applications.

[1] V. Jourdain and C. Bichara, Carbon 58, 2-39 (2013)

# Raman spectroscopy in graphene, nanotubes and layered materials

Andrea C. Ferrari

*Cambridge Graphene Centre, University of Cambridge, Cambridge, CB3 OFA, UK*
*(acf26@hermes.cam.ac.uk)*

Technological progress is determined, to a great extent, by developments in material science. Breakthroughs can happen when a new type of material or new combinations of known materials with different dimensionality and functionality are created. Raman spectroscopy is a well-established characterization technique for carbon nanomaterials and is being developed for layered materials [1]. Raman spectroscopy is an integral part of graphene research [2]. It is used to determine the number and orientation of layers, the quality and types of edge, and the effects of perturbations, such as electric and magnetic fields, strain, doping, disorder and functional groups [3]. This, in turn, provides insight into all $sp^2$-bonded carbon allotropes, because graphene is their fundamental building block. I will review the state of the art, future directions and open questions in Raman spectroscopy of graphene [3]. I will describe essential physical processes whose importance has only recently been recognized, such as the various types of resonance at play, and the role of quantum interference. I will update all basic concepts and notations, and propose a terminology that is able to describe any result in literature [3]. I will then show the implications for the understanding of the Raman spectra of nanotubes, highlighting the effects of electron-phonon coupling on their optical phonon dispersions and Raman spectra [4-6]. In particular on the different assignment of the $G^+$ and $G^-$ peaks in metallic and semiconducting nanotubes [6]. Finally, I will overview the Raman modes peculiar of multilayer structures, focussing on the interlayer shear mode of multi-layer graphene [7]. A variety of non-carbon layered materials can also be exfoliated to produce a whole range of two dimensional crystals [8]. Similar shear modes are present in all these materials, and their detection provides a direct probe of interlayer interactions [9].

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[2] A. C. Ferrari *et al.,* Phys. Rev. Lett. 97, 187401 (2006)
[3] A.C. Ferrari, D.M. Basko, Nature Nano. 8, 235 (2013)
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[5] M. Lazzeri *et al.,* Phys Rev B 73, 155426 (2006)
[6] S. Piscanec at al. Phys Rev B 75, 035427 (2007)
[7] P. H. Tan *et al.,* Nature Materials 11, 294 (2012)
[8] F. Bonaccorso *et al.,* Materials Today 15, 564 (2012)
[9] X. Zhang *et al.,* Phys. Rev. B 87, 115413 (2013)

**K1**

## Perspectives on carbon nanotube research

Mildred Dresselhaus

*Massachusetts Institute of Technology, USA (millie@mgm.mit.edu)*

The field of carbon nanotubes continues to expand in research popularity as we look into the future, but the focus now has moved more to improved fabrication techniques, characterization techniques, more sophisticated theory, and increasing inspiration from advances in graphene research. The focus of my presentation will be on the two areas of special interest to me: studies of double and triple wall nanotubes in ensembles and at individual nanotube level, and the transformation of one nanotube form to another by energy transfer.

**I1**

## Imaging the cell-carbon nanomaterial interface at high resolution

Alexandra Porter and Angela Goode

*Dept. Materials and London Centre for Nanotechnology, Imperial College London, SW7 2AZ, UK*
*(a.porter@imperial.ac.uk)*

The continued commercial up-scaling of carbon nanomaterials and their application needs to be accompanied by an understanding of the occupational health, public safety, and environmental implications of these materials. An increasing volume of literature on the toxicity of carbon nanomaterials is being published; however, the results of these studies are frequently inconclusive. The aim of our work is to relate the physicochemical properties (i.e. aggregation state, morphology and chemistry) of carbon nanotubes (SW- and MW-NTs) and graphene to their bioreactivity. I will describe results of recent work using aberration corrected high resolution and low loss electron energy-loss spectroscopy (EELS) techniques to track the uptake, trajectory and intracellular processing of individual carbon nanotubes and monolayer graphene by lung and neuronal cells and how they change as a function of time in cells. Implications of the interaction mechanisms of the carbon nanomaterials in the various different cellular environments for their long term reactivity will be discussed.

C1

## Vertically aligned double- and single-walled carbon nanotubes for electrochemical surfaces

Katherine E. Moore[1], Jingxian Yu[2], Benjamin S. Flavel[3], Joseph G. Shapter[1]

*1 Flinders Center for Nanoscale Science and Technology, Flinders University, Australia (katherine.moore@flinders.edu.au)*
*2 School of Chemistry and Physics, The University of Adelaide, Australia*
*3 Institute of Nanotechnology, Karlsruhe Institute of Technology, Germany*

Carbon nanotubes (CNTs) are a highly desirable material for incorporation into electrochemical and biological sensing devices, owing to their fast heterogeneous electron transfer, high surface area and electrochemical stability. We have recently shown that double walled CNTs (DWCNTs) demonstrated superior electron transport compared to single walled CNTs (SWCNTs) when electrochemical redox is isolated to the nanotubes only [1-2]. We attribute this to the selective outer-tube functionalisation with the inner tube retaining its undisrupted $sp^2$ network and hence it's intrinsic electronic properties. In this work, vertically aligned single- and double- walled CNT arrays were assembled on gold surfaces forming electrochemical electrodes. The CNTs were subsequently covalently loaded with a ferrocene modified α-aminoisobutyric acid peptide, followed by characterisation with cyclic voltammetry. The CNT electrode comprised of DWCNTs demonstrated significantly higher peak current compared to its single walled counterparts. This is attributed to a higher loading of the ferrocene modified peptide to the outer wall of the DWCNT due to a larger number of defects sites within the $sp^2$ carbon lattice. This indicates that DWCNTs may offer a useful alternative to SWCNTs in future electrochemical sensors and biosensors.

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[2] K.E. Moore, B.S. Flavel, C.J. Shearer, A.V. Ellis, J.G. Shapter, Electrochemistry Communications, 13 (2011) 1190-1193
[3] K.E. Moore, B.S. Flavel, J. Yu, A.D. Abell, J.G. Shapter, Electrochimica Acta, 89 (2013) 206-211

C2

## Electrical response of carbon nanotube yarns to liquid environments

Jing Qiu, Jeronimo Terrones, Alan H. Windle, James A. Elliott

*Department of Materials Science and Metallurgy, University of Cambridge, United Kingdom (jt451@cam.ac.uk)*

Continuous DC four-point probe measurements were carried on CNT yarns synthesised by a floating catalyst CVD process, with the aim of understanding the interactions between carbon nanotube assemblies and their surrounding chemical and physical environment (e.g. for sensing , catalytic and composite reinforcing applications). The electrical resistance of such samples was monitored while immersing and removing them from different liquids; namely acetone, cyclohexane, cyclohexanone, ethanol, n-methylpyrrolidone, toluene, and water.

All liquids tested caused a time-delayed, reversible (upon removal from the liquid) increase in resistance. The total resistance increase and the rate of increase were closely dependent on the affinity towards the yarn, assessed by means of the Hansen solubility parameters, and the polarity of the liquid. These trends, along with the observed radial swelling and axial elongation of the samples upon immersion, lead to an explanation of the phenomenon based on polar interactions of the liquids at capacitive inter-bundle junctions. The increase in resistance is caused by the opening of more of such junctions (impairing bundle interconnectivity) due to a new minimum-energy structural configuration resulting from an altered balance between nanotube/surrounding-medium interfacial surface energy and the elastic energy stored in CNT bundles bent around obstacles to minimise such interface.

I2

## Recording single molecule chemistry with nanotube electronic devices

Yongki Choi[1], Gregory A. Weiss[1], and Philip G. Collins[2]

*1 Department of Chemistry and 2 Department of Physics, University of California at Irvine,*
*California 92697, USA (collinsp@uci.edu)*

Nanoscale electronic devices like field-effect transistors have long promised to provide sensitive, label-free detection of biomolecules. Single-walled carbon nanotubes in particular have the necessary sensitivity to detect single molecule events and the bandwidth to monitor single molecule dynamics in real time. Recent measurements have demonstrated this premise by monitoring the dynamic, single-molecule processivity of three different enzymes: lysozyme [1-2], protein Kinase A [3], and the Klenow fragment of DNA polymerase I [4]. With all three enzymes, single molecules were electronically monitored for 10 or more minutes using nanotube devices. These long recordings allowed us to directly observe rare enzyme transitions to chemically inactive or hyperactive conformations. The high bandwidth of the nanotube transistors further allow every individual chemical event to be clearly resolved, providing a record of tens of thousands of turnovers by a single enzyme molecule. While the statistical means establish values for processivity and turnover rates, the measurements also reveal variability, dynamic disorder, and the existence of intermediate states. Initial success with three different enzymes indicates the generality and attractiveness of the nanotube devices as a new tool for single molecule science, and our focused research on transduction mechanisms provides the design rules necessary to fully generalize this architecture [2]. This presentation will summarize these rules, and demonstrate how the purposeful incorporation of just one amino acid is sufficient to fabricate effective, single molecule nanocircuits from a wide range of enzymes or proteins.

[1] Y. Choi, *et al.,* Science (2012) 335, 319-324; Y. Choi, *et al.*, JACS (2012) 134, 2032-5
[2] Y. Choi, *et al.*, Nano Lett. (2013) 13, 625-631
[3] P.C. Sims, *et al.*, JACS (2013) 135, *in press*
[4] T.J. Olsen, *et al.*, JACS (2013) 135, *in press*

C3

## Tunable near-field plasmonic effects in individual carbon nanotubes

Igor V. Bondarev[1], Maxim F. Gelin[2], and Areg V. Meliksetyan[1]

*1 Department of Physics, North Carolina Central University, Durham, NC 27707, USA*
*(ibondarev@nccu.edu)*
*2 Theoretical Chemistry, Technical University of Munich, Garching D-85747, Germany*

We discuss how low-energy collective inter-band plasmon excitations in individual single wall carbon nanotubes (CNs) can be used to tune their electromagnetic properties in the near-field. In small-diameter (~1 nm) semiconducting CNs, optically excited excitons can transfer their energy to plasmons non-radiatively [1]. This energy transfer process can be controlled via the quantum confined Stark effect by an electrostatic field applied perpendicular to the CN axis. This affects the exciton-interband-plasmon coupling in individual CNs and their optical absorption properties, both linear and nonlinear, accordingly. This is the unique feature of the confined quasi-1D geometry where the transverse electronic motion is quantized to form 1D-bands while the longitudinal electronic motion remains continuous. Strong local coherent fields (plasmons) generated in this way can be used in a variety of new tunable optoelectronic applications, such as near-field optical probing and sensing, optical switching, enhanced electromagnetic absorption, and materials nanoscale modification.

In hybrid metallic CN systems (those containing extrinsic atomic type species such as semiconductor quantum dots, extrinsic atoms, or ions), inter-band plasmons mediate near-field quantum effects such as resonance absorption, decay and bipartite entanglement [2]. These can be controlled and monitored by using non-linear optical experimental techniques, such as 2D photon-echo spectroscopy or double quantum coherence spectroscopy [3]. Our findings provide new understanding of the very important role played by low-energy inter-band plasmon excitations in CN systems, offering new principles for optoelectronic device concepts for future carbon nanotechnology.

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[3] M.F. Gelin, I.V. Bondarev, A.V. Meliksetyan, Chem. Phys. 413 (2013) 123-131

C1

## Can diamond nanowires form inside carbon nanotubes?

Zhen Zhu[1], David Tománek[1], Yanquan Feng[2]

*1 Physics and Astronomy Department, Michigan State University, USA (zhuzhen@msu.edu)*
*2 School of Physics, Beijing Institute of Technology, P.R. China*

We investigate the possibility of templated growth of diamond nanowires from functionalized diamondoid molecules enclosed in a carbon nanotube (CNT). Our *ab initio* density functional theory studies identify suitable candidate molecules and conditions, under which such molecules may fuse to narrow diamond nanowires with $C_8H_8$ or $C_7H_8$ unit cells inside a CNT. We find that the unique environment inside a narrow carbon nanotube, which can be suitably represented by a cylindrical potential, subjects enclosed molecules to a high pressure, caused by a "capillary" force. The surrounding narrow nanotube orients the enclosed molecules in a suitable way favoring fusion within the constraining volume. Our calculations indicate that $C_{10}H_{16}$ adamantane molecules do not fuse to diamond nanowires in a reaction that requires additional energy, but rather convert to carbon chains [1]. On the other hand, $C_{14}H_{18}(COOH)_2$ diamantane di-acid molecules may fuse in an exothermic reaction to $-C_8H_8-$ diamond nanowires in hydrogen atmosphere [2]. Our canonical molecular dynamics calculations at elevated temperatures indicate likely intermediate products that occur during these reactions and agree with experimental observations [1,2].

Supported by the National Science Foundation Cooperative Agreement No. EEC-0832785, titled "NSEC: Center for High-rate Nanomanufacturing".

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[2] Jinying Zhang, Zhen Zhu, Yanquan Feng, Hitoshi Ishiwata, Yasumitsu Miyata, Ryo Kitaura, Jeremy E. P. Dahl, Robert M. K. Carlson, Natalie A. Fokina, Peter R. Schreiner, David Tománek, Hisanori Shinohara, Angew. Chem. Int. Ed. 52 (2013) 3717

C2

## Development and commercialization of high dispersibility MWCNTs and MWCNT-based conductive composite and ink

Young Chul Choi, Hong Man Park

*CNT Division, Hanwha Chemical Corporation, Janggyo-dong, Jung-gu, 100-797 Republic of Korea*
*(youngchoi@hanwha.co.kr)*

Multiwalled carbon nanotubes (MWCNTs) possess excellent characteristics, such as strong mechanical properties, high electrical conductivity, high thermal conductivity, large energy storage capacity, and so on. These superb properties have been expected to open a new era of various applications, including nano-structured composite, energy storage vehicles, information displays, electronic devices, etc.

In this work, we have developed the commercial scale synthesis technology of high dispersibility MWCNTs and MWCNTs-based conductive composite and ink. In order to use MWCNTs as conducting fillers in composite and ink, an efficient dispersion of the nanotubes is a prerequisite. We found that aligned MWCNTs have much higher dispersibility than entangled ones. It is well known that the longer nanotubes result in higher conductivity of composite and ink. However, the dispersibility of aligned MWCNTs is inversely proportional to their length, and poor dispersibility causes low conductivity of composite and ink. It was therefore believed that there might be optimum length of MWCNTs for a certain dispersion process. It was found that the MWCNTs of ~60 μm in length showed the highest conductivity of polymer composite when prepared using twin extruder. On the other hand, the longer the nanotubes are, the higher conductivity the ink shows. This is because the process for ink preparation uses very strong dispersion process including sonication and/or milling for sufficient time. Not only did we develop the mass production of MWCNTs, composite and ink, but we also succeeded in commercialization of those materials. We would like to introduce several issues that have arisen during the marketing of MWCNT-based products, and give hints how to resolve those problems.

I2

# Quantification of dispersion degree in polymer/carbon nanotube nanocomposites

Mostafa Yourdkhani and Pascal Hubert

*Department of Mechanical Engineering, McGill University, Canada (pascal.hubert@mcgill.ca)*

Dispersion of carbon nanotubes (CNTs) inside polymers has been found as a challenging issue towards manufacturing of CNT/polymer nanocomposites. It has been shown that the performance of nanocomposites strongly depends on the state of dispersion [1]. Therefore, it is important to evaluate the dispersion degree of the product during the manufacturing process. Dispersion degree is usually assessed by qualitative analysis of microscopy micrographs; however, it is not always easy to distinguish between different states of dispersion. In the present work, a quantitative algorithm is developed to analyze the dispersion degree of CNTs inside polymer matrices. This algorithm can be used to analyze the micrographs obtained from optical or electron microscopy techniques. In this algorithm, first, a binary image of a given dispersion micrographs is produced. In the binary image, on-pixels represent the particle elements while off-pixels are considered as matrix elements. A key parameter is then defined as “nearest neighboring distance”, which is the distance between any matrix elements to its nearest neighboring particle element. The mean value of this parameter is used to quantify the dispersion degree; a dispersion index is defined by comparing the image of interest with the two correlated extreme cases of dispersion: aggregated and uniform dispersions. Using this dispersion index, dispersion degree can be quantitatively evaluated to determine whether it is desirable. Synthetic models are used to investigate the sensitivity of the algorithm to different dispersion scenarios. Besides, optical and electron microscopy images of CNTs/polymer nanocomposites are used to assess the functionality of the algorithm to the real micrographs.

[1] B. Fiedler, F.H. Gojny, M.H.G. Wichmann, M.C.M. Nolte, K. Schulte, Compos. Sci. Technol. 66 (2006) 3115-3125

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C7

# Carbon nanotubes as semi-flexible polymers: Measuring the entropic spring constant in CNT resonators

Arthur W. Barnard[1], Paul L. McEuen[2]

*1 Applied and Engineering Physics, Cornell University, USA (awb28@cornell.edu)*
*2 Kavli Institute at Cornell for Nanoscale Science, Cornell University, USA*

Carbon nanotubes (CNT) have been widely studied as vibrating nano-beam resonators in controlled vacuum environments, however it is known that they behave as semi-flexible polymers when in solution [1]. Recently, we have theoretically shown that these two pictures are intimately linked [2]; yet a decisive measurement that reveals how entropic effects govern the behavior of CNT resonators has remained elusive. A major barrier to accomplishing this is that traditional fabrication techniques lead to an unknown and uncontrollable built-in strain. To this end, we have developed an electrically-contacted nanotube tweezer platform that is capable of lifting a pristine CNT off of its growth substrate, directly applying strain to the free-standing doubly-clamped CNT, and electrostatically driving and detecting its motion.

With this platform, we have obtained complete maps of the mechanical frequency response of CNTs as a function of both gate voltage and strain, studying several tubes that are ~10 microns long and a few nanometers in diameter. The characteristic resonance behavior observed is highly non-linear in strain and does not fit into simple elastic models of beam mechanics. However, by adapting the tension-strain relationship that is well established for semi-flexible polymers, we are able to clearly rationalize our measurement and extract meaningful physical quantities including the persistence length, bending stiffness, and the non-linear entropic spring constant. These results show that room temperature dynamics of CNT resonators can be highly entropic, which thus imposes thermodynamic limits on the attainable quality factor of mesoscopic 1D resonators.

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# Tuesday

K2

# Towards an understanding of catalytic graphene and carbon nanotube growth

Stephan Hofmann

*Department of Engineering, University of Cambridge, United Kingdom (sh315@cam.ac.uk)*

The application potential of carbon nanotubes (CNTs) and graphene hinges entirely on the development of growth and integration techniques that are scalable and allow an adequate level of structural control. Chemical vapor deposition (CVD) now dominates the nanotube market and rapid progress is being made to develop it also for graphene manufacture. Central to the CNT and graphene growth process is thereby the use of a catalyst, in the form of a nanoparticle or poly-crystalline film, respectively. Despite an ever growing body of literature on empirical process calibrations, in both cases an understanding of the catalytic growth mechanisms is still largely missing even for common transition metal catalysts such as Ni. This leaves key questions unanswered, such as the level of structural growth selectivity/control that can be achieved for instance in terms of chirality for CNTs and in terms of poly-crystalline texture and layer control for graphene.

With a focus on diverse CNT and graphene applications in the electronics and display industry, we have been trying to address this current lack of understanding by using in-situ metrology, ranging from environmental scanning and transmission electron microscopy to high-pressure X-ray photoelectron spectroscopy, X-ray diffraction and scanning tunneling microscopy, to directly probe the atomic level mechanisms that govern the growth and device behavior of these nanomaterials in realistic process environments. This talk will review our current understanding of CNT and graphene CVD based on model catalyst systems [1-6], in particular highlighting the importance of kinetic aspects and size- and solubility-dependent mechanisms.

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[5] Kidambi *et al.,* J. Phys. Chem. C 116 (2012), 22492 [6] Dlubak *et al.,* ACS Nano 6 (2012), 10930

I3

# Continuous growth and patterning of carbon nanotube forests

John Hart

*University of Michigan, MIT (beginning July 2013), USA (ajohnh@umich.edu)*

Despite the rapidly growing commercial interest in carbon nanotubes and their applications [1], manufacturing of organized assemblies of CNTs, which retain promise to have exceptional bulk properties, largely remains an unmet challenge. I will present our research on efficient and scalable manufacturing of CNT forests, which connects fundamental growth insights to precision machine design. Synchrotron X-ray scattering is used to reveal the collective mechanism of CNT self-organization into vertically aligned “forests” [2], and to build population-based models of mechanical and chemical coupling during growth [3]. Insights from this work have enabled the design of a novel concentric tube reactor for efficient multi-zone roll-to-roll CVD on flexible substrates [4], and the adaptation of laser printing for large-scale patterning of nanoparticle toner as a CNT growth catalyst [5].

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[2] M. Bedewy, E.R. Meshot, M.J. Reinker, A.J. Hart, ACS Nano 5(11):8974-8989, 2011
[3] M. Bedewy, B. Farmer, A.J. Hart, *in preparation*, 2013
[4] E.S. Polsen, A.J. Hart, *in preparation,* 2013
[5] E.S. Polsen, A.G. Stevens, A.J. Hart, ACS Applied Materials and Interfaces, 5(9):3656-3662, 2013

# Investigation of the active component formation of Fe-Co catalyst during MWCNT growth by means of in situ methods

Dmitry Krasnikov[1,2], Vladimir Kuznetsov[1,2], Alexander Shmakov[1,2], Olga Lapina[1], Andrey Andreev[1,2], Arcady Ishchenko[1], Karina Elumeeva[1]

*1 Boreskov Institute of catalysis SBRAS, Russia (krasnikovdmitry@gmail.com)*
*2 Novosibirsk State University, Russia*

Multi-walled carbon nanotubes (MWCNTs) are known to be perspective component for numerical composite materials due to their unique mechanical properties and high thermal and electrical conductivity. Their properties mainly depend on the diameter distribution and defect concentration, which, in turn, depend on the catalyst nature and growth conditions. Previously it was demonstrated that the formation of the catalytic species and nucleation of the carbon deposits determine the selectivity and activity of nanotube growth process. Thus, the investigation of the catalyst active component formation is extremely important for the design of selective processes of MWCNT production. In the present work the formation of the active component of the bimetallic Fe-Co catalyst during MWCNT growth was studied using *in situ* synchrotron radiation XRD analysis. The XRD data in combination with the results of other physical methods (HRTEM, internal field $^{59}$Co NMR) can be used for the development of kinetic model and the optimization of the synthesis conditions to produce MWCNT with controlled properties in a fluidized bed reactor. For the first time we have obtained data confirming the stepwise formation of Fe-Co bimetallic alloy. It was found that the cobalt particles are formed at the first stage of catalyst reduction. These primary particles promote the reduction of Fe species with the subsequent formation of the alloy. Mono-component Fe catalyst demonstrates the simultaneous formation of Fe–C alloys with subsequent transformation into stable iron carbide. The *in situ* activation of the Fe–Co catalysts leads to the formation of highly dispersed alloyed particles with bcc structure type. Meanwhile, the stable carbide formation for such systems is not observed. The absence of stable carbides promotes carbon diffusion through metal particle providing much higher activity of multicomponent Fe–Co catalysts compared to that of monometal Fe catalysts. According to the XRD data, catalyst active component is solid or at least contains crystalline core during CNT growth. Pechini-type method of Fe–Co catalyst production demonstrates much higher MWCNT production with different structural properties than it was described before.

# In situ Raman investigations of the growth of carbon nanotubes

Vincent Jourdain[1], Hugo Navas[1], Matthieu Picher[1], Eric Anglaret[1], Raul Arenal[2,3], Etienne Quesnel[4]

*1 Laboratoire Charles Coulomb, Montpellier, France (vincent.jourdain@um2.fr)*
*2 Laboratoire d'étude des microstructures, UMR 104 CNRS-ONERA, Châtillon, France*
*3 Instituto de Nanociencia de Aragon, U. Zaragoza, Spain*
*4 CEA-LITEN, 17 rue des martyrs, 38054 Grenoble cedex 9, France*

The catalytic chemical vapour deposition (CCVD) of carbon nanotubes (CNT) is based on the decomposition of a carbon precursor on catalytically-active and shape-controlled surfaces [1]. We have investigated the mechanisms of CNT growth in CCVD by *in situ* Raman spectroscopy complemented by *ex situ* characterizations (TEM, XPS...) [2-4]. The purpose of this contribution is to present the main and latest results of this approach for the rationalization of single-walled CNT (SWCNT) growth and the control of SWCNT features. For most growth conditions and catalyst systems, our kinetic data are in qualitative agreement with the kinetic model proposed by Puretzky *et al.* and based on a progressive encapsulation of the catalyst particle by a carbonaceous layer [5]. Quantitative discrepancies are observed at the limits of the growth window, which are accounted for by allowing a variation of the density of active particles in the Puretzky's model. Our studies also highlighted how the growth conditions and the size of the catalyst particle influence the catalyst reduction and its consequences on the activation of CNT growth and on the CNT diameter distribution. Finally, we will present our latests results about the energetics of defect creation during SWCNT growth and the competition between the formation of SWCNTs and that of carbonaceous by-products.

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## I4

## Raman spectroscopy of chirality-enriched carbon nanotubes

Stephen K. Doorn

*Center for Integrated Nanotechnologies, Los Alamos National Laboratory, U.S.A. (skdoorn@lanl.gov)*

Access to carbon nanotube samples enriched in single chiralities allows the observation of new photophysical behaviors obscured or difficult to demonstrate in mixed-chirality ensembles. Recent examples include the observation of strongly asymmetric G-band resonance Raman excitation profiles resulting from non-Condon effects [1] and the unambiguous demonstration of Raman interference effects [2]. A summary of our results illustrating the asymmetric profile behavior observed for a wide range of semiconducting species with excitation in E22 will be given, along with a demonstration of Raman interference between E33 and E44 for select chiralities. We also present here our most recent results demonstrating the generality of the non-Condon behavior to include metallic species (specifically armchair chiralities). Additionally, the $E_{ii}$ dependence in non-Condon behavior with excitations from E11 thru E44 for both RBM and G modes will be discussed. Additionally, the complex response expected for the CNT 2-D mode has not yet been clearly defined. We present results on the dispersive and resonance behaviors of the 2-D mode. The response will be discussed in the context of the interplay of dispersive effects and resonance with the $E_{11}$ and $E_{22}$ transitions. The results will be compared to simulations that include all relevant electronic and phonon bands tied to the double-resonance process.

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## C10

## Boron nitride nanoribbons from in-situ unzipping during nanotube growth

Luhua Li, Ying Chen

*Institute for Frontier Materials, Deakin University, Waurn Ponds, Australia (luhua.li@deakin.edu.au)*

Boron nitride nanoribbons (BNNRs) have many interesting properties. They have been produced previously from unzipping boron nitride nanotubes (BNNTs) via two separate steps: BNNT growth and post-synthesis unzipping treatments. Here, we introduce an in-situ unzipping concept that simplifies the two steps into one. That is, unzipping happens during BNNT synthesis so that BNNRs can be directly harvested without the need for post-synthesis treatment. The resultant BNNRs are of high chemical purity and crystallinity according to near edge x-ray absorption fine structure (NEXAFS) spectroscopy, and prefer a zig-zag orientation.

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C11

# Lattice-directed growth of single-walled carbon nanotubes on surface: from orientation to chirality control

Jin Zhang

*Center for Nanochemistry, College of Chemistry and Molecular Engineering, Peking University, China*
*(jinzhang@pku.edu.cn)*

Single-walled carbon nanotubes (SWNTs) have been regarded as one of the promising candidates for future applications in nanoelectronic devices. However, how to grow SWNTs on surface with controlled structure is a bottleneck to the fabrication of nanoelectronic devices. Till now, the gas flow and lattice directed modes have been used to grow aligned SWNTs on surface. For the lattice directed mode, it is bases on the energy differences with the SWNTs selectively directed along some preferential orientations on single crystal substrates. Using the difference, the orientation and chirality of SWNTs on specific surface could be controlled. This talk will cover: 1) Quartz (001), MgO (001), and layered mica, which have the three-, four- and six- fold symmetries respectively, were used as the substrates to grow SWNTs and the produced SWNTs were displayed the preferential angles of 120° on quartz, 90° on MgO and 60° on mica; 2)An approach was developed to align the SWNTs on graphite surface, where the orientation of each SWNT shows a period of 60° and also depends sensitively on both its chiral angle and handedness. Moreover, by combining with the resonant Raman spectroscopy, the (n,m) index of each SWNT can be exactly determined from the (d,θ) plot.

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[2] J. Zhang *et al., submitted*

C12

# Modulating catalyst formation process to control diameter and density of single-wall carbon nanotube forests

Shunsuke Sakurai[1,2], Masayasu Inaguma[1], Don Futaba[1,2], Motoo Yumura[1,2], Kenji Hata[1,2]

*1 Nanotube Research Center, National Institute of Advanced Industrial Science and Technology (AIST) Central 5, 1-1-1, Higashi, Tsukuba, Ibaraki, 305-8565, Japan*
*2 Technology Research Association for Single Wall Carbon Nanotubes (TASC) Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki, 305-8565, Japan*

We have showed that essentially any Fe compounds could serve as catalysts for SWNT forest growth, and interestingly, the average diameters of the SWNTs were nearly identical (2.8–3.1 nm) [1]. We report here by decoupling the catalyst formation and SWNT growth processes, we performed a continuous and wide range control of the diameter (1.9–3.2 nm) and density (0.03–0.11 g $cm^{-3}$) of SWNT forests while the growth yield was preserved [2]. We found that the diameter and density were inversely correlated where low/high density forests would consist of large/small diameter SWNTs. The catalyst formation process was modeled by considering the competing processes, Ostwald ripening and subsurface diffusion. Interestingly, this model showed that the offsetting effects of these two processes can suppress the evolution of catalyst size at a specific particle size. By using this model, we explained the results where SWNT forests with similar average diameters grew regardless of the initial Fe catalyst [1], and how $H_2$ exposure decreased catalyst size.Finally, we have studied the growth kinetics of a series of SWNT forests continuously spanning a wide range of diameters (1.9–3.2 nm) [3], where we have found a linear relationship between the individual SWNT mass and the individual catalyst volume.

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**I5**

## Mechanical resonators based on nanotubes and graphene

Adrian Bachtold

*ICFO – The Institute of Photonic Sciences, Castelldefels (Barcelona), Spain (adrian.bachtold@icn.cat)*

Carbon nanotubes and graphene offer unique scientific and technological opportunities as nanoelectromechanical systems (NEMS). Namely, they have allowed the fabrication of mechanical resonators that can be operable at ultra-high frequencies and that can be employed as ultra-sensitive sensors of mass and charge. In addition, nanotubes and graphene have exceptional electron transport properties, including ballistic conduction over long distances. Coupling the mechanical motion to electron transport in these remarkable materials is thus highly appealing. Here, I will review some of our recent results on nanotube and graphene NEMSs, including mass sensing at the proton mass level, and force sensing with a sensitivity of ~10 zN/Hz$^{1/2}$.

**I6**

## Carbon-based mechanical resonators

Herre S.J. van der Zant

*Kavli Institute of Nanoscience, Delft University of Technology, The Netherlands*
*(H.S.J.vanderZant@tudelft.nl)*

Nano-electromechanical systems (NEMS) make use of electrically induced mechanical motion and vice versa. Carbon nanotubes are ideal building blocks of NEMS because of their unique (mechanical) properties and their low mass. This puts them in an unexplored regime of motion which approaches the fundamental detection limit set by quantum mechanics [1]. At room temperature, we use mixing techniques to probe the bending-mode vibration of a suspended carbon nanotube [2]; the gate voltage strains the carbon nanotube and thereby tunes its frequency. At low temperatures, mechanical vibrations are actuated by a nearby antenna and a record high Q-value of 150000 at a resonance frequency of 300 MHz is achieved [3]. Electron tunnelling and mechanical motion are strongly coupled resulting in single-electron tuning oscillations of the mechanical frequency and in energy transfer to the electrons causing mechanical damping [4]. By embedding a suspended carbon nanotube in a superconducting quantum interference device, its displacement is measured while the gate voltage pulls the tube close to the substrate [5].

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# Carbon nanotubes for piezoresistive electro-mechanical transducers incorporating a wafer-level technology

Sascha Hermann[1], A.Shaporin[1], J.Bonitz[2], S.Hartmann[1], S.Voigt[1], C.Kaufmann[1], R.D.Rodriguez[3], D.R.T.Zahn[3], J.Mehner[1], B.Wunderle[1], S.E.Schulz[1,2], T.Gessner[1,2]

*1 Chemnitz University of Technology, Center for Microtechnologies (ZfM), 09126 Chemnitz, Germany (sascha.hermann@zfm.tu-chemnitz.de)*
*2 Fraunhofer Institute for Electronic Nano Systems (ENAS), 09126 Chemnitz, Germany*
*3 Chemnitz University of Technology, Institute of Physics, 09126 Chemnitz, Germany*

Some single-walled carbon nanotubes exhibit a distinctive intrinsic piezoresistivity. This extraordinary behavior may be exploited in ultra sensitive displacement and force sensors [1, 2]. Driven by this aim we present our progress on the integration of suspended SWCNT arrays into microelectromechanical systems (MEMS). Thereby we focus on fabrication oriented wafer-level approaches for defined CNT-assembly, electrical/mechanical CNT contacting and integration of CNTs into a silicon-based MEMS. Since the performance of a CNT-based piezoresistive sensor depends on aspects like a reliable electrical/mechanical contact, the chirality distribution of CNTs in arrays as well defect density and impurities, this work's goal is a deeper insight in these important aspects. Therefore a MEMS stage was designed and fabricated. It enables an extended electrical and structural characterization of suspended CNTs under strain as well as a mechanical reliability test for CNT-piezoresistors and contacts. Thereby a wafer-level technology was applied combining CNT integration and MEMS fabrication, demonstrating a technology with a high application potential for sensor device fabrication. Through a specially designed wet processing system, the dielectrophoretic method was scaled up to wafer level allowing controlled CNT alignment and deposition. Aiming at high process control and reproducibility, the assembly process was analyzed using *in situ* Raman spectroscopy. The dynamics of the CNT assembly process was investigated giving insights into the complex interrelationship between electric field properties and dispersion parameters. Furthermore, we investigate the local chiral distribution of CNTs as well as the structural and electrical properties of CNTs under strain.

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P1

## Laser power dependence of laser-assisted alcohol chemical vapor deposition of carbon nanotubes

Kouichi Akahane[1], Naokatsu Yamamoto[1], Shinji Yasuda[2], Hiroshi Takai[2], Shun-ichi Umeda[3],
Shin-ichi Nakamura[3], Hideyuki Sotobayashi[3]

*1 National Institute of Information and Communications Technology, Japan (akahane@nict.go.jp)*
*2 Tokyo Denki University, Japan,*
*3 Aoyama Gakuin University, Japan*

Carbon nanotubes (CNTs) are attracting significant research attention because of their potential applications in micro- and nanodevices owing to their unique properties [1]. We have been developing laser-assisted alcohol chemical vapor deposition (CVD) to grow position-controlled and/or functional CNTs. In this study, we investigate the laser power dependence of CNT growth by laser-assisted alcohol CVD. CNTs were grown by laser-assisted alcohol CVD in a SUS vacuum chamber with a transparent viewport. The substrate holder was heated resistively. The continuous wave laser used for irradiation had a wavelength of 532 nm. The CNTs were grown on transparent quartz substrates with a single catalyst layer of 6-nm-thick Fe. The laser power was changed from 0.24 W to 1.2 W by using a neutral density filter. After 2 min of CNT growth without laser irradiation, the sample surface was semi-transparent, indicating that CNTs several micrometers in length were grown on the substrates. After 0.24 W laser irradiation, the sample surface exhibited black spot only at the laser irradiation point, whereas 1.2 W laser irradiation produced a black ring where CNT growth was enhanced. The center of the black ring on latter sample had a transparent surface. Therefore, the CNT growth strongly depends on the laser power in laser-assisted alcohol CVD.

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P2

## New approach for synthesizing individual, controlled diameter SWNTs for electronics

Fatima Z. Bouanis[1,2], Evgeny Norman[2], Vincent Huc[3], Marc Chaigneau[2], Jean L. Maurice[2],
Bérengère Lebental[1,2], Talal Mallah[3], Didier Pribat[4], Costel S. Cojocaru[2]

*1 Institut Français des Sciences et Technologies des transports, de l'aménagement et des réseaux, France (Fatima.bouanis@ifsttar.fr)*
*2 Laboratoire de Physique des Interfaces et Couches Minces, France*
*3 Institut de Chimie Moléculaire et des Matériaux d'Orsay, France*
*4 Departement of Energy Science, Sungkyunkwan University, Suwon, 440-746, Korea*

In this work we report, a robust and versatile approach for reproducible and controllable growth of single walled carbon nanotubes (SWNTs) using self-assembled monolayer (SAM) technique coupled with atomic hydrogen ($H_{at}$) pretreatment to control the catalytic metallic nanoparticles morphology and density. This new approach represents a first step towards a general route to control the yield, the diameter distribution and possibly the chirality of nanotubes. Precise morphology and chemical composition as well as density control of the metallic nanoparticles are achieved by a subsequent pyrolysis step under radical hydrogen atmosphere. Using the as-formed nanoparticles as catalysts, SWNTs are grown by hot filament chemical vapour deposition (HFCVD). They exhibit remarkable high crystalline quality, with well controlled yield and diameter strongly dependent on the initial catalyst species. Field effect transistors (FETs) with excellent performance characteristics were obtained using such in-place grown SWNTs as channel. The electronic properties of SWNTs can also be tuned using this approach. Indeed, the transistors obtained from RuTTP and $FeCl_3$ as catalysts precursors exhibit ON/OFF current ratio up to ~ $10^8$, indicative of the direct growth of mostly semi-conducting SWNTs. By contrast, devices obtained from $RuCl_3$ salts display ON/OFF current ratio well bellow $10^2$, indicating the direct growth of highly metallic specimens enreached SWNTs.

P3

# A novel approach for integrating horizontally aligned carbon nanotubes into devices by photolithography

P. Braeuninger-Weimer, T. Süss, C. Hierold

*Micro and Nanosystems, ETH Zurich, Switzerland (p.b.w@web.de)*

The controlled integration of carbon nanotubes (CNTs) into components such as carbon nanotube field-effect transistors (CNFETs) is one of the major challenges of CNT device fabrication. If randomly grown individual CNTs are to be contacted in a defined way, atomic force microscopy (AFM) or scanning electron microscopy (SEM) is often used to localize the CNTs with respect to a marker system. Then electron beam lithography is employed to define electrical contacts to the CNTs [1]. This is very costly in terms of time and not suitable for batch fabrication, since for each CNT contact an individual mask must be designed.

Here, a novel approach is presented, which allows controlled contacting of individual CNTs by photolithography (Karl Süss MJB4) utilizing a single photo mask. By exploiting the horizontal alignment of CNTs on quartz substrates [2] and a novel system of alignment marks, CNTs can be contacted by serial optical lithography exposure.

The CNT locations relative to a predeposited marker system is determined by AFM. A system of alignment marks on the sample and on the contact mask enables the precise placement of the contacts at the location of the individually selected CNTs. The marker system allows for a shift of +/- 25 µm in x and y direction, respectively.

By this novel approach, an average alignment accuracy of 0.2 ± 0.1 µm was measured by AFM. With this approach, CNFETs with single walled carbon nanotubes (SWNTs) were fabricated and measured.

In conclusion, this novel approach enables the fabrication of a large numbers of single nanotube FETs. This process provides an alternative to electron beam lithography for device designs requiring alignment precisions of up to 0.2 ± 0.1 µm.

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P4

# Semiconducting single-wall carbon nanotubes on demand by polymer wrapping

W. Gomulya[1], G.D. Costanzo[1], E.J.F. de Carvalho[1,2], S.Z. Bisri[1], V. Derenskyi[1], M. Fritsch[3], N. Fröhlich[3], S. Allard[3], P. Gordiichuk[1], A. Herrmann[2], S.-J. Marrink[1], M.C. dos Santos[2], U. Scherf[3], M.A. Loi[1]

*1 Zernike Institute for Advanced Materials, University of Groningen, Netherlands*
*2 Instituto de Física, Universidade de São Paulo, Brazil (eltonfc@if.usp.br)*
*3 Institute for Polymer Technology, Wuppertal University, Germany*

Current carbon nanotube (CNT) synthesis methods render heterogeneous samples, with wide distributions of electronic and mechanical properties. This limits the broad applicability of as-synthesized nanotubes in electronic and nano-mechanical devices. Thus, sorting techniques that separate tubes with properties of interest are gaining research attention. Very efficient separation by chiral angle of nanotubes with a diameter of around 1 nm can be obtained by spontaneous wrapping of fluorene-based polymers [1]. Even though many polymer structures have been tested, none has been able to discriminate CNTs larger than 1.2 nm in diameter.

In this work, we report on the ability of poly(9,9-dialkylfluorene-2,7-diyl) family of polyfluorenes to suspend nantoubes in a wide diameter range, from 0.8 nm to 1.6 nm depending on the length of the alkyl sidechain. These results come with spectroscopic evidence of high prevalence of semiconducting CNTs that allow for the fabrication of network field effect transistors with mobility up to 14 $cm^2/Vs$ for holes and 16 $cm^2/Vs$ for electrons, and on-off ratio of $10^5$ [2].

Based on molecular dynamics and molecular modeling simulations we provide a model based on the important role of the polyfluorene sidechains [3] that demonstrate how the diameter of suspended CNTs can be tuned by changing the sidechain length.

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**P5**

## Mist-CVD deposition of SWCNT films for transparent electrodes

K. Jantharamatsakarn and S. Chaisitsak

*Department of Electronics Engineering, Faculty of Engineering, King Mongkut's Institute of Technology Ladkrabang, Bangkok, 10520 Thailand (kcsutich@kmitl.ac.th)*

The floating catalyst CVD using ferrocene–ethanol mist [1] has the potential for large-scale production of SWCNTs (single-walled carbon nanotubes) at a low temperature, since it is a continuous process of both catalyst particle formation and nanotube growth occurring in the same reactor. In this work, the ferrocene-ethanol mist CVD under atmospheric pressure was successfully used to deposit web-like SWCNT films from the gaseous phase of onto a Si substrate and a membrane filter (~50 mm). The home-built vertical mist-CVD system was carried out without the use of $H_2$ or CO gases [2]. The tiny mist of ferrocene-ethanol was generated using a high-frequency ultrasonic vibration (~1.7 MHz). The effects of various parameters including furnace temperature, ferrocene/ethanol ratio, flow rate of carrier gas, and deposition time on the formation of SWCNTs were investigated using SEM, TEM and Raman spectroscopy. The furnace temperature and the flow rate of carrier gas were found to determine the diameter and crystallinity of nanotubes. The ferrocene concentration in ethanol strongly influenced the diameter distribution of nanotubes and the amount of impurity particles in the materials. The collected SWCNT films on a filter were directly transferred to a laminate sheet by using a hot press laminator. The properties of SWCNT films were investigated by UV-Vis spectrophotometer and four-point probe measurement. The high sheet resistance of 22 k$\Omega$ sq$^{-1}$ was observed for the as-transferred films. However, the initial results show that a sheet resistance of 8 k$\Omega$ sq$^{-1}$ could be achieved with a 65% transmittance at the wavelength of 550 nm after nitric acid or hydrochloric acid treatments (the transmittance of a plastic sheet was 80%). Further investigation in improving the electrical properties of the films is under progress and will be presented at the conference.

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**P6**

## Synthesis and structural characterizations of aligned carbon nanotubes: analysis of the central core

E. Charon, M. Pinault, P. Boulanger, M. Mayne-L'Hermite, C. Reynaud

*CEA-Saclay, DSM/IRAMIS/SPAM, Laboratoire Francis Perrin, Bat. 522, 91 191 Gif sur Yvette Cedex, France (emeline.charon@cea.fr)*

The aligned multi-walled carbon nanotube (MWNT) carpets present numerous potential applications such as nanoporous membranes [1]. Main works are based on theoretical studies from perfect CNT (without defects) which highlight very high speeds of flow through the porous central core of nanotubes [1]. However, experimental studies are less numerous and difficult to reproduce. One major difficulty is to adjust the size and the crystalline structure of the CNT and especially the morphology and structure of nanotube's central core.

In this study, aligned MWNT are grown by catalytic chemical vapour deposition using mixed aerosol containing both the carbon and metal precursors, enabling the nucleation of catalyst nanoparticles directly in the gas phase [2]. These aligned MWNT are rather straight but their central core needs to be specifically controlled. The control is focused on both the occurrence of catalyst-based nanoparticles inside CNT core and on the structural quality of graphene layer constituting the central core. Our study aims at determining the influence of different synthesis parameters on the central core characteristics. The approach is to combine a global analysis of the characteristics of the synthesis (yields, growth rate...) and of the samples (CNT length, diameter, and structure) with a local analysis of the central core in terms of filling with catalyst particles and of structural quality of graphene sheets.
By changing the composition of the gas phase in a wide range, reasonable synthesis yields and very clean CNT exhibiting diameter around 20 nm and with few defects regarding Raman spectroscopy (ID/IG ~0.3), were obtained. Concerning the central core, the blocking rate by the iron can be modulated and reach very low rates for special synthesis conditions while the internal graphene layers remain still defective and involve a high blocking rate.

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P7

# In situ refreshing enabled parts-per-quadrillion gas detection with pristine carbon nanotubes and graphene

Gugang Chen and Avetik R. Harutyunyan*

*Honda Research Institute USA Inc., 1381 Kinnear Road, Columbus, OH 43212, USA*
*(*aharutyunyan@honda-ri.com)*

Single-walled carbon nanotube (SWNT) and graphene are very promising for ultrasensitive gas detection since they consist solely of surface so that every atom is in direct contact with nearby analyte molecules. However, it is very challenging to achieve super-sensitivity due to virtually unavoidable interfering species present in the detection environment. This may partially explain why we are still far from what a pristine SWNT or graphene can offer even after more than a decade of research. Here we illustrate a novel route to address this issue. Through *in situ* refreshing of the sensor surface with continuous ultraviolet light illumination during the course of detection, we have observed 2 to 4 orders of magnitude better sensitivity than current state-of-the-art results for a range of gas molecules, and for the first time entered parts-per-quadrillion (PPQ) detection level at room temperature [1, 2]. The study further points out how to exploit the intrinsic sensitivities of other nanomaterials.

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P8

# Density-controlled CVD growth and selective removal by thermal-lithography for horizontally-aligned single-walled carbon nanotubes

Shohei Chiashi, Taiki Inoue, Keigo Otsuka, Daisuke Hasegawa, Saifullah Badar, Shigeo Maruyama*

*Department of Mechanical Engineering, The University of Tokyo, Japan*
*(*maruyama@photon.t.u-tokyo.ac.jp)*

Horizontally-aligned single-walled carbon nanotubes (HA-SWNTs) are often used for the fabrication of SWNT field-effect transistors (FETs). In order to improve SWNT-FET performance, high density and only semiconducting HA-SWNTs are desirable. Here, we showed the CVD gas pressure dependence of the HA-SWNT density [1] and discussed the alignment mechanism based on the incubation time of SWNT growth. Additionally, we applied the thermal lithography technique for selective removal of metallic SWNTs [2]. We used iron nanoparticles as the catalyst, ethanol vapor as the carbon source and R-cut crystal quartz substrates [3]. CVD growth was performed at 800 °C. Decreasing CVD gas pressure, the density of HA-SWNTs increased although the amount of grown SWNT simply decreased. At higher pressure, many SWNTs simultaneously start to grow (with uniform incubation time), get entangled each other and form bundle structure. The bundle structure disturb the interaction between SWNTs and the quartz substrate surface and degenerate the alignment growth. For selective removal of metallic SWNTs, we used thermal-lithography technique [2]. HA-SWNTs were covered with molecular glass thin film and applied electric voltage to HA-SWNTs. Only metallic SWNTs were Joule-heated and they became exposed owing to thermocapillary flow of molecular glass. By etching metallic SWNTs, the SWNT-FETs with higher on/off ratio could be obtained. We will discuss the lateral resolution of the thermal-lithography, which depend on the sample temperature and the applied voltage.

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**P9**

## A single step route to highly concentrated nanotube solutions

Adam J. Clancy[1], Takuya Morishita[1,2], Milo S. P. Shaffer[1,*]

*1 Department of Chemistry, Imperial College London, UK (*m.shaffer@imperial.ac.uk)*
*2 Toyota Central R&D Labs. Inc., Japan*

A one-step reduction and dissolution of single-walled carbon nanotubes (SWNTs) is demonstrated, giving rise to a fast, facile and scalable route towards high concentrations (>5 mg $ml^{-1}$) of anionic individualized nanotubes (nanotubide). The reactivity of these solutions with organohalides is quantified with regards to concentrations of reducing metal and SWNT, as well as metal carbon ratio, sterics of the grafted group and choice of halogen.

Reduction of SWNTs to nanotubide is the only known route to truly individualized nanotubes that does not require damaging sonication or unscalable ultracentrifugation [1] while simultaneously providing a route towards functionalization. [2] Simplifying nanotubide production and probing the subsequent reactions will facilitate advancements in a wide array of SWNT applications, particularly in high performance composites.

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**P10**

## Precursor-dependent reversible diameter modulation of vertically aligned single-walled carbon nanotubes

Erik Einarsson[1], Theerapol Thurakitseree[1], Akihito Kumamoto[1],
Christian Kramberger[2], Shohei Chiashi[1], Yuichi Ikuhara[1], Shigeo Maruyama[1,*]

*1 The University of Tokyo, Japan (*maruyama@photon.t.u-tokyo.ac.jp)*
*2 University of Vienna, Austria*

We synthesized vertically aligned single-walled carbon nanotubes (SWNTs) with a mean diameter of approximately 1 nm by chemical vapor deposition (CVD) of an acetonitrile-ethanol mixture [1]. The addition of no more than five volume percent acetonitrile in ethanol results in a dramatic reduction of the mean SWNT diameter. In the absence of acetonitrile, the mean diameter returns to the ~2 nm typical of ethanol-grown vertically aligned SWNTs. We also show the diameter can be modulated on the fly by the addition or absence of acetonitrile in the feedstock, and this diameter change is both reversible and repeatable [2].

We examined the interface between small- and large-diameter SWNTs by scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HR-TEM). Layers having different diameter can be separated from one another, but the separation is not always clear-cut. Further examination by HR-TEM revealed some of the SWNT junctions are actually continuous, whereas most are discontinuous across the interface [2]. Based on these findings, we propose that acetonitrile changes the growth mode from tangential to perpendicular [3], causing a marked reduction in SWNT diameter.

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# Separation of single-walled carbon nanotubes by 1-dodecanol mediated size exclusion chromatography

**P11**

Benjamin S. Flavel[1], Manfred M. Kappes[1,2], Ralph Krupke[1,3], Frank Hennrich[1]

*1 Institute of Nanotechnology (INT), Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany*
*2 Institute of Physical Chemistry, Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany*
*3 Institute of Materials Science, Technische Universität Darmstadt, Germany*

A simple, single column, high throughput, fractionation procedure based on size exclusion chromatography of aqueous/SDS (sodium dodecyl sulfate) suspensions of single-walled carbon nanotubes (SWCNTs) is presented. This procedure yields monochiral or near monochiral SWCNT fractions of semiconducting-SWCNTs (s-SWCNTs). The (n, m) separation of 15 different nanotube species with a purity of 16 – 93 % is shown. Furthermore, sorting was achieved without the need for a surfactant/eluent change. Upon tailoring the concentration of 1-dodecanol either through reduction of pH or the direct addition of alcohol to the raw starting material the originally strong interaction of s-SWCNT to the Sephacryl gel could be reduced, and allowed for diameter dependent fractionation.

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# Doping duration influence on N-MWNTs structures

**P13**

O. Guellati[1,2,3,4], I. Janowska[3], D. Bégin[3], M. Guerioune[1] and C. Pham-Huu[3]

*1 Laboratoire d’Etude et de Recherche des Etats Condensés (LEREC), Département de Physique, Université Badji Mokhtar, BP. 12, Annaba 23000, Algeria (guellati23@yahoo.fr)*
*2 Université Chérif Messaadia, BP. 1553, Souk-Ahras 41000, Algeria*
*3 Laboratoire de Chimie et d’Électrochimie des Surfaces (CES), FUNDP rue de Bruxelles 61, B-5000 Namur, Belgium*
*4 Laboratoire des Matériaux, Surfaces et Procédés pour la Catalyse (LMSPC), ECPM - CNRS, UdS, 25 rue Becquerel, 67087 Strasbourg, France*

Recently, nitrogen doping of CNTs has gained increasing attention because of their electronic properties in comparison with pure carbon nanotubes in different application as catalysis field [1, 2, 3]. In this investigation, we focalize on the synthesis of nitrogen-doped MWNTs by catalytic CVD, using ethane and ammoniac as carbon and nitrogen sources, over Fe-$Al_2O_3$ support. Furthermore, the variations in this doping time were applied ranging from 30 min to 120 min of the growth period in the mode (in-situ and out-situ). A strong correlation between ammonia injection duration and nitrogen concentration in the tubes was observed between (0,15 at.% to 2,5 at.%) in different coordination with Carbon or oxygen. These functionalized MWNTs were studied using High resolution TEM, FESEM, XPS, IR, BET, Thermal analysis and Raman spectroscopy in order to determine their structural characteristic, graphitization and cristallinity degree in quantitatively and qualitatively point of view.

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P14

# Growth of single-walled carbon nanotubes from solid solutions: chirality selective and growth dynamics

Maoshuai He[1], Hua Jiang[2], Juha Lehtonen[1], Esko Kauppinen[2]

*1 Department of Biotechnology and Chemical Technology, School of Chemical Technology, Aalto University, Finland (maoshuai.he@aalto.fi)*
*2 Department of Applied Physics, School of Science, Aalto University, Finland*

Chirality-selective growth of single-walled carbon nanotubes (SWNTs) by chemical vapor deposition (CVD) is of great importance owing to its good controllability and low cost. However, this process has been hindered by the limited control over the catalyst and the incomplete understanding to the SWNT growth mechanisms. In this contribution, we will introduce two types of $Co_xMg_{1-x}O$ solid solutions which are well designed and prepared aiming at structure-controlled growth of SWNTs. In a $Co_xMg_{1-x}O$ solid solution prepared by simple impregnation, the nucleation and subsequent growth of SWNTs on Co nanoparticles formed upon CO reduction were studied by *in situ* environmental transmission electron microscopy (ETEM). Our studies revealed that such prepared solid solution affords an epitaxial formation of Co nanoparticles with a narrow diameter distribution. In particular, the formed Co nanoparticles exhibited extremely high stability during SWNT nucleation and growth process. SWNTs with a very narrow chirality distribution were obtained by atmospheric pressure CVD process [1]. In another atomic layer deposit prepared $Co_xMg_{1-x}O$ solid solution, growth of SWNTs with a very high efficiency even under low CO pressure in ETEM chamber was achieved, which allowed the determination of individual SWNT growth rate. Ultra-low growth rates (0.3~0.8 nm/s) were observed for the SWNTs grown on this catalyst. In order to understand the reasons for such ultra-low growth rate, a thermodynamic model was developed to evaluate the growth rate. Careful studies on the experimental data demonstrated that the SWNT growth rate was not diameter sensitive, but suggesting that it could be chirality-dependent.

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P15

# Reaction-mechanism analysis on the CNT growth by eDIPS method using $^{13}$C carbon source

Takayoshi Hirai[1], Yuki Kuwahara[1], Masaharu Kiyomiya[1], Takeshi Saito[2,*]

*1 Technical Research Association for Single Wall Carbon Nanotube (TASC), Japan*
*2 National Institute of Advanced Industrial Science and Technology (AIST), Japan*

Direct-injection-pyrolytic-synthesis (DIPS) method is excellent for its high yield and low production costs. Our group has reported various synthetic techniques with DIPS method, and then proposed enhanced DIPS (eDIPS) method where the tube diameter distribution can be controlled gradually and selectively by simple tuning of injected two carbon source [1,2]. In order to further optimization of the production of carbon nanotubes, the growth mechanism involved in their formation must be understood. Here we report the results of reaction analyses using various $^{13}$C-labeled hydrocarbons as carbon sources. The eDIPS growth of CNTs was carried out as previously reported typical experimental procedures [1]. Feedstocks were prepared by dissolving appropriate amounts of ferrocene and sulfur compounds into suitable $^{13}$C-labeled or non-labeled organic solvents. As a second carbon source, $^{13}$C-labeled or non-labeled gaseous hydrocarbons were adopted. The ratio of carbon isotopes was evaluated by the G-band shift in the Raman spectra [3]. It was found that $^{13}$C is predominant in CNTs grown under the several reaction conditions using natural aromatic hydrocarbons (as a primary carbon source) and $^{13}$C-labeled ethylene (as a secondary carbon source). For example, under a reaction condition using natural toluene as a primary carbon source and $^{13}$C-labeled ethylene as a secondary carbon source at the ratio of $^{13}C/^{12}C= 2.5$, the percentage of $^{13}$C in produced CNTs was evaluated to be ca. 97%. On the other hand, using aliphatic hydrocarbon (as a primary carbon source) instead of aromatic hydrocarbons, the percentage of $^{13}$C in CNTs proportionally depended on the amount of the secondary carbon sources. These results show the clear correlation between thermal decomposition of carbon sources and growth of CNTs. This work has been supported by New Energy and Industrial Technology Development Organization (NEDO) project.

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P16

## Coalescence of triple-walled carbon nanotubes

Hiroyuki Muramatsu[1], Takuya Hayashi[2], Kazunori Fujisawa[2], Tomohiro Tojo[2], Yoon Ahm Kim[2], Morinobu Endo[2]

*1 Nagaoka University of Technology, Japan (muramatsu@mst.nagaokaut.ac.jp)*
*2 Shinshu University, Japan*

Connecting and welding of carbon nanotubes have been a challenge for designing structures with novel properties and for creating three-dimensional $sp^2$ carbon networks with improved physical properties. In this work, we report coalesced adjacent triple walled carbon nanotubes covalently, using catalytic boron atoms at high temperatures. The detail structure investigated by TEM, Raman, and XPS.

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P17

## Giant cations: generation of single-walled carbon nanotube polyelectrolytes via electrochemical oxidation

Stephen A. Hodge, Mustafa K. Bayazit, Hui Huang Tay, Milo S. P. Shaffer*

*Imperial College London, UK (*m.shaffer@imperial.ac.uk)*

We demonstrate the electrochemical generation of individually separate and distinct (*i.e.* discrete) single-walled carbon nanotube cations for which the term ‘nanotubium’ is coined. These species are generated following constant potential oxidation in highly stable electrolytes. (Electro)chemical charging of carbon nanotubes [1] allows enhanced solubility (electrostatic repulsion), purification (tailoring the charge/carbon stoichiometry), and covalent functionalisation [2]. Nanotubium species offer the exploration of a new library of nucleophilic grafting reactions, upon which we demonstrate a nucleophilic assembly reaction.

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**P18**

# The Marangoni effect in repositioning of deposited carbon nanotubes

Matti J. Hokkanen[1,†], Roope Lehto[1,†], Teemu Isojärvi[1], Juha Salmela[2], Sanna Haavisto[2], Markus Ahlskog[1], Jussi T. Timonen[1,*]

*1 University of Jyväskylä, Finland (*jussi.t.timonen@jyu.fi)*
*2 VTT Technical Research Centre of Finland, Jyväskylä, Finland.*
[†]These authors contributed equally.

The so-called Marangoni effect, or mass transfer (flow) along an interface of two fluids, is a well-documented hydrodynamic phenomenon driven by a surface tension gradient. The effect is known to play a major role in a variety of every-day phenomena, such as e.g. in the formation of the famous "tears of wine" [1]. While most past work has been focused on colloidal dispersions of particles deposited from an evaporating drop of liquid, there exists little information about the influence of Marangoni flow inside such a drop on repositioning of particles already existing on the substrate. Previous work on the Marangoni effect has also been hampered by lack of efficient methods to measure the related flow in situ. The situation has improved with the recent introduction of optical coherence tomography (OCT), by which flow patterns can be measured in three dimensions.

We studied the Marangoni flow in spherical drops of two-component liquids inserted on substrates containing a deposition of multiwalled carbon nanotubes (MWCNTs), and its effect on their repositioning. When such drops were evaporated, spherical imprints were formed on the substrate near the limiting (outermost) contact lines of the drops. The radial orientation of MWCNTs near these imprints were studied by scanning electron microscopy for drops of different mixtures of a volatile, fully wetting liquid, and a nonvolatile, incompletely wetting liquid (so called antagonist mixtures). The higher evaporation rate at the advancing front of the volatile component caused a concentration gradient in the radial direction of the drop, and thus a Marangoni flow. The velocity fields of these flows were measured using OCT.

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**P19**

# Synthesis of PANI/CN$_x$ composites by lithium intercalation and exfoliation of carbon nanotubes

Cristal M. Ibañez[1], André Galembeck[1,2], Humberto Terrones[3], Celso P. De Melo[1,4], Yadira I. Vega-Cantú[1,2,5,*]

*1 Programa de Ciências de Materiais, Universidade Federal de Pernambuco, Brazil*
*2 Departamento de Química Fundamental, Universidade Federal de Pernambuco, Brazil*
*3 Department of Physics, Penn State University, United States*
*4 Departamento de Física, Universidade Federal de Pernambuco, Brazil*
*5 Advanced Materials Department, IPICYT, México (*yivega.work@gmail.com)*

This work presents the synthesis of nanocomposites with nitrogen-doped mutiwalled carbon nanotubes (CN$_x$) and polyaniline (PANI). Exfoliation of CN$_x$ was carried out by lithium-ammonia intercalation followed by a thermal treatment to obtain unzipped CN$_x$ (ex-CN$_x$), using the method developed by Cano *et al.*, [1]. In this work, two different kinds of CN$_x$ were used: (i) intercalated and exfoliated CN$_x$ without acid treatment; (ii) CN$_x$ (without acid treatment) functionalized with aniline monomers in lithium-ammonia solution. The preparation of ex-CN$_x$/PAni composites was carried out by *in situ* by interfacial polymerization of aniline [2]. For the synthesis of ex-CN$_x$/PAni various weight percentages of CN$_x$ (1, 5, 10 and 20 wt. % based on the aniline monomer content) were dispersed in the monomer solution 0.97 g. All the samples were characterized by X-ray powder diffraction, Raman spectroscopy analysis showed increases in the D band intensity for ex-CN$_x$ and CN$_x$ functionalized with aniline monomer. Scanning electron microscope (SEM) and transmission electron microscopy (HRTEM) were used to observe the coating and morphology. The samples ex-CN$_x$/PAni composites were characterized by cyclic voltammetry (CV) and impedance spectroscopy to analyze the electronic properties.

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P20

# Direct observation of CVD synthesis of carbon nanotube using quadrupole mass spectrometry

Shuhei Inoue[1], Daisuke Nakahara[2], Yukihiko Matsumura[1]

*1 Energy and Environmental Engineering Division, Faculty of Engineering, Hiroshima University, Japan (shu18@hiroshima-u.ac.jp)*

*2 Department of Mechanical Science and Engineering, Hiroshima University, Japan*

As a method of synthesizing single-walled carbon nanotube (CNT), the chemical vapor deposition is the standard method. Ethanol is one of the typical carbon sources for synthesizing CNT, but it has been unclear the nucleation mechanism and the reason why its synthesis stops above 1000 °C. In this study, we conducted in situ mass spectroscopy during CVD synthesis using Q-mass. Since these several years, it has been considered that degradation of ethanol or condensation results in this phenomenon, because the double bond of carbon atoms were detected by FT-IR experiment. With respect to our quantitative analysis of experiment, however, the observed spectra seem to proceed to desireble direction as the temperature becomes higher; for example, the amount of generated ethylene and acetylene, which are considered to be precursor products for synthesizing CNT, becomes larger. Furthermore, when we synthesized CNT at 800 °C using the ethanol, which experienced 1000 °C or 1100 °C, we could derive pure CNTs. This indicates that the reason of the failure in synthesizing CNT at high temperature is not the degradation of ethanol and its condensation. The melting point of nano particles are expected to be lower than that of bulk materials due to Gibbs-Thomson effect. Shibuta and Suzuki [1] discussed its qualitative analysis using molecular dynamics simulation. Referring to their simulation, the melting point of nano particles used as a catalysts are estimated to be around 930 °C, which is quite near by the threshold temperature of synthesizing CNT. As a result, we concluded that at higher temperature the nano catalysts fuse or aggregate; in the former case carbon atoms never deposit and nucleates because carbon and metal are liquid phase, in the latter case multi-walled carbon nanotube are synthesized because the catalysts particles became larger. This assumption is in good agreement with experimental results.

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P21

# SWNTs growth with narrow diameter distribution using annealing-induced size-controlled Au-nanoparticles

Seung-Hwan Lee, Eun-Hye Kwak, and Goo-Hwan Jeong

*Department of Nano Applied Engineering, Kangwon National University, Chuncheon 200-701, Republic of Korea (ghjeong@kangwon.ac.kr)*

Since the electrical, physical and optical properties of single-walled carbon nanotubes (SWNTs) are dependent on their diameter and chirality, a number of researches have been dedicated to control the diameter or chirality so far mainly using a catalytic chemical vapor deposition (CVD) method [1]. As a catalyst for SWNTs synthesis, recent reports demonstrated the wide ranges of nanoparticles including some precious metals and various metal oxide nanoparticles can act as catalysts for SWNTs growth. We have been employed monodispersed Au nanoparticles for SWNTs growth since Au has a low melting temperature so that we could easily control the particle size by thermal evaporation. In addition, we can also expect melting point decrease in a nanoscale environment, which might be helpful for particle size control with relatively low temperature ranges [2].

Here, we demonstrate the formation of Au nanoparticles, size control and their validity in diameter controlled growth of SWNTs. The Au nanoparticles were obtained by high temperature annealing of the electron beam deposited Au thin films on mechanically exfoliated graphenes, SiO2 and ST-cut quartz wafers, respectively. We further performed repetitive thermal annealing to investigate the gradual decrease of particle size and grew SWNTs from them using chemical vapor deposition with methane source. The size of Au nanoparticles linearly decreased with annealing time and the produced SWNTs have very narrow diameter distribution. In the meeting, the size relationship between Au nanoparticles and resultant SWNTs will also be discussed.

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P22

# Large-scale SWCNT synthesis optimized for SWCNT-based highly flexible / highly conductive / highly transparent thin films and devices

Toni Endmann, Esther Roch-Talens, Claudia Richter, Andreas Leson, Oliver Jost

*Fraunhofer IWS Dresden, Germany (oliver.jost@iws.fraunhofer.de)*

Highly flexible / highly conductive / highly transparent (each of them or alltogether) carbon nanotube based thin films and devices are currently considered to be one of the most promising approaches to get carbon nanotube based devices into applications and the market. This is especially true if this can be combined with a kg-scale per week SWCNT synthesis method where the synthesized nanotubes can be tuned to show the desired properties.

The presentation will show some of the basics of nanotube growth control in our large-scale evaporation-based SWCNT synthesis. The formation of both 100% semiconducting SWCNTs and highly metallic SWCNT enriched samples (both at the kg-scale) is shown together with some insights into the reasons and growth mechanisms for this selective growth of metallic or semiconducting tubes. This is followed by outlining approaches controlling the length and bundle thicknesses of the as-synthesized SWCNTs leading to advantageous conditions for the fabrication of highly conductive and transparent SWCNT-based devices at later stages.

After that I will discuss the properties of films and devices fabricated from these property-optimized nanotubes with some emphasis on flexible, transparent and highly conductive films and devices. Transparent thin films still showing the bulk conductivity regime even at 98.5% transparency will be shown. Highly flexible / stretchable conductive nanotube/PDMS composites surviving even 10 million stretching cycles without any degradation of the initial high conductivity are shown.

P23

# String-like assembly of aligned single-wall carbon nanotubes in a single-chiral state

Hideki Kawai[1], Kai Hasegawa[1],Toru Nakatsu[2],Taishi Takenobu[3],Kazuhiro Yanagi[1]

*1 Tokyo Metropolitan University, Japan (yanagi-kazuhiro@tmu.ac.jp)*
*2 Kyoto University, Japan, 3. Waseda University, Japan*

Single-wall carbon nanotubes (SWCNTs) have one-dimensional tube-structures, thus can form their random networks in which the tubes are directed toward various directions, and various kinds of SWCNT devices such as field effect transistors, sensors, and conducting films are demonstrated on such SWCNT random networks. Recent progress of purification techniques enables us to obtain metallic, semiconducting, or single-chiral states of single-wall carbon nanotubes (SWCNTs). Although device performances are improved by using such high-purity samples, transport properties are strongly affected by their random structures due to the scattering at interfaces between the SWCNTs. Therefore, to control alignment of SWCNTs in such networks and to decrease or to align such interfaces is very important to improve device performance.

Here, we report a very simple technique to produce controlled assemblies of SWCNTs in a single-chiral state from solutions that were previously mono-dispersed. To obtain SWCNT aggregates, the ionic repulsion forces of the surfactants, which prohibit SWCNT aggregation, must be reduced. Usually, these ionic repulsion forces are reduced by adding salts and alcohols. However, when we added such reagents rapidly into the solutions, randomly aggregated SWCNTs (algae-like aggregation) were typically formed. In such algae-like aggregates, the SWCNTs were randomly oriented. However, we observed that when we adjusted the solution temperature and incubation time, string-like assemblies with diameters of approximately 10 μm and lengths of greater than 1 mm self-formed. Polarized Raman and scanning electron microscopy measurements clearly indicated that the SWCNTs were aligned. These assemblies exhibited good field effect performances, exhibiting an on/off ratio of $6.8\times10^3$ and a maximum mobility of 106.5 $cm^2 V^{-1}s^{-1}$.

P24

# Performance of carbon nanotubes directly grown on natural cellulose fibers as catalytic supports

Heeyeon Kim, Nam Jo Jeong, Hong Soo Kim, Seong Ok Han

*Korea Institute of Energy Research (KIER), Korea (heeyeon@kier.re.kr)*

Carbonaceous supports of high surface area and porosity were synthesized using natural cellulose fibers such as henequen, kenaf and rice straw for catalytic application. Natural cellulose fibers went through carbonization and specific surface treatment, then carbon nanotubes (CNTs) were directly grown on them for the increase in surface area. In $CO_2$ reforming of $CH_4$, Ni catalysts supported on CNT-grown cellulose supports showed higher catalytic activity and long-term durability compared to conventional $Ni/Al_2O_3$ catalyst, which is caused by high surface area and coke resistance of the former catalyst. Also, alkaline earth metals such as Ca and Mg promote the dispersion of Ni particles and sterically hinder the agglomeration of them. Our $CO_2$ reforming of $CH_4$ reaction was carried out at 700°C for 7 days for long-term durability test. Metal nano particles on carbonized cellulose structures were characterized by X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

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P25

# One-step synthesis of NbC nanowire within inner space of carbon nanotubes by template method

Keita Kobayashi[1], Satoshi Anada[2], Takeshi Nagase[1,2], Takeshi Saito[3,4], Masaharu Kiyomiya[4], Qing Wang[5], Ikuya Wakamori[5], Ryo Kitaura[5], Hisanori Shinohara[5], Hidehiro Yasuda[1]

*1 Research Center for Ultra-High Voltage Electron Microscopy, Osaka University, Japan (kobayashi-z@uhvem.osaka-u.ac.jp)*
*2 Division of Materials and Manufacturing Science, Osaka University, Japan*
*3 Nanotube Research Center, National Institute of Advanced Industrial Science and Technology (AIST), Japan*
*4 Technology Research Association for Single Wall Carbon Nanotubes (TASC), Japan*
*5 Department of Chemistry and Institute for Advanced Research, Nagoya University, Japan*

To increase the density of integrated circuits (ICs) for development of next-generation electric devices, carbon nanotubes (CNTs) encapsulating good conductor nanowire in their inner space is expected as one of the candidates for the alternative materials to a thin metallic wire due to their stability and structure. Moreover, encapsulated superconductor materials in CNTs are particularly desirable, because they should produce high-efficiency ICs. However, fusion or vaporization of guest materials is necessary for encapsulation of the materials into inner space of CNT by the template method. Although the encapsulation of Pb (Tc: 7.2 K) and Sn (Tc: 3.7 K) in CNTs has been reported [1], any super conducting ceramics has not been encapsulated into CNTs by the method due to their higher melting point. Therefore, development of novel method for encapsulating such refractory guest materials into CNTs is required. Based on these backgrounds, we have tried to encapsulate superconductive guest materials with higher melting point to CNT having thinner diameter. Consequently, we developed a simple method for encapsulating niobium carbide (NbC; melting point: ~3000 K; Tc: 10.5 K) in the inner space of CNTs with diameter of 1-3 nm [2]. In this presentation, we will report synthesis method of the NbC-encapsulated CNT and will outline their properties.

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P26

## Direct synthesis of the carbon nanomaterials on copper particles

T.S. Koltsova[1,2], I.V. Anoshkin[2], E.I. Kauppinen[2], O.V. Tolochko[1], A.G. Nasibulin[2]

*1 Material Science Faculty, State Polytechnical University, Polytechnicheskaya, 29, 195251 Saint-Petersburg, Russia (annelet@yandex.ru)*

*2 NanoMaterials Group, Department of Applied Physics, Aalto University School of Science and Technology, P.O. Box 15100 Puumiehenkuja 2, FIN-02150 Espoo, Finland*

In the present work we investigated the growth of carbon nanomaterials (nanofibers and graphene) on the surface of copper nano- and micro particles. The synthesis was carried out by chemical vapor deposition technique. Acetylene and ethylene were examined as carbon sources. Acetylene led to the formation of carbon nanofibers, whereas ethylene resulted in multilayer graphene appeared on the copper. Formation kinetics and mechanism of carbon nanostructures on the surface of copper particles were studied. The influence of hydrogen - carbon ratio in the gas phase on the structure and quantity of carbon product were examined. The structures of the synthesized fibers were analyzed. The mechanical tests of compacted copper - carbon composite materials showed significant increase in the hardness.

P27

## Low temperature synthesis and growth mechanism of single-walled carbon nanotubes from Pt catalysts in the alcohol gas source method

Hiroki Kondo, Naoya Fukuoka, Shigeya Naritsuka, Takahiro Maruyama*

*Department of Materials Science and Engineering, Meijo University, Japan (*takamaru@meijo-u.ac.jp)*

Single-walled carbon nanotubes (SWNTs) have been anticipated for application in a lot of future nanodevices. To fabricate SWNT devices in a conventional LSI process, it is desirable to grow SWNTs at low temperature in a high vacuum. Recently, we reported that, using Pt catalysts in the alcohol gas source method, SWNTs could be grown at 700°C under an ethanol pressure of $10^{-4}$ Pa, while keeping the yield comparable with that grown by conventional Co catalyst at $10^{-1}$ Pa [1]. This indicates that Pt catalysts are suitable for SWNT growth in a high vacuum. However, SWNT growth at low temperature using Pt catalysts has not been investigated sufficiently. In this study, we carried out SWNT growth at various temperatures with Pt catalysts, and demonstrated that SWNTs could be grown below 400°C. In addition, the grown SWNTs were characterized using SEM, TEM and Raman spectroscopy.

SWNT growth was carried out using the alcohol gas source method with Pt catalysts deposited on $SiO_2$/Si substrates [1]. The growth temperature and the ethanol pressure were varied between 350 and 700°C and between $1.0\times10^{-5}$ ~$1.0\times10^{-1}$ Pa, respectively. SEM results showed that the SWNT yield decreased as the growth temperature was reduced. In spite of the yield reduction, both G band and RBM peaks were observed in the Raman spectra even at 400°C, indicating that the growth of SWNTs. In addition, the average SWNT diameter became smaller, as the growth temperature was reduced, and the diameters of most of SWNTs grown at 400°C were below 1 nm. TEM and Raman results indicated that the reduction of catalyst size caused the decrease of SWNT diameter. Based on the relationship between catalyst size and SWNT diameter, we will discuss the growth mechanism of SWNTs from Pt catalysts.

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P28

## Chemical modification of carbon nanoparticles

Wojciech Krasodomski, Wojciech Mazela

*Oil and Gas Institute, Poland (wojciech.krasodomski@inig.pl)*

According to literature data, the addition of carbon nanoparticles to fuels and hydrocarbon oils can improve their properties, i.e. diesel fuel cetane number and octane number of gasoline [1] or tribological properties of greases [2]. The key problem is to obtain stable dispersions of carbon nanoparicles in hydrocarbon matrix.

This presentation exhibits results of research on the structure modification of carbon nanotubes, graphite oxide (GO) and graphene, to obtain organofilic materials, showing a strong affinity for hydrocarbons. Commercially available CNTs was oxidized in nitric acid [3], GO was obtained by modified method described by Hummer [4] from graphite. Oxidized carbon nanotubes and graphite oxide consists of covalently attached oxygen-containing groups such as hydroxyl, epoxy (oxirane), carbonyl and carboxyl groups. The presence of these functional groups makes CNT and GO susceptible to various chemical modifications. Organophilic carbon nanotubes, graphite oxide and graphene nanosheets dispersions were prepared from oxidizing form in two ways. First, directly synthesized in reaction with carboxylic acids, or oxirane derivatives using proper catalyst. Second, by multistep process typically consisting of an activation of oxygen-containing group (for example reaction with thionyl chloride), and next a main reaction with amines, alcohols or even alkoxides. Obtained organophilic carbon nanoparticles were characterized by FTIR spectroscopy and the Zeta Sizer measurement. Some of them were selected for further investigation to evaluate effectiveness of suspending in organic solvents, especially hydrocarbon oils.

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P29

## Study of the lateral growth of carbon deposits on MWNTs via ethylene decomposition.

V.L. Kuznetsov[1,2], D.V. Krasnikov[1,2], M.A. Shuvaeva[1], S.I. Moseenkov[1], A.V. Ischenko[1],
A.I. Romamnenko[2,3], E.N. Tkachev[3], O.B. Anikeeva[3], S. Bokova-Sirosh [4], E.D. Obraztsova

*1 Boreskov Institute of Catalysis SB RAS, Novosibirsk 630090, Russia (kuznet@catalysis.ru)*
*2 Novosibirsk State University, Novosibirsk 630090, Russia*
*3 Nikolaev Institute of Inorganic Chemistry SB RAS, Novosibirsk 630090, Russia*
*4 General Physics Institute RAS, Moscow, Russia*

Catalytic CVD carbon nanotube properties significantly depend on the presence of surface impurities and defects. Amorphous carbon and defective graphene flakes are most common impurities in MWNT surfaces. In this paper we have investigated the kinetics of carbon species deposition on MNWT surface during the ethylene decomposition at 600-750°C. The rate reaction equation was derived. The rate of the reaction is proportional of the nanotube surface area and ethylene pressure (reaction order with respect to ethylene close to 2). The activation energy of carbon deposition is close to that of the interaction of two ethylene molecules resulting in formation of radicals ($C_2H_5$ and $C_2H_3$ ~250 kJ/mol). HR TEM, Raman spectroscopy, XRD, Differential thermal analysis, temperature dependence conductivity and surface area measurements were used to characterize the structure of carbon deposits forming at variable temperatures, ethylene pressure and exposure time. The prolonged exposure of MWNTs in CVD conditions causes the significant changes of nanotube structure surface via the lateral growth of carbon layers. The variation of reaction time allows varying the thickness of deposited defective layers (up to doubling of NT diameter). These data are important for the optimization of operation parameters of catalytic reactors for the production high quality MWNT (especially in fluidized bed). These reaction can also be used for the functionalization of MWNTs.

**P30**

## Self-assembly of single-wall carbon nanotubes by the "coffee-stain effect"

Han Li[1], Friedrich Schöppler[1], Andreas Muzha[2], Tobias Hertel[1,*]

*1 Institute of Physical and Theoretical Chemistry, Department of Chemistry and Pharmacy, Julius-Maximilians University of Würzburg, D-97074 Würzburg, Germany (*tobias.hertel@uni-wuerzburg.de)*
*2 Institute of Organic Chemistry, Department of Chemistry and Pharmacy, Julius-Maximilians University of Würzburg, D-97074 Würzburg, Germany*

Thin films of single-wall carbon nanotubes (SWNTs) are expected to find use in electronic and photonic applications because of their unique electronic and optical properties. One of the primary challenges in making such films is to obtain control over film thickness and morphology over sufficiently large substrate areas. The coffee-stain effect has been recognized as a simple technique to produce various forms of self-assembled structures on solid surfaces [1] and has already been applied to polymer-, protein-, DNA- and nanoparticle- deposition [2]. In this study, we use the coffee-stain effect to fabricate self-assembled and aligned SWNT stripes or films from colloidal SWNT-SDS suspensions. We have identified the working range of surfactant- and SWNT concentrations within which stripe- or film- formation can be expected.

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**P31**

## Synthesis of carbon nanotubes from oil residue

Yongfeng Li and Kai Xu

*State Key Laboratory of Heavy oil Processing, College of Chemical Engineering, China University of Petroleum, Beijing,Changping 102249, China*

The heavy oil residue is a highly aromatic material, as a bottom product after the distillation of petroleum, and such byproduct has great potential as feedstock in making carbon materials because it contains a large amount of carbon-rich molecules. In our work, single-walled carbon nanotubes (SWNTs) were synthesized by a chemical vapor deposition (CVD) method using heavy oil residue as carbon source. Different kinds of metals as catalysts including transition metals (Fe, Co and Ni) and nonmagnetic metals (Au and Pt) are used in the growth of SWNTs. It was found that diameters of the as-grown SWNTs strongly depend on the type of catalysts [1]. Compared with the case of nonmagnetic catalyst, SWNTs synthesized from transition metal catalysts have a narrow diameter distribution.

In addition, our results demonstrate that SWNTs and double- and triple-walled carbon nanotubes (DWNTs and TWNTs) can be controllably synthesized by an arc discharge method using asphalt as carbon source. The morphology and structure of three kinds of products synthesized with Fe as catalyst were characterized by scanning electron microscopy, high-resolution transmission electron microscopy, Raman spectroscopy and energy dispersive X-ray spectroscopy. It was found that different buffer gases strongly affect the number on layers in the synthesized nanotubes [2]. Our findings indicate oil residue is a suitable industrial carbon source for the growth of different type nanotubes.

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P32

# A chirality selective growth of carbon nanotubes via twisted graphene nanoribbons

Hong En Lim[1], Yasumitsu Miyata[1], Ryo Kitaura[1], Yoshifumi Nishimura[1], Yoshio Nishimoto[1], Stephan Irle[1], Jamie H. Warner[2], Hiromichi Kataura[3,4] and Hisanori Shinohara[1]

*1 Department of Chemistry & Institute for Advanced Research, Nagoya University, Nagoya 464-8602, Japan*
*(noris@nagoya-u.jp)*
*2 Department of Materials, University of Oxford, Parks Road, Oxford, OX1 3PH, UK*
*3 Nanosystem Research Institute, National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki 305-8562, Japan*
*4 Japan Science and Technology Agency, CREST, Kawaguchi, Saitama 330-0012, Japan*

CNTs are commonly known as a roll-up graphene sheet which can be cleaved [1] to give strips of different widths, called graphene nanoribbons (GNRs). To date, we have learnt about the different ways by which a CNT can be unwrapped, however, how can these flimsy, strips of carbon be rolled to attain a tubular geometry remains elusive. Not until recently, Kit *et al.* proposed that the CNT can be formed through the twisting of GNR in their theoretical studies [2]. This inspires the study to construct the CNTs via this peculiar means of fabrication.

Herein, we report the first experimental realization of a thermally-induced, self-intertwining of GNRs for the preferential synthesis of CNTs with chiral indices of (7, 2) and (8, 1). The GNRs generated from the PTCDA, a perylene derivative, were transformed into CNTs in the inner space of a host template. Optical measurements performed on the newly grown CNTs revealed a significant enhancement in these two chiralities, matching the predicted chiralites for CNTs formed via the twisting of GNRs with a width of N=5. Our finding adds a radically new aspect to the present understanding of CNT synthesis, shedding much light on the future tuning of not only specific chiral tubes, but also contemporary nanomaterials engineering.

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P33

# Controllable growth of multi-walled carbon nanotubes or amorphous carbon over copper catalysts

Zhi-Yan Zeng, Yung-Chi Lin, Jarrn-Horng Lin

*Department of Materials Science, National University of Tainan, 33, Sec. 2, Shu-Lin St., Tainan 70005, Taiwan*
*(janusjhlin@mail.nutn.edu.tw)*

The controllable growth of amorphous carbon or carbon nanotubes (CNTs) is a promising route to obtain high-purity CNTs. Usually, the growth of CNTs is accompanying with the formation of amorphous carbon. Here, we have developed that the growth of bamboo-like multi-walled carbon nanotubes (CNTs) without the formation of amorphous carbons was performed using copper-based catalysts by catalytic chemical vapor deposition (CVD) with diluted ethylene at 700–900 °C. The as-grown CNT soot was characterized by transmission electron microscopy, thermogravimetric analysis and Raman spectroscopy. The weak metal–support interaction of a sulfate-assisted copper catalyst ($CuSO_4/SiO_2$) can provide high-purity growth with remarkable yields of CNTs (2.24–6.10 CNT/g Cu·h) at 850–900 °C. Additionally, hydrogen-assisted CVD can activate inert copper catalysts, e.g., $Cu(NO_3)_2/SiO_2$ or $Cu(CH_3COO)_2/SiO_2$, for the growth of CNTs.

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P34

# Metal-organic framework (MOF) as tailored precursors for hierarchical nanostructured carbons

Sivakumar Balakrishnan and Mainak Majumder

*Nanoscale Science and Engineering Laboratory (NSEL), Department of Mechanical and Aerospace Engineering, Monash University, Clayton, VIC 3168, Australia (mainak.majumder@monash.edu)*

Metal-organic frameworks are hybrid organic-inorganic materials in which the metal ions or clusters are linked by organic ligands to form materials with ordered porosity and geometrically located metal ions. MOFs have distinct advantages as a precursor to carbon materials in that: (i) the organic component can be selected to have aromatic groups, (ii) the metal ions can not only be chosen, but also distributed periodically, and can catalyse growth of nano-structured carbons, (iii) they possess a hierarchical porosity that is open in all directions which can be templated. Given the large family of MOFs known today and the ability to tailor them during synthesis, MDCs are likely to be actively researched in the immediate future. In the present work [1] we report a novel concept in tailoring the architecture of MOF-derived Carbons by isomorphously doping MOF-5, with catalytic transition metal ions such as $Ni^{2+}$ prior to carbonization. The carbon material demonstrates a 3D mesh of carbon nanofibers, loosely templating the MOF structure but with large electrical conductivity. The nanofibers possess a conical arrangement of graphene sheets as detailed by HRTEM and with excellent electrochemical properties. Given that the MOF can be produced in multigram scales, our approach enables bulk-scale production of carbon nanofibers, reliably without stringent control of process parameter required for Chemical Vapor Deposition route.

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P35

# Magnetic two-dimensional $sp^2$ carbon sheet of fused pentagons

Mina Maruyama and Susumu Okada

*Graduate School of Pure and Applied Sciences, University of Tsukuba, Japan*
*(mmaruyama@comas.frsc, tsukuba.ac.jp)*

Carbon molecules are known to form various polygonal conformations owing to flexibility of its bonding angle and length. These polygons can be a constituent unit for the various molecular patchworks with zero-, one-, two-, and three-dimensions by sewing these polygons. In addition to graphene, it is interested in exploring the possibility of the other two dimensional carbon allotropes consisting of carbon polygons. Among the polygons, pentagon (cyclopentadiene: $C_5$) and dodecagon (cyclododecahexaene: $C_{12}$) can completely cover up a 2 dimensional plane with hexagonal network of fused pentagons (acepentalene) . In this study, we explore the possible geometric structures and electronic properties of the 2D network of sp2 C consisting of fused pentagons (polymerized $C_{14}$) with dodecagon pores by using first-principles calculations based on density functional theory with local spin density approximation.

Our calculations show that the fused pentagon sheet is energetically stable, and the calculated total energy is about 0.6 eV/atom higher than that of graphene. Furthermore, the sheet keeps its sp2 bonding 2D network under the elevated temperature up to 800 K. The sheet is metal with flat dispersion band at the Fermi level leading to the ferromagnetic spin ordering.

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## Octopus and VLS mode growth of single-walled carbon nanotubes by molecular dynamics method

Shigeo Maruyama, Tomoya kawasuzuki, Takuya Noguchi, Kaoru Hisama, Shohei Chiashi

*Department of Mechanical Engineering, The University of Tokyo, Tokyo 113-8656, Japan*
*(maruyama@photon.t.u-tokyo.ac.jp)*

In order to explore the possible chirality-controlled growth process, the growth mechanism of single-walled carbon nanotubes (SWNTs) was studied by molecular dynamics simulations. We have adopted a newly developed Tersoff-type classical potential for carbon and several metal atoms, such as Co, Ni, Pt, Fe and Ti [1]. A genetic algorithm was employed to optimize the potential functions for various solid structures and metal-on-graphene model calculated by DFT. The nucleation and growth of an SWNT from a metal cluster of certain size and at certain temperature and pressure range are observed. Here, we observe two apparently different growth modes of SWNTs. A preferred structure at lower temperature is 'Octopus' mode where several carbon chains are wrapping the metal cluster. The preference of carbon chain structure on metal surface prohibited the transition to hexagonal structure which can lead to the full encapsulation of metal cluster. Because of this chain structure, the solid-state metal cluster can be a stable catalyst. Another structure appeared at higher temperature is 'VLS' mode where carbon atoms are dissolved in liquid metal cluster. The nucleation and growth of SWNTs is dynamics process depending on carbon feeding rate. The diameter of nanotube is similar to the metal cluster size for Octopus mode in contract to the VLS mode where the diameter is determined in the dynamically nucleated cap structure. These 2 modes may correspond to 'tangential' and 'perpendicular' modes observed in TEM [2]. These 2 different growth modes may explain the drastic diameter change observed in vertical aligned CVD growth by adding nitrogen in carbon precursors [3]. Here, we found that reversible and repeatable growth of 1 nm or 2 nm diameter SWNTs from the same catalysts [3].

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P37

## Properties of carbon nanotube/SiC heterojunctions formed by surface decomposition of SiC

Takahiro Maruyama[1,2],Takatoshi Yajima[2], Satoshi Sakakibara[2], Shigeya Naritsuka[2]

*1 Department of Applied Chemistry, Meijo University*
*2 Department of Materials Science and Engineering, Meijo University, Japan*
*(takamaru@meijo-u.ac.jp)*

Carbon nanotubes (CNTs)/semiconductor heterojunctions have been an important subject in nanoelectronics. However, it has been difficult to fabricate CNT/semiconductor heteojunctions, where CNTs and semiconductor surface were directly bonded at the interface, such as conventional semeiconductors. Recently, we have been investigating CNT growth by surface decomposition of SiC [1]. By this method, aligned zigzag-type CNTs with fairly uniform tube diameters can be selectively produced normal to the SiC surface. In addition, carbon atoms of the CNTs are directly bonded to SiC at the interface without any interlayers,indicating the formation of CNT/semiconductor heterojunction at the interface. In this study, we formed CNT/SiC heterojunctions and investigated the crystalline and electronic properties of the interface between CNTs and SiC using TEM and photoemission (PES).

CNT/n-type SiC heterojunctions were formed by surface decomposition of 4H-SiC(000-1). Through heating temperature and heating time, the CNT length could be controlled up to 4 μm. For the sample with CNTs of 180 and 230 nm in thickness, distinct rectifying behavior was observed in the current-voltage measurements. When the CNT length was 1500 nm, the leakage current was increased. From TEM observations, we concluded that the increase of the leakage current was due to the deterioration of crystalline quality of CNTs near the interface. We also carried out PES measurements for CNT/n-type SiC and the band bending at the interface will be discussed.

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**P38**

# Wafer-scale growth of highly vertically aligned carbon nanotubes on CVD-Ni catalyst for very high aspect ratio (A/R > 17) contact fabrication

Takashi Matsumoto, Daisuke Nishide, Munehito Kagaya, Yuichi Yamazaki, Makoto Wada,
Tatsuro Saito, Naoshi Sakuma, Akihiro Kajita, Tadashi Sakai

*3D Nano-Carbon Interconnect Research Group, Low-power Electronics Association and Project (LEAP), Japan*
*(matsumoto@leap.or.jp)*

Carbon nanotube (CNT) and graphene are promising candidates for future semiconductor material because of their special properties, such as ballistic transport and high thermal conductivity. In particular, CNTs are necessary for realization of high aspect ratio (A/R) contact fabrication in next generation 3D memory. We demonstrated very high A/R multi-walled carbon nanotube contact fabrication by integration of the 300 mm (or 200 mm) nano-carbon and metal CVD cluster tools. A key issue for practical application of high A/R CNT contact fabrication is how to form the catalyst on the contact bottom. The metal CVD technique is very useful for thin film formation in such ultra high A/R contact holes. We deposited a nickel catalyst layer (t < 3 nm) in the contact holes and exposed the Ni catalyst to reduction gas to enhance the catalytic ability for CNT synthesis. The CNT growth on high A/R TEG wafer was performed by thermal or plasma CVD with a precursor of $C_2H_4$ or $C_2H_2$ at low temperatures (<500 $^{O}$C). First of all, we analyzed and evaluated the CVD-Ni properties and its catalyst activities by SEM, TEM, XPS, EELS, and Raman scattering spectroscopy. As a result of the analyses, the CVD-Ni catalyst showed a similar surface state, crystal structure, and equivalent catalytic activity to PVD-Ni. The growth direction of CNTs on the CVD-Ni catalyst showed the preferred orientation of <110> is the same as that of the PVD-Ni catalyst. The CNTs grown on the CVD-Ni at 500 $^{O}$C clearly showed highly vertically aligned carbon nanotubes, and they were well filled from the bottom to the top of the contact holes. The CNT density in the contact hole was $2 \times 10^{11}$/cm$^2$, and the CNT diameter was 15-25 nm. Finally, we have achieved very high aspect ratio (L = 1750 nm, A/R > 17) and small diameter (< 100 nm) CNT contact fabrication by integration of the wafer-scale nano-carbon and metal CVD tools. This work was performed as part of the “Ultra Low Voltage Device Project” supported by NEDO and METI of Japan.

**P39**

# Growth of aligned carbon nanotubes on carbon substrates by CVD: role of an oxide sub-layer on CNT growth

Stéphanie Patel[1], Youssef Magga[1], Mathieu Pinault[1], Dominique Porterat[1], Sébastien Joulié[2],
Marc Monthioux[2], Cécile Reynaud[1], Martine Mayne-L’Hermite[1]

*1 Laboratoire Francis Perrin - DSM-IRAMIS-SPAM, CEA Saclay, 91191 Gif-sur-Yvette, France*
*(martine.mayne@cea.fr)*
*2 Carbones et Matériaux Carbonés, Groupe NanoMatériaux, CEMES, UPR A-8011 CNRS, BP 4347, F-31055*
*Toulouse cedex 4, FRANCE*

The properties of composites reinforced by carbon fibres depend not only on the properties of fibres and matrices, but also on the interface between them. Carbon Nanotubes (CNT) are currently being investigated to improve the interfacial adhesion. The innovative approach developed in the present study concerns the integration of aligned CNT directly on carbon fibres in order to improve the composite properties. The synthesis method of aligned CNT on carbon fibres based on Catalytic Chemical Vapour Deposition (CCVD) will be briefly reported. This synthesis process consists in two successive stages: deposition of a thin silica ceramic sub-layer on the carbon substrate surface followed by the growth of aligned CNT from a ferrocene-toluene aerosol mixture [1].

The determination of the chemical and structural characteristics of the interface (carbon substrate – ceramic sub-layer – aligned CNT) is of high importance in order to tailor the CNT characteristics and to control the final properties of the composites. We demonstrate that the length of CNT grown on carbon substrates is controlled by the thickness of the sub-layer and the synthesis duration. The analysis (SEM-EDX, STEM/X-EDS, XPS) of the structure and nature of the interface indicates that (i) an iron silicate phase is formed during the growth of CNT demonstrating that iron is diffusing through the silica sub-layer (ii) the diffusion depth of iron is estimated to be around 100 nm (iii) the silicate phase is ensuring a barrier role for iron diffusion in the carbon substrate.

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P40

## Tunable narrow chirality separations of large-diameter single-walled carbon nanotubes

Kevin S. Mistry[1,2] and Jeffrey L. Blackburn[2]

*1 University of Colorado, Boulder, USA (kevin.mistry@colorado.edu)*
*2 National Renewable Energy Laboratory, USA*

Highly enriched samples of semiconducting single-walled carbon nanotubes (SWCNTs) are sought for many applications such as nanotube FETs, photovoltaic absorber layers, and digital logic. These devices may require especially low metallic impurity levels and further benefit from large-diameter (d > 1.2 nm) nanotubes. One such strategy to produce scalable quantities of semiconducting SWCNTs uses fluorene-based polymers, but has not had much success at selecting large-diameter SWCNTs. Here, we demonstrate the ability to selectively enrich large-diameter semiconducting SWCNTs with no detectable metal SWCNTs at high yield, concentration, and throughput. We further report on the ability to tune the chirality distribution by selecting the appropriate polymer that can select a narrow or wide chiral angle range. In addition, we control the diameter range of the enriched SWCNTs by tuning the synthesis temperature of our laser vaporization SWCNTs. The diameter range can be tuned from ~0.8 nm with lower synthesis temperature to ~1.4 nm with higher synthesis temperatures. Lastly, we find our photoluminescence signatures to be brighter and narrower than comparable aqueous dispersions and can use this technique to probe unique phonon-coupled transitions in isotope-labeled samples.

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## Enhancing electrical conductivity of double-walled carbon nanotube fibers by p-doping with hydrogen peroxide

Aarón Morelos-Gómez,[1] Masatsugu Fujishige,[1] Sofia Magdalena Vega-Díaz,[2] Isamu Ito,[1] Tomoyuki Fukuyo,[3] Rodolfo Cruz-Silva,[2] Ferdinando Tristán-López,[2] Tomohiro Tojyo,[4] Katsuhisa Higashiyama,[4] Kazunori Fujisawa,[4] Kenji Takeuchi,[1] Takuya Hayashi,[4] Yoong Ahm Kim,[4] Mauricio Terrones,[2,5] Morinobu Endo[1,2] and Mildred S. Dresselhaus[6]

*1 Inst. Carbon Sci. Tech., Shinshu University, 4-17-1 Wakasato, Nagano-city 380-8553, Japan (amorelos@shinshu-u.ac.jp)*
*2 Res. Center for Exotic Nanocarbons (JST), Shinshu University, 4-17-1 Wakasato, Nagano-city 380-8553, Japan*
*3 MEFS Co., Ltd., Nagano-shi 380-0921, Japan*
*4 Fac. Eng., Shinshu University, 4-17-1 Wakasato, Nagano-city 380-8553, Japan*
*5 Dept. Phys., Dept. Mater. Sci. Eng. and Mater. Res. Inst., P. S. U., University Park, PA 16802, USA*
*6 Dept. Elec. Eng. Computer Sci. and Dept. Phys., M. I. T., Cambridge, MA 02139-4307, USA*

Double-walled carbon nanotube (DWNT) fibers are of great interest due to their electrical properties and lightweight. We present a detailed analysis to elucidate the mechanism by which hydrogen peroxide ($H_2O_2$) improves the electrical transport of DWNT fibers. These fibers were sonicated in $H_2O_2$ for several hours. We believe that molecular oxygen liberated after the $H_2O_2$ decomposition is physisorbed within intertube voids of the bundles of DWNTs, and resulted in p-doping of the outer nanotubes. Our observations reveal a decrease in the radial breathing mode intensity of the outer semiconducting tube walls, a G'-band shift towards higher frequencies and a smaller magnetoresistance effect. This p-doping caused a metallic behavior of the fiber at temperatures > 100 K. This method is simple, efficient and low cost, thus making it an ideal process to be applied in any laboratory and scaled up.

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# Low temperature growth of dense carbon nanotube arrays on conductive underlayers

Nuri Na[1,2], Yeong-Gi So[3], Yuichi Ikuhara[3], and Suguru Noda[2,4]

*1 Department of Chemical System Engineering, The University of Tokyo, Japan*
*2 Department of Applied Chemistry, Waseda University, Japan (noda@waseda.jp)*
*3 Institute of Engineering Innovation, The University of Tokyo, Japan*
*4 PRESTO, JST, Japan*

Low-temperature, dense growth of CNTs on conductive underlayer is very important for their application to electronic devices such as interconnects in ultra-large scale integrated circuits. Rapid growth of vertically-aligned CNT arrays has been established well [1,2], but at high temperatures (700~800 °C) on insulating underlayer ($AlO_x$, etc.) with a low CNT density (0.03~0.07 g/cm$^3$). There are some recent reports targeting at the interconnect application [3,4] but such growth remains still challenging.

Low process temperature, on the other hand, is beneficial to keep catalyst particles from coarsening on and alloying with the conductive underlayer. Ni particles were formed on the conductive TiN layer on $SiO_2$/Si by sputter deposition at 400 °C. Ni formed particles through nucleation and growth and the particle density as high as ~ $2.8\times10^{12}$ cm$^{-2}$ was realized by stopping the deposition prior to the percolation of the Ni particles. Then, CVD was carried out at 400 °C by feeding $C_2H_2$ at a pressure as low as 1-10 mTorr so as not to kill the catalysts. Resulting CNT films were as dense as 1.1 g cm$^{-3}$, with the number densities of CNTs and their walls as high as $1.5\times10^{12}$ and $1.2\times10^{13}$ cm$^{-2}$, respectively. Detailed microstructure analysis of catalyst particles and CNTs by atomic force microscopy, scanning electron microscopy with energy dispersive X-ray spectroscopy, and transmitting electron microscopy will be presented.

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P43

# The effect of adding N-containing compounds on the floating-catalyst chemical vapor deposition synthesis of single-wall carbon nanotubes.

Shigekazu Ohmori[1], Masaharu Kiyomiya[1], Takayoshi Hirai[1], Yuki Kuwahara[1,2], Takeshi Saito[1,2,*]

*1 Technology Research Association for Single Wall Carbon Nanotubes (TASC), Japan*
*(*takeshi-saito@aist.go.jp)*
*2 National Institute of Advanced Industrial Science and Technology (AIST), Japan*

Recently, it has been reported that the adoption of N(nitrogen atom)-containing compounds results in the production of narrower single-wall carbon nanotubes (SWCNTs) in the substrate-type chemical vapor deposition (CVD) synthesis. [1] Similar narrowing effect was also reported on the floating-catalyst CVD using carbon monoxide as a carbon source. [2] Although the modulation of the catalyst activity by the absorption of nitrogen atoms on the catalyst has been proposed as the origin of the narrowing effect [1], the detailed mechanism is still an open question.

In this work, we have investigated the effect of adding N-containing compounds into the feedstock in the efficient floating-catalyst CVD named the eDIPS method. [3] As a result, the variety in terms of the diameter distribution, yield, and optimum thermal condition in the CVD reaction has been observed according to the molecular structure of N-containing compounds. For example, in the case of using pyrazine as a N-containing compound, slight narrowing effect was observed. On the other hand, it was found that using thiazole instead of thiophene which is commonly used as a promoter in eDIPS method causes broadening of the diameter distribution. These results might contradict the suggested simple mechanism for the effect of N-containing compounds in the CVD production of SWCNTs. This work has been supported by NEDO.

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P44

## Growth of various forms of $sp^2$ hybridized carbon using water assisted chemical vapor deposition

Shashikant P. Patole[1,2,*], Jung-Hun Lee[1], Seul-Gi Kim[2], Ji-Beom Yoo[1,2,*]

*1 SKKU Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan University, Suwon 440746, Republic of Korea (*sppatole@skku.edu and jbyoo@skku.edu)*
*2 School of Advanced Materials Science & Engineering, Sungkyunkwan University, Suwon 440746, Republic of Korea*

In recent years $sp^2$ hybridized carbon structures like fullerene, carbon nanotubes (CNTs) and graphene have attracted a lot of scientific interest due to the useful properties possessed by these structures. Fullerene is an example of 0-dimensional system, CNT is an example of a 1-dimensional system and graphene is an example of 2-dimensional system of $sp^2$ hybridized carbon. As compared to $sp^3$ hybridized carbon which is present in diamond, $sp^2$ carbon shows its own unique properties due to differences in band structure and phonon modes. In this talk, CNT growth and a new form of 3-dimensional structures of $sp^2$ hybridized carbon using water assisted chemical vapor deposition will be discussed. These novel structures consist of a CNT-gaphene hybrid and a few layered graphene which forms a hollow spheres with around 10-60 nm inner diameter and 40 to 120 nm outer diameter. The continuous growth of hollow spheres from the catalyst on the substrate makes a freestanding membrane of hollow spheres. These structures possess unique properties, which are combination of properties of fullerene, graphene and rolled graphene structures like CNTs. It also shows promising applications in various fields including as an anode in the Li-ion batteries.

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## Receipt of nanostructured high-nitrogen steel powders by mechanical alloying

Nikolay Razumov, Anatoliy Popovich

*Saint-Petersburg State Polytechnical University, Russia (n.razumov@onti.spbstu.ru)*

In recent years, the interest of high-nitrogen alloy steels, especially corrosion-resistant ones, is constantly increasing. One major advantage of these steels compared to traditional analogous steels - their high strength. Nowadays there are many methods of obtaining high-nitrogen steels (melting under high nitrogen pressure or argon back pressure, plasma-chemical saturation of the melt, using as raw materials nitrides, nitrogen-rich alloys, etc.), that require the use of sophisticated equipment. Furthermore, high temperatures required for steel melting, almost inevitably produce coarse-grained materials, thus reducing mechanical properties. Austenitic steel grain size cannot be reduced by thermal treatment, hence multiple pressures treatment is requires that ultimately leads to an increasing of the technology cycle duration, the energy consumption and the cost of the material. In this regard, reduction of the high-nitrogen austenitic steels grain size has been studied intensively. Great importance in this task belongs to mechanical alloying technology.

The aim of this work is to study the phase formation and the influence of the mechanical activation atmosphere on the iron mechanical alloying process by austenite elements in the system Fe-Cr-Ni-Mn-N.

High-alloy austenitic powders with super equilibrium nitrogen content and the size of the austenite nanocrystals 30 - 36 nm were obtained as a result of mechanical alloying in an atmosphere of ammonia. It is important to note that using mechanical alloying without thermal treatment allow not only to obtain a certain composition of the alloy powder with nanocrystalline structure, but also to change the lattice (the original bcc lattice of iron into fcc). It should also be noted that hot rolling technology of the austenitic high-alloy powder alloys with super equilibrium nitrogen provides a sheet with preserved nanocrystalline structure, and that microhardness is much higher than the microhardness of a similar steel produced in the conventional way.

## P46

## Low temperature synthesis of magnetic nanoparticles -loaded multiwall carbon nanotubes

Liis Seinberg[1,3], Shinpei Yamamoto[2], Hiroshi Kageyama[1] and Mikio Takano[2]

*1 Graduate School of Engineering, Kyoto University, Japan*
*2 Institute for Integrated Cell-Material Sciences, Japan*
*3 The National Institute of Chemical Physics and Biophysics, Estonia (liis.seinberg@kbfi.ee)*

Reaction temperatures as high as 700 °C are typically necessary in order to produce MWCNTs. Although MWCNT synthesis at 650 °C is reported, this includes multi-staged procedure and external pressure [1]. The additional drawbacks of CVD and arc discharge method are the necessity of an external carbon source or a catalyst feedstock during the synthesis. Highly crystalline MWCNTs loaded with metallic Ni and Fe nanoparticle can be prepared by pyrolyzing nickel stearate or ferrocene under a flow of acetylene, respectively, at 800 - 1100 °C [2,3]. However, the pyrolysis is also suffering from high reaction temperature synthesis drawbacks since the reducing agents necessary to form metallic NPs, i.e., decomposed organic ligands and hydrocarbon feedstock, have poor reducing ability at low temperatures.

We have successfully synthesized multi-wall carbon nanotubes (MWCNTs) loaded with Ni or Fe nanoparticles by pyrolyzing metal organic salts with $CaH_2$. The use of $CaH_2$ enables formation of MWCNTs at temperatures as low as 400 °C, which is about half of the lowest reported temperature in the pyrolysis method and is even 100 °C lower than the lowest reported temperature in the CVD procedure [1]. The developed method also enables synthesis of metal NP-loaded MWCNTs without using any catalyst support or external carbon source. The extraordinary strong reducing ability of $CaH_2$ opens a new path to preparation of MWCNTs with loaded NP, not only Ni and Fe but possibly for Co and their metal alloys. The method is not limited to less-carbon rich metal organic salts.

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## P47

## Optical absorption cross section of individual multiwall carbon nanotubes in the visible region

Muhammad Imran Shahzad, Nadia Shahzad and Alberto Tagliaferro

*Department of Applied Science and Technology (DISAT), Politecnico di Torino, Italy (imran.shahzad@polito.it)*

The remarkable development in the use of carbon nanotubes (CNTs) as filler for polymers makes this field rather promising for various applications [1]. The outstanding properties of CNTs make CNT-Polymer composites appealing alternative materials, such as flexible optical filters and sensors [2]. To properly exploit such possibilities, the understanding of optical properties of CNTs is of tantamount relevance. The aim of the present work is to determine the optical absorption cross section of various types of multiwall CNTs (MWCNTs). This is achieved by preparing Polydimethylsiloxane (PDMS) composites films with four different types of MWCNTs having various diameters (30-50 nm and 6-10 nm) and lengths (10-30 µm and 0.5-2.0 µm). Different percentages (0.0% to 1.5%) of CNTs were mixed in PDMS matrix using high speed mechanical stirring (~1000 rpm) and ultrasonication (~37 kHz) to reach optimal dispersion. By using doctor blade technique, 100 µm thick uniform films were produced on glass. They were then thermally cured and detached from the glass to get flexible and self standing films. The surface morphological study was done by FESEM, which shows that CNTs are well dispersed in the PDMS. Raman spectroscopy and FTIR were employed to investigate the possible structural changes in the polymer composite. The reflection and transmission characteristics (both specular and diffused) were measured for all films. The absorption coefficient which represents the fractional absorption per unit length and is proportional to the concentration of absorbing sites (i.e. CNTs as PDMS is non-absorbing in visible regime) was extracted. The slope of absorption coefficient vs MWCNTs volume density represents the absorption cross section of a single MWCNT. Absorption cross section was found to be related with single MWCNT volume; it varies in the range $7.7 \times 10^{-12}$ cm$^2$ to $1.7 \times 10^{-9}$ cm$^2$ as single MWCNT volumes varies from $6 \times 10^{-17}$ cm$^3$ to $2 \times 10^{-14}$ cm$^3$.

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P48

## SWCNT growth by aerosol method using ethanol with ferrocene and premade metal nanoparticles

Shandakov Sergey, Rybakov Michael, Sevostyanov Oleg, Russakov Dmitrii

*Kemerovo State University, Russia (sergey.shandakov@gmail.com)*

An aerosol CVD synthesis is very attractive method to grow single-walled carbon nanotubes (SWCNTs) as one-step synthesis and SWCNT deposition on various surfaces. In this work we utilize the aerosol CVD method based on the introduction of ethanol-ferrocene aerosol particles produced by an ultrasonic nebulizer [1]. To produce SWCNTs with controlled properties the effects of additives such as premade metal nanoparticles (CuNi, CoFe) and sulfur have been studied. The synthesis products are studied using TEM and Raman spectroscopy.

These investigations show that the SWCNTs with diameter from 0.9 to 1.4 nm are produced. The results obtained by Raman spectroscopy show that an intensity ratio of modes D/G does not exceed 3-4 %, which suggests a small fraction of disordered carbon in the synthesis products. The SWCNT diameter distribution using the RBM and $G^-$- modes are calculated. The results show that a small addition of relatively large metal nanoparticles to ethanol-ferrocene solution leads to a narrower SWCNT diameter distribution. The effect of premade metal nanoparticles on SWCNT growth is discussed.

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P49

## Structural features and electrochemical properties porous carbon deposited on decomposition product of calcium tartrate

E.V. Shlyakhova, E.O Fedorovskaya, A.V. Okotrub, L.G. Bulusheva

*Nikolaev Institute of Inorganic Chemistry SB RAS (shlyakhova@gmail.com)*

Attraction of carbon materials for industry associated with combination unique chemical and physical properties. Both large surface area of carbon and its accessibility are necessary conditions for its electrochemical application.

Our approach consists in the deposition of carbon from gas phase to the surface of well-dissolved oxide produced by thermal decomposition of calcium tartrate. It is expected that introduction of a small amounts of iron ions in the starting compound may affect the structure of the deposited carbon. Inorganic template and residue of transition metal were removed with hydchloric acid. As a result a light black substance was obtained. Characterization of carbon material was done by microscopy and spectroscopy methods. Additionally its specific surface area and pore distribution was investigated. Electrochemical potential of the resulting material is defined. BET surface areas of the resulting materials are in a range of 854-931 m2/g. Mainly the carbon material is mesoporous structure. Pore average size is equal to 10-30 nm. According to the Raman data increasing the number of transition metal atoms up to 0.4 % leads to increasing the value of IG/ID.

Structural features of the carbon material provide a relatively high value of electrochemical capacity up to 300 F/g. It is shown that decreasing of iron concentration result in increasing of electrochemical capacity. Traditionally carbon material use as an electrode material for lithium-ion battery. The resulting material has produced large reversible capacity (about 550 mAh/g) which is higher than the capacities observed from graphite.

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**P50**

## Effect of synthesis temperature on the structure of carbon nanotubes and nanofibers

Simunin Mikhail, Nevolin Vladimir

*National Research University of Electronic Technology, Russia (vkn@miee.ru)*

Today, there are many methods for the synthesis of carbon nanotubes [1]. However, the control and management of the properties of carbon nanotubes is studied area. This report describes the effect of temperature on the synthesis of structural perfection of carbon nanotubes. We investigate carbon nanotubes of the synthesis technology from ethanol without the use of hydrogen as a reducing agent. [2] Synthesis of carbon nanotubes is carried out on the sol-gel nickel catalyst and sputtering palladium catalyst.

Transmission electron microscopy (TEM) images were obtained for carbon nanotubes produced in the temperature range from 550 to 900 °C. By electron diffraction and TEM-images of nanotubes determined the number of defects in the structure of the nanotubes and their degree of amorphization. With increasing temperature, the synthesis of carbon nanotubes on their electron diffraction showing greater reflections from crystal planes of the material. As a result, it has been shown that an increase in the synthesis temperature formed nanotubes with fewer defects and lower degree of amorphization.

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**P51**

## High precision catalyst deposition for location controlled growth of SWCNTs and their integration into field effect transistors

Massimo Spina, Axel Fanget, Jaćim Jaćimović, Primož Rebernik Ribič, László Forró, Arnaud Magrez

*Institute of Condensed Matter Physics, Ecole Polytechnique Fédérale de Lausanne, Switzerland (massimo.spina@epfl.ch)*

Single-walled carbon nanotubes (SWCNTs) are promising candidates to overcome some of silicon technology limits [1]. However, the existing synthesis processes remains restricted to the prototype level because of their lack of control of their electrical properties as well as the poor control of their spatial positioning on the device. Especially for FETs, SWCNTs need to be synthesized with a high degree of control with respect to their alignment and diameter in order to provide arrays of devices with reproducible characteristics [2]. Direct SWCNTs synthesis methods by Chemical Vapor Deposition are best in terms of fabrication output and process fabrication reproducibility. However, it requires precise catalyst positioning and accurate particle size control. We have developed a method based on e-beam lithography (EBL) to precisely deposit one single catalyst particle with controlled size. Briefly, a high resolution negative tone resist doped with Co is patterned by EBL. After Co is segregated from the resist at 800°C, the amorphous carbon residues are etched by soft oxidation. The process results of individual particles with a diameter of 1.5±0.2nm localized within an area of 300nm$^2$, corresponding to the initial patterned surface of resist. From those nanoparticles, high-quality SWCNTs with a diameter of 1.4±0.2nm are grown by CVD from Ethanol. Bottom-gated Field effect transistors with high on/off ratios ($10^4$-$10^5$), low off-currents and high mobility (up to 75000 cm$^2$V$^{-1}$s$^{-1}$) confirm the high quality of the SWCNTs grown and their potential role as substitute of silicon in the next MOSFET technologies.

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## Solution growth of carbon-nanotube wires

P52

Yuki Takagi[1], Yugo Oshima[2], Kazuhiro Yanagi[3], and Taishi Takenobu[1]

*1 Department of Applied Physics, Waseda University, Tokyo 169-8555, Japan (akenobu@waseda.jp)*
*2 RIKEN, Wako 351-0198, Japan*
*3 Department of Physics, Tokyo Metropolitan University, Hachioji 192-0397, Japan*

Carbon nanotube (CNT) is known as excellent material which has nano-scale one dimensional structure and great transport properties. In particular, macro-scale thin-film devices consisting of networks of CNTs are of interest due to their applicability to flexible and printed electronics. In networks of CNTs, junctions between CNTs prevent the efficient charge transport and their reduction by making aligned CNT films or wires is crucially important for macro-scale CNT applications. Therefore, it is strongly required to establish fabrication method of such wire-like CNT thin films. Very recently, solution based crystallization method for one of nano-carbon materials, C60, has been developed [1]. Here, we applied this method to another nano-carbon material, CNT, and tried to grow the high-density CNT aggregations.

CNTs were dispersed in N-methylpyrrolidone and the dispersion was dropped on substrate. Small hydrophilic substrate was put on large hydrophobic substrate to pin the droplet. Then, CNT wires were self-assembly fabricated. We used small piece of Si substrate as hydrophilic pining center and Si substrate modified with self-assembled monolayers (SAMs) as hydrophobic substrate. Because substrate surface energy and drying rate are important for growth of CNT wire, we optimized condition of fabrication process by preparing some types of SAMs and changing the drying condition. As a result, we satisfied fabricating macro-scale wire-like CNT thin films. In summary, we performed fabrication of wire-like CNT thin films via solution based growing method. This result enables us to fabricate separated and purified CNT wire which is expected to be used for physical properties research and high performance thin film device.

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## High-throughput separation of metallic and semiconducting single-wall carbon nanotubes; improvement in preparation of SWCNTs dispersion

P53

Takeshi Tanaka[1,2], Satoshi Asano[2], Mariko Kubota[2], Kaori Makino[2], Shunjiro Fujii[1,2],
Hiromichi Kataura[1,2]

*1 Nanosystem Research Institute, National institute of Advanced Industrial Science and Technology (AIST), Japan (tanaka-t@aist.go.jp)*
*2 Technology Research Association for Single Wall Carbon Nanotubes (TASC), Japan*

For the electrical application of single-wall carbon nanotubes (SWCNTs), separation between metallic (M) and semiconducting (S) SWCNTs is required. We developed M/S separation method using agarose gel [1], which allowed the low-cost and high-throughput separation using pilot-scale chromatography; however, the step of preparation for SWCNT dispersion restricted the throughput of the M/S separation. Here we report the improvement of the preparation of SWCNT dispersion. The processes of dispersion by sonication and purification by ultracentrifugation restricted the throughput, so we changed the dispersion method from sonication to Nanomizer treatment and used continuous ultracentrifugation for the purification. We also scaled up the column size to 8.5 liter and finally achieved 2 g/day production of separated SWCNTs through the whole process including dispersion, purification and separation. The result of thin film transistor using separated S-SWCNTs will be presented.

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P54

# Growth of single-walled carbon nanotubes with controlled diameters and lengths by an aerosol method

Ying Tian, Marina Y. Timmermans, Matti Partanen, Albert G. Nasibulin, Hua Jiang, Zhen Zhu, Esko I. Kauppinen

*NanoMaterials Group, Department of Applied Physics and Center for New Materials, Aalto University, Puumiehenkuja 2, 00076 AALTO, Finland (ying.tian@aalto.fi)*

Single-walled carbon nanotubes (SWCNTs) with desirable diameter are required for various applications particularly in electronics and photonics, since the diameter is an essential characteristic to determine their electronic and optical properties. In this work, we demonstrate an effective and simple approach for diameter-controlled growth of SWCNTs in an aerosol chemical vapor deposition (CVD) reactor based on ferrocene vapour decomposition in an atmosphere of CO [1]. The wide range modulation of SWCNT diameters from 1.1 to 1.9 nm gives possibility to effectively adjust the properties of SWCNTs to meet the needs for specific applications.

A detailed investigation of SWCNT products and related growth mechanism is presented as a function of the synthesis reactor temperature, water-cooled probe position and addition of a small amount of $CO_2$ during growth on the basis of combined analyses of transmission electron microscopy (TEM), scanning electron microscopy (SEM), Raman and ultraviolet-visible-near infrared (UV-Vis-NIR) absorption spectroscopy. The results show that increasing the temperature gives rise to the formation of high quality and large diameter SWCNTs. By monitoring the water-cooled probe position, both the bundle length and the diameter of the SWCNTs are effectively tuned due to the variation of the residence time and temperature profile in the reactor. An introduction of a small amount of $CO_2$ suppresses the growth of small diameter nanotubes and enlarges the mean diameter of SWCNT samples.

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P55

# Manipulation of Ni catalyst particle size, shape and areal density on TiN support layer for growth of vertical aligned CNTs

Jana Tittmann[1], Sascha Hermann[1], Holger Fiedler[1], Stefan S. Schulz[1,2], Thomas Gessner[1,2]

*1 Chemnitz University of Technology, Center for Microtechnologies, 09126 Chemnitz, Germany*
*(jana.tittmann@zfm.tu-chemnitz.de)*
*2 Fraunhofer Institute for Electronic Nano Systems (ENAS), 09126 Chemnitz, Germany*

Due to their promising electronic properties, vertical grown carbon nanotubes (CNTs) can be applied as vertical interconnects in integrated circuits. The main reason against the replacement of copper by CNTs in this technology is the still too low areal density. Consequently, the electrical resistance of CNT-Vias is larger than that of copper interconnects.

Here we show investigations of vertical CNTs grown on TiN/ Ni layers. This system is not only known to give a small contact resistance between metallization and CNTs but also to produce CNTs with high quality. Based on AFM measurements, changes in catalyst particle height and shape as well as in their areal density are determined. REM and Raman measurements demonstrate the dependence of the CNT length and quality on the thickness of both layers. To further increase the number of catalyst particles per area, an approach similar to [1] is tested. In this procedure a second catalyst layer is deposited on top of the already formed first catalyst particles. In contrast to Esconjauregui's combination of $Al_2O_3$ with Fe, Co and Ni, we use TiN and Ni to check the general validity of this approach for different systems. Besides that, we apply the approach for growth of multi- instead of single-walled nanotubes. We find that this leads to increase in the particle density by up to 600 %. But depending on the starting configuration of the system, shrinking to less than 50 % is also possible. By combining observations from several states of sample preparation, we draw the conclusion, that the first catalyst layer and the particles formed by it have a drastic impact on the final appearance and therefore on the final areal particle density.

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P56

## Synthesis of large diameter collapsed carbon nanotubes from chemical vapor deposition

Neenu Varghese[1], Andrej Znidarsic[2], Maoshuai He[1], Albert Nasibulin[1], Hua Jiang[1],
Abdou Hassanien[2], Esko Kauppinen[1,*]

*1 Aalto University, Espoo, Finland (*esko.kauppinen@aalto.fi)*
*2 National Institute of Chemistry, Slovenia*

Carbon nanotubes are cylindrical one dimensional nanostructures. However, when the diameter increases, cylindrical carbon nanotubes become energetically unstable and they tend to collapse forming flattened carbon nanotubes or nanoribbons [1, 2]. Nanotube collapsing causes band gap modification and the collapsed tubes exhibit electronic, mechanical and electromechanical properties different from that of non-collapsed tubes [3].

Large diameter singled and double walled carbon nanotubes (SWCNTs and DWCNTs) of 3-8nm in diameter have been synthesized employing chemical vapor deposition technique using iron as catalyst particles. Fe nanoparticles prepared by microwave reduction [4] was deposited on $Si/SiO_2$ substrate for the carbon nanotube growth. Transmission electron microscopy (TEM) and atomic force microscopy (AFM) provide evidence for the collapsed carbon nanotubes. Kinked, folded and twisted carbon nanotubes were observed in TEM suggesting that the nanotubes are flattened due to its large diameter. Raman spectra were measured on individual large diameter carbon nanotubes. Conductive AFM measurements on these nanotubes were carried out to study the electrical properties of the collapsed tubes and they were found to exhibit rectifying behavior.

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P57

## Improving the areal density of horizontal aligned ultralong carbon nanotubes by coarse substrates

Huanhuan Xie[1,2], Rufan Zhang[2], Yingying Zhang[1], Fei Wei[1,2]

*1 Center for Nano and Micro Mechanics, Tsinghua University, Beijing, China (yingyingzhang@mail.tsihghua.edu.cn)*
*2 Beijing Key Laboratory of Green Chemical Reaction Engineering and Technology, Tsinghua University, Beijing, China (wf-dce@tsinghua.edu.cn)*

Ultralong horizontally aligned carbon nanotubes (HA-CNTs) grown by chemical vapor deposition (CVD) have attracted extensive attention due to their relatively low defects and excellent properties. For the application of ultralong HA-CNTs, it is important to develop effective methods to grow HACNTs with high density, which is tightly connected with the quantity of active catalysts with optimized sizes, whereas catalyst nanoparticles on the smooth surface of silicon substrate tend to agglomerate into larger ones at high temperature [1]. Therefore, we proposed two methods to improve the areal density by using coarse substrates to reduce the catalyst sintering. First, coarse substrates were obtained by coating a layer of silica nanospheres on their surface [2]. Catalyst nanoparticles can be held on the surface of silica nanospheres or around silica nanospheres to keep small size which are suitable for the catalytic growth of ultralong CNTs. The areal density of ultralong HA-CNTs was improved by a factor of more than two. Second, graphene/graphite sheets (GP sheets) grown by CVD on copper foil was used to load catalysts to grow CNTs. It worth noting that metal nanoparticles resulted from the transferring process of GP sheets would act as catalysts for the growth of CNTs. The wrinkles on the GP sheets stuck the catalyst nanoparticles and blocked the agglomeration of catalyst nanoparticles. As a result, high areal density ultralong HA-CNTs arrays were grown out of GP sheets.

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**P58**

# High yield synthesis of narrow-chirality distributed single-walled carbon nanotubes

Bin Xu, Toshiaki Kato*, Koshi Murakoshi, Toshiro Kaneko

*Department of Electronic Engineering, Tohoku University, Sendai 980-8579, Japan (*kato12@ecei.tohoku.ac.jp)*

One dimensional single-walled carbon nanotubes (SWNTs) are potential materials for future nanoelectronics. Since the electronic and optical properties of SWNTs strongly depend on their diameter and chirality, the selective synthesis of SWNTs with desired chiralities is one of the major challenges in nanotube science and applications. Recently, we have demonstrated a narrow-chirality distributed growth of SWNTs by time-programmed plasma CVD [1]. In this method, we used very short time growth of SWNTs. Based on the systematic investigations, it has been revealed that there is a close correlation between incubation time ($t_i$) and SWNT structures. Since $t_i$ of the small diameter (or specific chirality) SWNTs is shorter than that of the larger (or other chiralities) ones, selective growth of narrow-chirality distributed SWNTs has been realized by adjusting the growth time during plasma CVD. Due to the short growth time, however, only small amount of narrow-chirality distributed SWNTs can be grown with this method.

In this study, we have improved previous time-programmed plasma CVD and established a new strategy to realize the mass production of narrow-chirality distributed SWNTs using pulse plasma CVD. When we carry out the pulse plasma CVD for SWNTs growth, it is found that the amount of SWNTs increases with an increase in the total growth time. Interestingly, it is also revealed that the initial narrow-diameter distribution of SWNTs can be maintained even after the long time pulse plasma CVD. We think this is because that only small diameter or specific chirality SWNTs can be grown during each pulse of plasma CVD due to their very short $t_i$. These results indicate that it should be possible to realize the mass production of narrow-chirality distributed SWNTs with our established novel approach.

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**P59**

# Conductivity-controlled growth of single-walled carbon nanotubes

Xiaojun Qin, Feng Yang, Fei Peng, Yu Liu, and Yan Li*

*Beijing National Laboratory for Molecular Science, Key Laboratory for the Physics and Chemistry of Nanodevices, State Key Laboratory of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China (yanli@pku.edu.cn)*

Single-walled carbon nanotubes (SWNTs) can be either metallic or semiconducting depending on their structures. The unique property makes SWNTs superior candidate materials for future nanoelectronics. However, the selective preparation of SWNTs has long been a big challenge in the area. The structure and property similarity of semiconducting and metallic tubes makes it very difficult to obtain SWNTs of identical structure even uniform conductivity. It is found from the band structure that metallic tubes have higher tendency to be oxidized. Therefore we developed a strategy to provide oxidizing environments by using certain catalyst supports during the chemical vapor deposition processes and directly grew semiconducting SWNTs. Nitrogen doping can remarkably increase the metallic property of SWNTs. Therefore, semiconducting and metallic SWNTs were acquired respectively.

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P60

# Synthesis of nitrogen-doped graphene with controlled nitrogen bonding configuration for oxygen reduction reaction

Satoshi Yasuda[1,2], Li Yu[1], Kei Murakoshi[1]

*1 Department of Chemistry, Hokkaido University, Japan (satoshi-yasuda@sci.hokudai.ac.jp)*
*2 JST-PRESTO, Japan*

Nitrogen-doped graphene exhibit oxygen reduction reaction (ORR) catalytic activity and consequently have attracted attention to the metal free cathode catalyst for fuel cells [1]. In general, there are three nitrogen bonding configurations within graphene, which are quaternary, pyridinic and pyrrolic nitrogen bonding configurations, and they are responsible for the ORR catalytic activities. However, it is still unclear which the configurations play important role in the actual activity for promoting ORR. To clarify the issue, development of selective synthesis technique of each nitrogen configuration in the graphene becomes a great challenge. In this study, we developed low temperature CVD synthesis based on surface polymerization of nitrogenous aromatic molecules as precursors, resulting in possibility of selective nitrogen configuration synthesis reflected on the molecular structure. Low temperature CVD was employed below 500 °C to inhibit thermal decomposition of the feedstock molecule and polymerize them. As feedstock molecules, we used two kinds of nitrogenous aromatic molecules which are pyridine and julolidine molecules. The thermal polymerizations of each molecule are expected to allow selective synthesis of pyridinic and quaternary nitrogen configurations in graphene, respectively. Raman spectra for both samples made from pyridine and julolidine showed distinguishable D- and G-bands, indicating graphitic carbon formation. XPS analysis revealed that each pyridine and julolidine-made nitrogen doped graphene mainly contain the pyridinic and quaternary nitrogen configuration as expected. These results showed that the surface polymerization technique has potential to synthesize nitrogen-doped graphene contained desired nitrogen configuration in the graphene. Rotating disk electrode voltammetry in oxygen saturated 0.1 M KOH solution was also performed for each sample and revealed that the pyridinic type is attributed to be the 4 electron reduction of ORR, while the quaternary type is 2 electron, indicating that the pyridinic type is effective promoter for ORR activity of graphene.

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P61

# Carbon nanotube films directly drawn from CVD system and their applications

Yongyi Zhang, Peng Gao, Geng Xu, Qingwen Li

*Division of Advanced Materials, Suzhou Institute of Nano-Tech & Nano-Bionics, Chinese Academy of Science, Suzhou 215123, PR China (yyzhang2011@sinano.ac.cn)*

Transparent carbon nanotube films was directly drawn out of CVD system and assembled into fibers and macro films (cloth). Compared with the other methods, it is much easier to obtain continuous CNT fibers and bulk CNT cloth in large area which is critical in many potential applications such as EMI, thermal management, and so on. In the poster, we will demonstrate the results for the continuous fabrication of CNT fibers and cloths by floating catalytic CVD system aiming at real application. The applications in light wires, EMI materials were also studied as well.

## P65

## Simple spectrometric determination of iron and aluminum contents in carbon nanotubes

Elsye Agustina, Jeung Choon Goak, Changjin Lim, and Naesung Lee*

*Faculty of Nanotechnology and Advanced Materials Engineering, Sejong University,*
*Seoul, South Korea (*nslee@sejong.ac.kr)*

In order to bring the excellence material carbon nanotubes (CNTs) to application level, the mass production is carried with involving combination of iron (Fe) catalysts on alumina support as the industrial requisition. However, the presence of these metal catalysts has been a barrier in areas requiring high-purity CNTs, such as lithium batteries [1] or semiconductor nanocomposites for high-voltage power cables [2]. Metallic ion species can deteriorate their electrochemical performances and cause breakdown in cable. Therefore, many synthetic techniques or purification processes have been developed to improve the purity of CNTs, which requires analytical tools or methods to measure extremely low concentration of metallic impurities remaining in CNTs. This study developed facile method to determine the amounts of Fe catalyst and alumina support by utilize the easily available UV-visible spectroscopy. Fe and Al were extracted by refluxing CNTs in an acidic solution with of temperature, reflux time, and solvent optimization. By TEM, metallic particles were observed to be encased in graphitic layers which potentially prevent the extraction. Therefore, ash residue was obtained by burning CNTs up to 900$^0$C and extracted with reflux. Fe and Al ions in the solution are able to form complex with 1,10-phenanthroline and Eriochrome Cyanine R produce red-color and pink-color, respectively, whose intensities are proportional to the concentration of each element in the solution. Series of standard solutions were designed to build the calibration equation. The effects of coexisting Fe and Al in CNTs on quantitative analysis were also elucidated by using the solutions of pre-determined compositions. Our facile quantitative analysis method of Fe and Al in CNTs by using UV-Vis spectroscopy has been validated by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

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## P66

## Electronic transport in multiwalled carbon nanotubes

Davie Mtsuko[1], A. Koshio[2], M. Yudasaka[2], S. Iijima[2], Markus Ahlskog[1,*]

*1 Department of Physics, P.O.B. 35, FIN-40014, University of Jyväskylä, Finland (ahlskog@jyu.fi)*
*2 NEC Research Center, Tsukuba, Japan*

We have measured the low temperature transport properties of single multiwalled carbon nanotubes (MWNT) of diameters (D) in the range 2-17 nm. Almost all previous work on MWNT's has been on tubes with diameters above 10 nm. In nearly all samples in this work, with $D < 10$ nm, the gate dependent conductance exhibits a gap whose size increases with the inverse tube diameter and increasing electrode separation. This so called transport gap is attributed, based on the experimental findings, on a combination of localization effects and narrow diameter induced gaps in the electronic band structure.

These results have significant similarities to the current research on graphene nanoribbons (GRN). As graphene does not intrinsically possess a bandgap, GNR's are fabricated, where a gap is created via quantum confinement due to the narrow width of the channel/nanoribbon. The size of the gap is then roughly in a similar inverse relation with the width of the constriction as in the case of the diameter dependence of the MWNT's in our work.

The transport gap has not generally been observed in the previous works on MWNT's because of the large diameters of the tubes in these. Our work, of which some early results were published previously [1], complements and bridges previous works on both single walled nanotubes and MWNT's, and also to the field of GNR's.

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## In-Sight project: In-line characterization of nanoparticles using a combination of analytical techniques in real time

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Julien Amadou[1], Mariëlle Wouters[2]

1 Nanocyl SA, R&D Department, Belgium (julien.amadou@nanocyl.com)
2 TNO, the Netherlands (marielle.wouters@tno.nl)

In-Sight is an SME-driven project aimed to achieve real-time characterization of nanoparticles (NP) during nanomaterial (NM) manufacturing. InSight is developing new tools as well as optimizing available techniques that are capable of real time NP measurements in order to provide valuable information for the nanoparticle user.

The In-Sight developed tools will enable monitoring real-time (including unexpected) changes in particles size, number and dimensions during particle processing. The outcome of the project will contribute to minimize batch failure, improved yield, troubleshooting scale-up. In addition, the in-line measurements will enable 'quality by design' throughout development of new products. In the first 18M, it has been shown that sample handling and measurement protocol are of extreme importance and require proper communication from producer to user.For further information, please visit www.fp7-insight.com

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## Nematic liquid crystals of carbon nanotubes and graphene

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C. Zamora-Ledezma[1,2], N. Puech[3], C. Blanc[4], C. Zakri[3], P. Poulin[3], E. Anglaret[4]

1 Centro de Física, IVIC, Altos de Pipe, AP 21827, 1204 Caracas, Venezuela
2 Centro de Investigaciones de Astronomia Francisco J. Duarte, 5101 Merida, Venezuela
3 Centre de Recherche Paul Pascal, CNRS and Univ. Bordeaux, 33600 Pessac, France
4 Laboratoire Charles Coulomb, Univ. Montpellier 2 and CNRS, 34095 Montpellier, France

Liquid crystal ordering is an opportunity to develop novel materials and applications with spontaneously aligned nanotubes or graphene particles. On the other hand, the organization of nanocarbons as liquid crystals provides new methodologies for the still challenging structural characterization of such materials.

In this talk, we will present a review of our recent results in the preparation and characterization of lyotropic LC made from concentrated aqueous suspensions, stabilized by surfactants, of single-walled carbon nanotubes (SWNT) or reduced graphene oxide (RGO) [1-5]. Homogeneously oriented SWNT LC can be prepared by shearing a drop between two glass plates [1]. The order parameter of SWNT LC was found to be very sensitive to waviness and entanglement of the nanotubes and the best orientational order was achieved after disentangling, shortening and sorting the nanotubes using ultrasonication and ultracentrifugation [2]. Anisotropic conductive films of nanotubes can be prepared by drying the LC. The anisotropy of conductivity of the anisotropic layers can be related to the order parameter through a simple analytical model assuming that the electrical resistance in a percolation path is proportional to the number of contacts [3].

Homogeneous orientation of RGO LC was achieved by centrifugating capillaries. Structural and thermodynamic characterizations provide statistical information on the dimensions of the graphene flakes, which are found to be comparable with those of neat graphene oxide flakes [4,5].

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**P69**

## Photocurrent generation in carbon nanotubes

Maria Barkelid, Val Zwiller

*Kavli Institute of Nanoscience, Delft University of Technology, The Netherlands (k.m.barkelid@tudelft.nl)*

The fundamental mechanism behind photocurrent generation in carbon nanotubes has for long been an open question. Initial studies suggested the photovoltaic effect, while more recent work has suggested a photothermal effect. Recent theoretical [1] as well as experimental [2] studies have established a fingerprint measurement for distinguishing between the photothermal and photovoltaic effect in graphene. It attributs multiple sign changes in the photocurrent as a function of gate voltage to the photothermoelectric effect, while a single sign change is indicative of the photovoltaic effect.

Here, we study metallic and semiconducting carbon nanotube p-n junction devices. The nanotube devices have an electrostatically defined p-n junction allowing investigation of the photocurrent as a function of charge carrier concentration. Measurements separately performed on metallic and semiconducting carbon nanotubes show that the photocurrent generation mechanism differs between the two nanotube species [3]. The metallic nanotubes demonstrate an evident six-fold pattern with multiple sign changes in the photocurrent response, a clear indication of the photothermal effect. In contrast, the semiconducting nanotubes display proof of the photovoltaic effect with a two-fold pattern and only a single sign-change of the photocurrent. This behavior have been confirmed on a total of three metallic and five semiconducting nanotube devices. Our results provide an understanding the physical processes which govern the photoresponse in carbon nanotubes, which is not only of fundamental interest, but also of importance for designing photodetectors and energy harvesting based on carbon nanotubes.

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## Humidity sensitivity of thin films based on dispersed multi-walled carbon nanotubes

A. Benchirouf[1], A. Jalil[1], G. Ovidiu[2], C. Müller[1], A. Al-Hamry[1], O. Kanoun[1], D. Zahn[2]

*1 Technische Universität Chemnitz, Measurement and Sensor Technology, Chemnitz, Germany*
*2 Technische Universität Chemnitz, Semiconductor Physics, Chemnitz, Germany*

The properties of thin films based multi-walled carbon nanotube (MWNT) dispersed in different surfactant types (anionic, nonionic) when exposed to humid environment in various temperatures were investigated systematically. The MWNTs dispersed in three different kinds of surfactants (sodium dodecylbenzene sulfonate (SDBS), sodium dodecylsulfate (SDS), and Triton X-100) were deposited on flexible polymer substrates (Polyethylene terephthalate - PET) through layer by layer drop casting deposition method to ensure high film homogeneity. The dispersion quality was characterized using Raman spectroscopy, in order to determine the relation between the dispersion quality and the sensitivity to humidity. The prepared probes were later exposed to humidity change at various temperatures. The I-V characteristics and the hysteresis of the MWNT-films are strongly depend on the amount of water, which gives the possibility to use MWNT thin film as humidity sensors. In the range of 10%–90% relative humidity (RH), the resistances of the MWNT films increase from 20%-30% and 103-278%, respectively, depending on the surfactant type and the concentration of CNTs and/or surfactant in the dispersion.

In particular, the MWCNT dispersed in anionic aromatic surfactants, such as SDBS, exhibit high sensitivity to humidity and good electrical properties at room temperature. Generally, the electrical measurements demonstrate that thin films based on MWCNTs have potential for humidity sensing applications.

## High-resolution TEM study on carbon nanotubes grown from permalloy nanoparticles

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A. Bonatto Minella[1,2], D. Pohl[1,2], C. Täschner[1], M. H. Rümmeli[1], R. Erni[3], L. Schultz[1,2], B. Rellinghaus[1]

*1 IFW Dresden, D-01069 Dresden, Germany (a.kiessling@ifw-dresden.de)*
*2 TU Dresden, Department of Solid State Physics, D-01062 Dresden, Germany*
*3 Empa, CH-8600 Dübendorf, Switzerland*

Carbon Nanotubes (CNT) were grown from $Fe_{20}Ni_{80}$ ("permalloy") nanoparticles on $Si/SiO_2$ substrates via plasma-enhanced chemical vapour deposition (PE-CVD) to study the internal interfaces of the as-grown CNT. For their characterization, aberration-corrected high resolution transmission electron microscopy (HRTEM) was carried out at a FEI TITAN$^3$ 80-300 operating at 80kV to reduce knock-on damages.

By growing carbon nanotubes (CNT) from permalloy catalyst nanoparticles two different types of CNT were formed: (i) SiC filled CNT and (ii) hollow, Si free CNT. The main role seems to play the hydrogen flow during the growth process since a high hydrogen flow leads to a strong etching of the Si substrate. The Si free CNT are interesting for the understanding of the CNT growth mechanism from catalyst nanoparticles. A recent work on FePt terminated CNT has revealed an energetically favoured facet for the release of carbon [1]. A similar behaviour is predicted from MD simulations for the CNT grown from permalloy nanoparticles. Preliminary results are in accord with this prediction. On the other hand, by changing the growth parameters we were able to produce CNT filled with SiC nanowires. These CNT exhibit a strongly distorted lattice. A model is proposed to explain the growth mechanism of these SiC filled CNT.

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## Controlling the chemical forms of nitrogen in multiwall carbon nanotubes with change of aerosol composition

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Lyubov G. Bulusheva[1], Yulia V. Fedoseeva[1], Alexander V. Okotrub[1], Antal A. Koós[2], Nicole Grobert[2]

*1 Nikolaev Institute of Inorganic Chemistry, SB RAS, 630090, Novosibirsk, Russia (bul@niic.nsc.ru)*
*2 Department of Materials, University of Oxford, Oxford OX1 3PH, UK*

Arrays of nitrogen-doped multiwall carbon nanotubes (MWCNTs) have been vertically grown on silicon substrates using an aerosol-assistant catalytic chemical vapour deposition (CCVD) method. To check the possibility controlling the chemical state of nitrogen in MWCNTs we changed the composition of the reaction mixture. Acetonitrile or benzylamine was taken as a nitrogen source, while ferrocene served as a catalyst source. We also replaced a portion of nitrogen-containing solvent by toluene which preserving the other CCVD parameters (temperature, ferrocene concentration, synthesis duration, gas flow) are constant. Electronic structure of the N-MWCNTs was studied using X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy. The first spectroscopy is surface-sensitive, and the second one probes the depth of nanotubes. We find that at low concentration of nitrogen-containing precursor in the reaction mixture the benzylamine promotes formation of graphitic-like nitrogen (direct substitution for carbon atom in nanotube walls), while both graphitic nitrogen and pyridinic-like (location of nitrogen at vacancy) nitrogen atoms are formed with the use of acetonitrile. From comparision of the XPS spectra measured with different excitation energy and NEXAFS data acquired at Auger and total-yield electrons we also discuss the distribution different forms of nitrogen (graphitic, pyridinic, and molecular) from the nanotube surface to the nanotube cavity depending on the aerosol composition.

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# Giant optical nonlinearity from carbon nanotubes filled with 1D arrays of dipolar molecules

J. Campo, S. Cambré, C. Beirnaert, C. C. Verlackt, W. Wenseleers

*University of Antwerp, Physics Department, Universiteitsplein 1, 2610 Antwerp (Belgium)*

Dipolar push-pull molecules, comprising a highly polarisable π-conjugated backbone with an electron donor and acceptor group attached to opposite ends, have been encapsulated inside single-wall carbon nanotubes (SWCNTs) to achieve a high 2nd order non-linear optical (NLO) response. A high molecular 2nd order NLO response (first hyperpolarisability β) is commonly achieved in polarisable and asymmetric molecules, but a macroscopic 2nd order NLO response also requires a noncentrosymmetric supramolecular arrangement. [1] In 3D bulk systems, dipolar molecules tend to align in a pair-wise anti-parallel way, thus cancelling each other's NLO response. Polar alignment is traditionally achieved by electric field poling of the dipolar molecules in a polymer matrix, followed by cooling below the glass transition temperature of the polymer to 'freeze' the molecular orientation. In contrast, for a 1D array of molecules encapsulated inside SWCNTs, an ideal supramolecular assembly occurs naturally, as the Coulomb interaction is then energetically most favorable for a parallel head-to-tail alignment. In such an assembly, the NLO responses of the individual building blocks will add coherently, thus resulting in a nanohybrid with a giant 2nd order NLO response. Here, we present the first evidence of this principle, using a prototypical dipolar chromophore encapsulated in various SWCNTs -samples. The encapsulation is evidenced by extensive wavelength-dependent fluorescence-excitation and resonance Raman experiments, studying the effect of the encapsulation on the vibrational and electronic properties of the SWCNTs and the encapsulated molecules. Wavelength-dependent Hyper Rayleigh scattering experiments [2,3] (i.e. second harmonic light scattering) reveal an increase of the NLO response of the nanohybrid with respect to the individual molecules by more than an order of magnitude.

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# Raman spectroscopy of carbon nanohoops

Hang Chen[1], M. R. Golder[3], S. K. Doorn[2], R. Jasti[3] A. K. Swan[1],

*1 Department of Electrical and Computer Engineering, and Photonics Center,*
*Boston University, Boston, MA 02215, USA*
*2 MPA-CINT, Los Alamos National Lab, Los Alamos, NM 87545, USA*
*3 Department of Chemistry, Boston University, Boston, MA 02215*

We present Raman analysis for Cycloparaphenylenes (CPPs) of different sizes ([6]-, [8-12]CPPs). [n]CPP molecules are carbon nanohoops reminiscent of a single unit of (n, n) armchair carbon nanotubes (CNTs).[1, 2] A plethora of Raman modes are observed in these spectra, including modes that are analogous the G band in CNTs, as well as peaks that are unique for carbon nanohoops. We have calculated the theoretical Raman spectra of [n]CPPs for n= 4~20 using density functional theory (DFT), which are then compared to the experimental spectra for the assignment of different modes. Theoretically, the even-numbered CPPs should have $D_{(n/2)d}$ symmetry, while the odd-numbered hoops have only $C_1$ symmetry. However, for certain Raman bands of the even-numbered CPPs, the experimental results seem to contradict this prediction. To address the problem, we have done further calculations by manipulating the geometry of even-numbered hoops. In addition, the peak positions for almost all Raman modes are found to be dependent on the size of the hoops from both the experimental and the calculated results. The effect of low temperature on the Raman features of the CPPs is also examined.

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## Resonant Raman spectroscopy of nitrogen-doped single-walled carbon nanotubes (N-SWNT)

Sara D. Costa[1], Theerapol Thurakitseree[2], Shigeo Maruyama[2], Cristiano Fantini[1], Marcos Pimenta[1]

*1 Dept. of Physics, Universidade Federal de Minas Gerais, Belo Horizonte, Brazil (sdcosta@fisica.ufmg.br)*
*2 Dept. of Mechanical Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo, Japan*

Vertically aligned nitrogen-doped single-walled carbon nanotubes (N-SWNT) were investigated via resonant Raman spectroscopy. In order to have a basis for comparison, two samples were used in the experiments: one grown with pure ethanol (SWNT) and another one grown with a mixture of ethanol/acetonitrile as feedstock (N-SWNT) [1]. Different laser energies in the ultraviolet, infrared and visible ranges (from 1.53 to 3.8 eV), were used to excite the sample and investigate its resonant behaviour. In order to create a map of the transition energy versus the radial breathing mode frequency, tuneable lasers were employed and a Raman spectrum was acquired every 2 nm.

The effects of the incorporation of nitrogen on the electronic and phonon structures were studied. Despite the low amount of nitrogen incorporated (0.2%), shifts in the optical transitions of the nanotubes were detected, showing modifications in the electronic properties upon doping. Additionally, the D and G' bands dispersive behaviour was studied.

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## Shot noise in suspended graphene at high magnetic fields

Antti Laitinen, Daniel Cox and Pertti Hakonen

*Aalto University, Finland (daniel.cox@aalto.fi)*

Graphene is an intriguing semimetal with, ideally, massless Dirac fermions as the carriers of electrical current. Recently the fractional quantum Hall state was observed in suspended graphene sheets having a mobility on the order of $10^5$ $cm^2/Vs$. Shot noise is one way to study the nature of charge transport in 2DEG and in graphene. It yields complementary information to conductance, and it has been employed to verify that the Landau level filling factor determines the effective charge of carriers in a 2DEG [1,2]. We have started such shot noise experiments on graphene. Our preliminary data display distinct noise around the field-induced transport gap. Correlations between noise and conductance have been analysed and the results are discussed in the light of the theories on the Quantum Hall effect.

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# Carbon nanomaterial containing polymer composites

Yvonne Demkiw, Kati Gharagozloo-Hubmann, Stephanie Reich

*Freie Universität Berlin, 14195 Berlin, Berlin, Germany (yvonne.demkiw@fu-berlin.de)*

Nano sized carbon material such as carbon nanotubes or graphene have superior physical properties. They are electrical conductive [1, 2], show high tensile strength [3] and have thermal conductivity of about 3000 to 6000 W/m K [4, 5, 6]. Their unique properties make them promising filler material for creation of composites with optimized performance.

The preparation of composite material with carbon nanomaterial is limited by the poor solubility and the lack of interaction between the carbon and the polymer matrix. After chemical modification of carbon nanotubes the tubes agglomerates can be destroyed; functionalized nanotubes can be incorporated homogeneously in the polymer matrix. The interaction with the composite material is enhanced by the functional groups such as carboxyl, carbonyl or hydroxyl groups, which leads to a further improvement of the composite properties.
Here we present a method for the functionalization of carbon nanotubes and report about the different polymeric composites with carbon nano material and their properties.

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# Aberration corrected STEM/EELS study of morphology-composition correlations in nitrogen-doped multi-wall carbon nanotubes

Fatma Dinc[1,*], Rebecca J Nicholls[1], Quentin M Ramasse[2], Nicole Grobert[1,*]

*1 Department of Materials, University of Oxford, Oxford, OX1 3PH, United Kingdom*
*(fatma.dinc@materials.ox.ac.uk, nicole.grobert@materials.ox.ac.uk)*
*2 SuperSTEM Laboratory, STFC Daresbury, Warrington, WA4 4AD, United Kingdom*

Nitrogen is a good candidate to fit into the hexagonal carbon network due to its similar atomic size to carbon. Even though nitrogen-doped carbon nanotubes (N-CNTs) have been studied so far in field emission, *in situ* electrical conductivity measurements, composites, dispersions and chemical sensing, we still have very limited understanding on their chemical and physical properties compared to their undoped counterparts.

This problem results from the fact that despite the large number of papers on N-CNTs, only a few of them validate the presence of nitrogen heteroatoms and report qualitative and quantitative analysis of the nitrogen content. Without investigating the concentration, the spatial distribution and most importantly the bonding type of nitrogen heteroatoms, we cannot efficiently exploit N-CNTs and N-CNTs applications remain a laboratory exercise.

Here, we have utilized electron energy loss spectroscopy (EELS) coupled with state-of-the-art aberration corrected scanning transmission electron microcopy (STEM) operated at 60 kV to investigate morphological and compositional variations in N-CNTs that we have synthesized by aerosol assisted chemical vapor deposition, from various C/N ratios. Three N-CNT morphologies occur and their distribution change in relation to C/N ratio used in the synthesis. Most importantly, we have found out that the nitrogen spatial distribution and concentration differ among morphologies, which gives us an insight on how to tune the properties of N-CNTs.

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# Carbon nanotube sensors: interplay between Schottky barrier and gas adsorption

Georgy Fedorov[1], Isha Dube[2], Anthony Boyd[2], Igor Gayduchenko[1], Makarand Paranjape[2],
David Jiménez[3], Paola Barbara[2]

*1 National Research University of Electronic Technology, Russia (gefedorov@mail.ru)*
*2 Department of Physics, Georgetown University, USA*
*3 Departament d'Enginyeria Electrònica, Universitat Autònoma de Barcelona, Spain*

Carbon nanotube field effect transistors (CNFETs) are extremely sensitive chemiresistors. Although their chemical sensing properties were discovered more than 10 years ago [1], the physical mechanism underlying their response is still unclear. Electrical changes can be caused either by charge transfer between adsorbed gas molecules and the nanotube channel, or by changes at the Schottky barriers between the carbon nanotube and the metal contacts. Previous work showed that in the case of sensors made with individual nanotubes, the response to $NO_2$ and $NH_3$ is mainly due to Schottky barrier modulation [2, 3].

Here we present numerical simulation based on existing models [4] to analyze the data by using measurements of metals work functions and their changes under gas exposure. Furthermore, we study the sensing mechanism of CNFETs where the channel is made of nanotube networks. We find that this case the carbon nanotube channel substantially contributes to the CNFET response. We explain the different behavior of CNFETs made with individual nanotubes vs. networks by considering gas adsorption occurring at the junctions between nanotubes forming the network.

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P81

# Commercially viable SWNT transparent conductive thin films from nanotubide inks

Siân Fogden, Ce Ma, Kee-Chan Kim, Kathleen Ligsay, Graham McFarlane

*Linde Nanomaterials, 1970 Diamond St, San Marcos, CA, USA (sian.fogden@linde.com)*

Although commercial interest has been growing into alternatives to doped metal oxides for transparent conductive thin films (TCFs), none have been able to achieve the required resistivity and transparency for commercial viability, commonly quoted in the literature as 100 ohms/sq at 90% transparency, without affecting other critical properties such as haze, environment stability, flexibility, hardness, adhesion and of course, cost. Single Walled Carbon Nanotubes (SWNTs) have shown great promise as an alternative material due to their outstanding electrical, optical and mechanical properties. However, up until now the resistivity and transparency requirements have not been met.

Using reduction dissolution technology to produce nanotubide inks, Linde Nanomaterials has been able to produce TCFs which exceed the resistivity and transparency requirements without affecting the other critical properties.

This reductive dissolution technology begins by reducing SWNTs in liquid ammonia followed by dissolution in a polar aprotic organic solvent without the need for additional mechanical energy. This mild dissolution technique results in solutions of long, undamaged, individualized SWNTs which can be deposited using spin or spray coating to make TCFs. This technique directly addresses the critical SWNT conductivity scaling factors of purity, length and bundle size to produce commercially viable TCFs. At the lab scale, photovoltaic devices made using these TCFs have been successfully produced. The developments presented here will pave the way for the mainstream use of SWNT based TCFs in both the touch and display markets.

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## J-aggregated dyes inside carbon nanotubes: from absorption isotherms to imaging applications

Étienne Gaufrès[1], Nathalie.Y.W Tang[1], François Lapointe[1], Nicolas Cottenye[1], Alexandre Favron[1],
Thomas Szkopek[2] and Richard Martel[1,*]

*1 Regroupement Québécois sur les Matériaux de Pointe and Département de Chimie, Université de Montréal, Québec H3C 3J7 (*r.martel@umontreal.ca)*
*2 Regroupement Québécois sur les Matériaux de Pointe and Department of Electrical and Computer Engineering, McGill University, Montréal Québec H3A 2A7*

Here, we report the discovery of a giant Raman scattering effect from encapsulated and aggregated dye molecules inside single-walled carbon nanotubes (dyes@SWNTs). Measurements performed on rod-like dyes, such as α-sexithiophene and β-carotene, assembled inside SWNTs as highly polarizable J-aggregates indicate a resonant Raman cross-section of ~$10^{-21}$ $cm^2/sr$, which is well above the CS required for detecting individual aggregates at the highest optical resolution. This high scattering cross section enables the determination of the encapsulation isotherms of the 6T inside carbon nanotubes. The shape of the isotherms indicated two regimes depending on the temperature and consisting of single and pair of molecules aligned head-to-tail. Finally, we developed using dyes@SWNT assemblies a library of nanoprobe labels with robust emission, multispectral capabilities and bio-compatibility for Raman imaging.

[1] E. Gaufrès. N. Y.W. Tang, F. Lapointe, J. Cabana, M.A Nadon, N. Cottenye, F. Raymond, T. Szkopek and R. Martel, *submitted*

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## Functionalized nanoparticles as viscosity reducers: MWCNTs in thermoplastic epoxy based matrix polymerized in-situ.

A. Petriccione[1,*], A. Martone[2], M. Zarrelli[2], V. Antonucci[2], M. Giordano[2]

*1 UNINA, University of Naples "Federico II", Italy (*angelo.petriccione@unina.it)*
*2 IMCB-CNR, Institute for Composite and Biomedical Materials, National Research Council, Italy*

Confinement and surface effects provided by nanoparticles have been shown to produce conformational changes to polymer molecules affecting the macroscopic viscosity [1]. Nanoparticles induce changes in polymer conformation and an increase in free volume which produce a significant decrease in viscosity. It can be generally attributed to the selective adsorption of the high molar mass fraction onto the nanoparticles surface when the polymer radius of gyration is greater than the nanoparticle radius [2].

Carbon nanotubes seems to be the ideal candidate to be used as viscosity reducers due both to their nanometric radius size, comparable to the gyration radius of polymer chains, and to their high surface to volume ratio [3]. On the contrary the increase of the nanotube content leads at percolation to the formation of a nanotube-polymer network hindering the viscosity reduction.

In this work we use multiwalled carbon nanotubes aggregates as viscosity reducers. Main idea is that nanotubes clusters retain a very high surface to volume ratio, able to induce the increase of the polymer free volume, possessing a much higher percolation threshold due to a very low aspect ratio. Hydrogen bridged stabilized aggregates of carbon nanotubes has been obtained by using hydroxyl and carboxyl functionalities.

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# Absorption and photoluminescence-spectroscopy of single-wall carbon nanotubes under potentiostatic control

Holger Hartleb, Caroline L. Rider-Dobson, Tobias Hertel*

*Institute of Physical and Theoretical Chemistry, Julius-Maximilians-University of Würzburg, Am Hubland, 97074 Würzburg, Germany (*tobias.hertel@uni-wuerzburg.de)*

We have studied spectroelectrochemical properties of highly enriched semiconducting (6,5) single-wall carbon nanotubes (SWNTs) in organic suspensions using a home-build setup. The experiment allows for quasi-simultaneous absorption and photoluminescence-spectroscopy of SWNT samples under potentiostatic control. The experiments thereby facilitate an investigation of the influence of electrochemical doping on absorption and emission spectra. The latter are known to be particularly susceptible to doping due to efficient non-radiative decay channels. Here we present initial results and highlight the role of exchange and correlation effects on optical spectra of these unique one-dimensional semiconductors.

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# Fermi energy shift in deposited metallic nanotubes: A Raman scattering study

Benjamin Hatting[1], Sebastian Heeg[1], Kenichi Ataka[1], Joachim Heberle[1], Frank Hennrich[2], Manfred M. Kappes[2], Ralph Krupke[2], Stephanie Reich[1]

*1 Freie Universität Berlin, Germany (benjamin.hatting@fu-berlin.de)*
*2 Karlsruhe Institute of Technology, Germany*

We report on the results of a comparison of the HEM Raman spectra of an enriched nanotube sample in solution and on a silicon substrate [1]. The metallic LO peak downshifts by 23 cm$^{-1}$ and broadens by 13 cm$^{-1}$ after the deposition. We explain our findings in terms of Fermi energy shifts, which influence the metallic LO peak due to the Kohn anomaly [2] and additional phonon relaxation channel [3]. The Fermi energy is shifted away from its intrinsic value in solution and closer towards its intrinsic value on silicon. As a result, the spectrum on silicon exhibits the lineshape that is characteristic of metallic nanotubes, while the lineshape in solution could potentially be mistaken as arising from semiconducting tubes.

We confirm our interpretation and quantify the observed Fermi energy shifts by performing in-situ electrochemical Raman measurements, which allow us to reproduce the spectrum observed in solution by deliberately shifting the Fermi energy. We arrive at a Fermi energy shift of -0.16 eV. Our results have implications for the application of Raman spectroscopy to distinguish metallic and semiconducting tubes by inspecting their HEM lineshape.

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## P86 Aharonov-Bohm oscillations in ballistic carbon nanotube ring

Akira Hida[1], Takayuki Suzuki[1,2], Koji Ishibashi[1]

*1 Advanced Device Laboratory, RIKEN-Advanced Science Institute, JAPAN (hida@riken.jp)*
*2 Department of Physics, Tokyo University of Science, JAPAN*

The phenomenon which the electrical resistance of the ring-shaped microscopic conductor changes periodically with the magnetic flux passing through the inside of the ring is known as the Aharonov-Bohm (AB) effect [1]. Since the AB effect originates in the wave nature of the electrons, it is ideal that a ring with ballistic transport property is used for the measurement. However, lithographic technique conventionally adopted to fabricate the rings has provided only the diffusive ones [2]. In this presentation, the AB oscillations observed in the ballistic ring which consists of a single-walled carbon nanotube (SWNT) are introduced.

In order to form a ring with a linear SWNT, both ends of it were connected covalently via carboxylic anhydride. Scanning tunneling microscopy revealed that standing wave patterns were clearly observed along a circumference of the ring, in other words, the electrons moved through the ring in the ballistic regime. For the conduction measurements under magnetic field, two electrodes of Au were fabricated on either side of a SWNT ring by means of atomic force microscope lithography technique [3]. At liquid helium temperature, giant-amplitude oscillations appeared in the magnetoconductance of the ring. The oscillations were well symmetric across zero magnetic field and had a period corresponding to an increase or decrease of the magnetic flux $h/e$. The obtained results indicated that an ideal single-channel AB ring was realized with a SWNT.

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## P87 Water adsorption on “hydrophobic” carbon nanotube surface

Yoshikazu Homma[1], Shohei Chiashi[2], Daiki Matsumoto[1], Junpei Shitaba[1],
Naoki Homma[1] and Takahiro Yamamoto[1]

*1 Tokyo University of Science, Japan (homma@rs.tus.ac.jp)*
*2 The University of Tokyo, Japan*

Water forms a wetting layer on a hydrophilic surface. This is an indispensable property for living cells and also influences the surface properties of materials in ambient air. Here, we show that water molecules form a stable adsorption layer of 1-2 monolayer thickness on the hydrophobic carbon nanotube surface at room temperature in moist ambient air [1]. Based on optical measurements of individual single-walled carbon nanotubes suspended between micropillars in water vapor together with molecular dynamics simulations, we found that the adsorption layer is a phase with large condensation energy, separated from ambient water vapor or even from liquid water. The condensation energy increases with increasing tube diameter, meaning that water molecules more easily adsorb on the surface when the tube diameter becomes infinity, i.e., on the graphene surface. The water adsorption layer is created by lateral hydrogen bonding of water molecules confined in the weak van der Waals potential of the nanotube surface. Paradoxically, the carbon nanotube with a thin wetting layer behaves as hydrophobic because of closed lateral bonding of water molecules in the layer.

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P88

## Electrical transport on in-situ-grown, suspended carbon nanotubes

Pasi Häkkinen, Alexander Savin, Pertti Hakonen*

*O.V. Lounasmaa Laboratory, Aalto University, Finland (*pertti.hakonen@aalto.fi)*

Single-walled carbon nanotubes (SWNTs) suspended between metallic electrodes offer versatile test systems for quantum dot (QD) and quantum wire physics. Superb mechanical properties of the SWNTs on the other hand allow investigation of high quality factor nanomechanical devices with resonance frequencies up to GHz range [1]. Growth of the SWNTs on superconducting electrodes as a final step of the sample fabrication further opens up possibility to study suspended high crystallinity Josephson junctions [2].

Our studies target the interplay between the mechanical motion and superconducting electrical transport in suspended SWNT devices. Our samples show clean four-fold QD transport behavior expected for individual SWNTs. We measure high mechanical quality factors on the order of 100 000 and a maximum resonance frequency of 276 MHz in a representative device. In addition, a small, gate-dependent critical current in the pA range is observed.

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## Estimation of conduction at CNT/SiC interface of vertically aligned and high density CNT on SiC

Masafumi Inaba[1], Megumi Shibuya[1], Yoshiho Masuda[2], Atsushi Hiraiwa[1], Michiko Kusunoki[2], Hiroshi Kawarada[1]

*1 School of Advanced Science and Engineering, Waseda University, Japan (inaba-ma@ruri.waseda.jp)*
*2 Eco Topia Science Institute, Nagoya University, Japan*

CNT forest is important for metallization. Metallic properties of CNT forest for Si-ULSI via structure have been reported[1]. However, CNT effective density is still not so high for large current density. CNT synthesized with SiC surface decomposition method (CNT on SiC[2]) exhibits the most densely packed CNT forest and has graphene sheets vertical to the SiC surface. Although metal/SiC interface is crucial to power device application of SiC, only one report[2] shows electric property of CNT/SiC interface, where the presence of Schottky barrier has been reported[3]. Here, quantitative current behavior at CNT/SiC interface is estimated.

Because of lateral conduction in CNT forest on SiC, isolated CNT area was formed with focused ion beam and was scanned by conductive AFM. CNT forest/SiC contact resistivity was lower than $5*10^{-9}$ ohm-cm$^2$ as reported previously. The conductivity depends on the isolated area and contact resistivity on CNT/SiC interface is evaluated to be about $10^{-2}$ ohm-cm$^2$. Note that the conduction shows the existence of optimal CNT length for contact. Contacting quality depends on CNT surface and CNT/SiC interface condition. When CNT length is less than 40 nm, initial graphene sheets remains and impedes vertical conduction. In the case of longer as 200nm, graphite structure parallel to CNT/SiC observed at the interface by cross sectional TEM and increase the contact resistance as a result. The smallest contact resistance at CNT/SiC has been obtained with CNT length at 100 nm, where the clearest vertical aligned CNT contact to SiC has been imaged by TEM.

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**P90**

# Collective optical resonances in networks of metallic carbon nanotubes

Tommi Isoniemi[1], Andreas Johansson[1], J. Jussi Toppari[1], Henrik Kunttu[2]

*1 Nanoscience Center, Department of Physics, University of Jyväskylä, Finland (tommi.isoniemi@jyu.fi)*
*2 Nanoscience Center, Department of Chemistry, University of Jyväskylä, Finland*

In carbon materials, actual optical plasmonics have this far been restricted to graphene, but the experiments we have performed provide novel evidence of plasmonic functionality in a different form of pure carbon [1]. We demonstrate optical resonances in thin films of single walled carbon nanotubes (SWCNTs) with a highly enriched (98 %) proportion of metallic chiralities. These resonances are measured in the Kretschmann configuration, and can be seen as intensity dips of up to 90 % in reflection spectra beginning at 360 and 650 nm at the critical angle for total internal reflection and moving to longer wavelengths for higher angles of incidence. Unexpectedly, they are only visible when the sample is excited with s-polarized light, the opposite of surface plasmon polaritons on thin metal films. The resonances are dispersive and intense only when the layer thickness is close to 100 nm, implying that a collective excitation might be responsible for the resonance. They are also sensitive to the dielectric environment, clearly distinguishing the data from normal total internal reflection absorption spectra. The length of the CNTs seems to be irrelevant, ruling out localized surface plasmon resonance, and increasing the amount of amorphous carbon only decreases the intensity of the resonance. Corresponding materials of semiconducting and unsorted SWCNTs with similar diameters (1.4 nm) do not display noticeable dispersive resonances. Although additional experimental and theoretical studies are needed to confirm the underlying mechanism, a magnetic plasmon resonance [2] due to intertube effects, possibly within bundles, is a possible explanation. A probable coupling to excitons can also be pointed out, as the resonances are found close to M11 and M22 transition energies of the SWCNTs. If the fundamental reason for the observed phenomenon is connected to a magnetic resonance, metallic SWCNTs might find applications in plasmonic metamaterials.

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**P91**

# Onset of rippling in MWCNTs studied with in situ TEM force measurements

H. Jackman, P. Krakhmalev, K. Svensson

*Department of Engineering and Physics, Karlstad University, Sweden (henrik.jackman@kau.se)*

When carbon nanotubes (CNTs) are bent they can deform in localized buckling or rippling deformations. The force-deflection relation is only linear up to a critical strain, where the rippling or buckling begins, and then the relation becomes non-linear with a concomitant drop in the bending stiffness (for a review see e.g. [1]). These two effects have important implications for the design of future nanoelectromechanical systems (NEMS) that utilize bending of CNTs. Several theoretical studies have investigated this phenomenon but there is still a lack of experimental data to compare with [1]. In a previous study we have measured the critical strain for the rippling onset of CVD-grown MWCNTs using *in situ* SEM force measurements [2]. We found that a large defect density in the MWCNT will shift the critical strains to higher values than theoretically predicted [3-4].

In this study we have performed *in situ* TEM force measurements on individual, arc-discharge grown, MWCNTs. We found values of the critical strain that are lower, compared to the values of the CVD-grown, owing to the high crystallinity of arc-discharge grown tubes. The values are comparable to previous predictions for SWCNTs [3] and thick MWCNTs [4], but there is also an influence from the geometry. We find a dependence of the critical strain on both the number of walls and the nanotube diameter, and we discuss this effect in terms of a radial stiffness that supports the outermost walls in a MWCNT.

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P92

## Tailoring oxidation of Al particles morphologically controlled by carbon nanotubes

Hye Yun Jeong, and Young Hee Lee*

*Center for Integrated Nanostructure Physics, Institute of Basic Science, Department of Energy Science, BK21 Physics Division, and Center for Nanotubes and Nanostructured Composites, Sungkyunkwan University (SKKU), Suwon 440-746, Korea (*leeyoung@skku.edu)*

Aluminum powder is used for energetic materials due to high energy density. Controlling oxidation rate, oxidation temperature, and reaction enthalpy are important parameters prior to practical use. Here, we engineered static and dynamic properties of oxidation of Al particles by mixing carbon nanotubes (CNTs) which have high thermal conductivity and large exothermic energy. Morphologies of Al/CNT mixture was engineered by a mechanical pulverization. Among various morphologies of Al/CNT mixture of i) CNTs adhered on the surface of Al particles, ii) CNTs partially embedded onto Al particles, forming an urchin type, and iii) CNTs fully embedded into aggregated Al particles, urchin type Al/CNT revealed the largest exothermic enthalpy at the lower oxidation temperature for both $\gamma$-$Al_2O_3$ and $\alpha$-$Al_2O_3$ phases. This was attributed to the fast heat transfer into Al particles via partially embedded CNTs having high thermal conductivity. Large exothermic enthalpy of -121.7 kJ/g was obtained in oxidation of Al/CNT mixture (10 wt% CNT) compared to that (-10.2 kJ/g) of pure Al particles and the mass of alumina of Al/CNT mixture after 1000 °C oxidation was increased by four times compared to pure Al particles. The exothermic enthalpy showed strong dependence on the CNT content, increasing to -188 kJ/g at 20 wt% CNT. The engineering ability of thermal properties in Al particles with CNTs opens a new research area for diverse use of solid fuel Al.

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## Understanding the elastodynamics and characterizing the elastostatics of repeatedly nanomanipulated single-walled carbon nanotubes atop vicinal crystalline quartz

Lucas C.P.A.M. Müssnich[1], Hélio Chacham[1], Jaqueline S. Soares[1], Newton M. Barbosa Neto[1,2], Luiz G. Cançado[1], Nitzan Shadmi[3], Ernesto Joselevich[3], Ado Jorio[1]

*1 Dept. de Física, Univ. Federal de Minas Gerais, Belo Horizonte, MG, 31270-901, Brazil*
*2 Instituto de Física, Univ. Federal de Uberlândia, Uberlândia, MG, 38400-902, Brazil*
*3 Dept. of Materials and Interfaces, Weizmann Institute of Science, Rehovot, 76100, Israel*

We investigate the elastodynamics and the elastostatics of single-wall carbon nanotube (SWNT) atop a vicinal crystalline quartz surface. We prescribe a dynamics to explain constant strain gradients observed in SWNT atop amorphous quartz, and show that it predicts new phenomena such as fixed points and strain avalanches. With the aid of an atomic force microscope apparatus and Raman spectroscopy, these new features are observed in nanomanipulated SWNT atop vicinal crystalline quartz. By analyzing a many -times nanomanipulated SWNT atop vicinal crystalline quartz, we suggest that these elements can be used to describe most observed strain profiles generated in the system. This raises the possibility of designing substrates to controllably strain engineer individual SWNT.

**P95**

## Fabrication of AgNW-SWCNT hybrid as the flexible transparent film heater

Taeyang Kim, Jeung Choon Goak, Naesung Lee*

*Faculty of Nanotechnology and Advanced Materials Engineering, Sejong University,*
*Seoul 143-747, South Korea (*nslee@sejong.ac.kr)*

Development of silver nanowire (AgNW) and carbon nanotube (CNT) as the active materials for the transparent film heater become the promising substitute material for ITO. AgNW as film possess the comparably optical property and electrical conductivity with those owned by ITO. Unfortunately, AgNW with only tens of nanometers diameter have low melting point which reduce its thermal stability. On the other hand, the high thermal conductivity CNT film is own high thermal stability due to its strong covalent C-C bond. As for the drawbacks, CNT has a higher resistance than ITO or AgNw film. In this study, the advantages of AgNW and CNT are combined by coating SWCNT on AgNW film. It is expected that the locally generated heat produced by AgNW is distributed through the SWCNT layer on the silver. Moreover, highlighting its form as the solution, AgNW and CNT hold the benefit due to their ability to be applied for large area. The composite film fabricated is then analyzed for its optical, thermal, and electrical properties. Single AgNW film is possessing resistance 36.3 Ω/sq at the transmittance of 94.4%. This AgNW layer is prepared by deposit the solution on thick glass substrate (5 × 5cm2, 3.2T) using spin coating. Single SWCNT film is prepared by spray coating method of the dispersed aqueous solution on the glass substrate. This film has 600 Ω/sq resistance at 91% transmittance. AgNW film showed the high heating characteristic which is able to reach temperature of 54 ° C when DC voltage of 8 V is applied. At 16V voltage, this temperature is increased to 140 °C but shows a tendency to decrease rapidly, as the AgNW are damaged by the high heat temperature. SWCNT film with resistance of 38.8 Ω/sq in 94.2% transmittance undergoes the temperature change of less than 1 ° C at 8 V DC voltages. SWCNT spray coating on AgNW films produce the sheet resistance of 37.8 Ω/sq at the transmittance of 85.6%. This composite transparent film showed the stable heating characteristics of ~ 135 ° C temperature change in the DC voltage of 16 V. It is assumed that by dispersing SWCNT, the excellent heat conduction occurs in AgNW may distribute uniformly and increased stability of the film.

**P96**

## Direct CVD synthesis of suspended double-walled carbon nanotubes and their characterization by TEM and optical spectroscopy

Sihan Zhao[1], Tomoya Kitagawa[1], Yuhei Miyauchi[2,3], Kazunari Matsuda[2], Hisanori Shinohara[1,*]
and Ryo Kitaura[1,*]

*1 Department of Chemistry & Institute for Advanced Research, Nagoya University, Nagoya 464-8602, Japan*
*(*noris@nagoya-u.jp and r.kitaura@nagoya-u.jp)*
*2 Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan*
*3 Japan Science and Technology Agency, PRESTO, Saitama 332-0012, Japan*

The physical properties of CNTs strongly depend on chirality, defects, the number of walls and encapsulated chemical species. Double-wall carbon nanotube is one of the most fundamental systems to examine the effect of inter-layer interactions on the electronic transitions. To study the inter-layer coupling in double-wall CNTs in detail, it is necessary to develop a direct preparation method of long and clean suspended individual double-wall CNTs on an open slit, which enables us to apply two complementary experimental techniques, Rayleigh scattering and TEM observations, on the same double-wall CNTs for characterizations of electronic transition energies in double-wall CNTs with defined inner and outer wall structures. Here, we report a preparation of suspended double-wall CNTs using the chemical vapor deposition (CVD) and also a characterization of their structure and optical properties.

Fe catalyst nanoparticles supported by MgO were deposited on the substrate with an open slit (~10 mm × 1.5 mm). After the deposition of Fe/MgO, suspended DWCNTs were grown by the alcohol catalytic chemical vapor deposition (ACCVD) method. The suspended DWCNTs have been characterized by TEM and Rayleigh scattering spectroscopy, and their chiral indexes and optical transition energies were identified. At presentation, we discuss the detailed experimental procedures and the interlayer coupling effects on the electronic transition energies in detail.

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P97

# The field emission peculiarities of nanodiode with nanotube cathode

German Kosakovskii[1,2], Zoya Kosakovskaya[1,2], Yurii Gulyaev[1], Evgeny Blagov[2],
Yurii Latyshev[1,2], Andrey Orlov[1,2], Anatoly Smolovich[1,2]

*1 Kotel`nikov Institute of Radioengineering and Electronics of RAS, Russia (german_kos@mail.ru)*
*2 Institute of Nanotechnology of Microelectronics of RAS, Moscow, Russia*

It is known the current-voltage characteristic (I-V) of the field emission diode with 3D cathode is determined by the non-linear nature of the tunneling of electrons to vacuum through the potential barrier near the cathode surface which is well described by the Fowler-Nordgeim function. Replacing of 3D cathode onto the 1D nanotube cathode has the following consequences:

(i) the nonlinearity of the I-V characteristic of nanodiode already will be determined by the interaction of two nonlinear processes: the tunneling process of electrons in a vacuum and the quantum-dimensional process of nanotube cathode conductivity. As a result the resonance peaks near Van Hove singularity and the threshold voltage appear on the I-V characteristic of the nanodiode [1].

(ii) the electrical contact of 1D nanotube cathode with metallic 3D electrode of the electron source cannot be adiabatic and the conditions for quantization of electrons arise the along of the nanotube axis. When the voltage will be more than the threshold voltage, the components of DC and AC current can appear in the electric circuit of diode [2].

In detail the mechanism of field emission in diode with nanotube cathode and the experimental data of our study of the emission properties will be discussed.

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# One-dimensional $N_2$ gas inside single-walled carbon nanotubes

Christian Kramberger[1], Theerapol Thurakitseree[2], Erik Einarsson[2], Shigeo Maruyama[2],
Yudai Izumi[3], Toyohiko Kinoshita[3], Takayuki Muro[3]

*1 University of Vienna, Austria (Christian.Kramberger-Kaplan@univie.ac.at)*
*2 The University of Tokyo, Japan*
*3 Synchrotron Radiation Research Institute, SPrinG8, Japan*

Vertically aligned forests of sub-nm thin SWCNT can be filled with $N_2$ molecules if a mixed acetonitrile/ethanol feedstock is used during CVD synthesis. The interior space of these SWCNT is sufficiently narrow (d < 1 nm) that the contained molecules are kept in a strictly one-dimensional arrangement. The linear arrangement of co-axially oriented $N_2$ molecules inside aligned single-walled carbon nanotubes is revealed by high resolution near-edge x-ray absorption spectroscopy. [1] The encapsulated $N_2$ molecules exhibit free stretching vibrations with a long electronic lifetime of the x-ray-excited anti-bonding $\pi^*$ states. Molecular dynamics simulations of $N_2$ inside (6,6) and (7,7) SWCNT confirm that narrow-diameter nanotubes (d < 1 nm) are crucial for stabilizing the linear arrangement of aligned $N_2$ molecules.

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**P100**

# Periodically patterned porous thin films of carbon nanotubes fabricated by polystyrene-nanosphere templating

Yuki Kuwahara[1], Takayoshi Hirai[2], Takeshi Saito[1]

*1 Nanotube Research Center, National Institute of Advanced Industrial Science and Technology (AIST), Japan*
*(takeshi-saito@aist.go.jp)*
*2 Technology Research Association for Single Wall Carbon Nanotubes (TASC), Japan*

Carbon nanotubes (CNTs) have been studied as one of emerging conductive materials for the application to transparent conductive films (TCFs) due to their unique properties such as high electrical conductivity, and transparency, accompanied by the mechanical strength and chemical stability. As for CNT-TCFs, the optimal film morphology for the high optical transparency and low electrical resistivity is one of the controversial issues. Therefore, the studies on the film fabrication techniques with controllability of their morphology are highly important. Such investigations will contribute to further improvements in conductivity and transparency of CNT-TCFs. It is well-known that the close-packed layer of ordered latex particles forms a hexagonal pattern that is frequently used as a template. In this study, we have fabricated periodically patterned CNT thin films with different pore-sizes by the templating method using polystyrene spheres (PSs), and investigated the relationship between the performance as CNT-TCFs and the film morphology. For the fabrication of the porous patterned CNT thin films, we combined PS template and filtration methods. At first, the PSs latex solution was filtered through membrane filter to form self-assembled close-packed layers on the membrane. Then, the CNT dispersion was poured on it and washed with ample amounts of Millipore water. After removing PSs, CNT films were transfer to glass substrates according to the method described by Wu *et al.* [1]. Patterned CNT films were observed by using SEM, AFM, and optical microscopy. The surface resistance and transparency of CNT films were also characterized. The study has been supported by the New Energy and Industrial Technology Development Organization (NEDO).

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**P101**

# Tailoring double walled carbon nanotubes by anchoring donor- and electron-acceptor moieties

Fernando Langa, María José Gómez, Myriam Barrejón

*Institute for Nanoscience and Molecular Materials, Univ. Castilla-La Mancha, Spain*
*(fernando.langa@uclm.es)*

Due to the coaxial structures, double walled carbon nanotubes (DWNTs) are mechanically, thermally and structurally more stable than single walled carbon nanotubes (SWNTs) [1]. Nowadays, there is an increase in interest in double-walled carbon nanotubes (DWCNTs) for both the elucidation of their physical properties and their possible applications as, for example, the fabrication of devices as field-effect transistors [2]. However, the influence on the electronic properties of DWCNTs of the covalent functionalization of the outer wall of DWCNTs with electron donors or electron acceptors is almost unexplored.

We have recently described the different behavior of dimethylanilino functionalized DWCNTs and SWCNTs in photoinduced electron transfer process (PET) [3], observing a shorter live of the radical ion pair in DWCNTs respecting to SWCNTs. In order to achieve a better knowledge on the behavior of functionalized DWCNTs, we report herein the covalent functionalization of these materials with electron donors (porphyrins) and electron acceptors (perylenes) as well as the photophysical behavior of these new hybrid materials.

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## Fano resonances in the midinfrared spectra of single-walled carbon nanotubes

François Lapointe[1], Étienne Gaufrès[1], Isabelle Tremblay[1], Nathalie Y-Wa Tang[1], Patrick Desjardins[2], Richard Martel[1,*]

*1 Regroupement Québécois sur les Matériaux de Pointe (RQMP) and Dép. de chimie, Université de Montréal, Montréal (Québec), Canada (*r.martel@umontreal.ca)*
*2 Regroupement Québécois sur les Matériaux de Pointe (RQMP) and Dép. de génie physique, École Polytechnique de Montréal, Montréal (Québec), Canada*

This work revisits the physics giving rise to the carbon nanotube phonon bands in the midinfrared. [1,2] Our measurements of doped and undoped samples of single-walled carbon nanotubes in Fourier transform infrared spectroscopy show that the phonon bands exhibit an asymmetric line shape and that their effective cross section is enhanced upon doping. We relate these observations to electron-phonon coupling or, more specifically, to a Fano resonance phenomenon. [3] We note that the dopant-induced intraband (not interband) continuum couples strongly to the phonon modes, and that defects created on the sidewall are scattering centers that increase the spectral amplitude of the resonance.

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## Fabrication of lateral-gated CuO nanowire emitters using electroplated Cu electrode and their field emission properties

Hansung Lee, Byung Jik Lim, In Ho Ha, Sung Hyun Kim, Churl Seung Lee, Kyung Il Lee*

*Korea Electronics Technology Institute, Korea (*leeki@keti.re.kr)*

Cupric oxide nanowires (CuO NWs) have a bandgap of 1.2 eV, and work function of 2.5-2.8 eV. Due to their high aspect ratio, large surface-to-volume ratio and quasi-onedimensional (Q1D) nanostructured CuO NWs have electrical, mechanical, magnetic and optical properties, as well as their unique applications. Many methods have been developed for the synthesis of CuO NWs such as, thermal oxidation, hydrothermal process, chemical vapor deposition (CVD), electrochemical deposition etc,. One of the simple process is the vapor-solid oxidation of thermal oxidation approach has been demonstrated to be particularly useful for the growth of vertically aligned CuO NWs with high crystalline quality.

Recently, it has been shown that good field emission properties for field emission displays by using self-assembled grown CuO NWs at low temperature [1]. In particular, the thermal oxidation method has advantages in applicability to a large area panel, simple process, and low cost in manufacturing. In order to apply these CuO NW emitters in field emission devices, how to strong adhesion into the cathode materials is one of the key issues because CuO layer naturally very weak adhesion material [2]. In this study, we fabricated CuO NW emitters with a lateral-triode structure by Cu electroplating and photolithography for field emission flat lamps. The width and pitch of CuO NWs stripes were 40 and 30 μm, respectively. The CuO NWs grow isotropic on the electroplated Cu electrode surface the diameter and length is about 50 nm and 7 μm, respectively. In this study, the details of the fabrication process of 4 in. lateral-gated CuO NW field emitters and their field emission characteristics in a field emission flat lamp will be reported.

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P104

## Effect of electrode surface roughness on field emission properties of lateral-gated carbon nanotube emitters

Churl Seung Lee, Hansung Lee, Byung Jik Lim, In Ho Ha, Sung Hyun Kim, Kyung Il Lee*

*Korea Electronics Technology Institute, Korea (*leeki@keti.re.kr)*

The phenomena of electron field emission from carbon nanotubes (CNTs) and their applicability to vacuum electronic devices such as field emission lamps and X-ray sources have been intensively studied. Although much effort has been made to commercialize CNT field emitter devices, several obstacles, in particular, field emission uniformity, emitter lifetime, cost competitiveness still remain to be overcome for commercialization [1]. In the screen-printing method, the CNT paste, which is the most major material in manufacturing the field emission devices using this method, has to be designed mainly in consideration of dispersion, printability, adhesion, conductivity, population of CNT emitters, etc. However, screen-printed cathode electrode surface is remarkable rough. Hence, both the magnitudes and the directions of the fields near the surface will be not uniform [2]. It will affect the uniformity and lifetime of the field emission flat lamp.

This study carried out a parametric approach to reducing the electrode surface roughness by using various fabrication method of electrode such as electroplating (EP), physical vapor deposition (PVD) processes. The morphologies and field emission properties of the electrode and CNT emitters were investigated. The electrode surface roughness of PVD, EP and paste electrodes were 12.6, 28.5, 69.4 nm, respectively. In this study, the details of the fabrication process of 4 in. lateral-gated CNT field emitters and their field emission characteristics in a field emission flat lamp will be discussed as well.

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P105

## Nanocomposites with superior mechanical properties – direct exfoliation of multilayered graphene into native nanocellulose matrix

Jani-Markus Malho[1], Päivi Laaksonen[1], Andreas Walther[2], Olli Ikkala[3] and Markus B. Linder[1]

*1 VTT Technical Research Centre of Finland, Tietotie 2, P.O. Box 1000, FI-02044, Espoo, Finland*
*(jani-markus.malho@vtt.fi)*
*2 DWI at RWTH, Aachen University, Forckenbeckstr. 50, D-52056, Aachen, Germany*
*3 Molecular Materials, Aalto University (formerly Helsinki University of Technology), P.O. Box 15100, FI-00076 AALTO, Espoo, Finland*

Nanofibrillated cellulose (MFC, NFC) is an excellent material with outstanding mechanical properties; however its full potential has not yet been able to transform into nanocomposite materials. A nanocomposite material was designed from NFC in combination with multilayered graphene. Remarkable mechanical performance was obtained by optimizing the processing of these two excellent materials alongside with the amount of multi-layered grapheme (1.25wt%); high toughness 22.3 MJ/m$^3$, high ultimate tensile strength 351 MPa, relatively high stiffness 16.9 GPa and high relative strain of 12 %. Multilayers of graphene are exfoliated directly into aqueous NFC matrix by a tip sonicator. After the exfoliation, the dispersions are vacuum filtered to remove the excessive amount of water to create a solid freestanding film. A small load is then applied to generate compression to prevent wrinkling before the nanocomposite is oven dried overnight. The method is facile and the energy consumption is quite small, thus it may be beneficial in industrial applications in the future. Based on these studies we are also suggesting an attractive interaction between NFC and graphene.

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## Evaluation of carbon nanotubes – oil dispersion stability

P106

Wojciech Mazela, Wojciech Krasodomski, Michał Pajda, Kamil Pomykała

*Oil and Gas Institute, Poland (mazela@inig.pl)*

According to literature, the introduction of nanotubes into liquid fuels can have a positive impact on: the processes of combustion, electrical conductivity, antiknock properties of gasoline [1], diesel fuel cetane number and octane number of gasoline [2]. However, the main problem is to obtain sufficiently stable dispersions of carbon nanotubes in liquid fuels [3].

This paper presents results of research on obtaining a stable dispersion of diesel fuel with multi-wall carbon nanotubes of different sizes, single-wall and modified multi-wall carbon nanotubes, which contain hydroxyl groups or carboxyl groups. The paper also evaluates the impact on the stability of dispersions of selected surfactants. Dispersions in the base diesel and commercial diesel were produced with the help of an ultrasonic disintegrator. The resulting samples were analyzed for the nature of the nanotubes, the type of dispersant and oil. The evaluation of the stability of the dispersion was performed by turbidimetry. In the case of multi-wall nanotubes, depending on their sizes, there was some difference in the ability to create dispersion in diesel fuel, although in any case, these dispersions are not stable enough. To obtain a dispersion, which stability exceeds 12 months it is necessary to use an appropriate dispersant. Stable dispersions with single wall nanotubes were not obtained. Both the base and commercial diesel fuel, regardless of dispersant used, the stability of the dispersion did not exceed several hours. Also modified multiwall nanotubes, containing hydroxyl groups or carboxyl groups, did not form stable dispersions in diesel. A little more stable dispersion of a few days old, was observed in the case of nanotubes dispersed in the commercial diesel fuel, which shows the stabilizing influence of various additives used during diesel production.

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## Dopants as morphology promoters: a fundamental study of the role of boron and sulfur in the formation of MWCNT junctions

P107

A.L. Elías[1], A. McCreary[1], L. Pulickal Rajukumar[1], A.L.M. Reddy[2], K Kalaga[2], N. Perea-López[1], M. Audiffred[1,3], D. Swanson[1], H.R. Gutiérrez[4], R. Vajtai[2], V. Meunier[5], B.G. Sumpter[6], P.M. Ajayan[2], H. Terrones[1], M. Terrones[1,7,*]

*1 Pennsylvania State University, USA (*mut11@psu.edu) 2 Rice University, USA*
*3 Universidad de Guanajuato, Mexico 4 University of Louisville, USA*
*5 Rensselaer Polytechnic Institute, USA 6 Oak Ridge National Laboratory, USA*
*7 Shinshu University, Japan*

Much has been said about the individual roles of sulfur [1] and boron [2] in the synthesis of carbon fibers and nanotubes (CNTs). We have studied the role of both boron and sulfur together throughout the synthesis of CNTs, via an aerosol assisted chemical vapor deposition (CVD) process. During our experiments, a solution containing Toluene ($C_6H_5CH_3$) and Ferrocene ($C_{10}H_{10}Fe$) together with small amounts of B and S precursors was pyrolyzed in an ultrasonic generator. The mist was carried by an Argon flow through the quartz reaction tube inside a furnace at temperatures ranging between 800-900 °C. The resulting material consists of CNT-based hierarchical structures. The incorporation of both boron and sulfur in the precursor solution induces CNT junctions, causing the micron-size carbon fibers to be decorated with radially grown CNTs that resemble "nanotentacles." The materials were characterized using SEM, HRTEM, EELS, TGA, XRD, XPS, and Raman spectroscopy. Finally, because of their high surface area, these synthesized structures have been tested for their possible application in supercapacitors and Li-ion batteries.

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**P108**

# Effect of MWCNTs purity in electrochemical response of near-percolation amperometric composites

J. Muñoz, J. Bartrolí, M. Baeza and F. Céspedes

*Sensors and Biosensors Group, Universitat Autònoma de Barcelona (UAB), 08193 Cerdanyola del Vallès (Bellaterra), Barcelona, Spain (josemaria.munoz@uab.cat)*

The main drawback in carbon nanotubes (CNTs) composite materials resides in the lack of homogeneity of the different commercial CNTs lots due to different amounts of impurities in the nanotubes, as well as dispersion in their diameter/length and state of aggregation. Nevertheless, the aspect ratio of the CNTs is one of the main parameters that determine their percolation behaviour and the conductivity of the composites [1]. The parameters of study for this work were the purity and the activation or non–activation of the raw CNTs. Three different series of multiwall carbon nanotubes (MWCNTs) dispersed on resin epoxy containing 1% to 20% in conductor material have been used to fabricate composite electrodes for electroanalytical purposes. Purity was characterized by Thermogravimetric Analysis (TGA), Transmission Electron Microscopy (TEM) and X–ray fluorescence (FP–XRF). The detection of functional groups on the carbon surface was conducte by (IR) spectroscopy. The optimum composition of the composite electrodes was characterized by Percolation Theory [2], Electrochemical Impedance Spectroscopy (EIS), Cyclic Voltametry (CV) and Atomic Force Microscopy (AFM). The feasibility of this approach in terms of electroanalytical response was demonstrated by means of the amperometric detection of ascorbic acid in water solution [3]. Preliminary studies showed that the composites with CNTs which contain an 11% in impurities had the best electrochemical and limit of detection (LOD) results. This study opens the way for the use of CNTs doped with metal nanoparticles for the optimization of amperometric (bio)sensors.

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**P109**

# Capacitance extraction of graphene field-effect transistors from time-domain pulse responses

Incheol Nam[1,3,4], Daewon Kim[1,3], Taegeun Kim[1,3], Keun Heo[1,3], Unjeong Kim[2], Chan-Wook Baik[2], Sungwoo Hwang[1,2,*], and Sangsig Kim[3]

*1 Research Center for Time-domain Nano-functional Devices, Samsung Advanced Institute of Technology, Yongin 446-712, Korea (*swnano.hwang@samsung.com)*
*2 Frontier Research Laboratory, Samsung Advanced Institute of Technology, Yongin 446-712, Korea*
*3 Department of Electrical Engineering, Korea University, Seoul 136-701, Korea*
*4 DRAM Product Engineering Team, Memory Division, Samsung Electronics Co., Hwasung 445-701, Korea*

We demonstrate a simple extraction method for capacitances in graphene field-effect transistors (GFETs). Intrinsic gate-oxide and parasitic capacitances from time-domain pulse responses are separately extracted by using a small-signal equivalent circuit model together with a differential equation of RC time constant. In particular, transient currents were measured in GFETs mounted on an aluminum coplanar waveguide, when rectangular pulses are applied to a gate electrode. The validity of the extraction method is proved in the case of MOSFETs under similar experimental conditions. Compared with previous calculations using a large-scale fixture for measurement, our characterization method is remarkably effective in nano-scale area without considering fixture designs [1, 2].

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P110

## Thermodynamics on soluble carbon nanotubes: how do DNA molecules replace surfactants on carbon nanotubes in water?

Yuichi Kato[1], Ayaka Inoue[1], Yasuro Niidome[1,2], Naotoshi Nakashima[1,2,3,*]

*1 Department of Applied Chemistry, Graduate School of Engineering, Kyushu University, Motooka 744, Fukuoka 819-0395, Japan*
*2 WPI-I2CNER, , Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan*
*3 JST-CREST*

Investigating the interactions between molecules and single-walled carbon nanotubes (SWNTs) is one of the central issues in carbon nanotube science [1].

We report *thermodynamics on soluble carbon nanotubes* that enables deep understanding the interactions between single-walled carbon nanotubes (SWNTs) and molecules[2]. We selected sodium cholate and single-stranded cytosine oligo-DNAs (dCn (n = 4, 5, 6, 7, 8, 10, 15, and 20)), both of which are typical SWNT solubilizers, and successfully determined thermodynamic properties (delta$G$, delta$H$ and delta$S$ values) for the exchange reactions of sodium cholate on four different chiralities of SWNTs ((n,m)=6,5), (7,5), (10,2), and (8,6)) for the DNAs. Typical results contain i) the dC5 exhibited an exothermic exchange, whereas the dC6, 8, 10, 12, 15, and 20 materials exhibited endothermic exchanges, and ii) the energetics of the dC4 and dC7 exchanges depended on the associated chiral indices and could be endothermic or exothermic. The presented method is general and is applicable to any molecule that interacts with nanotubes. The study opens a way for *science of carbon nanotube thermodynamics*.

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P111

## Synthesis and structural properties of carbon nanoscrolls

Alexander N. Obraztsov[1,2], Andrey L. Chuvilin[3,4], Rinat R. Ismagilov[1]

*1 M.V. Lomonosov Moscow State University, Department of Physics, Moscow, Russia (obraz@polly.phys.msu.ru)*
*2 University if Eastern Finland, Department of Physics and Mathematics, Joensuu, Finland*
*3 CIC NanoGUNE, Donostia-San Sebastian, Spain*
*4 IKERBASQUE, Basque Foundation for Science, Bilbao, Spain*

Carbon nanoscrolls (CNS) formed by spirally coiled graphene sheets is a peculiar yet not well explored member of carbon nanomaterials family [1]. The possibility to grow well crystallized conically shaped CNS with polygonal cross section by chemical vapor deposition (CVD) has been previously demonstrated [2]. Here we present a deeper insight into synthesis conditions, growth mechanism and the structure of CVD grown CNSs. The deposits containing CNSs as well as other graphitic and diamond forms of nanocarbon have been obtained on Si substrates using a direct current discharge plasma activated CVD system [3]. Carbon structures obtained at different stages of the synthesis have been further characterized by Raman, SEM and HR TEM in combination with FIB. Most of the CNS needles have shapes of twisted prisms with polygonal cross-sections similar to that reported in [2]. We have found that the CNSs, as well as graphene flakes presented in the deposits, grow perpendicular to the crystal facets from inside of the diamond micro-crystallites, formed at the initial steps of the CVD process. HRTEM investigation of the cross-sections of diamond crystals at the initial growth steps reveals the seeds of graphene and tubular structures in the bulk. These observations suggest a two steps growth process of well ordered graphitic structures during CVD: at a first step micron size diamond crystals are formed being full of strain-induced stacking faults (SF); at the second step diamond undergoes annealing and graphitic planes propagate in the bulk along the SFs, exit to the surface and continue growing from the vapor phase preserving flat or twisted crystalline structure as templated by diamond parent crystal.

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## P112 Electro-mechanical properties of polyurethane composite with carbon nanotubes network oxidized by $KMnO_4$ and $O_2$ RF plasma

Robert Olejnik[1,2], Petr Slobodian[1,2],Pavel Říha[3], Uroš Cvelbar[4], Petr Sáha[1,2]

*1 Polymer Centre, Faculty of Technology, T. Bata University, T.G.M. 275, 76272 Zlin, Czech Republic, (rolejnik@volny.cz)*
*2 Centre of Polymer Systems, University Institute, T. Bata University, Nad Ovcirnou 3685, 76001 Zlin, Czech Republic*
*3 Institute of Hydrodynamics, Academy of Sciences, Pod Patankou 5, 166 12 Prague 6, Czech Republic*
*4 Jozef Stefan Institute F4, Jamova cesta 39, 1000 Ljubjana, Slovenia*

The effect of functionalization of multi-walled carbon nanotubes using $KMnO_4$ oxidation and oxygen plasma treatment on the electrical resistance of nanotube network/polyurethane composite subjected to elongation has been studied. The layered composite is prepared by taking a non-woven polyurethane filtering membrane which is made by electrospinning, enmeshing it with carbon nanotubes and melding them into one. The testing has shown tenfold composite resistance increase for the composite prepared from $KMnO_4$ oxidized nanotubes in comparison to the network prepared from pristine nanotubes. The evaluated sensitivity of the treated composite in terms of the gauge factor increases linearly with strain from values around 5 at the start of deformation to nearly 45 at the strain 12 %. This is a substantial increase, which put the composite prepared from $KMnO_4$ oxidized nanotubes among ranges the materials and strain gauges with the highest sensitivity of electrical resistance measurement.

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## P113 Redox activity of encapsulated metal clusters tuned by metallic and semiconducting property of carbon nanotubes

Fan Zhang[1], Xiulian Pan[1,*], Yongfeng Hu[2], Liang Yu[1], Xiaoqi Chen[1], Peng Jiang[1] Xinhe Bao[1,*]

*1 State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences; Dalian 116023, China (*panxl@dicp.ac.cn and xhbao@dicp.ac.cn)*
*2 Canadian Light Source, 44 Innovation Boulevard, Saskatoon, SK, S7N 2V3, Canada*

An increasing number of studies reveal that confinement of metal or metal oxide nanoparticles inside carbon nanotubes (CNTs) often leads to significantly enhanced catalytic activity with respect to the same bare metal nanoparticles or those deposited on the outer walls of CNTs [1-3]. Such a different behavior originates from both the physical (spatial restriction of the channels) and chemical factors (interaction of confined species with the curved graphene walls) inside CNTs.

We demonstrate here that reactions confined within single wall carbon nanotube (SWCNT) channels can be further tunbed by their metallic and semiconducting properties. Taking encapsulated rhenium species as a probe, in situ Raman and XANES spectroscopies, which provide complementary information about the electronic state of carbon nanotubes and rhenium, reveal electronic interaction between encapsulated species and nanotubes. As a result, the reduction and oxidation activities of rhenium species differ significantly when they are encapsulated within metallic or semiconducting nanotubes.

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P114

# Nonlinear optical imaging and spectroscopy of individual carbon nanotubes with four wave mixing and second harmonic generation microscopy

M. Pettersson[1], J. Aumanen[1], P. Myllyperkiö[1], A. Johansson[2], O. Herranen[2], M. J. Huttunen[3], G. Bautista[3], H. Jiang[4], A. G. Nasibulin[4], E. I. Kauppinen[4], M. Ahlskog[2], M. Kauranen[3]

*1,2 Nanoscience Center, Department of Chemistry[1] and Physics[2], University of Jyväskylä, Finland*
*(mika.j.pettersson@jyu.fi)*
*3 Department of Physics, Tampere University of Technology, Tampere, Finland.*
*4 Department of Applied Physics and Center for New Materials, Aalto University, Finland.*

Due to difficulties in synthesizing homodisperse samples, it is important to investigate individual carbon nanotubes (CNT) with known structure. Raman and fluorescence spectroscopy are nowadays routinely used in investigations of individual CNTs but the huge potential of nonlinear spectroscopy has not been exploited much so far although it is anticipated to become an important characterization tool of SWCNTs. To this end, we are working with nonlinear spectroscopy and microscopy of individual carbon nanotubes, developing both time-resolved four-wave mixing (FWM) [1], as well as second harmonic generation (SHG) measurements [2]. We combine nanofabrication methods and electron microscopy in order to produce samples with structurally well-defined individual single wall carbon nanotubes (SWCNT). The signals are sufficiently strong allowing imaging of SWCNTs with good sensitivity. We discuss some technical aspects of the measurements and show that FWM imaging can be used to follow local photo-oxidation in individual SWCNTs.

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P115

# B-doped MWNT sponges: synthesis, structural characterization and oil absorption application

L. Pulickal Rajukumar[1], A. L. Elías[1], N. Perea-López[1], H. R. Gutiérrez[2], J. Wang[1], A. McCreary[1], W. Zhao[3], A. Roy[4], J. Suhr[3], R. Vajtai[5], P. M. Ajayan[5], B. I. Yakobson[5], H. Terrones[1], M. Terrones[1], B. G. Sumpter[6], V. Meunier[7]

*1 The Pennsylvania State University, USA (mut11@psu.edu) 2 University of Louisville, USA*
*3 University of Delaware, USA 4 Air Force Research Laboratory, USA 5 Rice University, USA,*
*6 Oak Ridge National Laboratory, USA 7 Rensselaer Polytechnic Institute, USA*

We report the synthesis and sorption capabilities of three dimensional B-doped multi-walled carbon nanotubes (MWNTs) structures. An aerosol assisted chemical vapor deposition (CVD) was used to synthesize the 3-D MWNT materials. The synthesis was carried out by atomizing a precursor solution of Toluene ($C_6H_5CH_3$) and Ferrocene ($C_{10}H_{10}Fe$) by the action of an ultrasonic generator under an Ar atmosphere. The B precursor was introduced directly into the precursor solution prior the CVD process. The Boron doping induces elbow-like features in the nanotubes that lead to the entangling of MWNTs, resulting in a macroscopic sponge morphology. Negative curvature regions in the graphitic lattice constitute favorable sites where B atoms can be embedded. Theoretical simulations demonstrated that B is more energetically stable in heptagon-like sites [1]. This has also been verified through elemental and microscopic analyses. The B-doped MWNT sponges have been found to be hydrophobic and oleophilic. Oil absorption experiments at different temperatures were performed on these doped sponges and high porosity, good recyclability and oil sorption capacity (>100 g/g) were observed. Mechanical testing was also performed while acquiring Raman spectra, in order to study the correlation between Raman shifts and applied strain.

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## P116 Absorbance of the free-standing SWCNT film under heating

Sergey D. Shandakov[1], Olivier Reynaud[2], Ilya V. Anoshkin[2], Ying Tian[2], Esko I. Kauppinen[2],
Albert G. Nasibulin[2]

*1 Kemerovo State University, Krasnaya st., Russia*
*2 Nanomaterials Group, Aalto University, Finland (olivier.reynaud@aalto.fi)*

Because of their outstanding optoelectronic properties, single-walled carbon nanotubes (SWCNTs) are promising material for many devices such as flexible displays, solar cells, capacitive touch sensors, thin films transistors [1]. It is crucial that any device made of SWCNT works the same way with time; therefore, it is important to verify the stability of the SWCNTs. However, significant changes in optoelectronics properties of SWCNT can be observed after exposure to air or oxygen [2].

Optical absorbance spectroscopy measurements results show that long-time exposure of SWCNT to air leads to the decrease of Van Hove transition (E11) intensity. In this contribution, we present the effect of heating on free-standing SWCNT films in ambient atmosphere after long exposure to air. We investigated effects of thermal and resistive heating (27-250 °C) in ambient atmosphere, and we show that the first van Hove transition inhibition can be removed after heating up to around 170 °C.

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## P117 Supramolecular functionalization of carbon nanotubes using poly(2,7-carbazole)s

Nicole Rice and Alex Adronov

*Department of Chemistry, McMaster University, Canada (adronov@mcmaster.ca)*

A novel 2,7-carbazole monomer unit was synthesized and used to prepare two poly(2,7-carbazole)s, a homopolymer and an alternating copolymer with 2,7-fluorene. Both polymers were obtained in relatively high molecular weight, and both display excellent solubility in common organic solvents. The carbazole polymers were able to effectively disperse single-walled carbon nanotube bundles in both THF and toluene using a relatively simple procedure to yield concentrated polymer-carbon nanotube samples that were stable for months. The polymer-coated carbon nanotube samples were characterized by thermogravimetric analysis, atomic force microscopy, absorbance spectroscopy, photoluminescence mapping and Raman spectroscopy. It was found that the polymers used in this study preferentially interact with carbon nanotubes having diameters of 1.15 nm or less. Additionally, absorbance and photoluminescence data indicates that the dispersions are enriched in semiconducting nanotubes. Strong carbon nanotube fluorescence was observed in both photoluminescence mapping and Raman spectra of thin films of our polymer-carbon nanotube composites, indicating that our polymers are capable of keeping single-walled carbon nanotubes effectively debundled after removal of solvent. [1]

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P118

## Understanding the $NO_x$ adsorption mechanisms on metallicity-sorted single-walled carbon nanotubes

Georgina Ruiz-Soria[1], Markus Sauer[1], Alejandro Perez[2], Duncan J. Mowbray[2], Paolo Lacovig[3], Matteo Dalmiglio[3], Silvano Lizzit[3], Kazuhiro Yanagi[4], Andrea Goldoni[3], Angel Rubio[2], Paola Ayala[1], Thomas Pichler[1]

*1 Faculty of Physics, University of Vienna, Austria (georgina.ruiz@univie.ac.at)*
*2 Nano-bio Spectroscopy Group and ETSF Scientific Development Center, Department of Materials Science, Faculty of Chemistry, University of the Basque Country, Spain*
*3 Sincrotrone Trieste, Italy*
*4 Department of Physics, Tokyo Metropolitan University, Japan*

The sensing capability of single-walled carbon nanotubes (SWCNTs) is directly related to their high surface-to-volume ratio, electronic properties and chemical reactivity. This has been thoroughly investigated and reported for different compounds. Nevertheless, the possibility of getting a more fundamental insight into the interaction of SWCNTs and gas molecules encounters several limitations. In this context, we have inspected the changes in the electronic properties of ultra clean sorted SWCNTs when exposed to $NO_2$ gas. Combining X-ray absorption and photoelectron spectroscopy, the adsorption mechanism was investigated and the chemical reaction pathway was determined. With this, we have found for the first time that this mechanism is strongly dependent on the metal character of the samples. Our results suggest that the decomposition and recombination of N-containing compounds are favored by the presence of semiconducting and metallic SWCNTs in different proportions, being physisorption the predominant process. However, a weak chemisorption was also identified, where metallic SWCNTs showed to be twice more reactive than the semiconducting ones. We have also resolved the vibrational structure of the system providing proof that weak covalent bonds can be formed between $(NO)_2$ and the remaining structural defects on the SWCNTs' sidewalls. Understanding the complex mechanism of $NO_2$ adsorption on SWCNTs has a key role in the further optimization for nanotube-based sensors and their application.

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## Electronic Raman spectra and origin of Fano resonance in metallic single-wall carbon nanotubes

Riichiro Saito[1], Eddiwi H. Hasdeo[1], Ahamad R. T. Nugraha[1], Kentaro Sato[1], Mildred S. Dresselhaus[2]

*1 Department of Physics, Tohoku University, Sendai 980-8578 Japan (rsaito@flex.phys.tohoku.ac.jp)*
*2 Massachusetts Institute of Technology, MA 02139-4307 USA*

In metallic single wall carbon nanotubes (m-SWNT), G band (in-plane optical phonon modes) Raman spectra becomes soft and broad because of the coupling of the G band phonon with an electron-hole pair (or exciton) excitation in the gapless linear energy sub-band, which is known as the Kohn anomaly effect [1]. However, the asymmetric spectral shape of the G band for m-SWNTs, also known as Breit-Wigner-Fano (BWF) line shape, is still not well explained theoretically. Since BWF line shapes are commonly observed in graphene or graphite intercalation compounds [1], electrons in the linear energy band of m-SWNTs should be expected to exhibit this asymmetry spectral shape. In this presentation, we explained the origin of BWF line shape by interference of phonon G band spectra and electronic Raman spectra (ERS). The ERS is observed in m-SWNTs [2] and the exciton-exciton interaction between a photo-excited exciton and an exciton in the metallic energy sub-band is relevant to the ERS. We calculated ERS spectra as a function of laser excitation energy and the Fermi energy which reproduce the experimental BWF spectral shape well. One surprising message in this calculation is that the direct Coulomb interaction between the two excitons vanishes at q=0 because of the symmetry of the two sub-lattices of graphene even though the Coulomb interaction at q=0 is generally considered to be a maximum. This surprising effect can be shown analytically, too. As an interference effect between the ERS and G band spectra, BWF spectral shape is calculated in which experimental BWF features can be analyzed [3].

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## P120

# Tunable metallicity dependent p-type doping in single-walled carbon nanotubes

Markus Sauer[1], Hidetsugu Shiozawa[1], Georgina Ruiz-Soria[1], Hiromichi Kataura[2], Kazuhiro Yanagi[3], Stefan Krause[4], Thomas Pichler[1]

*1 Faculty of Physics, University of Vienna, Strudlhofgasse 4, 1090 Vienna, Austria*
*(markus.sauer@univie.ac.at)*
*2 Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology, Central 4, Higashi 1-1-1, Tsukuba, Ibaraki 305-8562, Japan*
*3 Department of Physics, Tokyo Metropolitan University, 1-1 Minami-Osawa, Hachiouji, Tokyo 192-0397, Japan*
*4 Bessy II , Helmholtz Zentrum Berlin, Albert Einstein Straße 15, 12489 Berlin, Germany*

Recent studies on the intercalation of single-walled carbon nanotubes (SWCNTs) with molecules like K or $FeCl_3$ mostly neglect the influence of the nanotube metallicity on the resulting characteristics. Therefore we investigated the electronic structure of SWCNTs intercalated with $FeCl_3$ using highly pure metallic and semiconducting nanotubes as a starting material produced by state of the art metallicity separation techniques.Making use of X-ray photoemission and X-ray absorption measurement, the intercalated nanotubes were probed to discern their electronic properties. Strong p-type doping concomitant to a strong shift of the Fermi level is evidenced. Analysis of the valence band illustrates that semiconducting SWCNTs exhibit significantly higher doping after similar intercalation doses. For metallic SWCNTs the 1D Tomonaga-Luttinger-liquid is preserved over the whole intercalation range whereas semiconducting SWCNTs show a transition into a 3D Fermi liquid state already at very low doping. Together with results from Raman measurements this study poses another important step towards precisely tunable graphitic materials yielding a wide range of different properties when metallicity effects are taken into account.

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## P121

# CVD growth of multiwall carbon nanotube based structures

Muhammad Imran Shahzad[1], Denis Perrone[1,2], Nadia Shahzad[1,2], Alberto Tagliaferro[1]

*1 Department of Applied Science and Technology (DISAT), Politecnico di Torino, Italy*
*(imran.shahzad@polito.it)*
*2 Center for Space Human Robotics, Italian Institute of Technology (IIT), Torino, Italy*

The vertically aligned carbon nanotubes uniformly grown by CVD on a patterned surface feature interesting and unique mechanical, electrical and thermal properties which lead to a variety of potential application such as heat dissipation systems [1], field emission sources [2], conductive electrodes and micro mechanical devices [3].

This article reports on the columnar growth of Vertically Aligned Multiwall Carbon Nanotubes (VA-MWCNTs) on patterned Si surface. In the first part, we have developed a procedure of patterning the Silicon surface which allows the growth of predetermined MWCNTs structures. Secondly, we have focused on the growth of Carbon Nanotubes based structures by chemical vapor deposition technique at $850^0$C with Camphor and Ferrocene as carbon precursors and catalyst respectively. Field Emission Scanning Electron Microscopy is employed at low magnification to verify the accurate patterning and at high magnification to examine the surface morphology of carbon nanotubes structures. The dimensions of CNT structures are in the range of few hundred micrometers while the diameter of single MWCNT was in the range of 30-80 nm.

These MWCNTs based microstructures have several electrical and thermal applications. For instance they can be very useful for heat transfer systems as the lower thermal conductivity of fluids can be improved by the inclusion of nanotubes thanks to their peculiar 1-dimensional heat transfer characteristics.

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**P122**

## Theoretical prediction of thermoelectric properties of conical carbon nanofibers

Derek A. Thomas[1], Takahiro Yamamoto[2], Tomofumi Tada[1,3], Satoshi Watanabe[1]

*1 Department of Materials Engineering, University of Tokyo, Japan*
*2 Faculty of Engineering, Tokyo University of Science, Japan*
*3 Present: Materials Research Center for Element Strategy, Tokyo Inst. Technol., Japan*

The unique thermal and electrical properties of carbon systems, such as the high electrical conductivity of graphene [1] and high thermopower seen in multilayer graphene [2], make carbon nanostructures promising candidates for next generation transport applications. Carbon nanofibers can have a wide diversity of geometric underlying structures, and better understanding of the implications of nanostructure on transport properties is critical in building on complex integrated technologies.

The conical-helix nanofiber (CHNF) and cup-stacked nanofibers (CSNF) are annular graphite-like nanotubes. CHNF is formed by a helically wound graphene ribbon. Experiments suggest radically different thermal properties such as a two orders of magnitude decrease in thermal conductivity for conical nanofibers than for graphene [3], which agrees with our molecular dynamics estimates using CHNF and CSNF [4]. Because of the continuity of covalent bonding in CHNF and low thermal conductivity, we have estimated thermoelectric figure of merit of CHNF to have an upper limit of 3.8 [3]. In the present study, we investigate the electrical properties of carbon nanofiber structures within the nonequilibrium Green's function method using Atomistix Toolkit [5] to make a more quantitative estimate of the figure of merit. We also look at the effect of defects on thermopower and electrical conductivity to estimate the applicability of carbon nanofibers in thermoelectric applications.

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**P123**

## High current density and long term electron emission from optimized and patterned VACNTs for x-ray tomography applications

R. Ummethala[1], D. Leberl[2], S. F. Tedde[2], A. Leonhardt[1], B. Büchner[1], J. Eckert[1]

*1 Leibniz Institute for Solid State and Materials Research (IFW), Helmholtzstrasse 20, 01069 Dresden, Germany*
*(r.n.ummethala@ifw-dresden.de)*
*2 Siemens AG, Corporate Technology, Guenther-Scharowsky-Strasse 1, 91058 Erlangen, Germany*

Vertically aligned carbon nanotube (VACNT) bundles have been grown on patterned Si substrates with varying bundle sizes and were characterized regarding electron field emission. The substrates were patterned to obtain squares of 100 x 100 $\mu m^2$, 50 x 50 $\mu m^2$, 10 x 10 $\mu m^2$ and 5 x 5 $\mu m^2$ with a spacing of 20 µm, using electron beam lithography (EBL). The patterned substrates were sputtered with Fe catalyst layer and subsequently CNTs were grown by means of a direct current plasma enhanced chemical vapor deposition (DC-PECVD) reactor using ethylene as the hydrocarbon precursor, along with argon and hydrogen.

Electron field emission from such patterned VACNTs was measured using a spacer-based diode characterization setup. They were compared with each other and also with uniformly grown CNTs. The field emission from VACNTs patterned as 10 x 10 $\mu m^2$, in pulsed operation mode, exhibited a very high current of 321 mA and a current density of 5.7 A $cm^{-2}$ at an applied electric field of 14 V $\mu m^{-1}$. A stable current of 40 mA was recorded for a cumulative emission time of about 70 hours. The degraded structure of the CNTs was analyzed by using SEM and HR-TEM. The robust, well-aligned and optimally patterned VACNTs on Si substrate have a high potential to be applied as electron emitters in x-ray computed tomography and other electronic devices.

**P124**

## Novel photonics devices based on carbon nanotubes

M. Guézo[1], Q. Gu[1], G. Thomas[1], S. Loualiche[1], J. Le Pouliquen[1], T. Batte[1], O. Dehaese[1],
L. Bodiou[2], F. Grillot[3], Y. Battie[4], A. Loiseau[5], B. L. Liang[6]

*1 FOTON, UMR CNRS 6082, INSA, avenue des Buttes de Coësmes CS 14315, 35043 Rennes Cedex, France (maud.guezo@insa-rennes.fr)*
*2 FOTON, UMR CNRS 6082, ENSSAT,* 6 rue Kerampont BP 80518 22 305 Lannion Cedex, France
*3 Télécom ParisTech, Ecole Nationale Supérieure des Télécommunications, Laboratoire CNRS LTCI, 46 rue Barrault, 75634 Paris Cedex 13, France*
*4 LCP-A2MC, Institut de Chimie Physique et Matériaux (ICPM), 1 boulevard Dominique François Arago, 57070 METZ Technopôle, France*
*5 LEM,ONERA, BP72, 29 avenue de la Division Leclerc, 92322 Châtillon Cedex, France*
*6 Electrical Engineering Department, University of California at Los Angeles, Los Angeles, CA 90095, USA*

Nonlinear optical properties of carbon nanotubes (CNT) have been highlighted, in direct comparison with quantum wells (QW) for telecom applications [1]: CNT present ultrafast absorption dynamics and large 1D-excitonic nonlinearities. We aim at demonstrating the huge potential of CNT-based optical devices for high-bit-rate telecom applications, as simple-process and low-cost solution in comparison with QW-based devices [2]. Furthermore, we develop a novel structure of electrically-pumped active source, based on CNT. Such CNT-laser diode not only has great potential towards the development of future optoelectronic applications, but offers an excellent platform to study optical phenomena in one-dimension. Thus, we will present our research studies on passive as well as active photonics devices based on CNT for telecom applications.

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**P125**

## CdSe nanocrystal / carbon nanotube composites

Asmus Vierck[1], Cristina Palencia[2], Michaela Meyns[2], Mirjam Volkmann[2], Holger Lange[3],
Christian Klinke[2], Beatriz H. Juárez[3], Janina Maultzsch[1]

*1 Institute for Solid State Physics, TU Berlin, Berlin, Germany (avierck@physik.tu-berlin.de)*
*2 Institute of Physical Chemistry, University of Hamburg, Hamburg, Germany*
*3 Department of Physics, Columbia University, New York, USA*
*4 IMDEA Nanoscience and Universidad Autónoma de Madrid, Madrid, Spain*

Recently, hybrid nanomaterials based on semiconductor nanocrystals (NCs) and nanotubes (NTs) attracted a lot of interest due to their potential use in optoelectronic and photovoltaic devices. In order to enable such devices, detailed studies on their structural as well as electronic properties are required. Especially the subject of charge transfer arises to be crucial for possible applications. CdSe NCs have proven to be highly efficient light absorbers with a tunable bandgap, and by transferring light-induced charges they can effectively increase the photoconductivity of the attached NTs. Here, carbon nanotubes (CNTs) with a smaller and boron nitride nanotubes (BNNTs) with a wider band gap than CdSe are studied as composite components. CdSe-nanotube composites were prepared using one-pot synthesis by the hot injection method [1], which allows controlling the CdSe NC size and shape [2]. As opposed to the common method of creating artificial defects in CNTs to aid sidewall functionalization, our samples do not require such treatment as the NCs attach directly to the CNT sidewalls during growth. In this way we can ensure that the vibrational and electronic properties of the composite are governed only by the properties of the individual components and their interaction and not by linker molecules or randomly distributed defects. The influence of attaching CdSe to both CNTs and BNNTs will be discussed based on Raman spectroscopy and photoluminescence measurements. While the NC photoluminescence quenches after attachment, we show that the influence on most observed phonon modes is comparably small.

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P126

# The field emission mechanism of carbon nanotube at a small anode-cathode distance

Roman Voloshin[1], German Kosakovskii[2,3], Zoya Kosakovskaya[2,3,*],
Evgeny Blagov[3], Andrey Orlov[2,3] and Anatoly Smolovich[2,3]

*1 National Research University of Electronic Technology "MIET", Russia*
2 Kotel`nikov *Institute of Radioengineering and Electronics of RAS, Russia (*kosakovskaya@bk.ru)*
*3 Institute of Nanotechnology of Microelectronics of RAS, Moscow, Russia*

It is known the distance between the neighboring point cathodes into the matrix Spindt cathode is a few microns. For this reason the distance between the anode and the cathode is less than 1 micron. If the anode-cathode distance is less than the nanotube length, the anode and the nanotube cathode are united as the electrical dipole. The charge of the nanotube tip is formed the point charge on the anode surface. In this case the anode may emit the electrons like the nanotube at low voltage. If we change the polarity of the electrodes the I-V characteristic will be a symmetrical function.

In this study we investigated the field emission from carbon nanotubes when the distance between nanotube and anode less 1 mkm. The model of nanodiode was assembled into a scanning electron microscope Carl Zeiss NEON 40 and contained the nanotube emitter with diameter of 10 nm and a length 1 mkm which was attached to the surface of the Ni cathode. The end of tungsten anode has a diameter 200 nm. The nanotube-cathode distance was equal to 700 nm. The I-V characteristics were measured at voltages below 10 V with step 30 mV. It was found the emission current is observed at the change of the polarity of the electrodes of nanodiode when the vacuum gap between the anode and the nanotube is less than the length of the nanotube. It should be noted, that often the magnitude of emission current from the anode is more than the one from nanotube, what may be explained the good ohmic contact of 3D anode with 3D electron source. We observed the resonance peaks near Van Hove singularity and the threshold voltage on I-V characteristic.

The mechanism of the observed phenomenon will be discussed.

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P127

# Anomalous electric-field screening at the edge atomic sites of finite-length zigzag carbon nanotubes

Ayaka Yamanaka, Susumu Okada

*Graduate School of Pure and Applied Sciences, University of Tsukuba, Japan*
*(ayamanaka@comas.frsc.tsukuba.ac.jp)*

In this decade, carbon nanotubes (CNTs) are attracting much attention due to its possible application for semiconductor electronic devices in the next generation. In these devices, CNTs essentially feel an external electric field. Therefore it is urging us to unravel fundamental properties of CNTs under an electric field for designing and fabricating nanotube-based electronic devices. In our previous work, we elucidate that capped CNTs nonuniformly screen the external electric field depending on the local atomic arrangement due to the inhomogeneous charge distribution arising from the bond alternation [1]. In this work, we study the electronic properties of finite-length CNTs with the open ends which are terminated by hydrogen atoms to unravel the effects of the caps of nanotubes by performing first-principles total-energy calculations based on density functional theory. We consider the model system in which hydrogen-terminated finite-length CNTs are sandwiched by the two electrodes, which apply the electric field parallel to the CNT axis. We analyze the electrostatic potential on each C atomic site to uncover how the electric field affects on the electronic properties of the CNTs. Although the pentagonal rings associated with the nanotube-cap are absent, we find that the electrostatic potential also strongly depends on the atomic site as in the case of capped nanotubes. The fact indicates that the structure-dependent screening against the external electric field is essential for any CNTs irrespective to their edge morphology. Furthermore, in the zigzag nanotubes, we find that the unusual screening against the external field associated with the peculiar edge localized state [2].

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## P128 Carbon nanotubes bumps for off-chip electrical interconnects

Ray Chin Chong Yap[1,2], Christophe Brun[1], Dunlin Tan[1,2], Edwin Hang Tong Teo[1,2], Dominique Baillargeat[1], Beng Kang Tay[1,2]

*1 CINTRA CNRS/NTU/THALES, UMI 3288, Research Techno Plaza, 50 Nanyang Drive, Border X Block, Level 6, Singapore 637553, Singapore (ebktay@ntu.edu.sg)*
*2 School of Electrical and Electronics Engineering, Nanyang Technological University, Block S1, 50 Nanyang Avenue, Singapore 639798, Singapore*

Despite many challenges, carbon nanotubes (CNTs) is one of the key emerging materials for potential use in off-chip electrical interconnects. Off-chip interconnects processes are generally located at the backend packaging level, and its feature sizes are considerable large and have feature sizes in the microns levels. Typically off-chip interconnects methodology include flip chip and through silicon vias (TSVs) technology. Under More-than-Moore law, the significant of function integration (such as RF) and downscaling of packages dimensions will be one of the key future trends. However, at the same time of fulfilling the scaling trends, conventional metals are facing the limitations of electro-migration, scattering and skin depth effect at radio frequency. Hence compatible design integration and characterization of CNT at both DC and radio frequency must be explored.

The design integration processes to fabricate CNT bumps for flip chip application have been successfully demonstrated. By interconnecting CNT bumps to CNT bumps using a flip chip methodology, electrical conduction through CNTs to CNTs have been achieved [1]. Initially measurements at the DC and high frequency (up to 40 GHz) have also shown the potential of our fabrication methodology. In this work, the densities of the CNT bumps, barrier layers will be varied and addressed. It is believed that the densities of the CNT play a significant role to reduce the overall bump resistivity. A higher conductive and thinner barrier will also help to reduce the contact resistance of the CNT bumps. Different bumps designs will also be discussed. Characterization using DC 4-point probe and RF measurements using vector network analyzer will be demonstrated. With better designs, the performances of CNT bumps can be further improve and become closer to meet/be better than the current metal.

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## P129 Optical visualization and manipulation of individual ultralong carbon nanotubes

Rufan Zhang[1], Yingyingzhang[2], Qiang Zhang[1], Huanhuan Xie[1,2], Jingqi Nie[1], Fei Wei[1,*]

*1 Beijing Key Laboratory of Green Chemical Reaction Engineering and Technology, Department of Chemical Engineering, Tsinghua University, Beijing 100084, China (*wf-dce@tsinghua.edu.cn)*
*2 Center for Nano and Micro Mechanics, Tsinghua University, Beijing 100084, China*

It is of great significance to realize direct visualization and manipulation of individual carbon nanotubes (CNTs) for their characterizations and applications in ambient conditions. However, the observation of individual CNTs usually requires electron microscopes under high vacuum. Optical microscopes are much more convenient to be used, yet their resolution is low. Here, we report the visualization and manipulation of individual ultralong CNTs under optical microscopes by deposition of $TiO_2$ nanoparticles (NPs) on CNTs [1]. The strong scattering of $TiO_2$ NPs to visible light renders them visible by optical microscopes. Micro-Raman-spectroscopy measurement of individual CNTs is greatly facilitated by the optical visualization of CNTs. With the assistance of $TiO_2$ NPs, individual CNTs can be easily manipulated under an optical microscope at macroscopic scale and in ambient conditions. Based on our approach, various manipulation of ultralong CNTs, including cutting, transfer, fabrication of structures/devices, pulling out inner shell of multi walled CNTs, are demonstrated [2].

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P130

# Low-field electronic transport of carbon nanotube on hexagonal-boron nitride substrate

Zhengyi Zhang[1], Arend van der Zande[1], Mitsuhide Takekoshi[2], Xiao Guo[1], Philip Kim[2], James Hone[1]

*1 Dept of Mechanical Engineering, Columbia University, USA (zz2162@columbia.edu)*
*2 Dept of Physics, Columbia University, USA*

Carbon nanotube (CNT) is one of the best available systems to study one dimensional physics. However, so far most of the studies are based on the devices made of CNT on $SiO_2$/Si substrate, which introduces a large amount of trapped charges causing the long range scattering in conductance and spatial variation of the Fermi energy of CNT [1]. Moreover, recent studies showed that the surface polar phonon from $SiO_2$ is dominant in acoustic phonon-electron scattering in transport [2]. In order to achieve the best performance of CNT-FET device, we realize that thin hexagonal boron nitride(h-BN) would be an ideal substrate as it is atomically flat without any tangling bond, and it has the surface phonon energy twice of in $SiO_2$ which would not couple with electron at room temperature.

In this study, we perform the electronic transport measurements of ultra-clean CNTs transferred partially on thin flake of h-BN and partially on $SiO_2$ substrate. At room temperature, CNT on h-BN shows nearly hysteresis free low bias transport and much higher conductance compared with the one on $SiO_2$. And a clear coulomb blockade feature is observed at 2 K in vacuum, which was only obtained in clean suspended nanotubes before. These all suggest that h-BN is an ultraclean and uniform substrate for study of the intrinsic nature of CNT.

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P131

# In-situ TEM observation of zipper-like wall-to-wall coalescence of double-wall carbon nanotubes with home-made very high temperature compatible heating holder

Sihan Zhao, Ryo Kitaura*, Yasumitsu Miyata and Hisanori Shinohara*

*1 Department of Chemistry & Institute for Advanced Research, Nagoya University, Nagoya 464-8602, Japan (*r.kitaura@nagoya-u.jp or noris@cc.nagoya-u.ac.jp)*

We report, for the first time, the detailed *in-situ* TEM observation of wall-to-wall coalescence [1, 2] of double-wall carbon nanotubes (DWCNTs) at very high temperature (>2000˚C). Such observation is enabled by developing a home-made and very high temperature compatible TEM specimen heating holder equipped with a micro-sized carbon nanotubes (CNTs) network heater. This micro-sized CNT heater could reliably meet the necessity of sample heating to sufficiently high temperature (up to 3000˚C) while minimizing spatial drift of sample induced by the heating.

We observed that a single larger-diameter DWCNT is formed at the final stage through a zipper-like mechanism of wall-to-wall coalescence between two individual outer shells and two individual inner shells. The time sequential TEM images obtained throughout the reaction suggests the presence of the Stone-Wales type transformation, which provides insight on thermal reconstruction process of the nanocarbon materials.

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# Wednesday

**K3**

# Carbon nanotube-nanowires

Hisanori Shinohara

*Department of Chemistry & Institute for Advanced Research, Nagoya University, Japan*
*(noris@nagoya-u.jp)*

Putting atoms, molecules, and, even, nanowires of various kind into carbon nanotubes (CNT) is one of the most fascinating and exciting research topics in carbon nano-science and nanotechnology. By doing this, one can easily and drastically alter the electronic structures, electron transport and magnetic properties of CNTs, in which charge transfers between encapsulates and CNTs may oftentimes play crucial roles. In some cases, novel nanowires can be fabricated within carbon nanotubes which are not possible to produce in ambient conditions.

In this talk, I will discuss some novel structures, electronic and magnetic properties of nanowire-encapsulating carbon nanotubes. These include metal-nanowires [1-3], graphene nanoribbons [4] and diamond nanowires [5,6]. The carbon nanotubes encapsulating, for example, Eu-nanowires exhibit anomalous magnetic properties in low temperatures as compared with the solid Eu. We found that the internal space of CNTs may also facilitate to provide even diamond nanowires from the so-called (various) diamondoids.

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**I7**

# Chirality-controlled synthesis and electronic applications of single-wall carbon nanotubes

Chongwu Zhou

*Department of Electrical Engineering, University of Southern California, Los Angeles, CA 90089, USA*
*(chongwuz@usc.edu)*

Chirality-controlled synthesis of single-wall carbon nanotubes with predefined chiralities has been an important but elusive goal for almost two decades. Here we demonstrate a general strategy for producing carbon nanotubes with predefined chiralities by using purified single- chirality nanotubes as seeds for subsequent metal catalyst free growth, resembling vapour-phase epitaxy commonly used for semiconductor films. In particular, we have successfully synthesized (7, 6), (6, 5) and (7, 7) nanotubes, and used Raman spectroscopy to show unambiguously that the original chiralities of the nanotube seeds are preserved. In addition, we have performed electrical measurements on synthesized individual (7, 6) and (6, 5) nanotubes, confirming their semiconducting nature. I will also present the latest results of chirality-dependent growth rate study using vapour phase epitaxy. The vapour-phase epitaxy approach is found to be highly robust and should enable a wide range of fundamental studies and technological developments. Furthermore, I will report macroelectronics based on separated nanotube thin film transistors, including key technology components such as assembly of separated nanotube networks, high-yield fabrication of devices, and applications for AMOLED displays and printed electronics.

C14

## The study of micro-scale strain on flexible networked single-walled carbon nanotube electronic devices

Tae Geun Kim[1,4], Jong Seung Hwang[3,*], Un Jeong Kim[2], Sung Woo Hwang[1,2], and Sangsig Kim[4,*]

*1 Research center for Time-domain Nano-functional Device, Samsung Advanced Institute of Technology, Giheung, Yong-In, Gyeonggi, 446-712 Korea (*swnano.hwang@samsung.com and sangsig@korea.ac.kr)*
*2 Frontier Research Laboratory, Samsung Advanced Institute of Technology, Giheung, Yong-In, Gyeonggi, 446-712 Korea*
*3 School of Advanced Materials Science and Engineering, SKKU Advanced Institute of Nanotechnology, Sungkyunkwan University, Suwon 440-746, Korea*
*4 Department of Electrical Engineering, Korea University, Anam-dong, Seongbuk-gu, Seoul 136-713, South Korea*

The electrical properties of flexible field effect transistors (FETs) formed with single walled carbon nanotubes (SWCNTs) are systematically studied as a function of strain. The network SWCNT-FETs were fabricated on polyethersulfone (PES) substrate [1]. We found that the strain estimated from microscopic scale (nm) measurement by scanning electron microscopy (SEM) observation is significantly different from the strain calculated from macroscopic scale (cm) by factor of up to ~ 4. Micro-scale strain was estimated by in-situ measurement of length change with SEM equipped with the special bending jig. According to our close inspection by SEM, the large difference in strain obtained from two different measurement scales (micro- and macro-) can be attributed to formation of cracks and tears in the SWCNT network, or at the junction of SWCNT network and electrode during the strain process. Due to irreversible cracks and tear formation during the strain process, electrical properties such as on current level and field effect mobility are lowered by 4 % and 15 %, respectively.

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C15

## Towards high performance flexible supercapacitors based on carbon nanotubes

Woong Kim

*Department of Materials Science and Engineering, Korea University, Republic of Korea*

Development of high performance flexible supercapacitors requires the consideration of various aspects of materials ranging from physical flexibility and electrical and electrochemical properties to mechanical integrity of all the main components during bending cycles [1-3]. From these perspectives, we have been studying carbon nanotubes, gel electrolytes, current collectors, and supporting substrates. I will discuss how the structure of electrode materials and the composition of gel electrolytes affect the energy and power density of the supercapacitors, how we improve adhesion property between different materials, and whether asymmetric configuration can be accommodated to the flexible supercapacitors to improve energy density. Finally, development of stretchable supercapacitors will be briefly introduced.

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**C16**

## Electrolyte gated transistors of aligned carbon-nanotube thin film

Yoshifumi Wada[1], Jiang Pu[1], Yuki Takagi[1], Kazuhiro Yanagi[2], Taishi Takenobu[1,*]

*1 Department of Physics, Waseda University, Japan (takenobu@waseda.jp)*
*2 Department of Physics, Tokyo Metropolitan University, Japan*

Recently, electrolyte gated transistors (EGTs), which is using electrolyte for gate dielectrics, realize low voltage operation (<3V) and high on/off ratio (~$10^4$) of single-walled carbon nanotube (SWCNT) thin films [1]. This is due to electrochemical doping of semiconductor channel upon application of gate bias. However, because ion movement in electrolyte is necessary for electrochemical doping, high speed operation is extremely difficult. Here we tried to investigate the ion motion by measuring electrochemical impedance spectroscopy (EIS) for electric double layer capacitors (EDLCs), which is consist of two electrodes and electrolyte, and found out suitable structure for high-frequency response. Finally we applied this perception to SWCNT EGTs, which was aligned by recent reported solution process [2], and we realized 100 kHz response speed of gate electrolyte.

We measured EIS of laminate-structure EDLCs composed of ionic liquid, [EMIM][TFSI], and gold electrodes. Generally, limitation of frequency is determined as cut-off frequency. it linearly depends on inverse of ion resistance and EDL capacitance. To get higher frequency response, we employed asymmetric size electrode pair to get smaller capacitance with less increase of resistance. Because this structure successfully improved response speed of EDLCs, we applied this technique into transistors. For this purpose, asymmetric structure is very important and, to fabricate asymmetric EGTs, we used the aligned SWCNT film as transistor channel because of its small channel area. Using the aligned SWCNT films and EGT structure, we finally obtained high-speed response more than 100kHz in gate electrolyte of EGTs, which might be 1st step for future high-speed electronics based on electrolyte.

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**C17**

## Liquid-liquid interfaces: a suitable environment to prepare carbon nanostructures-based thin films

Rodrigo V. Salvatierra1, Sergio H. Domingues[1], Hiany Mehl[1], Vitor Hugo R. Souza[1],
Carlos E. Cava[1,2], Lucimara S. Roman[2], Marcela M. Oliveira[3], Aldo J.G. Zarbin[1]

*1 Department of Chemistry, Federal University of Parana (UFPR), Brazil (aldozarbin@ufpr.br)*
*2 Department of Chemistry, Federal University of Parana (UFPR), Brazil*
*3 Department of Chemistry & Biology, Technological Federal University of Parana (UTFPR), Brazil*

We have recently described a very versatile and efficient method to obtain homogeneous and transparent thin films of graphene- and carbon nanotubes-based polymer nanocomposites, through a chemical reaction at an aqueous-organic interface. In this work we show that this is a general method that can be extended to other kind of nanocomposites, as well as to prepare films based on one-phase composition material. The materials are directly obtained at the immiscible liquid/liquid interface as a free standing, transparent and self-assembled films. The films can be easily removed from interface and deposited over any kind of substrate, which represent a good advance in order to build efficient and reproducible devices. Thin, transparent, homogeneous and conducting films of CNTs, graphene, grahene/silver nanoparticles, CNTs/polyaniline, graphene/polianiline, CNTs/polythiophene and graphene/thiophene, deposited over ordinary and flexible substrates, will be presented. Application as ITO substitutes for transparent electrodes, in photovoltaic devices, sensors, electrochromic materials and as SERS substrates will be presented and discussed in light of the structure and morphology of the nanostructured films.

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# Electrical and thermal contacts between nanocarbon materials (graphene, nanotubes) and metals: the effects of conventional and localized annealing

S.A. Moshkalev, V. Ermakov, A.R. Vaz, A. Alaferdov, M.A. Canesqui, V.J. Silveira, R. Savu

*UNICAMP, Campinas, Brazil (stanisla@ccs.unicamp.br)*

One of important issues in nanofabrication is formation of reliable, low-resistance and stable contacts between nanostructured materials like graphene (monolayer, a few-layer and multilayer) or nanotubes and metal electrodes. For constantly decreasing sizes of contact areas in novel nanodevices, reduction of electrical and thermal contact resistivities becomes increasingly important, however the studies of these properties are currently very scarce. The methods used for controlled deposition of a few-layer and multi-layer graphene onto metal electrodes usually produce high-resistance contacts that need significant improvement. This can be done by means of conventional or localized annealing. Localized annealing, in turn, can be done using Joule heating by current or heating by focused laser beam. Here, three methods of annealing are compared, mechanisms of contact improvement with different metals are discussed, and advantages of localized laser annealing are demonstrated. For laser annealing, the same laser employed for confocal Raman spectroscopy is used, allowing for in-situ determination of local graphene (nanotube) temperature during the sample heating. The effect of localized laser annealing on dramatic improvement of electrical and thermal contacts between graphitic layers and initially rough metal (Ti, W, Au) surfaces is discussed [1]. Finally, the accuracy of thermal conductivity measurements for suspended multi-layer graphene flakes or nanotubes by an optothermal micro-Raman technique has been shown to depend critically on the quality of thermal contacts between the graphitic surface and metal electrodes used as a heat sink.

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# Template chemical vapor deposition synthesis of nanomesh graphene and its applications

Guoqing Ning

*State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing, Changping 102249, PR China (ngq@cup.edu.cn)*

Nanomesh graphene (NMG) that had nano-meshes, only one to two graphene layers and specific surface areas of up to 2038 $m^2 g^{-1}$ was produced in gram-scale by template growth on porous MgO layers [1]. Its unique porous structure gave excellent electrochemical capacitance (up to 255 $F g^{-1}$), charge-discharge cycle stability and rate performance as electrodes for supercapacitors. We further explored gas storage in the experimentally available porous graphene material [2]. Due to the existence of large surface corrugations, high stacking density of the NMG sheets was obtained by a SSA-lossless tightly stacking manner. Extraordinary methane storage capacities (236 v(STP)/v at 9 MPa and 274 K) and a high selectivity to carbon dioxide adsorption were obtained in the NMG samples. Our results indicate that porous graphene can be a promising material for energy storage and gas adsorption.

Furthermore, expanded vermiculite was used as layered templates in the CVD process to produce bulk materials containing graphene sheets of the order of hundreds of microns at a gram scale [3]. Meshes or carbon nanotubes can be introduced into the graphene sheets by template pretreating. Owing to the large sheet size, the as-obtained graphene sheets were easily fabricated into flexible graphene papers with low surface density and good conductivity, which exhibited greatly enhanced reversible capacity (1350 mAh/g at 50 mA/g) and cycling performance as anodes for lithium rechargeable batteries as compared to the graphene papers fabricated using reduced graphene oxide.

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C20

# Reconstruction of graphene layers under electric current

B.S. Archanjo[1], J. Campos-Delgado[2], B. Fragneaud[1], D.L. Baptista[3], C.A. Achete[1]

*1 Divisão de Metrologia de Materiais, Instituto Nacional de Metrologia, Qualidade e Tecnologia, Duque de Caxias, RJ, Brazil (bsarchanjo@inmetro.gov.br)*
*2 ICTEAM, Université catholique de Louvain, Louvain-la-Neuve, 1348, Belgium*
*3 Instituto de Física, Universidade Federal do Rio Grande do Sul, Porto Alegre, Brazil*

The quest for perfect graphene edges have kept many scientists captivated since its firsts observations. Based on the results of Joule heating of graphitic nanoribbons inside a TEM, where sharp zigzag and armchair edges were visualized [1], we were motivated to construct a device to induce Joule heating of nanoribbons in a configuration such that the sample could be studied outside the electron transmission microscope. In this work we will expose our different approach to build such device and the results of the electric transport experiments will be presented. CVD grown graphitic nanoribbons consist of many graphene layers stacked in AB configuration, their typical dimensions range from 50 to 300 nm in width, 20 nm in thickness and tens of micrometers in length. Joule heating experiments were conducted on this sample and healing of defects and sharp edge transformations were observed during electric current transport. We proposed to mount a carbon nanoribbon making contact on both ends of a conductive micro-wire placed itself on the void space of a TEM grid, using an nanomanipulator and Pt or C deposition to make contacts, the nanoribbons is placed across the wire bridging both ends. We have successfully constructed a TEM-electronic transport device in which the electron microscopy observation of a single nanoribbon and the electronic transport through it was possible. Our IV curves of the transport experiment show an interesting behavior that needs to be further investigated. We proved that the temperatures achieved by Joule heating are high enough to break the nanoribbon structure from the middle, away from the contacts that serve as heat sinks.

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**P135**

# Tailoring electrical properties of CNTs-polymer composites

Micaela Castellino, Massimo Rovere, Muhammad Imran Shahzad, Alberto Tagliaferro

*Applied Science and Technology Department (DISAT), Politecnico di Torino, Italy*
*(micaela.castellino@polito.it)*

Carbon nanotubes (CNTs) demonstrate remarkable conductive behaviours (electrical and thermal), which afford a number of promising applications [1]. Recently their outstanding properties have been considered in the development of CNT–polymer composites, with specific focus as a possible alternative materials for various applications, such as flexible electrodes, electronic paper, antistatic coatings and piezoresistive sensors [2].

In this study we focused our attention on the evaluation and modelling of electrical conductivity of CNTs filled epoxy resin. We discuss the results with regard to the influence of CNTs dimensions (length and diameter) and the influence of filler content (wt% and vol%). Thanks to the Dijkstra algorithm [3], we have implemented a simulation code, which could determine the route between electrodes having the minimum path in the polymer, for a chosen type of nanotubes (short MWCNTs), uniformly dispersed in a fixed volume. Then we have determined the path length (Dtot) in the polymer for all other 'similar routes'. The more the path inside the polymer, the more the composite results as a non-conductive materials, since the polymer has been considered as an insulator. We have compared these simulated results with experimental data for several wt% (0.5, 0.75, 1.0, 2.0, 3.0, 4.0 wt%), finding a perfect correspondence between modelling and experimental results. We tested also previous models like percolation theory and tunnelling, with much poorer results.

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**P136**

# Self-assembled films of multi-wall carbon nanotubes and iron-oxide filled carbon nanotubes used in gas sensors for oxygen detection

C.E. Cava[1], R.V. Salvatierra[2], A.J.G. Zarbin[2], L.S. Roman[1]

*1 Universidade Tecnológica Federal do Paraná (UTFPR), Londrina, PR, Brazil*
*(carloscava@utfpr.edu.br)*
*2 Universidade Federal do Paraná (UFPR), Department of Chemistry, Curitiba, PR, Brazil*

The interactions of carbon nanotubes (CNTs) with the atmosphere have been attracting the attention of many researchers in the last decade. Particularly, some studies have demonstrated the possibility of using CNTs to detect the oxygen gas. For instance, Collins *et al.* showed that the conductivity in a single CNT is changed when the material is exposed to the oxygen atmosphere. Besides, a precise explanation of how the interaction between oxygen and CNT occurs. They showed that the oxygen/CNT interaction is related to a physisorption process. Carbon nanotube films homogeneously deposited between the metal electrodes can increase the sensor's sensitivity. Recently, we developed a self-assembly method to obtain multi-wall carbon nanotube films applied in resistive gas sensor devices. This self-assembly method produces a homogeneous multi-wall carbon nanotube film with good adhesion to the substrate. The gas sensor device built by the self-assembly method presented a sensitivity 3.4 times higher than films made by regular casting deposition; a fast recovery time of 0.9 seconds could also be observed. In a complementary study, we have applied the same deposition method for iron-oxide filled carbon nanotubes which presented a sensitivity of 4.5% for 1% of oxygen with a recovery time of 4 min.

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# In situ refreshing enabled parts-per-quadrillion gas detection with pristine carbon nanotubes and graphene

Gugang Chen and Avetik R. Harutyunyan*

*Honda Research Institute USA Inc., 1381 Kinnear Road, Columbus, OH 43212, USA*
*(*aharutyunyan@honda-ri.com)*

Single-walled carbon nanotube (SWNT) and graphene are very promising for ultrasensitive gas detection since they consist solely of surface so that every atom is in direct contact with nearby analyte molecules. However, it is very challenging to achieve super-sensitivity due to virtually unavoidable interfering species present in the detection environment. This may partially explain why we are still far from what a pristine SWNT or graphene can offer even after more than a decade of research. Here we illustrate a novel route to address this issue. Through in situ refreshing of the sensor surface with continuous ultraviolet light illumination during the course of detection, we have observed 2 to 4 orders of magnitude better sensitivity than current state-of-the-art results for a range of gas molecules, and for the first time entered parts-per-quadrillion (PPQ) detection level at room temperature [1, 2]. The study further points out how to exploit the intrinsic sensitivities of other nanomaterials.

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P138

# Enhanced charge collection properties of quantum dot solar cells based on $TiO_2$ anatase nanorod arrays

Hyun Suk Chung and Hyun Suk Jung*

*School of Advanced Materials Science and Engineering, Sungkyunkwan University, Korea*
*(*hsjung1@skku.edu)*

The solar cells based on colloidal quantum dots have been studied widely because of their low fabrication cost and high light harvesting efficiencies [1]. Despite of these advantages, there are charge collection problems due to the constraint of the diffusion length [2]. The exploitation of advanced nanostructure is capable of solving the aforementioned charge collection problem by increasing surface area and reducing length of electron path. $TiO_2$ anatase nanorod may be one of solution. In this study, we synthesized $TiO_2$ anatase nanorod arrays with length of 200 nm using two-step sol-gel method. The morphology and crystal structure for the nanorod arrays were confirmed by using Transmission electron microscopy, Scanning electron microscopy and X-ray diffraction. The heterojunction QD solar cells based on the anatase nanorod were fabricated on fluorine-doped tin oxide and their photovoltaic properties were characterized. Compared with conventional $TiO_2$ nanoparticle based QD solar cells, these nanostructure solar cells exhibited better charge collection properties due to long life time measured by transient open circuit studies. Our finding demonstrates that the single crystalline anatase nanorod arrays are promising charge transport semiconductors for heterojunction QD solar cells.

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**P139**

## Self-assembled micro-honeycomb network of single-walled carbon nanotubes for heterojunction solar cells

Kehang Cui, Takaaki Chiba, Erik Einarsson, Shohei Chiashi, Shigeo Maruyama*

*Department of Mechanical Engineering, The University of Tokyo, Japan (*maruyama@photon.t.u-tokyo.ac.jp)*

The gap between the outstanding electrical and optical properties of an individual single-walled carbon nanotube (SWNT) and inferior performance of macro-scale SWNT devices is hindering its widespread applications. The smart assembly is necessary to play SWNT to its full potential. Here, we propose a self-assembled micro-honeycomb network (μ-HN) of SWNTs obtained by water or ethanol vapor treatment of as-synthesized vertically aligned SWNTs (VA-SWNTs) for heterojunction solar cells with higher performance.

The VA-SWNTs was synthesized by the standard alcohol-catalytic CVD method with Co/Mo dip-coated on Si/SiO2 substrate [1]. The fabrication process of the micro-honeycomb structured film was obtained by exposing the as-synthesized VASWNT to water vapor and drying under ambient environment afterwards. Each micro-honeycomb cell consists of capillary-aggregated walls and randomly oriented bottom that contacts the Si substrate. The SWNT film was transferred on top of the substrate which has a 3 mm × 3 mm bare n-type silicon contact window in the center using hot water transfer technique. By the vapor treatment, collapsed spaghetti-like SWNTs contact to the substrate in the middle of each honeycomb cell. Cell walls consist of cross-linked heavily bundled SWNTs. The pristine SWNT-Si heterojunction solar cell fabricated with μ-HN shows a stable fill factor of 72%, which is the highest fill factor reported to date [2, 3]. The improvement is attributed to the hierarchical structure of micro-honeycomb network. A PCE beyond 10% is achieved in the dry state after dilute nitric acid treatment.

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**P140**

## Thermoelectric modules made of p- and n-type single walled carbon nanotube composite films

Urszula Dettlaff-Weglikowska[1], Mingxing Piao[1], Gyutae Kim[1], Siegmar Roth[2]

*1 Korea University, School of Electrical Engineering, South Korea (udettlaff.w@gmail.com)*
*2 Sineurop Nanotech GmbH, Germany*

Single walled carbon nanotube (SWCNT) networks, composed of semiconducting and metallic nanotubes forming free standing mats (buckypaper) are known for high electrical conductivity and a reasonable value of the Seebeck coefficient. SWNT composites with polymers still show a high electrical conductivity, whereas their thermal conductivity is low due to blocked heat flow across the composite structure. We prepared and characterized thermoelectric materials based on thin films of SWCNT composites with polyvinylalcohol. Pristine SWCNTs incorporated in polymer matrix generated positive value of the thermopower and were used as a p-doped thermoelectric material. Polyethyleneimine (PEI) was studied as an n-type dopant for SWCNTs. Simultaneous change of majority charge carriers from holes to electrons upon addition of PEI caused the Seebeck coefficient to change sign from positive to negative providing an n-type thermoelectric material. A single p/n couple made of two composite strips containing 20 wt% of SWCNTs - pristine p-type and n-type PEI doped nanotubes - generated a TEP voltage of 92 μV per 1 K temperature gradient. By comparison, a single p/n couple made of two films made of polyvinylidene fluoride with 95 or 20 wt % of multi-walled carbon nanotubs conducting layers produced ~15 μV per 1 K temperature gradient, as recently reported for the multilayered carbon nanotube/polymer composite based thermoelectric fabrics [1]. In our study, the thermoelectric voltage generated by a single p/n polymer couple per 1 K was improved by factor of 6 through chemical functionalization of SWCNTs loaded to 20 wt%. A module composed of 5 electrically connected p/n junctions demonstrated a 25 mV voltage output by a temperature gradient of 50 K. The module generated 4.5 nW power, when a load resistance matched the internal module resistance of 30 kΩ.

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**P141**

## Nanocomposites of carbon nanotube and polyaniline applied as gas sensor device

Marcelo Eising[1], Rodrigo V. Salvatierra[2], Aldo J. G. Zarbin[2], Carlos Eduardo Cava[3], Lucimara S. Roman[4]

*1 PPG Engenharia e Ciência dos Materiais – PIPE, UFPR, Brasil (mareising@gmail.com)*
*2 Departamento de Química, UFPR, Brasil*
*3 Engenharia de Materiais, UTFPR, Brasil*
*4 Departamento de Física, UFPR, Brasil*

In this work we study the characteristics gas sensors devices based on carbon nanotube/polyaniline (CNT/PANI) nanocomposites. The active layer film of CNT/PANI was deposited on a chromium/gold (Cr/Au) interdigitated electrode, with electrical terminals to monitoring their electrical properties. When necessary, a UV light illumination from an LED is applied in order to enhance the limit detection. Due to the physical and chemical properties of CNT and PANI, the combination of these properties make these nanocomposites, materials with improved properties and great potential to be used in gas sensors. At this work, two types of CNT/PANI films dopping were studied, primary dopping using $H_2SO_4$ and applied to detect some kind of acid vapor, and another secondary dopping using *m*-cresol, applied to organic vapor detection. The CNT/PANI nanocomposite is synthesized in situ, using an innovative self-assembled method, from a biphasic system polymerization, with water and toluene. The film is formed in the water/toluene interface after 24 hours of mechanical agitation, then the glass substrate with the electrical conduction contacts, that is the bottom of the container where it is synthesized nanocomposite, getting the film deposited on these contacts.

Tests showed a short response time to adsorption and desorption of the studied gas molecules, and with sensibility $[S=(R - R_0)/R_0]$ around 6% for air flux intercalated with air+10% of saturated air of acetone $(CH_3)_2CO$, to films with secondary dopping. We also expand this study for others types of gases as: $O_2$, $N_2$, water vapor ($H_2O$) and ammonia ($NH_3$).

**P142**

## A three-dimensional carbon nanotube/graphene sandwich and its application in supercapacitors

Zhuangjun Fan[1], Jun Yan[1], Tong Wei[1], Fei Wei[2]

*1 Key Laboratory of Superlight Materials and Surface Technology, Ministry of Education, College of Material Science and Chemical Engineering, Harbin Engineering University, Harbin 150001, P. R. China (fanzhj666@163.com)*
*2 Beijing Key Laboratory of Green Chemical Reaction Engineering, and Technology, Department of Chemical Engineering, Tsinghua University, Beijing 100084, P. R. China*

Owing to its unique electrical, thermal, and mechanical properties, graphene has attracted great attention in various application areas, such as energy-storage materials, free-standing paper-like materials, polymer composites, liquid crystal devices and mechanical resonators. Among various approaches, the oxidation and reduction of graphite is one of the most effective methods in mass production of grapheme for industrial applications. However, the reduction of grapheme oxide (GO) results in always a gradual decrease of its hydrophilic character, which leads to irreversible agglomeration and precipitation, though GO itself is highly hydrophilic and can form stable dispersion in aqueous solvents. As a result, the unique 2D feature of graphene would be lost.

In this paper, for the first time, we report a novel strategy to prepare 3D CNT/grapheme sandwich (CGS) structures with CNT pillars grown in between the graphene layers by CVD approach. The CGS has been used successfully as electrodes in supercapacitors, and a maximum specific capacitance of 385 F g–1 has been obtained at a scan rate of 10 mV s–1 in 6 M KOH aqueous solution. After 2000 cycles, a capacitance increase of ca. 20% of the initial capacitance is observed, indicating excellent electrochemical stability of the electrode. This new carbon material is also expected to be useful as electrode material in Li-ion secondary batteries, as media for hydrogen storage, as catalysts for fuel cells, and as component for other clean energy devices.

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# Supercapacitor performance of arrays of aligned nitrogen-doped carbon nanotubes

Ekaterina O. Fedorovskaya, Alexander G. Kurenya, Lyubov G. Bulusheva, Alexander V. Okotrub

*Nikolaev Institute of Inorganic Chemistry, SB RAS, 630090, Novosibirsk, Russia*
*(fedorovskaya-eo@yandex.ru)*

Electrochemical capacitors, known as supercapacitors, have attracted great interest as promising energy storage devices due to their higher power energy density and longer cycle performance than the conventional dielectric capacitors. Recently, arrays of carbon nanotubes vertically grown on a substrate have attracted attention as a promising material for capacitor electrodes. Carbon nanotubes commonly possess large specific surface area, remarkable chemical inertness and physical stability. Direct contact of carbon nanotubes with conductive substrate provides fast charge/discharge and high stability of a capacitor. Nitrogen doping of carbon nanotubes increases structures defectness, which, in turn, leads to an increase surface area and the decrease the conductivity. In addition, the nitrogen can be integrated into the carbon structure by two ways – pyridine-like and three-coordinated nitrogen, which also affect the final physical properties of the nanotubes

Arrays of vertically aligned carbon nanotubes have been grown on silicon substrates using an aerosol-assistant catalytic chemical vapour deposition (CCVD) method. Acetonitrile was taken as a carbon source, while ferrocene was used as a catalyst source. Solution of 2 wt% ferrocene in acetonitrile with a small addition of Cr, Mo or W carbonyl was injected during one hour in CVD reactor heated up to 800° C. The length and defectness of carbon nanotubes were determined by scanning electron microscopy and Raman spectroscopy. The electronic state of nitrogen in the nanotubes was investigated by XPS spectroscopy. Electrochemical measurements were performed using cyclic voltammetry in 1 M sulfuric acid. The supercapacitor performance was related with the sample structure and nitrogen content.

P144

# Low resistance carbon nanotube – metal contact for interconnect applications

Holger Fiedler[1], Marius Toader[2], Sascha Hermann[1], Michael Rennau[1],
Michael Hietschold[2], Stefan E. Schulz[1,3], Thomas Gessner[1,3]

*1 TU Chemnitz, Center for Microtechnologies (ZFM), D-09126 Chemnitz, Germany*
*(holger.fiedler@zfm.tu-chemnitz.de)*
*2 TU Chemnitz, Institute of Physics, Solid Surface Analysis, D-09107 Chemnitz, Germany*
*3 Fraunhofer Institute for Electronic Nano Systems (ENAS), D-09126 Chemnitz, Germany*

Due to their unique electrical and thermal properties, carbon nanotubes (CNT) have the potential to replace Cu in the current state of the art interconnect technology. We prepared CNT based vertical interconnects (vias) and electrically characterized them. In contrast to our previous work [1], here a 1 nm Ta layer on top of a TaN diffusion barrier is employed as substrate bottom metallization. The electrical properties of the CNTs within the vias were checked by conductive atomic force microscopy (cAFM) after the planarization of the vias [2]. Averaging the resistance of the CNTs within five different vias in close proximity, we obtained a resistance of (11 ± 9) kΩ. For the most conductive CNT structure we even measured a resistance below 1 kΩ. This resistance value includes the contact resistance between the AFM tip (Pt surface) and the CNTs. Taking this and the number of shells into account we can conclude that the CNT-Ta contact resistance is close to the theoretical limit of 6.5 kΩ per shell. We attribute the improved contact resistance to the local formation of TaC at the CNT Ta interface. TaC can decompose in the presence of oxygen, which is why we measured the sample again six months after preparation. An increase of the individual CNT resistance by a factor of 3 to (35 ± 8) kΩ was observed. After annealing the sample at 450 °C in a reductive atmosphere the degradation of the contact is reversed and we measure a reduced resistance again.

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**P145**

# Rapid and easy patterning of carbon nanotube films and its application to transparent conductive films

Norihiro Fukaya[1], Dong Young Kim[2], Shigeru Kishimoto[1],
Suguru Noda[2], and Yutaka Ohno[1,*]

*1 Department of Quantum Engineering, Nagoya University, Japan (*yohno@nuee.nagoya-u.ac.jp)*
*2 Department Applied Chemistry, Waseda University, Japan*

Carbon nanotubes (CNTs) are quite promising material for transparent conductive films (TCFs) and interconnections of flexible devices without resource problems. For the formation of CNT interconnections, patterning of a thick CNT film on a plastic substrate is one of key processes. In this study, we propose the filtration and transfer process with patterned membrane filter to fabricate CNT patterns on a transparent plastic substrate on the basis of the floating-catalyst chemical vapor deposition technique (FC-CVD) [1]. We also apply this technique to produce CNT TCFs that consists of double layers of a uniform film and a grid of single-walled CNTs. By adding the grid, the performance of CNT TCFs were fairly improved over the tradeoff between transmittance and sheet resistance of conventional CNT TCFs with single layer CNT film. The sheet resistance at a transmittance of 80 % was reduced by 46 % from 95 Ω/sq. to 53 Ω/sq by adding the grid.

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**P146**

# Functionalization of multi-walled carbon nanotubes on the properties of carbon nanotube/epoxy composites

Li-Jun Cui, Wen-Yi Wang, Xiao-Bing Xu, Yan Meng, Jing Gao, Li-Ting Chen, Er-Xiong Ding,
Yan Wang, Hong-Zhang Geng

*State Key Laboratory of Hollow Fiber Membrane Materials & Membrane Processing, School of Materials Science and Engineering, Tianjin Polytechnic University, Tianjin 300387, P. R. China (genghz@tjpu.edu.cn)*

Functionalization of multi-wall carbon nanotubes (MWCNTs) was achieved by grafting carboxyl groups and amino groups to fabricate MWCNT/epoxy composites. Fourier transform infrared spectroscopy was used to detect the changes produced by functional groups on the surface of the MWCNTs. Different MWCNTs were incorporated into epoxy resin and the friction and wear behavior of MWCNT/epoxy composites was investigated using wear testing machine at different sliding speeds under different applied loads [1]. Cure behavior of composites was investigated by differential scanning calorimetry. Thermo-mechanical behavior was evaluated by dynamic mechanical analysis. Tensile strength, elastic modulus and maximum elongation were obtained and analysized [2]. Scanning electron microscopy was used to observe the worn surfaces and to characterize the fracture mechanism of composites and the dispersion state of MWCNTs in the epoxy. The results indicated that the functional groups had been grafted on the surface of MWCNTs. Compared with neat epoxy, the composites with MWCNTs showed a lower friction coefficient and wear rate, and the wear rate decreased with the increase of MWCNT loading. The introduction of MWCNTs also decreased the activation energy of the reaction and promoted the cure reaction. The addition of MWCNTs, especially amino-functionalized MWCNTs, clearly improved the tensile strength. The functionalized MWCNTs improved the interfacial bonding and made the dispersion of MWCNTs homogeneous in the matrix, giving the composites better mechanical properties.

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## Tunable and high power efficient MEMS supercapacitor based on vertically aligned carbon nanotubes

Arunabha Ghosh[1,2], Viet Thong Lee[1,3], and Young Hee Lee[1,3,4,*]

*1 Center for Integrated Nanostructure Physics, Institute for Basic Science*
*2 Sungkyunkwan Advanced Institute of Nanotechnology*
*3 Department of Energy Science and*
*4 Department of Physics, Sungkyunkwan University, Suwon 440-746, South Korea (*leeyoung@skku.kr)*

A tunable and high power efficient micro-supercapacitor was fabricated from vertically aligned multiwalled carbon nanotubes, exhibiting very fast charge storage capability, and hence an extremely significant addition to the recent rapid development of miniaturized charge storage devices. We have fabricated the micro-device by direct growth of vertically aligned multiwalled carbon nanotubes (CNTs) by thermal chemical vapor deposition. We obtained very high areal capacitance of 2.7 mF $cm^{-2}$ in $LiPF_6$ electrolyte at very high scan rate of 1 $Vs^{-1}$. Thus the device exhibited excellent power efficiency. Moreover the micro-device exhibited efficient and excellent tunable characteristics in terms of areal capacitance with variation in active materials' height. The areal capacitance was enhanced almost linearly with increasing height of the sample, with a very little change in gravimetric capacitance. A 2400 % (24 times) height increment resulted in almost 2300% increment in areal capacitance, which signifies excellent tenability of the device. At the same time, excellent gravimetric efficiency was observed. A 2300% increment in areal capacitance resulted in a negligible amount of loss in gravimetric capacitance, which is less than 14 %. This indicates very good efficiency of the device, which is caused by easy electrolyte access to the active material, which can be ascribed to well align CNTs and regularly spaced structure. This phenomenon leads to successful fabrication of a MEMS-supercapacitor of variable capacitance, which capacitance is easily controllable by varying height of active material, exploiting the linear relationship of height and capacitance, at the same time aligned structure preserve high power efficiency.

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## High-power airborne ultrasound emitters – Structural optimization of carbon-based fibrous materials

Matthias Guderian, Maxim Daschewski, Andrea Harrer, Jens Prager, Marc Kreutzbruck, Heinz Sturm, Asmus Meyer-Plath*

*BAM – Federal Institute for Materials Research and Testing, Berlin, Germany*
*(*asmus.meyer-plath@bam.de)*

Airborne ultrasound is a useful tool for non-destructive materials testing. Carbon based fibrous materials were found to be very effective emitters of ultrasound by means of the thermoacoustic effect. Here, a systematic approach is presented to optimize the ultrasound emission effectiveness of nanostructured carbon materials. It is based on comparing carbon fiber materials of different fiber diameter, including carbon fibers, carbon nanofibers and carbon nanotubes. Careful optimization of fiber diameter as well as web thickness and density allowed designing highly efficient ultrasound generation with frequencies up to 350 kHz. Hierarchically structured emitter materials consisting of electrospun carbon nanofibers with a carbon nanotube overgrow were found to offer highest sound pressures together with mechanical stability. In contrast to conventional piezo or polyelectrete ultrasound emitters, the new carbon fiber-based emitters are capable of producing very short and powerful ultrasound pulses that are free of ringing oscillations. This makes them especially useful for ultrasound impulse spectroscopy.

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## Fabrication of stable pn junction single-walled carbon nanotube films for solar cell applications

Yoshihiro Abiko, Toshiaki Kato, Rikizo Hatakeyama, Toshiro Kaneko

*Department of Electronic Engineering, Tohoku University, Sendai 980-8579, Japan*
*(hatake@ecei.tohoku.ac.jp)*

Stable n-type thin film transistors (TFTs) are fabricated with Cs encapsulated single-walled carbon nanotubes (Cs@SWNTs) prepared by a plasma ion irradiation method [1-3]. The transport property of SWNTs-TFTs clearly changes from the p- to n-type characteristic after the Cs plasma irradiation. Based on the systematic investigations, it is revealed that there is an optimum ion energy for the effective Cs encapsulation, which is around 50 eV. Furthermore, it is also found that the n-type feature is stable even under air, water, and high temperature (< 400 °C) conditions. The pn junction structure is also formed by position selective doping of Cs. The rectifying features are clearly observed for the pn junction SWNTs-TFTs. The solar cell performances are also systematically investigated. This very stable pn junction TFTs is important for the practical development of SWNTs-based solar cell applications [4].

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P151

## Electrically-conductive composite nanomaterial

L. Ichkitidze[1], V. Podgaetsky[1], S. Selishchev[1], E. Blagov[2], A. Pavlov[2], V. Galperin[3], Y. Shaman[3], E. Kitsyuk[3]

*1 National Research University of Electronic Technology (MIET), 124498, Moscow, Russia*
*(leo852@inbox.ru)*
*2 Institute of nanotechnology of microelectronics RAS, 119991, Moscow, Russia*
*3 Scientific Manufacturing Complex “Technological Centre”, 124498, Moscow, Russia*

Specific conductivity S of the composite nanomaterial layers with micron and submicron dimensions, consisting of carboxymethyl cellulose (CMC) and multiwalled carbon nanotubes (MWCNT) was investigated. Ultradispersed aqueous suspension was deposited on soft (aluminum foil, plates made from polyester and polyimide, cotton fabric, office paper) and solid (coverslip, silicon wafers with silicon oxide layer) substrates by silk-screen printing. Electrical resistance was measured by four-probe method and by the method of square on surface from which the conductivity S and conductivity per square of surface were calculated taking into account layer’s geometric dimensions.

Conductivities of the layers significantly increased after the annealing of the samples in air environment (up to 5 times) or hydrogen environment (up to 200 times). The samples of the composite nanomaterial based on MWCNT possessed by 4-6 orders of magnitude higher conductivity values than the control samples based on CMC, or CMC and soot K-354. Obtained values of specific bulk conductivity (~40 kS/m) and surface conductivity (~0.2 S) had the same orders which were obtained for the layers of “buckypaper” based on both MWCNT. Numerous bends of soft substrates didn’t affect on conductivity of the layers with thickness 5 μm.

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# Double-walled carbon nanotube transparent conductive film for next generation flexible device

Naoki Imazu, Takashi Oi, Hidekazu Nishino, Kenichi Sato, Osamu Watanabe, Shiro Honda
and Motoyuki Suzuki*

*Toray Industries, Inc., Japan (*motoyuki_suzuki@nts.toray.co.jp)*

Transparent conductive film (TCF) is used for electrode of various electric devices such as display, touch panel, electric paper, solar cell and so on. Recently, flexibility is demanded for these applications. Conductive material of traditional TCF is indium tin oxide (ITO), but it is impossible to bend ITO TCF because of its brittleness. One of promising material for flexible TCF is carbon nanotube (CNT). CNT TCF have attracted great interest since the pioneer report by Wu *et al.,* but as its transparent conductivity is inferior to that of ITO, it have not introduced to the market until now. In order to enhance transparent conductivity, CNT should be highly dispersed. We found that high dispersion consistent with high conductivity by using Double-Walled CNT (DWCNT).

DWCNT is synthesized by our original Cat-CVD process. The features of our DWCNT are as below; High purity (The percentage of DWCNT is over 90%), Low volume resistivity ($4.4*10^{-4}$ Ωcm) and High crystalline quality (G/D ratio is over 80). Using highly dispersed CNT liquefaction and precise coating technology, we have produced CNT TCF by wet coating process. Our CNT TCF has very high transparent conductivity, which are currently among the top in the world. And it has great characters such as high flexibility (bending and stretching durability), high environmental stability, and neutral color. This CNT TCF can be used for electric paper such as a digital book and a digital signage which are spreading in recent years. We made trial product of electric paper using CNT TCF. The transparent conductivity for this electric paper is 2500 Ω/sq, 92% TT and 500 Ω/sq, 90% TT (including PET substrate).

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**P154**

# Construction of robust binder-free architectures for high-performance lithium-ion battery electrodes

Xilai Jia[1], Yunfeng Lu[2], Fei Wei[1]

*1 Beijing Key Laboratory of Green Chemical Reaction Engineering and Technology, Department of Chemical Engineering, Tsinghua University, Beijing 100084, P. R. China (wf-dce@mail.tsinghua.edu.cn)*
*2 Department of Chemical and Biomolecular Engineering, University of California Los Angeles, CA 90095, USA*

Electrochemical energy storage devices like lithium-ion batteries are of great interest in commercial electronics, and being extending to electricl vehicles, grid and other applications. Nanocarbon networks can highly improve their performance to realize the extended potential. Herein, highly robust, flexible, binder-free lithium-ion battery electrodes were constructed consisting of high-aspect-ratio carbon nanotube (CNT)-interweaved networks and electrochemical active materials. The composite electrodes possess hierarchically pore networks and long-range electron conductive pathway, which achieve rapid electron and ion transport for electrochemical energy conversion and storage. Further, as a novel type of electrodes compared to traditional carbon black-polyvinylidene fluoride bound ones, the engineering design of binder-free electrodes have been discussed for maximum utilization of battery materials.

High-aspect-ratio CNTs meet dispersion probloms in preparation of their nanocomposites. We proposed to convert sol-like CNT dispersions into their gel networks, and successfully prepared more efficient high-aspect-ratio CNT nanostructural composites. Typical architectures, including CNT/nanocrystal [1], CNT/nanowire [2], CNT/nanosheet and CNT/cluster-like microparticle [3], were fabricated to demonstrate the efficiency of the those binder-free electrodes. In such composite nanostructures, long-range CNT conductive networks and hierarchical pores highly improved the kinetics of ion and electron reactions. Therefore, as-fabricated battery electrodes show significantly improved performance such as high capacity, high rate-capability and excellent cycling stability.

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**P155**

# Suspended carbon nanotube double quantum dots with recessed rhenium bottom gates

Minkyung Jung, Jens Schindele, Stefan Nau and Christian Schönenberger

*Department of Physics, University of Basel, Klingelbergstrasse 82, CH-4056 Basel, Switzerland (minkyung.jung@unibas.ch)*

Suspended carbon nanotube systems have been developed for ultraclean quantum dots with high yield [1,2]. In this work, we developed suspended carbon nanotube devices with recessed Rhenium (Re) bottom gates. Trenches in $SiO_2$ are opened by electron beam lithography (EBL) and anisotropic reactive ion etching with CF4 and followed by a wet etch step using buffered HF. After etching, both the depth and width of the trenches are 100 - 140 nm. An isotropic wet etch (buffered HF) creates an undercut in the trenches, preventing flags on the Re bottom gates during the sputtering process. The Re bottom gates which are formed at the trench by sputtering are 40 nm thick and 70 nm wide. Carbon nanotubes are then grown on the predefined Re bottom gate substrate by chemical vapor deposition (CVD) at 950 C. It is found that the Re surface is insensitive to the growth conditions. Carbon nanotubes are suspended over trenches. Finally, 5/65 nm layer of Ti/Au is deposited as source and drain contacts.

All measurements have been performed at 4.2 K. First, the entire nanotube is tuned to be p-doping (p’) by applying high negative back gate voltage so that the nanotube has good ohmic contacts. Depending on the left and right bottom gate voltages, single or double dots can be formed in p’-p-n-p’, p’-n-p-p’, p’-p-p-p’ or p’-n-n-p’ regime. The device in p’-p-n-p’ and p’-n-p-p’ regime exhibits very clean n-type single dot behavior, showing the filling of electrons from the first electron in the quantum dot. In p’-n-n-p’ regime, double quantum dot transport behavior is observed. Interestingly, quasi-periodic excited states are observed in bias triangles. This could be a signature of electron-phonon coupling due to the suspended double dots.

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**P156**

## Fabrication and characterization of polymer gel based flexible supercapacitors

Yu Jin Kang[1], Sang-Jin Chun[2,3], Sung-Suk Lee[2], Bo-Yeong Kim[2], Jung Hyeun Kim[3], Haegeun Chung[4], Sun-Young Lee[2,*] and Woong Kim[1,*]

*1 Department of Materials Science and Engineering, Korea University, Seoul 136-713, Republic of Korea*
*2 Department of Forest Resources Utilization, Korea Forest Research Institute, Seoul 130-712, Republic of Korea*
*3 Department of Chemical Engineering, University of Seoul, Seoul 130-743, Republic of Korea*
*4 Department of Environmental Engineering, Konkuk University, Seoul 143-701, Republic of Korea*

We have successfully fabricated all-solid-state supercapacitors with high flexibility, excellent elechtrochemical properties and mechanical integrity. The supercapacitors were made up of bacterial nanocellulose papers (BNC), carbon nanotubes (CNTs) and triblock copolymer gel electrolytes. A flexible electrode was fabricated by depositing CNTs on the BNC papers via vacuum filtration method. The polymer gel electrolyte was prepared by adding poly(styrene-block-ethylene oxide-block-styrene) (PS-PEO-PS) triblock copolymer in ionic liquid, bis(trifluoromethylsulfonyl)imide ([EMIM][NTF$_2$]). The polymer gels showed excellent ion mobility comparable with neat liquid electrolytes. The specific capacitance of the supercapacitors was 50.5 F/g at current density of 1 A/g. The flexible supercapacitors generally maintained electrochemical properties over 200 bending cycles. Furthermore, they showed good cyclability with specific capacitance changing only 0.5% after 5000 charge-discharge cycles. The BNC/CNT/polyemrgel supercapacitors may have a great potential in the field of basic material research and the flexible energy storage devices [1].

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**P157**

## Nanotube based biosensor for accurate thrombin detection on flexible substrate

I.A. Komarov[1],*, I.I. Bobrinetsky[1], A.V. Golovin[2], A.O. Zalevsky[2],*

*1 National Research University of Electronic technology, Russian Federation (bobrinet@mail.ru)*
*2 Moscow State University, Russian Federation (aozalevsky@gmail.ru)*

Biological sensors is a promising area of nanomaterials applications. Single wall carbon nanotubes (SWCNT) have high specific surface area as well as high sensivity to environment which make them applicable as interface between biological targets and electronic devices [1]. In that case a signal from small biological objects could be taken in easy-to-use form.

In the present work we describe assembly of high-sensitive biosensor at flexible substrate sensitive to human thrombin - key protein of blood coagulation cascade. We showed consistency of sensor response results with those obtained by molecular dynamics simulations and quantum mechanics calculations. SWCNT were modified with thrombin binding aptamer to form a sensitive layer on a flexible substrate. Formation of aptamer-protein complex changes aptamer conformation which affects charge distribution on nanotube's surface and results in changes of sensor resistance. As we showed the resistance of the structure decreased in ~45%. Reaction time is about 100 seconds. We used albumin protein as a control sample. The resistance decreased in 16% that is much less than response on thrombin.

Combination of experimental and computational methods gives deep understanding of underlying mechanisms which is crucial for successful development of highly specific highly sensitive sensors based on unique features of aptamers and single wall carbon nanotubes. These is the first time the carbon nanotube-based aptasensor was made on flexible substrate.

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**P158**

## $MoS_2$ decorated carbon nanotubes arrays

V.O. Koroteev[1], M.A. Kanygin[1], E. Imawa[2], L.G. Bulusheva[1], A.V. Okotrub[1]

*1 Nikolaev Institute of Inorganic Chemistry SB RAS (koroteev@niic.nsc.ru)*
*2 CIRIMAT UMR CNRS 5085, France*

Combining carbon nanotubes (CNT), possessing high electrical conductivity, with semiconducting nanoparticles allows creating a new class of low-dimensional hybrid materials with unique electronic, optical and luminescent properties. Hexagonal lattices of graphitic materials and molybdenum sulfide $MoS_2$ allow jointing these compounds in a hybrid. There are a few methods proposed to cover nanotubes with $MoS_2$, but all of them are destructive for CNT arrays, since requires nanotube dispersion [1-2]. Preserving the nanotube alignment in a hybrid with $MoS_2$ is important for the materials used as field cathodes or lithium ion batteries anodes [3].

We propose the approach of $MoS_2$ deposition on carbon nanotubes arrays, which allows preserving array structure, detaching arrays from the substrate and depositing molybdenum disulfide particles over it. The deposition was carried using hydrothermal procedure. As the result, freestanding CNT arrays decorated with molybdenum disulfide flower-like particles were obtained. The samples were examined using scanning electron microscopy, electron dispersion spectroscopy, Raman spectroscopy and x-ray photoelectron spectroscopy. XPS data reveals different forms of Mo and S-atoms in the samples, which could be attributed to different sulfides. Sample composition changes with changing the reagents content was examined. Raman depth profiling was done to estimate the amount of $MoS_2$, penetrated inside the array. Li intercalation performance of the films was measured in galvanostatic regime. In this case, CNTs are working as nanowires, while $MoS_2$ serves as lithium storage material.

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**P159**

## Coaxial fiber supercapacitor using all-carbon material electrodes

Viet Thong Le[1,2], Heetae Kim[2], Arunabha Ghosh[1,3], Jaesu Kim[1,2], Jian Chang[1,2], Quoc An Vu[1,2],
Duy Tho Pham[1,2], Young Hee Lee[1,2,3,*]

*1 Center for Integrated Nanostructure Physics, Institute of Basic Science,*
*2 Department of Energy Science,*
*3 Sungkyunkwan Advanced Institute of Nanotechnology, Sungkyunkwan University, Suwon 440-746,*
*Republic of Korea (*leeyoung@skku.edu)*

Self-sustainable textile electronics require electronic and energy storage devices. Different types of fiber supercapacitors with twisted structure using a single metal, polymer wire or carbon nanotube yarns have been demonstrated, revealing several drawbacks in terms of structural stability and robustness, as well as low energy and power density. In this report, we designed a coaxial fiber supercapacitor, which consists of carbon microfibre bundles coated with multiwalled carbon nanotubes as a core electrode and carbon nanofibre paper as an outer electrode. The ratio of electrode volumes was determined by a half-cell test of each electrode. The capacitance reached 6.3 mF $cm^{-1}$ (86.8 mF $cm^{-2}$) at a core electrode diameter of 230 μm and the measured energy density was 0.7 μWh $cm^{-1}$ (9.8 μWh $cm^{-2}$) at a power density of 13.7 μW $cm^{-1}$ (189.4 μW $cm^{-2}$) which were much higher than the previous reports. The change in the cyclic voltammetry characteristics was negligible at 180° bending, with excellent cycling performance.

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# Single-walled carbon nanotube-$TiO_2$ photoanodes for dye-sensitized solar cells

Jiyong Lee[1,†], Hosung Kang[2,†], Seunghyun Baik[1,3,*]

*1 Department of Energy Science, Sungkyunkwan University, Suwon 440-746, Korea*
*2 SKKU Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan University, Suwon 440-746 Korea*
*3 School of Mechanical Engineering, Sungkyunkwan University, Suwon 440-746, Korea (*sbaik@me.skku.ac.kr)*
[†]These authors contributed equally.

Dye-sensitized solar cells (DSCs) have attracted considerable attention due to the cost-effective high efficiency. Photoanodes based on $TiO_2$ particles or nanotubes have been intensively investigated to improve photovoltaic performance for DSCs. Single-walled carbon nanotubes (SWNTs) were also explored as building blocks for photovoltaic devices. Due to the recent progress in nanotube separation according to electronic types, metallic or semiconducting SWNTs were investigated for photovoltaic devices. Here we investigated photoanodes of DSCs by combining SWNTs and $TiO_2$ particles. Semiconducting as well as metallic SWNTs separated by the density gradient ultracentrifugation method were obtained from Nano Integris. The nanotubes were integrated on $TiO_2$ particles using the layer-by-layer structure. The metallic SWNTs provided a better performance. The metallic SWNT/$TiO_2$ photoanode achieved 16% improvement in current density and 12% improvement in overall efficiency under the AM 1.5 condition.

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# Electrical characterization of single-walled carbon nanotube field effect transistors with graphene electrodes

Miri Seo[1], Junhong Na[2], Hoyeol Yun[1], Byeong-Joo Lee[3], Seung Hwan Lee[3], Goo-Hwan Jeong[3],
Gyu Tae Kim[2], and Sang Wook Lee[1]

*1 Division of Quantum Phases and Devices, School of Physics, Konkuk University Seoul, 143-701, Korea (leesw@konkuk.ac.kr)*
*2 Department of Electrical Engineering, Korea University, Seoul, 136-713, Korea*
*3 Department of Nano Applied Engineering, Kangwon National University, Chuncheon, 200-701, Korea*

Electrical properties of a field effect transistor (FET) structures which are composed of single-walled carbon nanotube (SWNT) channel and graphene electrodes. Aligned arrays of SWNTs were synthesized by thermal chemical vapor deposition (CVD) method on quartz substrate. The micro scale contact electrodes and following circuit structures were defined by photo lithography on the large area graphene produced by CVD with Ni and Cu foil. Micro contact transfer method made it possible to move the arrays of SWNTs from quartz to $SiO_2$ substrate and to place the patterned graphene structures on top of the SWNTs. From the gate voltage dependence of current voltage characteristics of these FETs, we studied the junction properties between graphene and SWNT.

**P162**

# Carbon nanotube thin film transistors: towards all-printed devices

F. Cheng, J. Ding, N. Du, G. Dubey, J. Dunford, P. Finnie, C. Homenick, A. Hrdina, R. James‡,
M. Jakubinek, C. Kingston, J. Lefebvre, Z. Li, G. Lopinski, P. Malenfant, B. Simard, S. Zou

*National Research Council Canada, Ottawa, Ontario, K1A 0R. (jacques.lefebvre@nrc.ca)*
*‡Communications Research Centre Canada, Ottawa, Ontario, K2H 8S2*

In this presentation, I will cover our recent activities related to carbon nanotube transistors for applications in printable electronics. Aspects currently addressed include source and drain contacts, gate dielectric and transistor channel. For the dielectric, we selected one with high dielectric constant, good capacitance, and importantly, compatible with a printing process. For the transistor channel, two aspects are being addressed: ink formulation with an important focus on semiconductor enrichment (chromatography & conjugated polymer extraction), and ink deposition using three methods, drop-cast, inkjet and aerosol. I will highlight mobility numbers in excess of > 20 $\mathrm{cm}^2$/Vs and current On/Off ratio >$10^4$ for transistors obtained using semiconductor enriched carbon nanotubes with a diameter distribution centered at 1.3 nm.

**P163**

# Solution-processed carbon nanotube and graphene supercapacitors

Suvi Lehtimäki, Juho Pörhönen, Sampo Tuukkanen, Donald Lupo

*Organic Electronics Group, Department of Electronics and Communications Engineering, Tampere University of Technology (TUT), Finland (suvi.lehtimaki@tut.fi)*

Supercapacitors are energy storage devices which have properties between those of batteries and conventional capacitors [1]. Compared to batteries, they can provide a larger power, and because of the electrostatic charge storage mechanism, the cycle lifetime is much longer [2]. The most common material used in supercapacitors is activated carbon, which is very porous and thus has a large specific surface area. It is not, however, very conducting, leading to a need for separate current collector materials as well as conductive additives. Carbon nanomaterials, such as carbon nanotubes (CNT) and graphene, offer a promising new direction for supercapacitor development: being both microporous and electrically conducting, they can be used as the sole electrode material [3,4]. Furthermore, they can be formulated into printable inks, facilitating very simple, high-throughput manufacturing.

Here we report supercapacitors fabricated on flexible PET substrates from printable CNT and graphene based inks. The CNT material is a composite with carboxymethyl cellulose [5], where the polymer is wrapped around the nanotubes improving solubility and processability. The graphene ink used here is a composite of graphene and PEDOT:PSS, the latter of which improves the material's conductivity further. The electrolyte is aqueous lithium chloride, which provides not only more facile preparation and handling, but also disposability due to its non-toxicity. These devices are suitable for some applications such as energy harvesting and ambient intelligence.

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**P164**

# Surface characterization and modification of carbon nanotubes for application in cement-based composites

Anastasia Sobolkina[1], Viktor Mechtcherine[1], Cornelia Bellmann[2], Vyacheslav Khavrus[3], Steffen Oswald[3], Diana Maier[3], Silke Hampel[3], Manfred Ritschel[3], Albrecht Leonhardt[3]

*1 Institute of Construction Materials, Faculty of Civil Engineering, Technische Universität Dresden, D-01062 Dresden, Germany*
*2 Institute of Physical Chemistry and Polymer Physics, Leibniz Institute of Polymer Research Dresden, HoheStrasse 6, D-01069 Dresden, Germany*
*3 Leibniz Institute for Solid State and Materials Research (IFW), Helmholtzstrasse 20, D-01069 Dresden, Germany (a.leonhardt@ifw-dresden.de)*

To use efficiently superior mechanical properties of nanotubes (CNTs) for mitigation of crack initiation and propagation in cement-based composites, an adequate interaction between CNTs and cement matrix must be provided. In this study, various types of CNTs synthesized using acetonitrile, cyclohexane, and methane were investigated with regard to their physicochemical surface properties. Significant differences in the polarity as well as in wetting of the CNTs were revealed by combing electro-kinetic potential and contact angle measurements. The hydrophilicity of CNTs increased by utilisation of carbon sources in the following order: cyclohexane, methane, acetonitrile. The XPS analysis applied for an estimation of the chemical composition at the CNT surface yielded nitrogen atoms incorporated into the tube structure by application of acetonitrile as a carbon source. It was found that the active nitrogen-containing sites increased the polarity of the CNTs, imparting them with Lewis basic characteristics and improving their wetting behavior. To enhance the compatibility of the graphene sidewalls of the CNTs with cement matrix, the nanotubes were coated with silica via a sol-gel method. A strong dependency of silica deposition on the CNT nature was observed. The mechanism of silica adsorption through interfacial bond formation was discussed.

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**P165**

# Selective sorting of semiconducting single-walled carbon nanotubes with fluorene-xanthenoxanthene copolymer for high-performance TFTs

Hongbo Li*, Fan Zhang, Na Lv, Song Qiu, Zheng Cui and Qingwen Li*

*Suzhou Institute of Nanotech and Nanobionics, Chinese Academy of Science, Suzhou 215123, P. R. China. (*hbli2008@sinano.ac.cn and qwli2007@sinano.ac.cn)*

Recent research in single-walled carbon nanotubes (SWNTs) based thin-film field transistors (TFTs) has witnessed remarkable evolution as a result of combined efforts in the selective sorting of semiconducting (s-) SWNTs and solution-processable device fabrication. Some conjugated polymers have been recently used for the selective sorting of s-SWNTs and made it possible to fabricate the uniform s-SWNT TFTs at a large scale via the dip- and spin-coating method, showing the important improvements in sorting processing, solution processing and device performance [1-2].

Unfortunately, although a lot of conjugated polymers have been used for the selective dispersion SWNTs, only few fluorene and thiophene based polymers are proved to be capable of selectively suspending the s-SWNTs, due to their polymer structure dependence. Therefore, it is quite desirable to explore more novel polymers for the s-SWNT sorting towards high-performance TFTs. Herein, we report that an alternating conjugated copolymer of fluorene and peri-xanthenoxanthene, as a dispersant, could be used for the selective sorting of the s-SWNTs. Furthermore, via the dip-coating method, the fabricated s-SWNT network presented the excellent device performance with the charge-carrier mobility of 4-6.1 $cm^2/V{\cdot}s$ and the on/off ratio of $10^7$-$10^8$.

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**P166**

# New-type planar field emission display with superaligned carbon nanotube yarn emitter

Peng Liu, Yang Wei, Kai Liu, Liang Liu, Kaili Jiang, Shoushan Fan

*Tsinghua-Foxconn Nanotechnolgy Research Center, Department of Physics, Tsinghua University, Beijing 100084, China (pengliu@mail.tsinghua.edu.cn)*

With the superaligned carbon nanotube yarn as emitter, we have fabricated a 16 × 16 pixel field emission display prototype by adopting screen printing and laser cutting technologies. A planar diode field emission structure has been adopted. A very sharp carbon nanotube yarn tip emitter can be formed by laser cutting. Low voltage phosphor was coated on the anode electrodes also by screen printing. With a specially designed circuit, we have demonstrated the dynamic character display with the field emission display prototype. The emitter material and fabrication technologies in this paper are both easy to scale up to large areas.

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**P167**

# Carbon nanotubes for field emission based movement detection

Sergei Loschek[1], Sascha Hermann[1], Sebastian Voigt[2], Alexey Shaporin[2],
Jan Mehner[2], Stefan E. Schulz[1,3]

*1 Chemnitz University of Technology, Center for Microtechnologies, Germany (sergei.loschek@zfm.tu-chemnitz.de)*
*2 Chemnitz University of Technology, Microsystems and Precision Engineering, Germany*
*3 Fraunhofer Institute for Electronic Nano Systems (ENAS), Chemnitz, Germany*

Carbon nanotubes (CNTs) are excellent field emitters. The small diameter enhances the microscopic electric field strength at the CNT tips so that macroscopic field strengths of 1 - 2 V/µm are sufficient to start the field emission [1]. Therefore field emitting CNTs open new approaches for devices and applications like scanning electron microscopy and field emission displays [2].

In this work field emitting CNTs are of particular interest for highly sensitive displacement sensor applications. To exploit the field emission properties we deposited metallic single walled carbon nanotubes on electrodes and created a gap between the nanotubes and the electrodes to enable the field emission. The gap formation was done by a lithographical and an electrically induced breakdown technique. While the lithographical gap formation uses wafer-level processes of the back-end of line (BEOL) technology and creates gap sizes of several 100 nm up to ~1 µm, the electrically induced breakdown is a self-limiting and self-aligning process with resulting gap sizes of approximately 100 nm. The electrically induced breakdown was performed consecutively on each structure. Depending on the gap formation process and the resulting gap widths macroscopic field strengths in the range of 0 - 200 V/µm were applied. The field emission properties in different atmospheric conditions were studied and compared. In addition to the experimental work numerical simulations to investigate the gradients in field strength and current densities depending on the dynamic gap size and the CNT alignment for the single CNT and CNT forests were performed. Real contact configurations and CNT shapes were used in 3D multi-domain simulations.

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P168

## Areal capacitance of manganese oxide enhanced graphene on cotton substrate/textile

Peter Lynch, Paul King, Thomas McLean Higgins, Jonathan Coleman

*Trinity College Dublin, Ireland (lynchp9@tcd.ie)*

E-textiles have the potential to make our current devices more convenient. Wearable energy would be necessary to power E-textiles and could also be used to assist conventional devices. Supercapacitors, an electrochemical analogue to the electrostatic capacitor, can be readily fabricated on a textile substrate [1]. The usefulness of a fabric capacitor is limited by the area it occupies making the capacitance per unit area the most appropriate metric for comparison.

In this work the cotton layer provides a macroscopically porous network on which Graphene, added by a simple dip and dry method used in the fabrics industry [1], serves as a conductive layer over the cotton while Manganese Oxide, deposited by electroless deposition [2], provides a pseudocapacitive material to give the fabric an appreciable capacitance. Using a safe aqueous electrolyte ($Na_2SO_4$) facilitates aplicati0n to wearable energy. The main advantages of this process are its simplicity and cost effectiveness.

Capacitances for two electrode systems exceeding 0.2F/cm$^2$ have been achieved with energy density of 19.2 µWh/cm$^2$ and power density of 40.6 mW/cm$^2$. A t-shirt sized device could have energy and power densities in the tens of milli-Watt hour and tens of Watts range.

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P169

## Spintronic application of carbon nanotubes

Sayani Majumdar[1,2], Esko Kauppinen[1]

*1 Department of Applied Physics, Aalto University School of Science, 02150 Espoo, Finland*
*2 Department of Physics and Astronomy, University of Turku, 20014 Turku, Finland*

Quantum mechanical degree of freedom of electrons namely “spins” are at the center of many spintronic device concepts. Active control over spin polarized transport in magnetic nanostructures will enable low power operation and new functionalities to future logic, memory, and sensor technologies. In a conventional spin-valve or magnetic tunnel junctions, two ferromagnetic (FM) electrodes are separated by a thin nonmagnetic barrier and the giant or tunneling magnetoresistance depends critically on the spin polarization of the electrodes. Also the spin transporting material and their interface with the FM electrode is a key issue in these device structures as significant amount of the injected spins get lost in these spacers.

Hybrid inorganic/organic spintronics is a subject of great interest among condensed matter physicists due to the possibility of exploiting best of both worlds. While inorganic FMs possess very high spin polarization, $\pi$-conjugated organic semiconductors are attractive for transporting polarized spins spintronics, due to their low spin-orbit and hyperfine coupling. However, as the organic semiconductors are mainly hydrocarbons they contain significant amount of H atoms in their side chains and the hyperfine field from these H atoms can make the spin-polarized carriers to precess around these local spins and lose their polarization before reaching the receiving electrode. So, it has been theoretically predicted that fully carbon based systems like carbon nanotube (CNT) and graphene could be better choice for spin polarized transport where spin-orbit coupling is small because of the weak atomic spin–orbit splitting in carbon and due to absence of H atoms, hyperfine field is almost negligible.

In spite of all these predictions, spintronic devices made of CNT and graphene has so far been unable to show significant improvement. In this presentation we will briefly review spintronic application of the CNTs highlighting on the achievements so far, major challenges and the future prospects of this emerging field.

## P170

## Carbon nanotube based ultra-high-speed blackbody emitters

Hideyuki Maki, Tatsuya Mori, Yohei Yamauchi

*Department of Applied Physics and Physico-Informatics, Keio University, Yokohama 223-8522, Japan*

Here we report on a novel ultra-high-speed blackbody emitter based on carbon nanotubes (CNTs). Using a nonsuspended CNT thin film in direct contact with a substrate, we observed high-speed blackbody emission with the response speed of 1 Gbps (experimentally) and 10 Gbps (theoretically), which is > $10^6$–$10^7$ times higher than that of a conventional incandescent emitter with a filament and is higher or comparable to a light-emitting diode (LED) and a laser diode (LD) (~100 Mbps or ~10 Gbps, respectively). We theoretically show the mechanisms of this high-speed response, which is due to the high heat dissipation to the substrate in the thin CNT film[1]. We also demonstrate the modulation under a rectangular input, the 500-ps-width pulsed light generation and the real-time optical communication. These results are the first report on high-speed light emission and optical communication in a CNT emitter including CNT electroluminescence arising from an electron-hole recombination. This blackbody emitter can be applied as a high-speed light source for optical or optoelectronic circuits because of its fast modulation speed, micro size and direct formation on a Si wafer. This emitter can also be expected to be applied as an ultrafast white light source for a compact time-resolved measurement system because the pulsed continuum light (like a supercontinuum light) can be generated from one chip. Moreover, this CNT-based emitter can be fabricated without separation of metal and semiconductor CNTs; therefore, wafer-scale mass-produced CNTs can be used for the fabrication of this emitter. This novel emitter will open new applications for blackbody emission, which conventionally has been limited to applications of illumination or heating lamps.

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## P171

## Multifunctional and environmentally friendly nanocomposites between graphene or graphene oxide and natural rubber

C.F.de Matos,[1] Fernando Galembeck,[2] Aldo J.G Zarbin[1]

*1 Universidade Federal do Paraná- UFPR, PR, Brazil (carola@ufpr.br)*
*2 Universidade Estadual de Campinas - UNICAMP, SP, Brazil*

This work describes a green route to multifunctional nanocomposites materials obtained between natural rubber latex (NR) and both i) graphene (rGO) and ii) graphene oxide (GO). The graphene structures used in this study were obtained by a modified Hummers method. Aqueous solution with different concentration of GO and aqueous dispersion of rGO (prepared with surfactant cetyl trimethylammonium bromide - CTAB) were mixed with natural rubber latex under magnetic stirring followed by sonication. The slurries obtained were cast onto a flat plastic mold (10×5×5 cm) and dried in an oven under air at 70 °C for 24 h. The nanocomposites were characterized by TEM, SEM, AFM, X-ray diffraction, Raman and infrared spectroscopies. The thermal, electrical and mechanical properties were evaluated by thermogravimetric analysis, resistivity measurements (four-points) and dynamical mechanical analysis (DMA). Spectroscopic data, XRD and DMA indicated an increase in structural organization of the polymer, which means that the carbon nanostructures induce crystallization in the polymer (proportional to the amount of carbon nanostructures). The occurrence of fillers networks in the polymeric matrices provided significant improvements in the electrical, chemical and mechanical properties, in comparison to the unfilled polymer. For example, the electrical resistivity varied from $10^7$ (NR) to $10^3$ $\Omega cm^{-1}$ after the addition of 2 wt% of rGO and the storage modulus increased from 3.8 (NR) to 6.49 MPa (~73%) with only 2 wt% of GO.

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P172

## Room temperature single charge memory using all surrounded carbon nanotube channel

Kazuhiko Matsumoto, Takafumi Kamimura

*Institute of Scientific and Industrial Research, Osaka University , Japan*
*(k-matsumoto@sanken.osaka-u.ac.jp)*

A single charge memory operated at room temperature is one of the candidates for the device beyond CMOS. The device was realized by the all arounded carbon nanotube channel FET. The single wall carbon nanotube (CNT) was wrapped by the double layered insulator of $Al_2O_3$ (3 nm) and $SiN_x$ (27nm), and by the top gate metal. Even when the low top gate was applied, the electric field concentration occurs because of the narrow CNT diameter of 1nm, high electric field is concentrated to the channel, and charge in the CNT channel was injected to the interface of $Al_2O_3$/ $SiN_x$ and trapped there. When one charge was trapped, the next charge was stopped for the injection because of Coulomb blockade phenomena. By one charge injection and storage, the threshold of the memory shift and works as a single charge memory. In order to operate at room temperature, the channel length should be as small as less than 10nm. Using ALD system, the channel gap as small as 10nm was realized. In the dependence of the drain current on the top gate bias measured at room temperature, the drain current begins to increase by increase of the gate bias. At the certain gate voltage, however, the drain current suddenly decreases and again begins to increase following the increase of the gate bias. Therefore, the drain current shows the weak oscillation along the gate bias. The period of the oscillation is 220mV. The decrease of the drain current is attributed to the single charge injection from CNT channel to the $Al_2O_3$ and $SiN_x$ interface trap, which make the shift of the threshold voltage of 220mV. The threshold voltage shift is regulated by the Coulomb blockade phenomenon which stops the next charge to be injected to the trap. The around trip of the gate bias produces the hysteresis. The width of the hysteresis was also regulated by the single charge injection and shows the stepwise increase. The increase of the hysteresis was just the same as 220mV, which corresponds to that of the single charge injection. The single charge memory will be one of the candidates for the ultra low power consumption device beyond CMOS age.

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## Touch-induced n-IR fluorescence modulation in transparent stretchable polymer-SWNT composite films

Rujun Ma[1], Mini Mol Menamparambath[2], Pavel Nikolaev[2,3], Seunghyun Baik[2,4,*]

*1 SKKU Advanced Institute of Nanotechnology, Sungkyunkwan University, Suwon, 440-746, Korea*
*2 Department of Energy Science, Sungkyunkwan University, Suwon, 440-746, Korea*
*3 Present address: UES Inc. and Air Force Research Laboratory, Dayton, OH, 45433, USA*
*4 School of Mechanical Engineering, Sungkyunkwan University, Suwon, 440-746, Korea*
*(*sbaik@me.skku.ac.kr)*

Optical transparency with stretchability in electronics is today's one of the most advanced topics for a wide range of device applications. Here we fabricated transparent stretchable composite films made of single-walled carbon nanotubes (SWNTs) and polymers [1]. The composite films retained near-infrared (n-IR) fluorescence of SWNTs by individual dispersion of nanotubes. Two different types of polymers were investigated (PVDF-HFP and PDMS), and the composite films were formed by solvent casting and curing. The maximum strain was as high as 600%. The fluorescence intensity, normalized by Raman G-mode, did not significantly vary as a function of strain. However, the n-IR fluorescence systematically changed as a function of temperature. Besides, the fluorescence intensity increased or decreased when touched by stainless steel or polymer rods [1]. The cycleability was excellent. The sub-micron spatial resolution could be obtained based on the calculated distance between nanotubes. The n-IR fluorescence from SWNTs in stretchable polymeric matrixes may enables optical touch sensing devices eliminating electrical interconnects [1].

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**P174**

## Polymer electrolyte fuel cell catalyst based on carbon nanotubes shows remarkable durability

Mohamed R. Berber[1], Tsuyohiko Fujigaya[1,2], Naotoshi Nakashima[1,2,3]

*1 Department of Applied Chemistry, Kyushu University, Fukuoka 819-0395, Japan*
*2 WPI-I2CNER, Kyushu University, Fukuoka 819-0395, Japan*
*3 JST-CREST*

Polybenzimidazole (PBI) is known to show proton conduction after acid doping and recognized as a promising polyelectrolyte for high temperature polymer electrolyte fuel cell (HT-PEFC) because the PBI exhibits an excellent proton transfer even under dry condition at higher temperature over 100 °C.

We have reported PBI adsorbed onto the surface of carbon nanotubes (CNTs) and acts as the good dispersant of CNTs [1]. By taking the advantage of uniform wrapping of PBI on CNTs surface, we utilized this composite (CNT/PBI) as a novel carbon supporting materials for the loading of platinum (Pt) nanoparticles to fabricate an electrocatalyst for PEFC [2,3].

The catalyst shows excellent Pt utilization efficiency mainly due to the formation of ideal interfacial structure around Pt. We fabricated the PEFC membrane electrode assembly (MEA) using the obtained composite (CNT/PBI/Pt) after doped with acid, and measured the fuel cell performance using hydrogen and air as fuels [4]. At the meeting, we report the durability of the MEA based on this CNT composites.

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**P175**

## Polymer reinforcement with $SiO_2$/MgO coated multiwall carbon nanotubes

K. Nemeth[1], L. Kovacs[1], B. Reti[1], Zs. Dugar[2], K. Belina[2], K. Hernadi[1]

*1 Department of Applied and Environmental Chemistry, University of Szeged, Szeged*
*(hernadi@chem.u-szeged.hu)*
*2 Department of Materials Engineering, Kecskemét College, Kecskemét*

Multiwall carbon nanotubes (MWCNTs) have excellent mechanical, electrical, magnetic properties and high aspect ratio, which make them an ideal reinforcing agent for high strength polymer composites. Complete inorganic coverage on their surface might help to reduce the aggregation of MWCNTs and also to overcome consequent dispersability problem. Polymer filler materials – talc or dolomit – are often used in the industry to improve mechanical properties. The surface treatment improves the interaction between polymer matrix and carbon nanotube [1-4].

In this work MWCNTs were coated with talc-like mixed oxides to facilitate their incorporation into the different polymer (PA,PE,PP) matrices. Silica-magnesia oxides were synthesized from different silica precursors and magnesia salts by different methods. As-prepared materials were characterized by TEM, SEM, Raman spectroscopy and XRD. In order to investigate the change of polymer's properties MWCNT nanocomposite samples were implicated into the matrix. MWCNT/ polymer composites were investigated by SEM and Raman spectroscopy. Mechanical and thermal (melting and crystallization) properties of our composites were measured by dynamic mechanical analysis (DMA) and tensile test.

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## Multifunctional material based on carbon nanotube/ Prussian blue nanocomposite film

P176

Edson Nossol[1], Arlene B.S. Nossol[1], Alan M. Bond,[2] Aldo J.G. Zarbin[1]

*1 Federal University of Paraná, Brazil (edsonnossol@ufpr.br)*
*2 Monash University, Australia*

Prussian Blue (PB), $Fe_4[Fe(CN)_6]_3.xH_2O$ ($x$=14-16), has an open framework structure constituted by alternating face centered cubic lattices of $Fe^{3+}$ and $Fe^{2+}$ cations, distinguishable by their different coordination to the $CN^-$ ligand. Electrodeposited thin films with this structure show the simultaneous presence of two redox couples, semiconductor characteristics and have the capability to reversibly intercalate different cations. Based on the exceptional electrochemical properties of carbon nanotubes (CNTs) such as high current density and heterogeneous electron transfer rate, mechanical stability and electrocatalytic effect on redox process of different compounds, the preparation of carbon nanotube/Prussian blue (CNT/PB) nanocomposites has attracted a great interest of the scientific literature. A new methodology to prepare PB nanostructures based on an in situ electrochemical reaction between the iron-based compounds present in the cavities of CNTs and the ferricyanide ions in solution was developed in our group [1]. This work reports the preparation of homogeneous, transparent and electroactive films of CNT/PB nanocomposites using this new method. PB electrosynthesized as nanocubes over the CNTs walls showed intimate contact between PB and CNTs, which improved the stability and redox properties of PB. The electrodeposition of PB and the chemical interaction between PB and CNTs were attested by cyclic voltammetry, X-ray diffraction, UV-Vis and Raman spectroelectrochemistry and *in situ* electrochemical techniques. The CNT/PB composite film presented as a multifunctional material, showing its application as $H_2O_2$ sensor with a very high sensitivity and low detection limits [1]; as a new electrode material for environmental treatment of water samples using different Fenton processes [2]; and as a eletrochromic device [3], with a good response time and excellent stability upon the application of several double potential cycles.

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## s-SWNT as active layer for silicon photonics

P177

A. Noury[1], E. Gaufrès[2], X. Le Roux[1], L. Vivien[1], N. Izard[1]

*1 Institut d'Electronique Fondamentale, CNRS-UMR 8622, Université Paris Sud, 91405 Orsay, France (nicolas.izard@u-psud.fr)*
*2 Regroupement Québécois sur les Matériaux de Pointe and Département de Chimie, Université de Montréal, Montréal, Québec H3C 3J7, Canada*

Silicon photonics was under intense investigation over the last years, as it is very promising in order to replace electronics in microprocessors. However, bulk silicon is an indirect bandgap material unable to emit light. Among explored solutions to overcome this limitation, one is based on active layers of semiconducting single wall carbon nanotube (s-SWNT). Carbon nanotubes are a promising material due to their ability to emit, modulate and detect light at telecom wavelength.

We report the integration of extracted s-SWNT, emitting mainly at 1.3 µm, on several photonics structures, from simple evanescent waveguide to micro-cavities. Full integration process is reported, from nanotube powder to s-SWNT optical emission on top of silicon waveguides. We show that it is possible to maintain optical properties of carbon nanotubes while deposited in thin films on top of a silicon-on-insulator (SOI) substrate. Coupling efficiency is in the order of 10% [1], and we showed very good thermal resilience at 100°C, which is encouraging for future applications. We investigate the effect of more complex structures, such as micro-cavities, on the photoluminescence intensity of s-SWNT. This is an important milestone in the area of 'Carbon Nanotube Photonics'.

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## P178

## High-mobility carbon nanotube thin-film transistors based on transfer and printing techniques

K. Higuchi[1], S. Kishimoto[1], Y. Nakajima[2], T. Tomura[2], M. Takesue[2], K. Hata[2],
A. Kaskela[3], A. G. Nasibulin[3], E. I. Kauppinen[3], and Y. Ohno[1,4]

*1 Dept. of Quantum Eng., Nagoya Univ., Japan (yohno@nuee.nagoya-u.ac.jp)*
*2 Research and Development Center, Bando Chemical Industries, Japan*
*3 Dept. of Applied Physics, Aalto Univ., Finland, 4 MIDE, Aalto Univ., Finland*

Among many kinds of thin-film transistors, carbon nanotube (CNT) thin-film transistors (TFTs) have attractive features such as high mobility, flexibility, and transparency. CNT thin films also have a good processability. In this work, we introduce high-speed flexographic printing technique in the device fabrication process. The devices are fabricated by fully lithography-free and ambient-pressure processes.

We fabricated bottom-gate CNT TFTs on a polyethylene naphthalate (PEN) film with the flexographic printing technique, which is a kind of high-speed typographic prints with a flexible relief plate made of photopolymer. The inks of silver nanoparticles and polyimide were respectively used for the electrodes and insulator. A CNT thin film grown by the floating-catalyst CVD was transferred as our previous work [1]. CNTs outside the channel region were etched by the ambient pressure Ar/$O_2$ plasma. The device with a channel length of 115 μm showed a high mobility of 157 $cm^2$/Vs for the rigorous model [2] (112 $cm^2$/Vs for parallel plate model) with on/off ratio of about $10^4$.

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## P179

## Carbon nanotube thin film transistors for printed electronics

Kimmo Ojanperä[1], Patrik Laiho[2], Antti Kaskela[2], Toma Susi[2], Ari Alastalo[1], Esko Kauppinen[2]

*1 VTT, Printed Functional Solutions, Finland (kimmo.ojanpera@vtt.fi)*
*2 Department of Applied Physics, Aalto University School of Science, Finland*

We present single-walled carbon-nanotube (SWCNT) thin-film transistors (TFT) fabricated on a plastic substrate using a hybrid manufacturing method. The device structure is a bottom-gate top-contact (BGTC) configuration. The SWCNT network for the TFT channel was collected onto a nitrocellulose membrane filter directly from a floating catalyst CVD reactor [1], and press transferred onto a plastic PEN substrate followed by the dissolution of the filter in acetone. Before the press transfer, the gate electrode was shadow-evaporated and a polyimide dielectric layer spun-cast on the substrate. Finally, the source and drain electrodes were inkjet-printed on top of the percolating SWCNT network.

The TFTs were characterized in ambient conditions by transfer curve measurements using a Keithley 4200 Semiconductor Characterization System. The TFTs had mobilities on the order of 4 $cm^2$/Vs and on/off-ratios over $10^3$, with the measurement voltage ranging from -10 V to +5 V. The TFT performance was limited by the combination of materials, impurities, statistical variation of the deposition processes, and the roughness of the substrate and the solution-processed surfaces. The demonstrated process can be used to fabricate, for example, backplane circuits of flexible displays.

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P180

# Photo and electroluminescent properties of composites from carbon nanotubes and CdS nanoparticles separated by a polymer dielectric layer

A.V. Okotrub[1], L.G. Bulusheva[1], M.A. Kanygin[1], S.V. Larionov[1], A. A. Zarubanov[2], K. S. Zhuravlev[2]

*1 Nikolaev Institute of Inorganic Chemistry SB RAS, Lavrentieva 3, Novosibirsk 630090, Russia*
*(spectrum@niic.nsc.ru)*
*2 Rzhanov Institute of Semiconductor Physics SB RAS, Lavrentieva 13, Novosibirsk 630090, Russia*

Simple and effective methods for synthesis of the hybrid material from the CdS nanoparticles (NP) on CNTs are proposed. CNT arrays were grown on silicon substrates using aerosol assistant chemical vapor deposition (CVD) method. The size and the shape of the CdS NP formed on CNT were found to depend on the temperature of water or other organic solutions. Electron microscopy study revealed a direct contact between CdS nanoparticles and CNT surface. X-ray photoelectron spectroscopy examination of the CdS/CNT hybrid material detected surface oxidation of the grown nanoparticles. The synthesis methods allow preserving alignment of CNTs in the array and uniform decorating the CNTs with CdS nanoparticles or deposition only on nanotubes tips. Formation of the continuous CdS/CNT interface indicates that nucleation and growth of the NP take place directly on the nanotube surface. Electroluminescent properties of synthesized materials were studied on a set-up elaborated for measurement of field electron emission characteristics. When the CdS NP are deposited on carbon nanotubes, the intensity of this band decreases significantly. Furthermore, the kinetics of the photoluminescence decay becomes faster, which brings evidence of an additional channel for the quantum-dot deexcitation. The analysis of the experimental data demonstrates that the Förster energy transfer from CdS NP to carbon nanotubes is most probably responsible for this channel. Preliminary deposited between the CNT and NP layers from polymer PMMA with 10 - 50 nm thickness increases efficiency photoluminescence on $10^2$.

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# Thermal-magnetic-electric oscillator based on spin-valve effect

Hee Chul Park[1], A. M. Kadigrobov[2], S. Andersson[3], D. Radic[4], R. I. Shekhter[5], M. Jonson[5,6,7], and V. Korenivski[3]

*1 School of Computational Sciences, Korea Institute for Advanced Study, Seoul, Korea*
*2 Theoretische Physik III, Ruhr-Universitat Bochum, Bochum D-44801, Germany*
*3 Nanostructure Physics, Royal Institute of Technology, Stockholm SE-106 91, Sweden*
*4 Department of Physics, Faculty of Science, University of Zagreb, Zagreb 1001, Croatia*
*5 Department of Physics, University of Gothenburg, Göteborg SE-412 96, Sweden*
*6 School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh EH14 4AS, Scotland, UK*
*7 Division of Quantum Phases and Devices, School of Physics, Konkuk University, Seoul 143-701, South Korea*

A thermal-magnetic-electric valve with the free layer of exchange-spring type and inverse magnetoresistance is investigated. The structure has S-shaped current-voltage characteristics and can exhibit spontaneous oscillations when integrated with a conventional capacitor within a resonator circuit. The frequency of the oscillations can be controlled from essentially dc to the GHz range by the circuit capacitance.

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## Nanocomposites based on conducting polymers / aligned carbon nanotubes for electrochemical storage in ionic liquid media

Mathieu Pinault[1], Florent Tatard[1], Marina Porcher[2,3], Sébastien Lagoutte[3], François Tran-Van[2], Fouad Ghamouss[2], Martine Mayne-L'Hermite[1], Pierre-Henri Aubert[3]

*1 CEA-Saclay, DSM/IRAMIS/SPAM, Laboratoire Francis Perrin, Bat. 522, 91 191 Gif sur Yvette Cedex, France (mathieu.pinault@cea.fr)*
*2 PCM2E, EA 6299, Université François Rabelais, Tours, France*
*3 LPPI, EA 2528, Université de Cergy-Pontoise, France*

One of the obstacles in electric transportation is the use of autonomous electrical power sources (rechargeable batteries, fuel cells, etc.). Recently, with the development of supercapacitors, electronically conducting polymers (ECPs) have been suggested as promising materials for electrode elaboration [1-3] considering its use with ionic liquid and its nanostructuration to improve its limited [4].In this study, we present the elaboration of nanocomposites made of poly(3-methylthiophene) (P3MT) as ECP electrodeposited onto nanostructured electrode [5] made of aligned multiwalled carbon nanotubes (CNTs) obtained by aerosol-assisted CCVD [6-7]. We will present the optimization of the electropolymerization parameter leading to controlled thickness of the ECP on the CNT acting as a template electrode and to the homogeneity of the coating in the depth of the carpet (TEM, SEM coupled with EDX), depending on several parameters (concentration, current density, galvanostatic profile...). Preliminary results concerning the elaboration and the performance of nanostructured ECP/aligned nanotubes will be presented, showing a significant increase of the specific capacitance Cm of the nanocomposite (180 F/g) and the possibility to obtain self-supported and flexible nanocomposite carpets.

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## Flexible energy storage circuit for a piezoelectric harvester

Juho Pörhönen, Suvi Lehtimäki, Donald Lupo, Sampo Tuukkanen*

*Organic Electronics Group, Department of Electronics and Communications Engineering, Tampere University of Technology (TUT), Finland (*sampo.tuukkanen@tut.fi)*

Printing technologies are applicable for low-cost manufacturing of flexible, light-weight and large-area electronics. Potential applications are e.g. flexible displays, RFID antennas, batteries and solar cells. Our printing laboratory at TUT is equipped with a wide range of tools for patterning and deposition as well as tools for structural and electrical characterization of materials and devices.

This work is related to a project aiming at an autonomous fully printed activity and movement sensor. The sensor concept has great potential for energy harvesting applications as well. The sensor circuit is composed of a piezoelectric element, a voltage doubler [1] and a supercapacitor [2]. We are concentrated on the development of the supercapacitor which can be assembled on the same substrate with printed rectifying diodes [3]. Here, we demonstrate the functionality of the circuit by charging the supercapacitor using a commercial piezoelectric element. Towards the end of the project we aim at a fully integrated structure on the same substrate.

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# Tuning the localization behavior of CNTs in immiscible polymer blends by a reactive component

Petra Pötschke, Marén Gültner, Andreas Göldel

*Leibniz Institute of Polymer Research Dresden (IPF), Germany (poe@ipfdd.de)*

Polymer blends combine the characteristics of the specific polymers and in some cases even synergistic property effects are created. Hereby, in immiscible blends their morphology significantly influences the property profile of the materials. In many cases, co-continuous morphologies are found to be especially advantageous. Adding functional fillers into polymeric matrices is another possibility to generated materials with improved properties. Combining both, blending and filling, can create blend composites with outstanding properties, e.g. the incorporation of carbon nanotubes (CNTs) in insulating polymer blends can improve their electrical, mechanical and thermal properties. Interestingly, in immiscible polymer blends in most cases a selective localization of CNTs in one of the phases is observed which is mainly due to thermodynamic reasons and was found to be very fast and complete.

In the contribution it is shown that chemical reactions or strong interactions between functional groups on the nanotube surface and one of the polymer phases may also influence the localization behavior. By adding a reactive substance miscible with one blend component and able to react with functional groups of CNTs the localization behavior can be tuned, which will be shown on the example of PC-SAN with a reactive component (RC) containing maleic anhydride groups. Thereby, the localization behavior of $NH_2$ modified multiwalled CNTs (MWCNT) will be compared with that of unmodified MWCNTs and singlewalled CNTs (SWCNTs). Due to thermodynamic reasons, in absence of RC all types of CNTs localize in the PC phase of the blends, whereas after addition of the MA containing RC, which is fully miscible with SAN, the MWCNTs show a localization change towards SAN, depending on the RC content, which was not found for the used HiPCO SWCNTs.

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# Flexible and transparent UV sensors based on hybrid SWCNT-ZnO tetrapod films

Simas Rackauskas[1], Kimmo Mustonen[1], Marco Mattila[2], Olga Klimova[3], Hua Jiang[1],
Oleg Tolochko[3], Harri Lipsanen[2], Esko I. Kauppinen[1] and Albert G. Nasibulin[1]

*1 NanoMaterials Group, Department of Applied Physics, Aalto University, Finland (simas.rackauskas@tkk.fi)*
*2 Department of Micro and Nanosciences, Micronova, Aalto University, Finland*
*3 Material Science Faculty, Saint-Petersburg State Polytechnical University, Russia*

SWCNT thin film electrodes were fabricated by one step dry deposition technique from the filter to a polyethylene terephthalate (PET) substrate [1]. Flexible transparent UV sensors were fabricated by drying droplet of zinc oxide tetrapod (ZnO-T) solution between two transparent single-wall carbon nanotube (SWCNT) film contacts, on PET substrate. UV sensing phenomenon originates from the alteration of the charge carrier density under the UV-light irradiation [2]. High performance of the device, compared to a single ohmic contact sensor, is associated with the multiple barriers. The local electric field at the barrier area reduces the electron-hole recombination rates, resulting in an increase in free carrier density. Rapid photocurrent response and recovery is related to quick changes in interfacial region, instead of the whole surface [2]. It is also known that the higher the potential barrier, the faster the current recovery. Response measurements of the device show that such a SWCNT with ZnO-Ts photosensor is suitable for detection of low levels of UV light. Moreover the high resistance of 60 TΩ in the off state shows great potential for practical application in UV sensing [3]. Fabricated flexible transparent UV sensors showed 45 fold current increase under UV irradiation with the intensity of 30 $\mu W/cm^2$ at the wavelength of 365 nm and response time of 0.9 s.

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**P186**

## Photocatalytic activity of $TiO_2$/MWCNT nanocomposites with different $TiO_2$ phase compositions

Balázs Réti[1], András Dombi[2,3], Klara Hernadi[1,2,*]

*1 Department of Applied and Environmental Chemistry, University of Szeged, Hungary (*hernadi@chem.u-szeged.hu)*
*2 Research Group of Environmental Chemistry, Institute of Chemistry, University of Szeged, Hungary*
*3 Institute of Material Sciences and Engineering, University of Szeged, Hungary*

Decomposition of harmful pollutants in air and water can be achieved by advanced oxidation processes (AOPs). A novel AOP method is photocatalysis. This technique is using light irradiation and solid material to generate highly reactive oxygen containing radicals to oxidize harmful chemicals. Titanium dioxide ($TiO_2$) is a promising material for this purpose due to it is chemically stable, cheap, not toxic and biocompatible. Furthermore there is possibility to achieve even better efficiency by combining $TiO_2$ with multiwall carbon nanotubes (MWCNT) to create nanocomposite material [1, 2].

Titanium dioxide/MWCNTs composites were prepared by acid catalyzed sol-gel method using titanium-isopropoxide and ethanol as precursor and solvent respectively. The asprepared product was annealed at different temperatures to get different anatase/rutile ratios. The crystallity and the phase composition were measured by powder XRD method. With increasing annealing temperature the rutile content also increased. The TEM investigation of the samples revealed that titania nanoparticles were bound onto the surface of MWCNTs. Raman spectroscopy also confirmed the crystallity of the $TiO_2$ and slight changes were noticed in connection with the MWCNT bands. The photocatalytic activities of the composites were evaluated in salicylic acid decomposition in a homemade photoreactor under UV-A irradiation ($\lambda_{max}$= 365 nm). At the given MWCNT content, regarding the photocatalytic activity the optimum anatase/rutile content was found.

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**P187**

## Graphene nanoribbon inelastic transport based molecular sensor

Carlos Ritter[1], R. B. Muniz[2] , S. S. Makler[3], and A. Latgé[2]

*1 School of Physics, Trinity College Dublin, Dublin 2, Ireland*
*2 Instituto de Fisica, Universidade Federal Fluminense SN, 24210-360 Niteroi-RJ, Brazil*
*3 Instituto de Fisica, Universidade Federal Fluminense SN, 24210-360 Niteroi-RJ, Brazil*

Graphene is known for some special electronic transport properties like high electron mobility and balistic transport. In the particular case of graphene nanoribbons (GNRs), the edges can play an important rolle concerning chemical bonding, the electronic distribution and transport. We have developed a single pi-band tight-binding model for a molecular nano-sensor based on phonon-assisted inelastic quantum transport calculations done within the Green's functions formalism (without considering the spin degrees of freedom). In our model a molecule adsorbed to a single carbon (belonging to the GNR) is described as a single phonon mode whose electron-phonon coupling and phonon energy should depend on the local binding potential and the molecule's mass. We show that the transport properties of the GNR can give a "signature" of the particular adsorbed molecule and that the intensity of these "signatures" depend strongly on the geometries and/or GNR lattice chirality. Moreover, this nano-sensor is expexted to have sensitivity to very low concentrations of the foreign molecule.

## Hybrid thin films of unsubstituted polythiophene and in situ synthesized carbon nanostructures

**P188**

Rodrigo V. Salvatierra[1], Carlos E. Cava[1,2], Marcela M. Oliveira[3], Lucimara S. Roman[2],
Aldo J. G. Zarbin[1]

*1 Department of Chemistry – Universidade Federal do Paraná (UFPR), Curitiba, Brazil (rodrigovs@ufpr.br)*
*2 Department of Physics - Universidade Federal do Paraná (UFPR), Curitiba, Brazil*
*3 Department of Chemistry and Biology, Universidade Tecnológica Federal do Paraná (UTFPR), Curitiba, Brazil*

Polythiophenes (PT) are the most studied in the class of conjugated polymers. However, the simplest form – the unsubstituted PT – is limited by its improcessability whereby thin films cannot be produced, thus not utilizing its properties (like stability, charge transport), which are potentially superior related to its soluble counterparts (e.g., P3HT). In a previous work, we developed a liquid-liquid interfacial (water/oil interface) route to obtain self-assembled thin films of polyaniline and carbon nanotubes [1,2]. Adapting this route to the interfacial polymerization of thiophene, we observed a dramatic effect of solvents used in the polymerization of thiophene with solid iron chloride ($FeCl_3$). Testing four different solvents (benzene, toluene, chloroform and n-hexane), we found that hybrid thin films were synthesized with the aromatic solvents – toluene and benzene – in which the iron chloride promotes the polymerization and crosslinking of benzene or toluene, producing small graphene nanostructures along with the PT [3], leading to distinct properties of the polymer, like more conjugated samples, different absorption characteristics and significant hole mobilities (~$10^{-3}$ $cm^2.V^{-1}.s^{-1}$). Also, the effect of adding external carbon nanotubes was evaluated and its interaction with the polymer and in situ generated graphene structures.

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## Effect of nitrogen doping on electromagnetic properties of CNTs and CNT-based composites

**P189**

Olga Sedelnikova, Mikhail Kanygin, Lyubov Bulusheva, Alexander Kyrenya, Igor Asanov,
Alexander Okorub

*Nikolaev Institute of Inorganic Chemistry, Russia (o.sedelnikova@gmail.com)*

Peculiarities of geometry and properties of carbon nanotubes (CNTs) allow finding CNTs applications in different fields, particularly, for designing new shielding covering materials. The electronic properties and dielectric response of CNTs can be modified by inserting a foreign element, in particular nitrogen atoms, in the graphitic network. The content as well as the chemical states of incorporated nitrogen is dependent on the synthetic conditions. Improvement of conductivity of CNTs due to doping demonstrated earlier [1] could improve dielectric response of polymer composites with nitrogen-doped CNTs (N-CNTs) in comparison with pure CNT-based materials.

Nitrogen-doped and pure carbon CNT-based composites were fabricated using the forge rolling method for investigating their dielectric properties in static regime. Composites containing 1, 2, 3, and 4 wt.% of CNTs or N-CNTs were prepared. Measurements with perpendicular and parallel orientations of electric field relative to the nanotubes in polymer matrix were performed. The perpendicular permittivity measures for composites filled with pure carbon or doped nanotubes for all concentration was found to be the same as for the unloaded polymer matrix. For parallel polarization of electric field, we found enhancement of composite permittivity. However, this effect is considerably less pronounced for the N-CNT-based plates. To explain the miscellaneous effect of nitrogen doping on the dielectric response of CNT-based composites the DFT calculations (B3LYP) were used. The static polarizability was found to be dependent on mutual positions and form of the incorporated nitrogen atoms. Particularly, our calculations predict a decrease in the static polarizability of a CNT with the pyridinic nitrogen formation.

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# Carbon nanotubes – poly(3-hexylthiophene) nanohybrid material for organic electronic applications

Gianfranco Sfuncia[1], Silvia Giordani[2], Giovanni Marletta[1]

*1 Università degli Studi di Catania and CSGI, Italy (gianfranco.sfuncia@gmail.com)*
*2 Trinity Biomedical Sciences Institute - Trinity College Dublin, Ireland*

Single-wall carbon nanotubes (SWNT), given their peculiar electronic properties, are promising material for a wide set of organic electronic applications. Chemical vapour deposition synthesized SWNT were first purified using a well-established acid oxidation protocol [1] followed by a base washing step [2]. Best conditions in terms of oxidation temperature and time are investigated to obtain disentangled nanotubes and reduce amorphous carbon impurities as evidenced by Raman spectroscopy. Atomic Force Microscopy provided further proof of the enhanced purity and dispersibility gained and near infra-red photoluminescence spectroscopy showed that nanotubes, specifically the semiconducting ones, still exhibit their typical emission spectra, proving that their electronic properties remains undamaged after the oxidation process.

Purified nanotubes were then mixed with poly(3-hexylthiophene), (P3HT), a semiconducting polymer to create a nanohybrid material having a type II heterojunction [3], therefore potentially intriguing as active layer in hybrid polymer solar cell. Various deposition techniques were used to easily obtain thin SWNT/polymer nanocomposite films and their different morphologies were inspected by AFM in order to find best conditions in terms of nanostructuring and phase separation, i.e., critical parameters influencing excitons dissociation and charge transport in polymer solar cells. Their electrical behavior was studied by current – voltage curves recorded in dark and light conditions, showing marked differences in the conductivity of the composite material with respect to the polymer alone.

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# Optimization of carbon nanotube surface chemistry for atomic layer deposition via non-covalent functionalization

Cameron J. Shearer, Nina Buller, Dominik Eder

*Institute of Physical Chemistry, Westfälische Wilhelms-Universität Münster, Germany*

Nanocarbon-inorganic hybrid materials are an exciting new class of material which are finding application in catalysis, sensors, energy storage and energy conversion. Atomic layer deposition (ALD) is the perfect technique to prepare model nanocarbon-inorganic hybrids due to its ability to form conformal coatings on porous substrates with atomic control of film thickness and the possibility to coat multi-component layers. For uniform ALD coatings hydrophilic surfaces are required therefore nanocarbon surfaces must be modified. Covalent modification, such as oxidation, has been shown to facilitate ALD but the disruption of $sp^2$ bonding degrades the intrinsic properties of the nanocarbon.

Here we compare the ALD of ZnO onto modified CNT films functionalized both non-covalently and covalently. The ALD coatings are compared in respect to coating thickness/uniformity and crystal structure. We study small linker molecules consisting of 1, 2 and 4 aryl groups, namely benzyl alcohol, naphthalene carboxylic acid and pyrene carboxylic acid. In addition to non-covalently modified CNTs we compare ALD deposition onto acid treated CNTs and polypyrolle wrapped CNTs. ZnO coverage and uniformity is evaluated via gravimetric analysis and scanning electron microsopy. X-ray powder diffraction and transmission electron microscopy are used to investigate changes to the deposited ZnO crystal structure with varying nanocarbon surface chemistry.

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## Preparation of carbon fibers from polyacrylonitrile (PAN)/ carbon nanotubes (CNT)composite by electrospinning process

Eugene Shulga, Liis Laumets, Kati Kongi, Sven Lange, Ilmar Kink

*University of Tartu Institute of Physics, Estonia (jevgenis@fi.tartu.ee)*

Polyacrylonitrile (PAN) is currently the predominant precursor for carbon fibers [1-3]. Carbon nanotubes (CNT) can be well dispersed in PAN resulting in PAN/CNT composite fiber modulus consistent with theoretical predictions [4,5] or higher [6].

Long and thin (50-250 micrometers in length, 10-20 in diameter) Multiwalled carbon nanotube/Polyacrylonitrile (MWNT/PAN) composite nanofibers were prepared by electrospinning from PAN/DMSO solution system, with and without addition of surfactants (Green tea extract and Polyethylene glycol). The beads formation was observed with increasing of MWNT content. Composite nanofibers was heat treated at different temperatures 700 to 1500 C. Resulted fibers was characterised by Scanning Electron Microscopy and Raman spectroscopy. Influence of PAN and MWNT concentration on fibers mechanical properties and morphology will be discussed.

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## Multi-wall carbon nanotubes – polyethylene composites produced by using pre-adsorbed catalyst on the surface of carbon nanotubes

Mariya Shuvaeva[1,2], Nina Semikolenova[1], Vladimir Kuznetsov [1,2], Sergey Moseenkov[1], Arcadii Ischenko[1], Mikhail Matsko[1], Nina Rudina[1], Vladimir Zakharov[1]

*1 Boreskov Institute of Catalysis SB RAN, Russia (mas@catalysis.ru)*
*2 Novosibirsk State University, Russia*

Multi-wall carbon nanotubes (MWNTs) have been widely regarded as an attractive candidate for the use as fillers in the composite materials due to their extraordinary mechanical and electrical properties. Incorporation of carbon nanotubes into the polymer matrix results in significant improvement of polymer properties – mechanical strength, electrical conductivity, fracture toughness, electromagnetic shielding properties. In the present work we have investigated the influence of the MWNTs pre-treatment conditions on the catalytically active component adsorption and uniformity of MWNT distribution in the polyethylene matrix (PE) for the preparation of MWNT/PE composites by in situ polymerization method. MWNTs were synthesized by CVD ethylene decomposition over bimetallic Fe-Co catalysts at 680°C. The study was carried out using MWNTs with an average diameter of 7.8 nm. MWNTs both as synthesized and after oxidation pre-treatment were used. For investigation of the structure of MWNT/PE composites, TEM, SEM, DSC were used. We have found that the controlled oxidation treatment of MWNTs increases the adsorbing ability of TIBA-TiCl4 polymerization catalyst system with the much higher catalytic activity, producing the required amount of PE in the shorter time. It provides homogeneous distribution of catalyst particles along the nanotubes and finally homogeneous coverage of nanotubes surface with PE. For the first time we have observed the Ti-containing catalyst species of the size 2-3 nm on the MWNT surface, stabilized in polymer matrix. The results suggest promising directions for composite MWNT/PE preparation via the catalyst distribution on the surface of MWNTs followed by polymerization of ethylene. MWNT/PE composites with high concentration of homogeneously distributed nanotubes are perspective as polymer carbon nanotubes conductive master batches.

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## Light emitter based on purified semiconducting single-walled carbon nanotube films

Yuji Suzuki, Hideyuki Maki*

*Department of Applied Physics and Physico-Informatics, Faculty of Science and Technology, Keio University, Japan (*maki@appi.keio.ac.jp)*

An electrically-driven carbon nanotube (CNT) emitter has attracted attention as a small-sized electroluminescence (EL) emitter in photonic or optoelectronic integrated circuits owing to its small footprint and emission at telecom wavelength. The EL emitter with an individual CNT has insufficient emission intensity to use this emitter for optical application. In addition, due to its insufficient intensity, the relaxation time of EL has not been reported so far, although the photoluminescence(PL) lifetime has been already reported (from tens to hundred ps)[1]. So, we fabricated CNT-film EL emitters [2] using purified semiconducting CNTs to evaluate the relaxation time of EL. The CNTs have (7,6) chirality 50% of all tubes. Dispersions of CNTs drop on $SiO_2$/Si substrate and CNT film is formed. Two Pd electrodes are evaporated on the CNT film. We measured emission spectra under DC bias and obtained bright emission from this device compared with an individual s-CNT. We observed the spectra which involve few peaks related to chiralities. The polarization dependence of the emission is in good agreement with $\cos^2\theta$. Previously, it has been reported that the EL emission from an individual s-CNT has polarization dependence. Therefore, this result indicates that the observed emission is due to the electron-hole recombination. We evaluated the response speed of this device by Time-resolved measurement. We applied 600-ps-width pulsed bias voltage. The measured emission also has about 600-ps width. This indicates that the response speed of EL of s-CNT is very fast. This is the first demonstration of high-speed EL from s-CNTs. This work was partially supported by Grants-in-Aid for the Encouragement of Young Scientists from the MEXT and by the A-step from JST.

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**P195**

## Gate voltage dependent transport mechanism in carbon nanotube thin film transistors

Marina Y. Timmermans[1], Yutaka Ohno[2], Dong-ming Sun[2], Kestutis Grigoras[3], Albert Nasibulin[1], Takashi Mizutani[2] and Esko I. Kauppinen[1]

*1 Nanomaterials Group, Department of Applied Physics, Aalto University School of Science,*
*P.O. Box 15100, FI-00076 AALTO Finland*
*2 Quantum Nano-Device Group, Department of Quantum Engineering, Nagoya University, Furo-cho,*
*Chikusa-ku, Nagoya 464-8603, Japan*
*3 Microfabrication Group, Department of Micro and Nanosciences, Aalto University School of Science,*
*P.O. Box 13500, FI-02015, Finland*

Recent studies have focused on integrating networks of CNTs as an active material for thin film transistors, with very promising outcomes for future flexible large-area electronics. The understanding of operation principles and physics of CNT TFTs is indispensable in order to obtain desired functionality and further device improvements. Here we report temperature dependent behavior of CNT networks with respect to the gate voltage in the range between 77 K and 430 K. CNTs are synthesized by the floating catalyst (aerosol) CVD method and deposited directly onto the substrate in the form of a random network. The temperature dependence in the range of gate voltages which correspond to the on-state of the device is found to follow the behavior expected for variable range hopping. Closer to the off-state of the device, the number of the conducting paths available for transport is decreased. Therefore, thermionic emission transport mechanism over the barriers governs the current passage at the tube-to-tube junctions, the effect of which becomes more pronounced at sub-threshold voltage, which is indicated by strong temperature dependence.

## Electrical and optical properties of SWNTs-based composites

**P196**

Fernando Torres-Canas[1,2], Manuel Perez[2], Christophe Blanc[2], Camilo Zamora-Ledezma[1,3], Pedro Silva[1], Eric Anglaret[2]

*1 Laboratorio Física de la Materia Condensada, Centro de Física, IVIC, Altos de Pipe, AP 21827, 1204 Caracas, Venezuela*
*2 Laboratoire Charles Coulomb, Univ. Montpellier 2 and CNRS, 34095 Montpellier, France*
*3 Centro de Investigaciones de Astronomía Francisco J. Duarte, 5101 Mérida, Venezuela*

Most of the current SWNTs production today is used to process bulk composite materials and thin films for exploiting their intrinsic properties at the macroscopic scale. However, the poor control of their distribution and orientation lead to unorganized architectures and limited properties [1]. Besides mechanical properties, electrical and optical properties are the most widely studied. However, various kinds of photoluminescent (PL) nanotube-based composites can be prepared only when the tubes are well dispersed as individuals in the composites [2-4]. Indeed, contacts between nanotubes quench the PL intensity. On the other hand, contacts are required to obtain some electrically conductive materials.

In this work we propose and compare different strategies to sort and control the number and nature of contacts in order to control both the PL and electrical (conductivity) properties of SWNTs-based composites [2-4]. These approaches include the control of the quantity of SWNTs, the quantity and nature of the dispersing agents used to disperse them, and their orientational order. We especially work on thin films and thin layers of polymer composites, as well as inorganic gels. Different optical spectroscopy techniques, i.e. absorption, Raman and photoluminescence spectroscopies, are used to study the dispersion and orientation of the nanotubes [2-4]. Electrical measurements are achieved using two and four point probes.

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## Effect of the structural quality of carbon nanotubes on the antidegradation and electrical conductivity of carbon nanotubes/rubber composites

**P197**

Koji Tsuchiya, Tomoya Nagaoka, Yoshiyuki Takahashi, Hirofumi Yajima*

*Faculty of Science, Tokyo University of Science, Japan (*yajima@rs.kagu.tus.ac.jp)*

Carbon nanotubes (CNTs) have been expected to be effective as filler materials in polymer matrices because of their outstanding electrical/mechanical properties and peculiar structures. However, it is difficult for CNTs to be dispersed in polymer matrices because they form highly entangled agglomerates (bundles) owing to strong *van der Waals* interaction. In our previous study [1], we found that the rotation-revolution mixing technique can achieve a homogeneous dispersion of CNTs in a rubber matrix without a serious breakage of the CNTs, which leads to an improvement in electrical properties and a considerable decrease in percolation threshold of the composite. The present study demonstrated the thermal and mechanical degradation behavior and electrical properties of isoprene rubber (IR) composites containing multi-walled carbon nanotubes (MWNTs) prepared using the rotation-revolution mixing technique. The thermal and mechanical degradation of the rubber were suppressed by the addition of MWNTs, and the antidegradation degree was enhanced with an increase in defects of the MWNTs. The disordered structure of MWNTs possesses a high radical scavenging ability, because there exist high charge densities around the defects involved in a high affinity for radicals (polymer radicals or peroxy radials) generated by the heat and mechanical treatments. The electrical percolation thresholds of the MWNT/IR composites also depended significantly on the structural quality of the MWNTs and exhibited a minimum value of 0.5 phr MWNT loading at a D/G ratio of approximately 0.5, where D and G refer to the amounts of disordered and crystalline graphite in the MWNTs, respectively. The findings obtained in this study provide us with a useful index for preparing a promising rubber composite material with outstanding electrical behavior and high antidegradation ability.

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# The potential sunlight harvesting efficiency of single walled carbon nanotube solar cells

Daniel Tune, Joseph Shapter

*Centre for Nanoscale Science and Technology, The Flinders University of South Australia, Australia*
*(daniel.tune@flinders.edu.au)*

Recently, laboratory-scale solar cells have been demonstrated which show clear evidence of the successful exploitation of semiconducting single walled carbon nanotubes (SWNTs) as primary absorbers of sunlight energy. The unique properties of SWNTs may allow for high efficiency solar cell devices however little progress has been made to quantify this. Also, all SWNT species have their own peculiar absorption features covering different regions of the spectrum. So, which nanotube species are most appropriate for solar cell applications? How much of the power in the terrestrial solar spectrum could this material harvest? Shockley and Queisser used detailed balance calculations to derive a fundamental limit to the power conversion efficiency of a single junction solar cell. However these calculations are based on several assumptions, at least one of which does not apply in the case of SWNTs. One assumption is that all photons with energy greater than the semiconductor bandgap are absorbed. This requires a smooth continuum of states above and below the gap, as is the case with bulk semiconductors such as silicon but, due to the one dimensional confinement of electron and phonon states in a SWNT, it's density of states contains discrete van Hove features, which render the assumption invalid. Also, it is assumed that the absorption of one photon produces only one exciton. Whilst this is true for most semiconductors, there is evidence to suggest that SWNTs may exhibit multiple exciton generation from single photons.

An in-depth analysis of the potential of SWNTs to harvest sunlight will be presented, using the best currently available data to simulate the absorption properties of different semiconducting SWNT species and thus calculating a species-dependent potential sunlight harvesting efficiency. Then, the same model is used to simulate relevant multijunction scenarios including a high efficiency device absorbing in the visible and a similar device with an absorption profile tailored to harvest primarily in the infrared, whilst minimising absorption in the visible.

P199

# Modifying native nanocellulose aerogels with carbon nanotubes for mechanoresponsive conductivity and pressure sensing

Miao Wang[1], Ilya V. Anoshkin[1], Albert G. Nasibulin[1], Juuso T. Korhonen[1], Jani Seitsonen[1], Jaakko Pere[2], Esko I. Kauppinen[1], Robin H.A. Ras[1,*], and Olli Ikkala[1,*]

*1 Department of Applied Physics, Aalto University School of Science, Finland*
*(*olli.ikkala@aalto.fi and robin.ras@aalto.fi)*
*2 VTT Technical Research Centre of Finland, Finland*

Here we combine the best aspects of NFC and CNT aerogels in their hybrids in a synergistic manner, both forming separately aerogels. In more detail, we foresee that the mechanically excellent NFC nanofibers, as available from widely abundant sustainable plant-based sources and facile processes could be templates for functionalization by small weight fractions of CNT, thus combining the bulk availability of NFC and advanced electrical properties of CNT. Incorporating both NFC and CNT within the aerogels allows to combine the attractive features of both components: the wide availability, easy processing, and sustainability of the NFC majority component and the advanced electrical properties of the CNT minority component. We have described the first such hybrid aerogels, denoted here as hybrid nanofiber/nanotube aerogels, because both components have the tendency to form aerogels separately. The aerogels have been freeze-dried from aqueous hybrid gels. The hybrid nanofiber/nanotube aerogels are ductile, with reduced brittleness, as promoted by the particular native structure of NFC, which is retained by directly cleaving it from plant cell walls without dissolution steps. The aerogel morphology can be tuned by the freeze-drying process, as slow cooling by immersion of a hydrogel sample into liquid nitrogen leads to nanofiber aggregation into sheets, whereas quick cooling in liquid propane suppresses the sheet formation and allows fibrils in thin samples. We foresee that combining nanocellulosics and carbon nanotubes allows a wide variety of responsive electroactivity, pressure sensing, and functional materials, combining the best aspects of both nanofiber components even towards larger scale applications. [1]

[1] M. Wang *et al.*, Adv. Mater. (2013) ASAP

P200

## Simple and scalable dispersion of semiconducting arc-discharged carbon nanotubes by dithiafulvalene/thiophene copolymers for thin film transistors

Huiliang Wang[1], Jianguo Wei[2], Zhenan Bao[2]

*1 Department of Materials Science and Engineering, Stanford University, US (whl0903@stanford.edu)*
*2 Department of Chemical Engineering, Stanford University, US*

Semiconducting single-walled carbon nanotubes (SWNTs), with high charge carrier mobility and solution processibility, hold a great promise for high-performance low-cost thin film transistor applications. However, separating semiconducting SWNTs from metallic ones in large quantities still remains a challenge. It has been reported that conjugated polymers such as polyfluorene or polythiophene can sort small diameter semiconducting SWNTs. Large-diameter SWNTs are longer, less prone to defects and easier to align than small diameter SWNTs and hence are potentially better for electronic applications. In this work, we have developed a simple and scalable method to disperse and sort large-diameter arc-discharged SWNTs using dithiafulvalene/thiophene copolymers. We found that by altering the number of thiophene repeating units in the polymer backbone, the polymer rigidity and wrapping conformation can be tuned, resulting in a selective dispersion of semiconducting SWNTs. From Small Angle X-ray Scattering (SAXS) measurements and Molecular Dynamics (MD) simulations, we found that the amounts of SWNTs dispersed are proportional to the available contacts sites from the polymers and the increased polymers flexibility leads to improved selectivity. Thin film transistors showed on/off ratios greater than 104 from polymer sorted SWNTs, confirming preferential sorting of semiconducting SWNTs. The sorted, concentrated and stable large-diameter semiconducting SWNT solutions have great potential for applications in TFTs, sensors and semiconductor active layer in solar cells.

[1] H. Wang et al., ACS Nano, 26, pg. 2659-2668, 2013

P201

## Efficient fabrication of carbon nanotube micro tip arrays by tailoring cross-stacked carbon nanotube sheets

Yang Wei, Peng Liu, Feng Zhu, Kaili Jiang, Qunqing Li, and Shoushan Fan

*Department of Physics and Tsinghua-Foxconn Nanotechnology Research Center, Tsinghua University, Beijing 100084, P. R. China (WeiYang@tsinghua.edu.cn)*

Carbon nanotube (CNT) micro tip arrays with hairpin structures on patterned silicon wafers were efficiently fabricated by tailoring the cross-stacked CNT sheet with laser. A blade-like structure was formed at the laser-cut edges of the CNT sheet. CNT field emitters, pulled out from the end of the hairpin by an adhesive tape, can provide 150 µA intrinsic emission currents with low beam noise. The nice field emission is ascribed to the Joule-heating-induced desorption of the emitter surface by the hairpin structure, the high temperature annealing effect, and the surface morphology. The CNT emitters with hairpin structures will greatly promote the applications of CNTs in vacuum electronic devices and hold the promises to be used as the hot tips for thermochemical nanolithography. More CNT-based structures and devices can be fabricated on a large scale by this versatile method.

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**P202**

# $Fe_3O_4$ sheath on aligned CNTs synthesized by one-step sputtering as an anode material for LIBs

Yang Wu, Yang Wei, Jiaping Wang, Kaili Jiang and Shoushan Fan

*Department of Physics, Tsinghua-Foxconn Nanotech Research Ctr., Tsinghua University, Beijing, China*

Transition metal oxides have recently been identified as a promising candidate for the anode material of lithium ion batteries (LIBs). The reversible lithium storage in transition metal oxides (e.g. $Fe_3O_4$, $Co_3O_4$, $MnO_2$, etc.) takes place via a conversion mechanism. In contrast to prevalent synthesis that requires delicate wet chemistry methods, we employed ordered carbon nanotube (CNT) films to template the growth of nano-sized $Fe_3O_4$ via a sputtering approach. [1] Such CNT films were directly drawn from super-aligned CNT arrays grown on 8-inch silicon wafers. This one-step synthesis was carried out in a lab-designed apparatus that integrated both film drawing technique and magnetron sputtering. High purity Fe metal plates were used as targets. The CNT film was coated with sputtered Fe while it was drawn through the two opposite sputtering guns. The Fe deposition was spontaneous converted to a $Fe_3O_4$ sheath presumably by the $O_2$ impurity in the sputtering chamber. The complete oxidation was also confirmed with XRD and XPS. The size of $Fe_3O_4$ coating was analyzed and it turned out that it was easily controlled by the speed of CNT film drawing.

The electrochemical characterization suggested that the specific capacity of CNT-$Fe_3O_4$ composite anodes was dependent on the size of the $Fe_3O_4$ sheath. As the average size of $Fe_3O_4$ was regulated $Fe_3O_4$ ca. 7 nm (corresponding to 60 wt% of $Fe_3O_4$), the optimal capacity of CNT-$Fe_3O_4$ anodes was achieved (1200 mAh $g^{-1}$ with a 90% capacity retention after 100 cycles, or 800 mAh $g^{-1}$ based on the total mass). The specific capacity of over 1100 mAhg-1 at 1C rate was also remarkable. The excellent electrochemical performance could be attributed to CNTs that served as both scaffolds and conductors. Finally, the contribution of CNT in the same voltage window (0.1–3 V) and plausible originations to the extra specific capacity will be discussed.

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**P203**

# Silicon-coated carbon nanofiber mat for anode of lithium ion battery

Fei Yao[1,2], Bing Li[1], Kangpyo So[1], Jian Chang[1], Vu Quoc An[1], Didier Pribat[1],
Costel Sorin Cojocaru[2], Hongyan Yue[1], Sishen Xie[1] and Young Hee Lee[1,*]

*1 Institute of Basic Science, Center for Integrated Nanostructure Physics, Department of Energy Science,*
*BK21 Physics Division, Sungkyunkwan University, Suwon 440-746, Republic of Korea*
*2 LPICM CNRS, École polytechnique, Palaiseau 91120, France*

Si-coated carbon nanofiber (Si/CNF) mat was fabricated by electrochemical method for the anode of lithium ion battery (LIB). The free-standing CNF mat was first fabricated by electrospinning of polyamic acid followed by stabilization and carbonization, and then the as-prepared CNF mat was used for Si electrodeposition through cyclic voltametry (CV).[1] Spaghetti or granule-like Si was obtained by varying the deposition conditions. This Si/CNF mat was directly used as an anode material, which involves neither binders nor additional metal substrate. The best performance was achieved in spaghetti-like Si due to its highly porous nature which can accomodate the volume expansion and large surface area which benifits efficient charge transfer of ions at the electrode/electrolyte interface. The optimized Si/CNF mat anode after annealing at 1000 °C delivered initially a capacity of 1545 mAh/g and 1354 mAh/g after 50 cycles at 0.1 C rate with an average fading rate of 0.34 % per cycle, improving the capacity of pure CNF mat (280 mAh/g at the 50th cycle. Our X-ray photoemission spectroscopy and electrochemical analysis revealed that the formation of Si-C bond through high temperature annealing can enhance the adhesion between silicon and carbon at the interface which benefited the cyclic performance of the anode material ultimately.

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P204

## Study on stability of chemically-doped n-type carbon nanotube thin film transistors

Tomohiro Yasunishi, Shigeru Kishimoto, and Yutaka Ohno

*Dependent of Quantum Engineering, Nagoya University, Japan*
*(yohno@nuee.nagoya-u.ac.jp)*

The networks of single-walled carbon nanotubes (CNTs) have attracted much attention as an active layer of thin-film transistors (TFTs). Techniques for p/n control have been proposed by utilizing chemical doping; however, the mobility of the n-type devices reported so far are still much lower than those expected for CNT-TFTs, ranging from 1 to 10 cm$^2$/Vs. In this study, we realized n-type CNT-TFTs with high mobility as 70 cm$^2$/Vs (on/off: ~10$^5$) by the transfer process [1] and solution-based chemical doping technique with PEI. The stability of the device will also be discussed.

Acknowledgments: This work was partially supported by '08 NEDO Grant, NICT, ALCA/JST, and Grant-in-Aid for Scientific Research of JSPS.

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P205

## A dispersion method for improving the electrical conductivity of long SWCNT/rubber composites

Howon Yoon[1], Motoi Yamashita[1], Seisuke Ata[1], Motoo Yumura[1,2], Kenji Hata[1,2,*]

*1 Technology Research Association for Single Wall Carbon Nanotubes (TASC), Japan*
*2 National Institute of Advanced Industrial Science and Technology (AIST), Japan (*kenji-hata@aist.go.jp)*

The superior mechanical, electrical, and thermal properties and their high aspect ratio make CNTs an excellent filler material for composites. Although the potential of CNTs is well-recognized, it is not easy to disperse them while retaining the intrinsic properties of the pristine CNTs. This is because CNTs are usually supplied in the form of heavily entangled bundles. Therefore, ever-increasing interest in applying CNTs in many different fields has led to continued efforts to develop dispersion technique. In order to select a proper method for CNT dispersion, various types of dispersion techniques should be evaluated and compared. However, most of studies have been focused on the optimum dispersion condition employing only one or two types of methods. Although some reviews compared and listed commonly used dispersion methods, it is still not established that which dispersion methods is appropriated for which kinds of CNTs. When determining a suitable dispersion method, the feature of employed CNTs, such as the length, wall number, and pristine structure of CNTs should be taken into account.

Here, we focused primarily on the use of many types of dispersion methods, as a new approach for exploring the appropriated dispersion method of aligned long SWCNTs (length from 500 to 1,000 μm). We have compared three general classes of dispersion mechanisms, such as turbulent flow, cavitation, and mechanical force, which encompassed 10 different dispersion methods. From this work, we have found that the mechanism of turbulent flow, as represented by nanomizer and high pressure jet-mill methods, showed unique and superior dispersion ability for long SWCNTs that was advantageous to make highly conductive rubber and polymer composites. The results were interpreted that the biaxial shearing forces caused an exfoliation effect to homogeneously disperse the long SWCNTs while suppressing damage.

## P206

## CNT networking in MEHPPV-CNT composite-based organic light emitting diodes

SeGi Yu[1], Beomhee Won[2], So-Yeon Jun[1]

*1 Dept. Physics, Hankuk University of Foreign Studies, Yongin 449-791, Korea (ROK) (segiyu@hufs.ac.kr)*
*2 Dept. Physics, Syungkyunkwan University, Suwon 440-746, Korea (ROK)*

Organic light emitting devices (OLEDs) have been widely researched partly due to the recent commercialization of OLED TVs in 2013. Together with small molecular weight organic materials, large molecular weight organic materials, i.e., polymers, are focused for roll-to-roll process. Numerous methods are tried to utilize the recent advances in low-dimensional nanostructures [1]. Carbon nanotubes (CNTs) have been used in organic-based devices, and the performances of many CNT-organic composite devices were enhanced. However, there were few remarks on the level of current or the current of the CNT-incorporated organic devices were even increased, which indicates poor power efficiency. It is crucial to control the properties of CNTs for this purpose. CNT-incorporated OLEDs, which were operated in alternating current (AC) driving mode, were consisted of four layers, i.e., top metal electrode, a cyanoethyl pullulan (CRS)-based dielectric layer, poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEHPPV)-based emitting layer, where CNTs were mixed, and a bottom indium tin oxide (ITO) electrode from the bottom on the glass substrate. The length of CNTs was shortened by the mechanical method [2]. CNTs in MEHPPV-CNT composite were varied from 0.006 to 0.15wt%. CNT-incorporated OLEDs were brighter than the reference sample, and the turn-on voltages of the devices roughly reduced 50%. One of main reason for this reduction in the current is thought to be the micro-capacitor effects caused by CNT networking in MEHPPV [3]. The existence of conducting nature of CNTs in the organic materials yields to high values in the capacitance, which might be explained by the measurement of impedances of the devices. The network of CNTs would lead to the percolation phenomena, which is carefully controlled in order for low current operation, i.e., high impedance. The detailed explanation of high bright and low current of CNT-incorporated OLDEs will be explained in the presentation.

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## P207

## Carbon nanotube/sulfur composite cathode for Li-S battery

Qiang Zhang, Jia-Qi Huang, Wei-Zhong Qian, Fei Wei

*Beijing Key Laboratory of Green Chemical Reaction Engineering and Technology, Department of Chemical Engineering, Tsinghua University, Beijing 100084, China (zhang-qiang@mails.tsinghua.edu.cn)*

Owing to the multiple-electron-transfer electrochemistry of light element-sulfur, the Li-S battery is with a high theoretical capacity and energy density of 1672 mAh $g^{-1}$ and 2600 W h $kg^{-1}$, respectively. However, the insulating nature of S and $Li_2S_x$ (x=1 or 2), the low utilization of active phase, and the fast capacity degradation hinder the practical application of S cathode material. Novel electrolyte and advanced cathode materials are urgently anticipated to overcome these technical obstacles. With the rapid progresses on industrial mass production and commercialization of carbon nanotubes (CNTs), validating the concept of CNTs as the framework for advanced Li-S batteries is highly attractive. A composite cathode containing CNT@S coaxial nanocables is available. The Li ion storage performance of NCT@S is found to be greatly improved. To further improve the Li ion storage performance, polyethylene glycol (PEG) was used as a barrier to enhance the discharge capacity, improve the Coulombic efficiency, and inhibit the shuttle effect as well. The reason we selected PEG as the barrier was based on the fact that PEG could trap the highly polar polysulfide species by the interaction between the ether groups and polysulfides. The PEG modified SWCNT@S cathode afforded a reversible capacity of 1005, 639, and 413 mAh g-1 for the 1st discharging at 0.5 C, 100th discharging at 1.0 C, and discharging at 10.0 C, respectively. The cycling stability of discharging capacities should be improved by excellent entrapment of S-containing compounds for Li storage during charge-discharge process. Therefore, CNTs are promising scaffolds for Li-S battery with much improved property, and the as-obtained composite which contains CNTs based coaxial nanocables is a novel structural platform for the design of advanced functional materials with robust electron and thermal conductive pathway for energy storage, catalysts, and other applications. New insights on the multiple-electron-transfer electrochemistry based on related nanocarbon/sulfur cathode were also provided to shed light on extraordinary Li storage performance.

P208

# Photo-enhanced, titanium dioxide nanotube and carbon nanotube modified air-breathing biofuel cell

Adrianna Zloczewska[1], Robert Lynch[2], Marcin Opallo[1], Martin Jönsson-Niedziolka[1]

*1 Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland (azloczewska@ichf.edu.pl)*
*2 Department of Physics, and Materials and Surface Science Institute (MSSI),*
*University of Limerick, Ireland*

Biofuel cells (BFCs) are expected to be future micropower sources [1]. Recently we obtained a very efficient air-breathing biocathode for dioxygen reduction which can be used in BFCs [2]. It was composed of single-walled carbon nanotubes (CNTs) functionalized with 1-pyrenesulfonic acid [3] co-immobilised with the enzyme bilirubin oxidase in a silicate matrix. On the other hand there is an interest in obtaining a source of renewable energy harvested directly from the sun. The most commonly used material for these photoelectrochemical cells is nanoparticulate titania. Recently $TiO_2$ nanotubes appeared to be also interesting because of the ability to form photoanodes with increased: effective surface area and conductivity.

We present different approaches for the construction of a photo-enhanced BFC containing the biocathode modified with CNTs and the photoanode made of $TiO_2$ nanotubes. Both of them uses the fact that the power output of such a cell is dependent on the incident light intensity and that their voltage might be greater than the voltage of the biofuel cells without the photoanode. First approach is based on the idea presented by Moore *et al.* [4] - a sensitized photoanode where the dye is regenerated by the β-nicotinamide adenine dinucleotide. In the second approach we use the non-sensitized anode and the enzyme catalase .

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P209

# Irradiation-induced surface changes of CNT-containing polymer-based nanocomposites

Anne-Kathrin Barthel, Volker Wachtendorf, Heinz Sturm, Asmus Meyer-Plath*

*BAM – Federal Institute for Materials Research and Testing, Berlin, Germany*
*(*asmus.meyer-plath@bam.de)*

The processing of carbon nanotubes (CNTs) and polymers into nanocomposites has been widely studied for the development of new high-performance materials. In many cases improved material properties have been found, including increased mechanical stability, electrical conductivity and reduced heat release in case of fire. It is expected that manufacturing and use of CNT-containing polymer products will steadily increase. For reasons of environmental protection and consumer safety, it is therefore necessary to examine the entire life cycle of these materials. The present study focuses on the emission propensity for nanoscale components during use and at the end of the product life. The present work used accelerated artificial weathering to examine weathering-related degradation mechanisms of CNT-containing polymers and to assess whether and under what conditions degradation might give rise to the release of individual or agglomerated nanotubes and nanoscale composited fragments. The photodegradation of nanocomposites based on polyamide, polycarbonate and polyethylene that contained multi-walled CNTs of type "Baytubes C150P" was studied under three different types of exposures: dry, alternating dry and wet, as well as spectrally-resolved irradiation. Resulting surface changes were evaluated with complementary chemical and microscopic characterization techniques. For sufficiently high radiation dose, substantial degradation of the polymer matrix was observed for a part of the studied polymers. It resulted in an uncovered CNT network at the sample surface. Exposed to environmental processes or used under abrasive conditions, loosely-bound CNT networks may by individualized into aerosols or liquid dispersions. Also first indications of a photooxidation of uncovered CNT networks were found. Weathered CNT-containing polymer nanocomposites may therefore become a source of CNTs that are chemically and morphologically different from the originally incorporated CNTs. By investigation of potential exposure mechanisms of CNTs in polymer composites, the present work contributes to the risk assessment of CNT-containing products.

# Thursday

**K4**

# Advanced optical coupling in carbon-based nanosystems

Stephanie Reich

*Fachbereich Physik, Freie Universität Berlin, Germany (reich@physik.fu-berlin.de)*

Coupling two nanosized systems through their optical excitations yields fascinating effects. For example, elastic and inelastic scattering of light as well as light emission increase by orders of magnitude. The coupling may also result in a resonant exchange of optical excitations between two nanoscale partners, induce charge transfer in excited states, and so forth. In our presentation we will review the recent research in the field of optically coupled nanosystems. Carbon nanotubes and graphene are ideal test beds to study nanoscale optical phenomena. They can be used to design and implement model systems for plasmon-enhanced light scattering and resonant energy transfer processes. Plasmon-enhanced Raman scattering will be induced in graphene and carbon nanotubes by dimers of gold nanoparticles. The cavity between the particles is a place of highly enhanced electromagnetic fields, which is sensed by Raman scattering. As an exemplary system for excitation energy transfer we demonstrate functionalized carbon nanotubes with attached dye molecules. Light absorbed by the dye will be transferred and emitted by the tube. The wide choice of optical excitation energies in nanotubes and molecules allow tuning resonances and level alignment. We will discuss future ideas for using carbon-based nanostructures in optical coupling and technology.

# Carbon based high performance nanoelectronic and optoelectronic devices and circuits

Lian-Mao Peng

*Department of Electronics, Peking University, Beijing 100871, China (lmpeng@pku.edu.cn)*

Ballistic n-type carbon nanotube (CNT) based field-effect transistors (FETs) have been fabricated by contacting semiconducting single wall CNTs (SWCNTs) using Sc or Y [1,2]. Together with the demonstrated ballistic p-type CNT FETs using Pd contacts [3], this closes the gap for doping free fabrication of CNT based ballistic CMOS [4], high performance optoelectronic devices [5-6], and integrated circuits [7,8]. The feasibility of this doping free CMOS technology has been demonstrated by fabricating CMOS circuits, including a full adder circuit, on a $SiO_2$/Si substrate, demonstrating perfect symmetric device characteristics for the n-type and p-type CNT FETs based on the same single walled CNT. This CNT based CMOS technology only requires the patterning of arrays of parallel semiconducting CNTs with moderately narrow diameter range, e.g. 1.6-2.4 nm, instead of the more stringent chirality control on the CNT. This may lead to the integration of CNT based CMOS devices or entire carbon based circuit with increasing complexity and possibly find its way into logic and optoelectronic circuits. The development of high performance CMOS circuits also requires high quality gate dielectric with high dielectric constant. Although various high-κ dielectrics have been demonstrated to be technically compatible with carbon-based devices, it is proved to be very difficult to grow uniform thin high-κ film directly on the surface of CNTs or graphene via a general method, for example, atomic layer deposition (ALD). Utilizing the excellent wetting behavior of yttrium on $sp^2$ carbon framework [2], ultrathin (about few nm) and uniform $Y_2O_3$ layers have been directly grown on the surfaces of CNT and graphene without using noncovalent functionalization layers or introducing large structural distortion and damage. A top-gate CNT FET adopting 6nm $Y_2O_3$ layer as its top-gate dielectric shows excellent device characteristics, including an ideal subthreshold swing of 60 mV/decade (up to the theoretical limit of an ideal FET at room temperature). The high electrical quality $Y_2O_3$ dielectric layer has also been integrated into a graphene FET as its top-gate dielectric with a capacitance of up to 1200 nF/cm$^2$, showing an improvement on the gate efficiency and on state transconductance of over 100 times when compared with that of its back-gate counterpart [9-10].

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C21

# Carbon nanotube quantum dots as highly sensitive THz spectrometers

Mohamed Rinzan[1], Gregory Jenkins[2], H. Dennis Drew[2], Serhii E. Shafraniuk[3], Paola Barbara[1]

*1 Department of Physics, Georgetown University, Washington, DC 20057*
*(barbara@physics.georgetown.edu)*
*2 Department of Physics, University of Maryland, College Park, MD 20742*
*3 Department of Physics and Astronomy, Northwestern University, Evanston, IL 60208*

The THz region of the electromagnetic spectrum, comprising the frequency range between microwaves and infrared radiation, from 100 GHz to about 10 THz, holds great scientific interest for applications in several fields, from medical imaging to security screening. However, sources and detectors in this frequency range are scarce, thereby hindering the development of THz technology. Recently, advances in materials and experimental techniques have revealed new promising avenues for THz devices.

Here, we show that carbon nanotube quantum dots are especially suitable for practical, highly sensitive detectors with spectral resolution. Studies of THz response from quantum dots have been so far elusive, due to the difficulty to couple THz radiation to the dots. Our on-chip antenna design dramatically increases the coupling of THz radiation to the dot, yielding extremely sensitive, broad-band, THz quantum detectors. Their response is due to photon-assisted single-electron tunneling and it is substantially enhanced by a novel radiation-induced nonequilibrium cooling of the electrons, causing a sharp height increase of the Coulomb blockade peaks [1]. The increased response due to THz cooling allows operating temperatures easily reached with close-cycle cryostats.

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C22

# Highly Conductive CNT Thin Films for Organic Solar Cells

Aminy Ostfeld, Amelie Catheline, Ana Claudia Arias*

*University of California, Berkeley, USA (*acarias@eecs.berkeley.edu)*

Current transparent electrodes in electronic devices are made of indium tin oxide (ITO). Although it has the best electrical properties required for electronic applications, several drawbacks, such as its cost, its brittleness, have to be overcome to comply with the next generation of organic electronic devices. In this context, carbon nanotubes (CNTs) have been under investigation for several years, due to their excellent electrical and mechanical properties, to replace the ITO electrodes.

Using high quality CNT inks, transparent and highly conductive films have been made to prepare solar cells. CNT inks have been prepared by liquid ammonia reduction in order to fully individualized the CNTs without damaging them[1], as it is commonly done by usual dispersion techniques, such as functionalization, ultrasonication and/or ultracentrifugation. This method allows to keep long CNTs in solution with excellent electrical properties.

Our work is focused on organic solar cells on glass and on flexible substrates to study the CNT properties and to compare their efficiency to ITO. As the CNT transparent electrodes reach the electrical properties of ITO, solar cells with similar efficiency have been obtained regardless the use of CNTs or ITO. In addition, the study of the different organic layers and interfaces between the substrate, the CNTs and the active layer provide a better understanding of the solar cell. Moreover, CNT networks can be used to prepare flexible electrodes, thus new solar cell designs can be envisioned.

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I9

## How to make graphene superconducting

Francesco Mauri

*CNRS, Universite Pierre et Marie Curie, France (francesco.mauri@impmc.jussieu.fr)*

Graphene represents a physical realization of many fundamental concepts and phenomena in solid state-physics, but in the long list of its remarkable properties a fundamental one is missing, i.e. superconductivity. Superconductivity has instead been observed in several graphite-intercalated compounds (GICs). Here we show how one can create and engineer a superconducting transition by adatoms' doping [1]. Density-functional theory calculations show that the occurrence of superconductivity depends on the adatoms' chosen, in close analogy to the case of GICs. However, most surprisingly, and contrary to the case of GICs, Li-covered graphene is found to be superconducting at much a higher temperature with respect to Ca-covered graphene.

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C23

## Non-covalent functionalization, dispersion, and processing of graphene

Micah J. Green

*Department of Chemical Engineering, Texas Tech University, USA (micah.green@ttu.edu)*

This work focuses on the central concept of producing graphene from graphite without covalently functionalizing the graphene basal plane; such graphene may be stabilized, dispersed, and processed for use in a range of high-performance materials. In particular, our group has shown that both polyvinylpyrrolidone as well as pyrene derivatives can naturally absorb to the graphene surface, create repulsive (steric and electrostatic) forces, and prevent aggregation [1,2]. This allows for graphene dispersion in a wide range of organic solvents and composite precursors without compromising graphene structure. Such dispersions are stable against aggregation even when subjected to extreme temperature changes, pH changes, and freeze drying. The graphene/stabilizer ratio obtained by this method is exceptionally high relative to conventional surfactants. The mechanism of stabilization by pyrene derivatives were investigated as a function of the type and number of functional groups, counterions, and the electronic interaction between the functional groups and the basal plane.

Polymer nanocomposites formed from these dispersions include graphene-loaded epoxy and graphene-loaded polyvinyl alcohol films and nanofibers; these composites consistently show enhanced modulus, strength, and electrical conductivity. We also demonstrate novel results in the area of graphene aerogel templating to achieve an ultralow percolation threshold. These dispersions also show promise for applications to organic solar cells, conductive films, and inkjet-printed electronic devices.

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C24

# Graphene: a chemical, optical, and topographic characterization with a confocal Raman-AFM-SNOM

Ute Schmidt and Olaf Hollricher

*WITec GmbH, Ulm, Germany (ute.schmidt@witec.de)*

The unique chemical, mechanical, electrical, and optical properties of graphene lead to its many application possibilities such as: single molecule detectors, high-strength low-weight new materials, design of new semiconductor devices, etc. An important goal however, is the detection of such angstrom-thick two dimensional sheets and precisely determine the number of layers forming the graphene flake. The aim of this contribution is to show how the confocal Raman AFM - SNOM can contribute to the characterization of such small materials and devices. In the past two decades, AFM (Atomic Force Microscopy) was one of the main techniques used to characterize the morphology of nano-materials spread on nanometer-flat substrates. From such images it is possible to gain information about the physical dimensions of the material, without additional information about their chemical composition, crystallinity or stress state. On the other hand, Raman spectroscopy is known to be used to unequivocally determine the chemical composition of a material. By combining the chemical sensitive Raman spectroscopy with high resolution confocal optical microscopy, the analyzed material volume can be reduced below 0.02 $\mu m^3$, thus leading to the ability to acquire Raman images with diffraction limited resolution from very flat surfaces [1, 2]. Furthermore, using SNOM (Scanning Near-field Optical Microscopy) technology, it will be shown for the first time how the transparency of different graphene sheets is changing as a function of the number of layers. The combination of confocal Raman microscopy with AFM and SNOM is a breakthrough in microscopy. Using such a combination, the high spatial and topographical resolution obtained with an AFM can be directly linked to the chemical information provided by confocal Raman spectroscopy and its transparency properties obtained with SNOM.

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C25

# Enhanced photoresponse in quasi-1D graphene nanostructures

Ya-Qiong Xu[1,2], Tu Hong[1], Yunhao Cao[1], Zeynab Jarrahi[2], and Alex H. Huffstutter[1]

*1 Department of Electrical Engineering and Computer Science*
*2 Department of Physics and Astronomy, Vanderbilt University, Nashville, TN, USA (yaqiong.xu@vanderbilt.edu)*

Graphene has become one of the most promising materials for future optoelectronics due to its ultrahigh charge-carrier mobility, high light transmission, and universal absorbance in the near-infrared (NIR) and visible spectral ranges. However, a zero band gap and ultrafast recombination of the photoexcited electron-hole pairs limit graphene's potential in photovoltaic generation [1, 2]. Recent studies have shown that hot carriers can enhance photovoltaic generation in graphene p-n junctions through the photothermoelectric effect (PTE) [3-5]. It is, therefore, desirable to synthesize graphene nanostructures with intrinsic PTE-induced photocurrent response.

Here we report a simple method to synthesize quasi-one dimensional (quasi-1D) twisted graphene ribbons that can produce strong photocurrent response with about two orders of magnitude enhancement. Scanning photocurrent and photoluminescence measurements reveal that the photocurrent response is primarily attributed to the PTE and that the NIR photo-induced emission may arise from thermal radiation. These results may offer a new way to fabricate graphene-based optoelectronics with enhanced photoresponse.

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## Transport, magnetism and spin relaxation phenomena in graphene-based materials

I10

Stephan Roche

*CIN2 (ICN-CSIC) and Universitat Autonoma de Barcelona,Catalan Institute of Nanotechnology, Campus UAB, Bellaterra, Spain (stephan.roche@icn.cat)*

The origin of spin relaxation in graphene-related (nanotube, two-dimmensional graphene) is currently a highly debated issue, with reported spin diffusion times about 1 nanosecond that is three orders of magnitude lower than expected, whereas the nature of relaxation fluctuates between Elliot-Yaffet and Dyakonov Perel mechanism with no consensus and puzzling experimental features. All these issues also point towards revisiting the way such fundamental length scales are usually extracted in experiments (Hanle Measurements, two-terminal magnetoresistance), prior to the development of spin manipulation and revolutionary carbon-based spin devices. This talk will discuss intriguing new phenomena concerning magnetic proximity effect induced on graphene related materials by the presence of magnetic insulators and spin relaxation induced by locally strong spin-orbit coupling realized by single ad-atom deposition (Ni, Co, Au, In...). We will explore the effect of spin-orbit interaction induced by dilute ad-atom deposition on graphene and show that it is possible to monitor the spin-dynamics of initially polarized states that propagate in graphene, and to estimate at a quantitative level the spin precession times and spin-relaxation times as a function of charge density. From a comparison to the momentum scattering time we infer an unprecedented type of relaxation mechanisms which differs from conventional Dyakonov-Perel and Elliot-Yafet mechanisms

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## Graphene systems with external perturbations

I11

Young-Woo Son

*Korea Institute for Advanced Study, Seoul, Korea (hand@kias.re.kr)*

Interactions between graphene systems and applied forces or inserted molecules often result in very interesting consequences that are sometimes useful as well. In this talk, I will present a couple of theoretical works exploring those aspects in various graphene systems. First, I will discuss an ideal strength of graphene as function of doping. There have been several works on variations of electronic structures in graphene systems with external forces. However, the effect of variation of electronic degree of freedom on their mechanical properties has not been explored well. It is shown that the ideal mechanical properties of graphene are strong functions of doping due to distinct electron-phonon interactions in graphene systems. Second, I will also discuss another aspect of realization of interesting electron-phonon interactions in bilayer graphene in spectroscopic measurements. When two layers in bilayer graphene slide each other, interlayer electronic interactions couple to intralayer phonon degrees of freedom that changes Raman and IR spectroscopic signals. Third, if time allowed, I will present a possible explanation on a recent astonishing experiment showing the unimpeded water permeation through graphene oxide membrane. It is shown that the interlayer distance and ice formation are important factors for perfect water penetrations and for complete blocking for other gases and liquids.

**C26**

# Charge noise in multiwalled carbon nanotubes

Olli Herranen, Deep Talukdar, Markus Ahlskog

*Nanoscience Center, Department of Physics, University of Jyväskylä, Finland (olli.herranen@jyu.fi)*

Low frequency noise properties of nanoscale electronic devices are quite distinct from the ubiquitous silicon devices. For example, in the diffusive regime low frequency noise follows the Hooges's empirical relation which gives a $1/N_c$ scaling of noise magnitude, where $N_c$ is the number of charge carriers. The scaling, however, breaks down for ballistic nanoscale transistors as in that regime the definition of $N_c$ becomes unclear. In case of schottky barrier CNT devices and many other nanoscale devices in the diffusive regime Hooge's formula has been found to be applicable (see e.g. [1-2]). However, for ballistic devices it is necessary to find explanation that can be described with different phenomenon as Tersoff has done by introducing the charge noise model [3].

Almost all of the previous noise studies from CNTs are concentrated in SWNTs devices and very little is known about noise properties of multi-walled carbon nanotube (MWNT) devices. Intermediate sized MWNTs (< 15 nm) are good ballistic conductors without any considerable effect of the contacts which is usually the problem with SWNTs. Therefore they offer interesting model system to study the transport and noise properties of ballistic nanoscale devices. Here we report a noise study of intermediate sized semiconducting MWNTs that are in ballistic or quasi-ballistic regime. We show that the gate dependence of the noise fits well with the charge noise model proposed by Tersoff. These results enable to understand the noise properties of MWNTs and help to utilize them for future applications.

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**P210**

# Fermi energy-dependent structural deformation of single-wall chiral carbon nanotubes

Eduardo B. Barros[1], Bruno G. Vieira[1], Antonio G. Souza Filho[1],
Mildred S. Dresselhaus[2]

*1 Universidade Federal do Ceará, Brazil (ebarros@fisica.ufc.br)*
*2 Massachusetts Institute of Technology, U.S.A*

It is well known that the electronic and vibrational properties of carbon nanotubes are sensitive to charging effects. However, in spite of many years of dedicated research, the underlying process which is responsible for these changes has not been well described. On the other hand, ever since the seminal work by Yang *et al.* [1] it has been known that structural deformations such as axial, radial and torsional strains can be responsible for strong modifications of the electronic band structure of carbon nanotubes. Although both effects, charging and strain, are known to affect the electronic properties of CNTs the connection between the two processes have for a long time been overlooked. In this work, we investigate this connection by calculating the structural and electronic properties of charged carbon nanotubes by performing an extended Tight-binding calculation using Density-Functional-Theory-based Tight-binding parameters between neighbors up the the 7th nearest neighbors as a function of the interatomic distances, following the procedure of Vercosa *et al.* [2] The energy of the nanotube is calculated assuming that the electron population follows the Fermi-Dirac distribution for a given chemical Fermi-Energy ($E_F$). As the Fermi energy is varied, the total charge of the nanotube changes simulating a charging effect. Our results show that the relaxation of the electronic stress generated by an extra charge on the nanotube causes axial, radial and torsional strains which directly affects the electronic band structure of carbon nanotubes. Furthermore, we show that the torsional strain plays a major role on this relaxation process and is mainly responsible for the changes in the optical transition energies. Torsional strains of up to 2% were obtained for an (8,7) nanotube for a Fermi energy of about 1 eV, causing changes of more than 0.5 eV to the optical transition energies.

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**P211**

# Understanding high frequency transport in low-dimensional graphitic carbon and superlattice systems

Somnath Bhattacharyya[1,2], George Chimowa[1,2,] M. V. Katkov[1]

*1 Nano-Scale Transport Physics laboratory, School of Physics, University of the Witwatersrand, Johannesburg, South Africa (somnath.bhattacharyya@wits.ac.za)*
*2 Centre of Excellence in Strong Materials, South Africa*

Developing hybrid super-structures including carbon nanostructures for quantum information science is widely sought after and we show a possible route in carbon superlattice structures based on experimental results as well as theoretical analysis which also incorporates high-speed switching capabilities. We propose a theoretical model of disordered carbon superlattice structures where the local density of electronic states is controlled by changing the $sp^3$-C bond alternation as well as the hopping disorder parameter of the $sp^2$-C regions [1]. In addition the incorporation of nitrogen atoms in carbon networks was modeled as a combination of disorders which vary both in correlated and uncorrelated manners. Resonant peaks associated with C and N sites in these structures show a conductance cross-over under variation of the nitrogen concentration in these structures which can explain the observed negative differential resistance in diamond-like carbon superlattices as well as the conductivity cross-over in nano-crystalline diamond films [2], [3]. Detailed analysis of transport measurements over a wide range of temperatures, magnetic fields and also frequency shows an enhanced characteristic length in these systems that supports switching of complex impedance in the range of 65 GHz. High frequency transport properties of carbon superlattice structures are compared to carbon nanotube and graphene devices which can demonstrate ballistic conductance features.

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**P212**

# First principles and tight binding studies of graphene and SWNT growth

Kim Bolton[1], Shayesteh Haghighatpanah[1], Anders Börjesson[1], Abas Mohsenzadeh[1],
Hakim Amara[2], Christophe Bichara[3]

*1 School of Engineering, University of Borås, SE 501-90 Borås, Sweden (kim.bolton@hb.se)*
*2 Laboratoire d'Etude des Microstructures, ONERA-CNRS, BP 72, 92322 Châtillon Cedex, France*
*3 CINAM, CNRS and Aix Marseille University, Campus de Luminy, 13288 Marseille, France*

First principles and tight binding based Monte Carlo methods have been used to grow of graphene and SWNTs both in the absence and presence of Ni catalysts. The proper selection of temperature (T), chemical potential (P) and number of structural relaxation steps (S) allowed for the growth of defect-free graphene sheets.[1] This is important to study the formation and healing of defects.

In contrast, the conditions used for graphene growth do not lead to continued growth of defect-free SWNTs and the nanotubes close to form capped structures. Under these conditions a catalyst particle is necessary to maintain an open nanotube end, which is required for the elongation of the nanotube. In fact, efficient growth of SWNTs requires a larger chemical potential, which also adds carbon atoms to less reactive sites. Since this increases the probability of growing defective structures, it indicates that there may be a narrower (T,P,S) parameter window for nanotube growth.

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**P213**

# Effects of atomic distribution on the electronic properties of boron carbonitride nanotubes

A C M Carvalho[1,2], J Lawlor[1], T A Souza[2] , M Ferreira[1]

*1 School of Physics, Trinity College Dublin, Ireland (carvalac@tcd.ie)*
*2 GDENB, Departamento de Fisica e Quimica – ICE – Universidade Federal de Itajuba Avenida BPS, 1303, Itajuba – MG, Brazil*

Tubular structures of boron nitride, also known as BN nanotubes (BNNT), have been proposed theoretically back in 1994 [1] motivated by the structural similarities between hexagonal boron nitride (h-BN) and graphene. Theoretical and experimental studies of other tubular structures were subsequently driven by the synthesis of BNNT in 1995 [2]. Boron Carbonitride ($B_XC_YN_Z$) nanotubes are among such tubular structures and remain in focus due to its technological potential. In the case of the $B_XC_YN_Z$ nanotubes, theoretical calculations have revealed that these nanotubes may display intermediate electronic properties that lie somewhere in between pure carbon and boron nitride nanotubes. This suggests that it might be possible to engineer the physical properties of such tubes by an adequate control of the atomic concentrations.

In this work, electronic properties of $B_XC_YN_Z$ nanotubes optimized [3] by semi-empirical techniques are presented. In addition, results obtained by Density Functional Theory are compared with those based on Green's function theory. We indicate that the electronic properties of $B_XC_YN_Z$ nanotubes depend not only on the chemical composition but also on the atomic arrangement of B, C, and N atoms in the tubular structure.

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P214

# Ab initio molecular dynamics study of liquid water on NaCl(100) surface

Jian-Cheng Chen

*1 Department of Applied Physics, FI-00076 Aalto, Finland*
*2 Department of Chemistry, Aalto University, FI-00076 Aalto, Finland*
*(jian-cheng.chen@aalto.fi)*

By employing *ab initio* molecular dynamics (AIMD), we have simulated the liquid water-solid surface interaction of 256 water water on a (4×4) NaCl(100) unit cell, equilibriumed at a time scale of 50,000 fs. In this system, our AIMD results show that these water molecules occupy approximately in four layers. The liquid water density distribution has a maximum peak of 1.40 g/cm$^3$ in the first layer 2.8 Å above the NaCl surface. The water density decreases to 1.10 g/cm$^3$ in the fourth layer. The first layer water is about 1 ML on NaCl(100) surface, in which the oxygen atoms mainly occupy Na sites statistically. The liquid water structure appears when water is further away from the NaCl(100) surface by about 7.0 Å from oxygen-oxygen radial distribution function. To understand the dissolving process of NaCl into liquid water, we have calculated the dissolve barriers of $Cl^-$ and $Na^+$ ions from flat, vacancies,stepped and the corner of the island on the NaCl(100) surfaces using constraint method.

The barrier heights for producing Cl- or $Na^+$ ions on flat NaCl(100) surface are 0.78 eV and 0.75 eV, respectively. The dissolve barriers for $Cl^-$ and $Na^+$ ions on stepped surface are 0.19 eV and 0.13 eV respectively. The barriers for producing $Cl^-$ or $Na^+$ ions from the corners of island on NaCl(100) surface are 0.12 eV and 0.11 eV, respectively. These results indicate that the dissolving process of NaCl crystal starts from the corners of an island or a step surface. Thus, departure of the $Na^+$ ion has slightly lower barriers than dissolving $Cl^-$ ion at the initial stage. However when more $Na^+$ ions are dissolved, the $Na^+$ and $Cl^-$ ions have approximately the same barrier height as tested on the stepped surface.

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P215

# Effects of thermal boundary resistance on thermal conductivities of three-phase biological systems containing carbon nanotubes

Feng Gong[1], Dimitrios V. Papavassiliou[2] and Hai M Duong[1]

*1 Department of Mechanical Engineering, National University of Singapore, Singapore*
*(mpedhm@nus.edu.sg)*
*2 School of Chemical, Biological and Materials Engineering, The University of Oklahoma, USA*

The effective thermal conductivities of 3-phase biological systems were calculated by an off-lattice Monte Carlo method using random walk algorithm. The 3-phase biological systems consist of a normal tissue containing spherical cancer cells and single-walled carbon nanotubes (SWNTs) distributed randomly on the cancer cell surface. For the first time, the effects of thermal boundary resistances of normal tissue-cancer cell, cancer-cell-SWNT and SWNT-tissue as well as SWNT morphologies (concentrations, orientations and aspect ratios) on the effective thermal conductivity of the biological systems were studied comprehensively. Results showed that the effective thermal conductivity decreased as the thermal boundary resistance between tissue and cancer cell increased, but increased with the rise of thermal boundary resistance between cancer cell and SWNTs as well as the resistance between tissue and SWNTs. The model can be also applied to predict the effective thermal conductivities of 3-phase nanocomposites with carbon nanotubes, nanoparticles and polymer.

**P216**

# Ab initio molecular dynamics study of the effect of water on carbon nanotube growth

Wataru Hashizume[1] , Kohei Shimamura[1], Rizal Arifin[1], Tomoya Oguri[2],
Yasushi Shibuta[2], Fuyuki Shimojo[1], and Shu Yamaguchi[2]

*1 Department of Physics, Kumamoto University, JAPAN*
*2 Department of Materials Engineering, The University of Tokyo, JAPAN*

The catalytic chemical vapor deposition (CVD) method is one of the most popular techniques for the synthesis of carbon nanotubes [1]. A water-assisted super growth CVD method is developed by K. Hata *et al.* [2], in which a small amount of water vapor enhances the activity and lifetime of the catalysts. Recently, the dissociation of various carbon source molecules on the catalytic metal has been investigated by ab intio molecular dynamics (MD) simulations [3]. However the effect of water on the dissociation process of the carbon sources molecules is still unknown. In this study, we perform *ab initio* molecular dynamics simulations to investigate the effect of water on carbon nanotube growth as well as the molecular dissociation. The model system consists of 32 nickel atoms, 37 ethylene molecules, and a hydroxyl group. Carbon open-chain C-C-C-C is produced around a hydroxyl group. Time evolution of the gross atomic charge and the overlap population shows that the hydroxyl group is contributed to generate the carbon open-chain. In the presentation, our recent results will be introduced after the brief review of computational works on this topic.

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**P217**

# The origin of SWCNT's chirality and strategies toward SWCNT's chirality-selection in growth

Feng Ding[1], Li Li[1], Ziwei Xu[1], Tianying Yan[2]

*1 Institute of Textile and Clothing, Hong Kong Polytechnic University, Hong Kong, China*
*2 College of Chemistry, Nankai University, Tianjin, China*

The assignment of the chiral indexes, (n,m), to a single walled carbon nanotube (SWCNT ) during its initial nucleation has been a long term mystery. [1-4] Here we present an atomic analysis of the nucleation of SWCNT on the catalyst surface by both *ab initio* calculation, atomic simulation and geometry analysis. It is reveals that the 6th pentagon formed during the nucleation of a matured SWNT cap has a full control over the SWCNT's chirality, or, in another word, any arbitrary SWCNT can be formed by varying the position of the 6th pentagon only. Detailed kinetic analysis indicates that the appearance of the 6th pentagon on the SWCNT's cap is a random process in the vapor-liquid-solid (VLS) experiments. This finding leads to a conclusion that the assignment of the SWCNT's chirality in the VLS growth is a random procedure thus SWNT of any chirality has equal probability of be formed during the nucleation. Detailed analysis of large amount of experimental data validated this theoretical discovery. [5-6]

Although the analysis indicates that chirality-selected growth of SWCNTs within the VLS growth experiments is not feasibly, the SWCNT's chirality can be controlled using solid catalyst particles to bias the addition of the 6th pentagon. This well explains most previous experimental control on the SWNTs' chirality, such as the CoMoCat [6] and the preferred growth of conducting SWNTs [7]. Based on our *ab initio* calculations, a strategy of control SWCNT's chrality is emerged and its feasibility is discussed. [6]

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## Ti decoration of single-wall carbon nanotubes and graphene by density functional theory computations

P218

M.A. Gialampouki, Ch.E. Lekka

*Department of Materials Science and Engineering, University of Ioannina, Ioannina, 45110, Greece*
*(mgialab@cc.uoi.gr)*

Ti nanostructures on Single-Wall Carbon Nanotubes (SWCNTs) have attracted considerable attention due to their potential applications in electronic nanodevices and molecular adsorption [6, 7]. We report on Density Functional Theory (DFT) results referring to $Ti_N$ (N = 1, 2, 3, 7, 13) nanoclusters and Ti-nanowires (monoatomic, bcc(110) or hcp(0001) aligned) on carbon substrates. In the Ti adatom case, two new equivalent positions emerged that trisect the line joining the hexagon normal to the tube's axis sides. These sites accommodate the dimers and trimers in compact linear and 2D triangular forms, respectively, and the $Ti_7$ and $Ti_{13}$ in 3D conformations. For NWs' cases the cylindrical shape of SWNT turns to ellipsoid and the wires inside the SWNT appear to be more stable compared to the outside cases. For all cases, we found that Ti adsorbates introduce new electronic states close to and at the Fermi level. Despite the significant charge transfer from adsorbates to substrates, these otherwise reduced Ti-nanostructures induce substantial charge screening in their surrounding substrate's atoms and appear eventually as charged locations. These findings enlighten the early stages of Ti deposition, predict possible active sites, and may be of use for the design of metal-carbon coatings for applications in catalysis and nanoelectronics.

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## Molecular dynamics simulations of CNT/palladium interface exposed to mechanical load

P219

Steffen Hartmann[1], Ole Hölck[2], Bernhard Wunderle[1]

*1 University of Technology Chemnitz, Germany (steffen.hartmann@etit.tu-chemnitz.de)*
*2 Fraunhofer IZM, Germany*

We present our recent advances in molecular dynamics simulations of a pull-out test of carbon nanotubes (CNTs) embedded in palladium. As results we show force-displacement relations for quasi-static displacement controlled tests. We choose palladium because of its high potential as an electrical contacting material in CNT devices [1,2]. In our model we assume a van der Waals interaction between carbon and palladium atoms and approximate this with a Lennard Jones potential.

With our simulations we try to understand the mechanical behavior and interface quality of CNTs embedded in noble metals which is of importance for future sensor applications. There CNTs are envisaged as sensor elements due to their outstanding piezoresistive gauge factor [3]. To provide the electrical connection a metal electrode has to be integrated for determination of the CNT's resistance. The incommensurate interface [4] between the lattices of CNTs and metals lead to a behavior that is independent on embedding length. We report on pull-out forces which were determined to be in the nano Newton range. Further we show the influence of defects on the pull-out forces. Additionally we pursue supporting experiments for comparison with our theoretical findings. To this purpose we present results of our sample preparation and methods to experimentally obtain the force-displacement relation.

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## P220

## Controlled coupling of carbon nanotubes into plasmonic cavities probed by plasmon enhanced Raman scattering

Sebastian Heeg[1], Antonios Oikonomou[2], Roberto Fernandez-Garcia[3], Stefan A. Maier[3], Aravind Vijayaraghavan[2], Stephanie Reich[1]

*1 Freie Universität Berlin, Berlin, Germany (sebastian.heeg@physik.fu-berlin.de)*
*2 Manchester University, Manchester, UK*
*3 Imperial College London, London, UK*

Optical coupling of light and matter in the nanoscale regime is of key fundamental interest in basic research as well as applications. One of the most spectacular cases of this coupling at optical wavelengths can be observed in surface enhanced Raman scattering. Here, localized surface plasmon resonances of metallic nanoparticles generate highly localized, strongly enhanced near-fields which may increase the Raman intensity of a given inelastic scatterer by orders of magnitude. Single-walled carbon nanotubes, the model system to investigate physical phenomena in one dimension, constitute an ideal test bed to investigate optical coupling in the nanoscale; their vibrational and optical properties are well known[1] and - in contrast to molecules - their location and orientation relative to a plasmonic system can be readily obtained experimentally.

Here we demonstrate the controlled placement of a small carbon nanotube bundle in a plasmonic cavity formed by two closely spaced gold nanodiscs via dielectrophoretic deposition[2]. We observe a Raman signal enhancement of the order of $10^3$ which we confirm by spatially resolved Raman measurements. The nanotube bundle is oriented perpendicular to the plasmonic dimer axis. Therefore, rotating the polarization of the excitation switches on (polarization parallel to dimer) or off (polarization parallel to bundle) the interaction between the plasmonic cavity and the nanotube, with the latter providing an ideal reference. We discuss the feasibility of our interface as a model system to investigate the nature of plasmon enhanced Raman scattering in particular and optical coupling at the nanoscale in general.

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## P221

## CdS nanotubes – Synthesis and characterization

Mengyao Zhang, Liu Huang, Jia G. Lu

*University of Southern California, Department of Physics, Los Angeles, CA, USA*

We have fabricated CdS shell by a facile two-step, solution-based approach consisting of first growing ZnO nanowire in zincammonia complex solution, followed successive ion layer adsorption and reaction for depositing CdS layers to form the shell. [1] Crystal structural analysis, electrical properties, Raman and photoluminescence (PL) characteristics are evaluated. An intense near band edge luminescence is observed between 485 - 491 nm. It shows several distinct PL features originated from free and bound excitonic recombinations. The peaks are identified. Furthermore, the strain associated with a lattice contraction of $\Delta c/c$ is evaluated using the $\Delta w/w=(1+3\Delta c/c)^{-\gamma}-1$, where $\Delta w$ is the 1-LO phonon energy shift from its bulk value, and $\gamma$ is the Grüneisen parameter, 1.1 for CdS. [2]

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## Selective vertical growth of ZnO nanowires for electronic skin

**P222**

Yeri Jeong[1], Jeong Hee Shin[1], Seung Nam Cha[2], Jung Inn Sohn[2], Jae Eun Jang[1,*]

*1 Department of Information and Communication Engineering, Daegu Gyeongbuk Institute of Science and Technology (DGIST), Daegu 711-873, South Korea (*jang1@dgist.ac.kr)*
*2 Department of Engineering Science, University of Oxford, Oxford OX1 3PJ, U.K*

The five senses, which are sight, hearing, taste, touch, and smell of human, are essential elements in our life. If these senses are imitated as electrical devices, they can be applied to android robots or implanted to human body to support disabled people. Particularly, with the sense of touch, recent studies have developed an artificial electronic skin that has the ability to sense and respond to touch pressure. Existing touch sensors simply detects pressure or pressure distribution. However, due to its simplicity, these sensors have a limitation in mimicking the touch senses of human. To allow a human touch feeling on the electronic skin, it requires a high resolution touch sensor similar to human cell dimension. Therefore, we focus on one-dimensional ZnO structure that is ideal for self-powered touch sensing by converting nano-scale mechanical energy into electrical signal owing to its coupled piezoelectric and semiconductive properties with resolution effect [1].

We carried out several experiments to acquire better electrical characteristics of ZnO nanowire. The patterned conductive layer such as metal electrode is an essential part to make e-skin structure using nanowire. The verticality of grown nanowire on the metal layer, which is one of the most important parameters for high sensing efficiency, is poorer than that of grown on Si substrate. However, by changing substrate and structure condition, our nanowire can obtain similar or enhanced performance as of nanowire grown on Si substrate. As a result, a better electrical signal was detected from pressed nanowires. We prove that this new suggested structure has a high probability of self-powered e-skin system using nanowire structure.

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## Carbon nanotubes on boron nitride substrate: Effects of doping, defect, and electric fields

**P223**

Seoung-Hun Kang[1], Gunn Kim[2,*], Young-Kyun Kwon[1,*]

*1 Department of Physics and Research Institute for Basic Sciences, Kyung Hee University, Korea (*ykkwon@khu.ac.kr)*
*2 Department of Physics and Graphene Research Institute, Sejong University, Korea (*kimgunn@gmail.com)*

Using the desnity functional theory, we investigate the structural and electronic properties of the semiconducting carbon nanotube (CNT) on hexagonal boron nitride (hBN) substrates with or without defects under an external electric field to examine not only their good effects, but also bad effects of whether the electronic states originated from the hBN substrate would influence the CNT states near the Fermi level causing some problems in CNT devices. We apply the electric field strength from -0.2 V/Å to +0.2 V/Å, and introduce various dopants (K, Cl, and Ni) on the defective hBN substrate as well as the perfect one. The perfect hBN substrate does not modify the electronic structure of the CNT exhibiting the improved device performances, compared with conventional substrate such as $SiO_2$. However, the hBN substrate with some vacancy defects might be a poor substrate, on which the electronic conduction could occur when gate voltage is applied.

**P224**

## Fabrication of highly integrated graphene nanoribbon field effect transistors

Toshiaki Kato, Rikizo Hatakeyama, Toshiro Kaneko

*Department of Electronic Engineering, Tohoku University, Sendai 980-8579, Japan*
*(kato12@ecei.tohoku.ac.jp)*

Graphene nanoribbons combine the unique electronic and spin properties of graphene with a transport gap that arises from quantum confinement and edge effects. This makes them an attractive candidate material for the channels of next-generation transistors. Although nanoribbons can be made in a variety of ways, the reliable site and alignment control of nanoribbons with high on/off current ratios remains a challenge. Plasma chemical vapor deposition (CVD) is known as fruitful method for the structural-controlled growth and damage-free functionalization of nano carbon materials such as carbon nanotubes (CNTs) [1-3] and graphene [4,5]. We have developed a new, simple, scalable method based on the advanced plasma CVD method for directly fabricating narrow (~23 nm) graphene nanoribbon devices with a clear transport gap (58.5 meV) and a high on/off ratio (>$10^4$). Since the establishment of our novel graphene nanoribbon fabrication method, direct conversion of a Ni nanobar to a graphene nanoribbon is now possible. Indeed, graphene nanoribbons can be grown at any desired position on an insulating substrate without any post-growth treatment, and large-scale, two- and three-dimensional integration of graphene nanoribbon devices should be realizable [6].

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**P225**

## Electron transport through chemically linked armchair carbon nanotubes

Tomi Ketolainen, Ville Havu, and Martti Puska

*COMP / Department of Applied Physics, Aalto University, Finland (tomi.ketolainen@aalto.fi)*

Novel carbon nanostructures have attracted a considerable amount of interest in recent years. Carbon nanotubes (CNTs), for example, have shown excellent electronic, mechanical, and thermal properties. Therefore, CNTs are considered as the material for future nanoelectronics. In addition, carbon nanotube networks are being investigated [1]. The CNT networks combine good electrical conductivity with high mechanical strength leading to thin films that are both durable and flexible. These films could be used in modern display technology as transparent electrodes.

To understand the conductivity of the whole CNT network, one has to first consider the electron transport through a single carbon nanotube junction (CNJ). The transport properties of CNJs depend, e.g., on the chirality and diameter of nanotubes and the angle between them. Moreover, the pressure applied to the junction affects the conductivity.

We present an outline of our project where we examine the transport properties of CNJs that are linked chemically with organic molecules and transition metal atoms. We perform *ab initio* calculations of these junctions using the FHI-aims code [2]. FHI-aims also includes an implementation of the Landauer-Büttiker formalism, which makes it possible to calculate the electron transport through a nanotube junction. A particular goal of this work is to find new ways to improve the conductivity of CNJs and the whole CNT network.

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P226

## Suppression of exciton-electron scattering in doped single-walled carbon nanotubes

Satoru Konabe[1], Kazunari Matsuda[2], Susumu Okada[1]

*1 Graduate School of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan (konabe@comas.frsc.tsukuba.ac.jp)*
*2 Institute of Advanced Energy, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan*

Strong Coulomb interaction in single-walled carbon nanotubes (SWCNTs) leads not only to stable bound state of exciton and trion but also to interesting dynamical properties of the many-body exciton states and exciton-carrier state. Recently it was found that phase relaxation by the elastic scattering among the excitons dominantly contributes to the linewidth of optical spectra [2], much larger than the contribution of the Auger exciton recombination caused by the inelastic scattering among the excitons [3]. For doped SWCNTs, besides the elastic scattering between excitons, it is expected that the elastic scattering between excitons and charged carriers play a crucial role for determining the phase relaxation of the excitons.

In the present paper, we perform theoretical investigation on the dephasing process caused by the elastic scattering between excitons and electrons to unravel the dynamical processes of excited states in doped SWCNTs. Our calculation of the linewidth predicts that this scattering process shows strong suppression and nonlinearity associated with the doped electron density. This anomalous behavior is caused by a cusp-like structure in the dispersion relation of exciton that originates from the logarithmic singularity ascribed to the exchange self-energy [5].

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P227

## First-principles study of optical properties in small-diameter carbon nanotubes

Takashi Koretsune and Susumu Saito

*Tokyo Institute of Technology, Japan (koretune@stat.phys.titech.ac.jp)*

Electronic structures of carbon nanotubes can be basically understood using the electronic structures of graphene with some curvature effects. In small-diameter nanotubes, however, it has been known that the electronic structures are drastically modified due to the curvature; for example, (5,0) tube should be semiconducting in the naïve cutting line picture while density-functional theory (DFT) predicts the metallic behavior[1]. Furthermore, electron-phonon coupling is expected to increase with decreasing a diameter[2]. Thus, small-diameter nanotubes can have new possibilities for future application. To utilize the small-diameter nanotubes, it is of great importance to clarify the electronic properties, optical absorption/emission properties and Raman scattering from first principles.

To this end, we study all the small-diameter nanotubes using first-principles calculations and predict the absorption/emission properties and the frequencies of radial breathing mode (RBM). It is found that the electronic state that originates from graphene state around the M point in the hexagonal Brillouin zone plays an important role to understand the electronic structures of small-diameter nanotubes. Due to the energy-level decrease of the M-point state in the conduction band, several small-diameter nanotubes become non-luminescent, which agrees with the experiment[3]. Furthermore, we find that the RBM frequencies have chirality dependence as well as diameter dependence.

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**P228**

# Hydrocarbon chains formation from carbon nanotubes in the presence of CO and $H_2$ molecules: A molecular dynamics simulation study

F. López-Urías[1], A. L. Elías[2], S. Talapatra[3], Kanchan Mondal[3], Bobby G. Sumpter[4], Vincent Meunier[5], H. Terrones[2], M. Terrones[2,6]

*1 Advanced Materials Department, IPICYT, México.*
*2 The Pennsylvania State University, USA*
*3 Southern Illinois University, USA*
*4 Oak Ridge National Laboratory, USA*
*5 Rensselaer Polytechnic Institute, USA*
*6 Shinshu University, Japan*

The capacity of carbon nanotubes to catalyze hydrocarbons in the presence of atmospheres rich in carbon monoxide and hydrogen has opened a new route in fuel generation. In the present investigation, molecular dynamics (MD) simulations in conjunction with a force field potential were performed on single-walled carbon nanotubes (SWNTs), in contact with CO and $H_2$ molecules. The MD simulations were carried out with the canonical ensemble NVT at different temperatures (100-600 K) and simulation times (1-20 ps). MD results showed that the final structures exhibit the presence of different species such as methane, ethane, methanol, ethanol and long carbon chains, among others. It was found that the hydrocarbon chain formation is due to the partial destruction of the SWNTs wall in combination with the dissociation of CO and $H_2$ molecules helped by the temperature increment. We consider that our results could improve the understanding of experiments on CNT-based liquid fuel production.

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**P229**

# Optical absorption and selection rule in twisted bilayer graphene

Pilkyung Moon[1] and Mikito Koshino[2]

*1 Korea Institute for Advanced Study, Republic of Korea (pmoon@kias.re.kr)*
*2 Tohoku University, Japan*

Recent epitaxial growth technique realized twisted bilayer graphene in which two layers of graphene are stacked with rotational fault [1]. The interference between two lattice periods leads to the formation of a Moiré pattern, creating a superlattice potential in the graphene [2]. We theoretically investigate the optical absorption property of twisted bilayer graphenes with various stacking geometries, and demonstrate that the spectroscopic characteristics serve as a quite robust fingerprint to identify the rotation angle between two layers [3]. We find that the optical absorption spectrum consists of a series of characteristic peaks ranging from terahertz to ultraviolet frequencies, which are associated with the van Hove singularity in the superlattice band structure. We calculate the optical conductivity in two different methods, the tight-binding model and the effective mass model based on the Dirac equation, and show that the effective model nicely reproduces the tight-binding results for small rotation angles. More importantly, we analytically explain the optical selection rule which is peculiar to twisted bilayer graphene. Our results not only give a convenient way to identify the geometry of twisted bilayer graphene but also provide useful information for opto-electronic application.

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# Atomic scale insight in manipulating the SWCNT nucleation process

P230

Erik C. Neyts

*University of Antwerp, research group PLASMANT, Dept. Chemistry, Universiteitsplein 1,*
*2610 Wilrijk-Antwerp, Belgium*

Future applications of carbon nanotubes depend to a large extent on our ability to control the exact structure of the tubes. Plasma enhanced chemical vapor deposition (PECVD) is a possible route towards additional control over the growth process, and thus the CNT structure, compared to traditional CVD growth [1].

We developed a novel reactive hybrid MD/MC simulation model to investigate how various PECVD-specific factors may be applied to manipulate and enhance the nucleation and growth of SWCNTs. Specifically, the electric field and ion bombardment are studied. We find that both factors in a limited but well-defined parameter window contribute to SWCNT nucleation and growth. We demonstrate that the electric field (1) allows a lower C-concentration required for the initial nucleation step; (2) induces an increased growth rate at reduced temperature; and (3) permits vertical alignment of the growing SWCNT [2]. We propose a diffusion/migration competition mechanism to explain and make plausible these results.

Second, we also demonstrate how Ar-ion bombardment enhances the nucleation process in a narrow energy window. The enhanced cap nucleation is explained by a ion-collision induced graphene network restructuring mechanism [3]. This simulated prediction is fully corro-borated by subsequent experiments. Moreover, we also performed simulations demonstrating SWCNT growth at temperatures as low as 500 K [4]. These results open new possibilities towards enhanced structural control during the SWCNT nucleation and growth process.

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# Ab initio molecular dynamics study of dissociation of ethanol on nickel cluster in metal-catalyzed growth of carbon nanotubes

P231

Tomoya Oguri[1], Kohei Shimamura[2], Yasushi Shibuta[1], Fuyuki Shimojo[2], and Shu Yamaguchi[1]

*1 Department of Materials Engineering, The University of Tokyo, JAPAN*
*2 Department of Physics, Kumamoto University, JAPAN*

The formation mechanism of carbon nanotubes and the role of catalytic metals in the growth of single-walled carbon nanotubes (SWNTs) via a catalytic chemical vapor deposition method has been widely studied [1]. However, the dissociation process of carbon source molecules on the metal catalyst is not well understood yet because it is difficult to observe the initial stage of SWNTs formation directly in the experiment. Thus, we have investigated the dissociation process of various carbon source molecules on the catalytic metal by the *ab intio* MD simulation [2,3]. In this study, dissociation of ethanol molecules on the nickel cluster is investigated by *ab initio* molecular dynamics and nudged-elastic-band (NEB) simulations to unravel the initial stage of metal-catalyzed growth process of carbon nanotubes via an alcohol catalytic chemical vapor deposition. It has been observed that both C-C and C-O bonds in ethanol molecules are dissociated on the nickel cluster, which is followed by the formation of various reaction products such as hydrogen atoms and molecules, carbon monoxide, oxygen atom, water, ethylene, methane and their fragments. In addition, the NEB analysis indicates that the activation energy of the C-H bond dissociation in the fragment molecules on the nickel cluster is approximately one-eighth of the value obtained from the bond-dissociation energy of the C-H bond without the influence of the nickel cluster. It indicates the nickel cluster acts as the activator of the dissociation process of carbon source molecules by reducing the activation energy. In the presentation, our recent results will be introduced after the brief review of recent computational works on this topic.

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## P232

# Computational study on geometrical, electronic and thermal properties of rigidly interconnected carbon nanofoam

Sora Park[1], Young-Kyun Kwon[1,*], and David Tománek[2]

*1 Department of Physics and Research Institute for Basic Sciences, Kyung Hee University, Seoul, 130-701, Korea (*ykkwon@khu.ac.kr)*
*2 Physics and Astronomy Department, Michigan State University, East Lansing, Michigan 48824-2320, US*

Using *ab initio* density functional calculations, we investigated the structural and electronic properties of schwarzite having $sp^2$ carbon minimal surfaces with negative Gaussian curvature. Such a system consisting of the core part with local negative Gaussian curvature and the interconnection part with (4,4) carbon nanotube segments was calculated to be metallic and very rigid. [1] We found that these schwarzite structures can be doped by electron donors as well as acceptors, making it a promising candidate for the next generation of alkali ion batteries. We also proposed a structure of two interpenetrating, but disconnected schwarzite lattices as a potential application for the super-capacitor.

Further we studied the thermal and electrical conductivities of the system including schwarzite. Using direct molecular-dynamics simulations based on the Tersoff potential, we explored the dependence of the thermal conductivities on different number of core parts and length of interconnection part along a specific axis. The results show that the core parts of schwarzite, which are making the interconnection along other axes, play a role as scattering centers in the system resulting in reduced phonon mean free path and the thermal conductivities as compared with those of CNTs. Further, we investigate the thermoelectric properties of the system by examining the Seebeck coefficient and the figure-of-metrit values.

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## P233

# Molecular dynamics study of transformation of graphene flake to fullerene under electron beam irradiation

Andrey M. Popov[1], Irina V. Lebedeva[2], Andrey A. Knizhnik[2,3], Elena Bichoutskaia[4]

*1 Institute of Spectroscopy Russian Academy of Science, Troitsk, Moscow, Russia, (popov-isan@mail.ru)*
*2 Kintech Lab Ltd., Moscow, Russia*
*3 NRC "Kurchatov Institute", Moscow, Russia*
*4 School of Chemistry, University of Nottingham, Nottingham, United Kingdom*

Irradiation-induced processes in transmission electron microscope have lately attracted considerable interest. Here we present the algorithm for molecular dynamics study of such processes taking into account their characteristic features: 1) only interactions between incident electrons and atoms which lead to changes of atomic structure are predominantly considered, 2) fast irradiation-induced events and slow annealing of the structure between these events are simulated separately at different temperatures [1]. This algorithm is applied for simulation of graphene flake to fullerene transformation observed recently [2]. The interaction between electron beam and atoms is described by energy and momentum transfer.The structure analysis during the irradiation-induced transformation of graphene flake to fullerene is performed by visualization of process and monitoring the number of two-coordinate atoms and of pentagon, hexagon, heptagon and octagon rings. The transformation is revealed to occur through following stages: 1) fast formation of polygons different from hexagons at the flake edges, 2) a few attempts of formation and destruction of a bowl-shaped region during which the numbers of polygons different from hexagons increase whereas the number of two-coordinated atoms stays around the initial value, 3) formation of a bowl-shaped region followed by very fast zipping opposite edges of the flake. The emission of only few atoms is observed during the transformation. Therefore bond reorganization rather than formation of vacancies determines the atomic mechanism of the transformation.

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## MD simulations of DLC-carbon nanotube hybrid materials

**P234**

Wei Ren, Kai Nordlund

*Department of Physics, University of Helsinki, Finland (wei.ren@helsinki.fi)*

Since both carbon nanotubes and diamond-like carbon (DLC) have excellent mechanical properties, and nanotubes also have very interesting electrical properties, forming composites between the two could provide for a very durable electrically active material. Vacuum arc discharge deposition with an average C energy of about 50 - 70 eV is a standard way to make DLC. Hence DLC-nanotube composites could be formed by doing vacuum arc deposition on carbon nanotubes. We are carrying out molecular dynamics simulations of vacuum arc deposition on carbon nanotube bundles and in particular examine the $sp^3$ bonding fraction of the forming materials and the amount of damage in the nanotubes.

After we tested the full Brenner potential which leads to the formation of DLC similar to vacuum arc deposition experiments, we started to simulate a bundle of CNTs irradiated consequtively by 30 – 100 eV C atoms. The good news is that we do observe the formation of an increasing amout of $sp^3$ bonded C atoms starting from a purely $sp^2$ bonded system. But the fraction of $sp^3$ atoms is very low so far. Meanwhile, experiments of deposition on a single CNT bundle did not observe DLC. One of the possible reason for the low $sp^3$ atoms is the side pressure free in the simulations. To test the idea that the problem is the lack of side pressure, we are now running deposition on a periodic system where pressure can build up along the sides. DLC formation is expected to be observed.

## Ab initio molecular dynamics study of dissociation of methane on nickel surface in graphene synthesis via a CVD technique

**P235**

Yasushi Shibuta[1], Rizal Arifin[2], Kohei Shimamura[2], Tomoya Oguri[1],
Fuyuki Shimojo[2], and Shu Yamaguchi[1]

*1 Department of Material Engineering, The University of Tokyo, Japan (shibuta@materialt.u-tokyo.ac.jp)*
*2 Department of Physics, Kumamoto University, Japan*

The formation mechanism of carbon nanotubes and graphenes has been widely discussed from both the experimental and computational points of view. At the present, most of the computational studies focusing on the growth process of carbon nanotubes and graphenes employs isolated carbon atoms and therefore ignores the initial dissociation process [1]. Under such circumstance, we have investigated the dissociation of methane molecules on the nickel(111) surface using the *ab initio* molecular dynamics simulation in order to discuss the initial stage of graphene growth via a chemical vapor deposition (CVD) technique [2]. The methane molecule is dissociated into isolated carbon and hydrogen atoms via CH3 and CH fragment molecules with chemisorbing the nickel(111) surface. After the multistep dissociation, isolated carbon atoms are buried into the subsurface space between nickel layers via the diffusion through hollow sites. As the dissociation of methane progresses, dissociated hydrogen atoms cover the nickel surface with hopping on the nickel atoms, which inhibit further adsorption and dissociation of methane molecules. However, hydrogen molecules from hydrogen atoms are not generated on the nickel surface during the calculation. In the presentation, our recent results will be introduced after the brief review of recent computational works on this topic.

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## P236 Percolation in realistic hybrid carbon nanostructures networks

Louis-Philippe Simoneau, Alain Rochefort

*École Polytechnique de Montréal, Engineering Physics Department and Regroupement québécois sur les matériaux de pointe (RQMP), Montréal, Canada (louis-philippe.simoneau@polymtl.ca)*

Most transparent electrodes used today in electronic displays and photovoltaic devices are rigid, brittle and expensive. Carbon nanotubes (CNT) or graphene nanoribbons (GNR) networks do not show such drawbacks, and they exhibit very appealing structural, mechanical and electron structure properties. However, due to the complex internal structure of these networks, very few fundamental properties are well known. We have developed a Monte Carlo (MC) method to generate and to study the percolation of charge in such networks. Our model includes several variables that allow us to control the characteristics of the networks, and possibly to optimize the performance of the resulting device.

Our MC algorithms generate random 2D or 3D networks that can be tuned to simulate very realistic networks by directly using experimental data (size, junction resistance) in conjunction with relevant case-specific conditions: hardcore overlap, curliness, preferential distributed orientation, partial local crystallization, or heterogeneous mixture of materials. We have evaluated the total conductance of different CNT networks on the basis of individual contacts conductance represented by numerous specific statistical distributions. Our results show that the length, diameter, orientation and chirality distributions within the percolative network of the CNT networks have a great importance on the resulting electrical performances. Although we observed that low resistance percolation paths dominate the electrical transport, the conductivity of the networks weakly depends on the statistical distribution of the junction resistance. In contrast, the type of distribution for the structural parameters such as a preferential orientation of CNT in the network has a drastic effect on the resulting electrical properties. Our most recent developments using hardcore interpenetration allow us to better evaluate the sensitivity of the percolation threshold and to explore the importance of the network thickness. We also examine the effects of the presence of well-organized bundle of CNTs or other heterogeneous elements such as GNRs on the overall electrical properties of the network.

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## P237 Impurity effects on electronic transport in carbon nanotubes wave packet dynamics simulation

Yukihiro Takada, Takahiro Yamamoto

*Faculty of Engineering, Tokyo University of Science, Japan*

Understanding of impurity effects on electronic transport in semiconducting single-walled carbon nanotubes (SWNTs) is a key issue toward establishment of future ultra-fast switching devices utilizing their high mobility. Recent experiments have shown that the impurity and/or defect scattering in an SWNT causes Anderson's localization even at room temperature, originating from its low dimensionality and phase coherency of electrons [1]. In general, Anderson's localization can occur when the tube length is much longer than the localization length, which indicates the typical width of the localized wave function. However, relationship between the localization length and the intensity of impurity potential has not been sufficiently clarified yet.

In this study, we numerically investigate the effects of impurity scattering on the coherent electronic transport in semiconducting SWNTs with randomly distributed impurities using the wave-packet dynamics method [2], focusing on the effects of impurity-potential strength on the localization length. The obtained results are as follows.

(i) The wave packet shows the ballistic propagation in an SWNT just after it starts to diffuse, and then the localization occurs with time evolution.
(ii) The localization length of an SWNT decreases rapidly as the intensity of impurity potential increases.

Inferring from these results and the coherent length of SWNTs [2], we conclude that Anderson's localization can take place even at room temperature, which is consistent with recent experimental results.

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P238

# Band gap tuning of carbon nanotubes through covalent functionalization – A systematic tight binding study

David Teich, Gotthard Seifert

*Physikalische Chemie, Technische Universität Dresden, Germany (david.teich@chemie.tu-dresden.de)*

Carbon nanotubes are wellknown for their remarkable electronic properties. Since the semi-conducting characteristics are directly affected by the nanotube's chirality, CNTs show a promising potential for applications in semi-conducting device fabrication. Special interest is given to the use as semi-conducting material in field effective transistors. Because of their high linearity in the current-voltage-characteristic, CNTFETs are good candidates for high frequency analogous transistors applied in mobile technology systems. However, the nanotube's chirality cannot be well controlled during the synthesis which makes the fabrication of CNTs with unique band gaps to a difficult task. One opportunity to tune the band gap is the modification of the nanotube surface through covalent functionalization. Using a tight binding model and density functional based tight binding method we calculate the band structure of CNTs with different functionalization patterns. The systematic analysis of the dependence of the band gap energy on the functionalization degree gives information on the efficiency of band gap tuning through covalent functionalization.

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P239

# Ropes of carbon nanotubes: from natural coiling to nanomechanical energy storage

David Tománek[1], David Teich[2], Zacharias G. Fthenakis[1], Gotthard Seifert[2], and Sumio Iijima[3]

*1 Physics and Astronomy Department, Michigan State University, USA (tomanek@pa.msu.edu)*
*2 Physikalische Chemie, Technische Universität Dresden, Germany*
*3 Faculty of Science and Technology, Meijo University, Japan*

Even though single-wall carbon nanotubes occur most abundantly in ropes, little is known about the energy cost and structural changes associated with twisting of such ropes. We defy the computational challenge posed by the uncommon geometry of a twisted rope by accommodating the helical symmetry in our computational approach, which is based on *ab initio* density functional theory. We find that natural coiling may occur in ropes containing chiral nanotubes and is driven by the tendency to optimize the orientational alignment of neighboring nanotubes. Our calculations help identify conditions, under which straight nanotube bundles prefer to form a helix on energy grounds, and we find agreement between our results and high-resolution transmission electron microscopy observations [1]. Twisting a nanotube rope by applying an external torque requires an investment in deformation energy with contribution from not only twisting, but also stretching, bending, and compression of individual nanotubes. We quantify these energy contributions and find that twisted nanotube ropes may reversibly store up to 8 MJ/kg in nanomechanical energy, which is an order of magnitude higher than the energy density of advanced Li-ion batteries [2].

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# Production, structure and properties of novel metallic-DND nanostructured composites

E.S. Vasilyeva[1], S.V. Kidalov[2], J. Puguang[1], S.A. Kotov[1], V.V. Sokolov[2], M.V. Tomkovich[2]

*1 Saint-Petersburg State Polytechnic University, Russia (katrinfr@inbox.ru)*
*2 Ioffe Physical-Technical Institute of the Russian Academy of Sciences, Russia*

Traditionally dispersion strengthened (DS) copper and nickel based alloys are widely used for electrode materials for lead wires, relay blades, tribology, contact supports and electrode materials for spot welding [1-2]. The superior mechanical and thermal properties make nanodiamond effective filler for composites. DND powder is produced by detonation synthesis using carbon-containing explosives such as trinitrotoluene (TNT) and hexogen [3].

Advanced composite materials based on copper and nickel matrix with uniform distribution of ultra- dispersed DND nanoparticles, controlled microstructure and superior mechanical and physical properties were produced by solution spray-dry technique. The size of DND particles in the Cu, Ni -based composite has been varied in range of 3-5 nm up to 100 nm with concentration in range of 1-5 wt. %. Final powder has particles mean size in range of 0.5-5 μm as function of production parameters, porous structure and high developed surface. Influence the different stages of processing on true density, mechanical properties, structure and composition were studied by the range of methods. Application of spray dray method promises the great benefits in materials structure and properties for production of micron sized powders with uniformly distributed nano- dispersed phase.

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# Relationship between carrier mobility and bandgap in low- dimensional carbon materials

Jinying Wang, Zhongfan Liu*, Zhirong Liu*

*Peking University, China (*zfliu@pku.edu.cn and LiuZhiRong@pku.edu.cn)*

The intact graphene has a zero bandgap and subsequent low on-off ratio, while modifications on graphene to open the bandgap always bring about dramatic reduction of mobility. Therefore, how to build a graphene device performing both large on-off ratio and high carrier mobility is one of the most attractive topics. Herein, we investigated the intrinsic mobility of graphene-related systems theoretically. A ubiquitous linear dependence of the effective mass on bandgap was demonstrated to cause the inverse mobility-gap relationship in graphene. Moreover, the deformation-potential constant $E_1$, which also affects the mobility greatly, was found to be determined by both bandgap and the strain dependence of Fermi energy [1]. An effective tailoring of $E_1$ is essential for pursuing high mobility in graphene-related systems. Based on this, we further found that some specific boron-nitride-embedded graphene had low $E_1$ and mobility comparable to that of graphene when its bandgap is nonzero. And their transport polarities (whether electron or hole transport dominates) could be tailored by strain. Our results indicate that this hybrid material is promising for transistor devices [2].

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## Aluminum/boron nitride nanotube composites

P242

Maho Yamaguchi[1,2], Amir Pakdel[1], Chunyi Zhi[3], Yoshio Bando[1], Dai-Ming Tang[1,4],
Konstantin Faerstein[5], Dmitry Shtansky[5], Dmitri Golberg[1,2,*]

*1 WPI Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), Japan (*golberg.dmitri@nims.go.jp)*
*2 Graduate School of Pure and Applied Science, University of Tsukuba, Japan*
*3 Department of Physics and Materials Science, City University of Hong Kong, Hong Kong, China*
*4 Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, China*
*5 National University of Science and Technology (MISIS), Russian Federation*

Al/Carbon nanotube (CNTs) composites have become of great interest with respect to utilizations in automotive, aircraft and aerospace industries [1]. However, CNTs have drawbacks for such applications such as absorption of light and ease in bundling and buckling. Boron nitride nanotubes (BNNTs), while having quite similar structures to CNTs, are particularly known for their remarkable mechanical properties, no absorption of visible light, high thermal, chemical and oxidation stabilities, and straight needle-like morphologies. We have fabricated different “scale” Al/BNNTs composites – “nanocomposites”, “microcomposites” and “macrocomposites” [2,3]. “Nanocomposites” were fabricated by magnetron sputtering. A variety of Al coatings were uniformly put onto BNNTs [2]. Individual Al/BNNT hybrid mechanical properties were measured using *in-situ* TEM. Melt-spinning was selected for “microcomposites” to fabricate Al/BNNTs ribbons up to 1 m long. Conventional tensile tests were performed on them [3]. Finally, “macrocomposites” were fabricated by spark plasma sintering (SPS) and obtained pellet samples were tested with respect to hardness and compressive strength. Various degrees of Al reinforcement due to embedded nanotubes were documented for various samples and various testing modes.

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## Gas sensing with Carbon Nanotubes

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Zeila Zanolli[1], J.-C. Charlier[2]

*1 PGI-1 and IAS-1, Forschungszentrum Jülich, Germany (z.zanolli@fz-juelich.de)*
*2 IMCN, Université catholique de Louvain (UCL), Belgium*

The remarkable electronic and transport properties of carbon nanotubes (CNTs) make them very promising for a wide variety of applications in nanoelectronics and spintronics. In particular CNTs could be used as detection element for gas sensing nanodevices thanks to their high surface-to-volume ratio and to the high sensitivity of their physical properties to external perturbations. However, the response of pristine CNTs to gases is weak due to the intrinsically inert $sp^2$ carbon network that characterizes the sidewalls of CNTs. Hence, the functionalization of the CNT external surface is mandatory to improve both the sensitivity and the selectivity of CNT-based gas sensors.

In this talk, various approaches to address this issue using *ab initio* and Nonequilibrium Green’s Functions techniques will be presented. First, the effect of the controlled introduction of defects and of reactive molecular species on the CNTs sidewalls [1] will be considered. Then, the exploitation of the extraordinary catalytic properties of metal nanoclusters (NC) in designing sensors based on CNT-NC hybrid systems will be illustrated [2-3]. In those devices the functionalized CNTs act as sensing unit and gas detection is achieved by macroscopic measurements of the conductivity of CNT mats. A novel detection method based on local magnetic moment measurements of CNTs decorated with magnetic NCs will also be proposed [4]. For small cluster sizes, the strong CNT-NC interaction induces spin-polarization in the CNT. The adsorption of a benzene molecule is found to modify the CNT-NC local magnetization enough to be detected via magnetic-AFM or SQUID magnetometry. The present *ab initio* simulations predict these CNT-NC hybrid systems to exhibit an extraordinary sensitivity to gas molecules with respect to other conventional methods.

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# Insights in the synthesis of carbon nanotubes from computer simulation

M. Diarra[1,2], A. Zappelli[1], H. Amara[2], F. Ducastelle[2], C. Bichara[1]

*1 CINaM – CNRS and Aix Marseille University – France*
*2 LEM – CNRS and ONERA - France*

The outstanding physical properties of novel carbon-based materials (nanotubes, graphene...) strongly depend on their structure: chirality for SWNTs, number of layers and stacking for graphene. However, materials produced are far from being ideal and a direct synthesis of nanotubes with designed structure and properties is not yet achieved.

In order to get an atomic scale insight into the nucleation and growth mechanisms of SWNT's, we use a carefully assessed tight binding model for nickel and carbon [1, 2] to numerically investigate different aspects of the CCVD synthesis process. Owing to significant technical improvements of our grand canonical Monte Carlo code [2], we can extend previous calculations [3] of carbon adsorption isotherms to nanoparticles (NPs) up to ~2.5 nm diameter, in a broad temperature range. We thereby study the chemical and physical states of the metal catalyst as a function of size, temperature and carbon chemical potential conditions corresponding to nucleation and growth of SWNTs [4]. We then study the interfacial properties of the NPs with respect to $sp^2$ carbon walls, show that they strongly depend on the amount of carbon dissolved, and emphasize their role in the growth of tubes. Finally, we try and identify conditions in the growth parameter space that lead to the formation of defectless nanostructures, in order to investigate the chiral selectivity issue.

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# Electronic transport properties of metallic carbon nanotubes with metal contacts: size effects and contact resistance

Andreas Zienert[1], Jörg Schuster[2], Thomas Gessner[1,2]

*1 Chemnitz University of Technology, Germany (andreas.zienert@zfm.tu-chemnitz.de)*
*2 Fraunhofer ENAS, Germany*

Carbon nanotubes (CNTs) are promising candidates for applications in microelectronic devices. The atomically well defined quasi one-dimensional geometry allows for a ballistic electron flow through short tubes at low bias. Their mechanical and thermal stability and their ability to carry high current densities make them an ideal replacement of copper lines in future interconnects. However, large contact resistances between CNTs and metal electrodes are a major obstacle.

In the present work we study the contact quality and length-dependent transport properties of short to medium-sized (6,0) CNTs in end-to-end contact with the metals Al, Cu, Pd, Pt, Ag, and Au. Electron transport calculations are based on the non-equilibrium Green's functions formalism combined with density functional theory as well as a self-consistent version of the extended Hückel theory with a new set of parameters for carbon.

From the average conductance of the CNT-metal systems follows a ranking of the metals regarding their ability to form low-Ohmic contacts with CNTs: Ag ≤ Au < Cu < Pt ≤ Pd < Al. Similar trends are observed for the respective contact distances and binding energies.

Depending on the CNT length, pronounced oscillations of the conductance of CNT-metal systems are observed. This is interpreted by the length dependency of electron transmission spectra. A detailed investigation of the local density of states of the devices and their respective isolated parts (electrodes, infinite, and finite CNTs) gives a visual link between electronic structure and transport properties. It is shown that the electronic states in short CNTs are significantly altered by the presence of metallic contacts.

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# Interaction of multi-walled carbon nanotubes with biomaterials and their biodistribution

Shigeaki Abe[1], Kosuke Ishikawa[1], Yasutaka Yawaka[1], Fumio Watari[1], Rei Kurosaki[2], Tomoya Takada[2], Desharin Santida[2], Katsutoshi Nakayama[2], Daisuke Hayashi[2], Tomoya Takada[2]

*1 Hokkaido University, Japan (sabe@den.hokudai.ac.jp)*
*2 Asahikawa National College of Technology, Japan*

Recently, carbon nanotubes have received a great deal of attention because of their unique physical properties and the variety of their applications in the electronic, mechanical, and chemical fields. In addition, carbon nanotubes have also been used as a platform for various uses, including biomedical applications, because carbon nanotubes appear well suited as a biomaterials. A wide variety of applications in the biomedical field have been developed in recent years. For example, carbon nanotubes are known to be good scaffolds for cell culturing because of their cell adhesion ability. Characteristics of carbon nanotubes as adsorbents for chromatographic protein adsorption have also been actively studied. To control the characteristics of carbon nanotubes as biomedical materials, interaction mechanism of proteins with carbon nanotubes should be elucidated [1, 2]. However, the mechanism of the interaction has not been reported enough. Thus, we carried out their surface modification by mild chemical reaction and then obtained hydrophilic carbon nanotubes that were presented carboxyl groups on the surface. By comparison of the hydrophilic carbon nanotubes and unmodified ones, we investigated the effect of the surface properties [3]. The behaviors were explained by the difference in the dominance of hydrophobic interaction and ionic interaction between carbon nanotubes and the proteins. We also visualized their biodistribution in mice for estimation of their biocompatibility [4]. Though the injected CNTs were observed in some organs, they did not cause significant acute toxicity. We also estimated their cytocompatibility for hepatocytes because the CNTs accumulated in the liver through blood circulation.

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# Graphene growth on Ni (111) surface: molecular dynamics simulation

Rizal Arifin[1,3], Yasushi Shibuta [2], Kohei Shimamura[1], Fuyuki Shimojo[1], and Shu Yamaguchi[2]

*1 Department of Physics Kumamoto University, Japan (rizal.arifin@gmail.com)*
*2 Department of Material Engineering, The University of Tokyo, Japan*
*3 Department of Informatics Engineering, Muhammadiyah University of Ponorogo, Indonesia*

Graphene is considered as the most promising candidate of the carbon based electronic devices in future because of its extraordinary electronic properties such as high electron conductivity due to high carrier mobility [1]. Therefore, many researches have been conducted to find the best mechanism of graphene production. Growth of the graphene on the crystal surface, especially metal surface, becomes popular methods because it can produce high quality and large-area graphene sheets and it provides the low-energy route for its production. Ni is intensively studied recently as easily accessible substrate for graphene growth which is possible either to move the graphene to the other substrate or left it as freestanding graphene [2]. This study of graphene growth on Ni (111) surface is the continuation of our previous study of methane dissociation into carbon atoms on the Ni surface as the carbon-source molecules for the graphene growth process [3]. In this study, we investigate the graphene growth process from the carbon atoms located randomly on the Ni (111) by *ab initio* molecular dynamics (MD) simulation. We perform MD simulation at the several different annealing temperature and different composition of carbon atoms. In the presentation, our recent result will be introduced after the brief review of recent computational work on this topic.

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P252

## Functionalization of single-walled carbon nanotubes and their integration on wafer level

Thomas Blaudeck[1], David Adner[2], Sascha Hermann[1], Stefan E. Schulz[1,3], Heinrich Lang[2], Thomas Geßner[1,3]

*1 Chemnitz University of Technology, Center for Microtechnologies, Chemnitz, Germany*
*(thomas.blaudeck@zfm.tu-chemnitz.de)*
*2 Chemnitz University of Technology, Inorganic Chemistry, Chemnitz, Germany*
*3 Fraunhofer Institute for Electronic Nano Systems (ENAS), Chemnitz, Germany*

Attempts for a functionalization of single-wall carbon nanotubes (SWCNTs) have been paid attention for chemical reasons, for example to achieve solvent compatibility [1]. Furthermore, the topic has incurred a driving force towards aggregated, hybrid materials [2] especially for optoelectronic applications. Besides these, aggregates consisting of SWCNTs, functionalized molecules and metallic or semiconductor nanoparticles are envisaged as building blocks in nanoelectronic sensors [3]. To this end, scalable technological solutions for the integration of the functionalized SWCNTs on wafer level, *e.g.* into microelectronic circuitry and micro and nanoscopic electromechanical systems (MEMS, NEMS), are a key issue.

In this contribution, we report about different technical approaches to perform a side-wall functionalization of single-wall carbon nanotubes with (R-)oxocarbonylnitrene linkers with the aim to couple metallic nanoparticles in a way compatible to wafer-level integration. One promising approach comprised the extension of the protocols by Holzinger *et al.* [1] to long-chained ethylene glycol units. Characterization of the linker included IR, Raman and NMR spectroscopy. For integration on wafer level, a heatable microfluidic channel system was designed and applied on dielectrophoretically aligned SWCNTs on silicon substrates (150 mm diameter) with the possibility to monitor the process by *in-situ* Raman spectroscopy. The functionalization step with the linkers resulted in a change of the D-band of the SWCNTs.

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P253

## Study of the contact between neural cells and carbon nanotubes

I.I. Bobrinetskiy[1], G.E. Fedorov[2], I.A. Suetina[3], A.V. Romashkin[1]

*1 National Research University of Electronic Technology, Russia (vkn@nanotube.ru)*
*2 National Research Center "Kurchatov Institute", Russia*
*3 Ivanovskiy Institute of Virology, Russia*

Carbon nanotubes (CNT) are one of promising nanotechnology products. Unique electronic properties, high mechanical strength, excellent flexibility and large specific surface area of nanotubes make them suitable for creating novel biocompatible composite materials for bio-nano-electronics application. Currently one of the major challenges for biotechnology is maintaining the exchange of electric signals between biological objects and electronic devices. CNTs can be used for neuron signal processing and transmission for surgery and electronic implants integration. CNT can also be used as transducers in biological molecular detectors and sensors.

In this work we investigate the possible technological routes for maintaining an electrical contact between biological objects and carbon nanotubes. In order to improve the contact between cells and CNTs the latter have to be functionalized by biological surfactant like protein, DNA, etc. Here we used the CNT/bovine serum albumin (BSA) composite. We demonstrate an increase in proliferation when a voltage of about 100 mV is applied to CNT/BSA film [1]. We also compare properties of nanotube films fabricated using two different techniques. One type of films was made by depositing CNTs from BSA solution while the second type was a CVD as-growth film. We investigated formation of the "artificial synapse" between CNT and neural cells [2]. We discovered that intensity of G-band Raman shift increases for CNT/BSA film at specified points under axon. We suggest this phenomenon to better signal propagation by ion concentration increasing.

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## Raman response of graphite intercalation compounds revisited

**P254**

Julio Chacón[1], Ludger Wirtz[2], A. Y. Ganin[3], M. J. Rosseinsky[3], and Thomas Pichler[1]

*1 Faculty of Physics, University of Vienna, Austria*
*2 Physics and Material Sciences Research Unit, University of Luxembourg, Luxembourg*
*3 Department of Chemistry, University of Liverpool, United Kingdom*

We present a detailed in-situ Raman analysis of Stage I to VI potassium graphite intercalation compounds (GICs). In the case of Stage I ($KC_8$), an intrinsic and a defect modulated Raman response was observed [1]. We prove that the intrinsic G-line of $KC_8$ is at 1510cm$^{-1}$, and it is strongly dependent on the actual defect content in the sample, which has important implications for the electron-phonon coupling responsible for superconductivity. From a comparison with Stage I $CaC_6$ and $LiC_6$, we highlight that the Raman active modes alone are not sufficient to explain the superconductivity within the electron-phonon coupling mechanism in $CaC_6$ and $KC_8$ [2]. The Raman response of Stage II ($KC_{24}$) is conformed by a single G-line at 1610cm$^{-1}$, which is a useful benchmark for the identification of the intercalation stage in highly doped GICs. In the case of Stage III to VI, the G-line exhibit two components plus a single 2D -line. We demonstrate the presence of two nearest layer environments: heavily charged graphene layers adjacent to an intercalant layer and basically uncharged graphene layers sandwiched between other graphene layers electronically decoupled [3]. This allow us to unambiguously identify the Raman response of strained charged and uncharged graphene layers and to correlate it to the in-plane lattice constant determined by XRD, which for instance can be used to identify for internal induced strain in nanoelectronic and optoelectronic devices as well as the local interfacial strain in graphene polymer composites on an absolute value.

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## Significant parameters on graphene synthesized by chemical vapor deposition using ethanol

**P255**

Ajjiporn Dathbun and S. Chaisitsak

*Department of Electronics Engineering, Faculty of Engineering, King Mongkut's Institute of Technology*
*Ladkrabang, Bangkok, 10520 Thailand (kcsutich@kmitl.ac.th)*

A high quality graphene film on a copper foil was successfully grown by a CVD process using ethanol as a carbon source. The effect of growth temperatures (650-850°C), reaction times (5-50 min), pressure (2-40 mbar) and post-CVD cooling process rates (slow-cooling, fast-cooling and fast-cooling under ethanol exposure) on the formation of graphenes was investigated by Raman spectroscopy and scanning electron microscopy (SEM). The graphene film deposited under the optimal conditions showed features of a high quality such as a high $I_{2D}/I_G$ ratio of ~8, a low $I_D/I_G$ ratio of 0.18 and a narrow full width half maximum (FWHM) of Lorentzian-shaped 2D peak of ~35 cm$^{-1}$. It was found that the quality of graphene film could be enhanced by optimizing the pressure, growth temperature and time, while the number of graphene layer was less sensitive to the cooling rate. However, the fast cooling process under ethanol exposure was found to be a key process for obtaining graphenes with a large domain size. The sheet resistance (Rs) and transmittances of graphene films transferred onto a glass substrate were ~2kΩ/sq and ~95%, respectively. These findings may help to fabricate high-quality and large-domain graphenes on a copper foil for electronic applications.

## P256

## A highly selective non-radical diazo coupling provides low cost semi-conducting carbon nanotubes

Léa Darchy[1], Nassim Hanifi[1], Fabien Vialla[2], Christophe Voisin[2], Pierre-Alain Bayle[3], Luigi Genovese[4], Caroline Celle[5], Jean-Pierre Simonato[5], Arianna Filoramo[1], Vincent Derycke[1], Pascale Chenevier[1,6]

*1 CEA Saclay, IRAMIS, Service de Physique de l'Etat Condense (URA 2464), Laboratoire d'Electronique Moleculaire, F-91191 Gif sur Yvette, France*
*2 Ecole Normale Superieure, Laboratoire Pierre Aigrain (UMR 8551), F-75005 Paris, France*
*3,4,5,6 CEA Grenoble, INAC-SCIB3 (UMR-E 3 CEA, UJF-Grenoble 1), INAC-SP2M4 (UMR-E 9001 CEA, UJF-Grenoble 1), LITEN-DTNM5, INAC-SPRAM6 (UMR 5819 CEA, CNRS, UJF-Grenoble 1), 17 rue des Martyrs, F-38054 Grenoble, France*

Despite their recognized potential for low cost, flexible and high frequency electronics and photovoltaic, semi-conducting carbon nanotubes (sc-CNTs) did not lead to industrial development yet because they are synthesized as a mixture with metallic carbon nanotubes (m-CNTs). Sorting has been widely studied but cost remains high. Here, the proposed CNT chemical treatment uses diazoether with unprecedented selectivity, avoiding m-CNT and sc-CNT separation. Conventional diazonium coupling, partly selective for m-CNTs, induces extinction of nanotube conductivity [1]. The diazoether proved 50 times more selective as shown by luminescence, Raman spectroscopy and electrical conductivity. Treated CNT solutions containing inactive m-CNTs and highly preserved sc-CNTs were used in transistors with highly increased ON/OFF ratio. Furthermore, the diazoether/CNT reaction is based on an unexpected coupling mechanism: a stoichiometric, radical-free reaction instead of a radical chain reaction for diazonium. This cheap and versatile treatment opens the way to large scale use in printed electronics, with here a demonstration of printed transistors.

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## P257

## The impacts of single-walled carbon nanotubes on soil microbial communities

Lixia Jin[1], Yowhan Son[2], Jared DeForest[3], Yu Jin Kang[4], Woong Kim[4], Haegeun Chung[1]

*1 Department of Environmental Engineering, Konkuk University, Republic of Korea (hchung@konkuk.ac.kr)*
*2 Division of Environmental Science and Ecological Engineering, Korea University, Republic of Korea*
*3 Department of Environmental and Plant Biology, Ohio University, USA*
*4 Department of Materials Science and Engineering, Korea University, Republic of Korea*

Due to rapid developments in nanotechnology, nanomaterials may be released into the soil environment with unknown consequences. The effects of single-walled carbon nanotubes (SWCNTs), a widely used nanomaterial, on soil microbial communities was investigated by incubation of soils treated with powder and suspended forms of SWCNTs. To determine changes in microbial community composition, phospholipid fatty acid (PLFA) profiles was analyzed at 25th day of the incubation experiment. The biomass of major microbial groups including Gram-positive, Gram-negative, and fungi showed a significant negative relationship with SWCNT concentration. The relative abundance of Gram-positive and Gram-negative bacteria showed a positive relationship with SWCNT concentration while that of fungi showed a negative relationship. Furthermore, SWCNT treatment at different concentrations significantly altered the soil PLFA profiles. Our results may serve as foundation for establishing scientific guideline on regulating the release of nanomaterials such as SWCNTs to the natural environment.

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## Graphene quantum point contacts in the ballistic regime

Paul Clark, Hendrik Ulbricht

*School of Physics and Astronomy, University of Southampton, Southampton, United Kingdom, SO17 1BJ*
*(p.clark@soton.ac.uk)*

Graphene offers a new and unique opportunity to recreate and adapt quantum optics experiments with electrons. Work in coherent manipulation of electrons has been historically focused on the quantum Hall regime in structured GaAs devices. Recent advances in substrates for graphene allow the investigation of quantum optics in the ballistic regime. Nano structuring graphene allows a direct method to control the allowed motional quantum states of electrons in such solids. A quantum point contact (QPC) is an important building block to realise quantum optics experiments in graphene as it can act as a coherent source and as an electronic beam splitter. Graphene devices have been fabricated with structures for a QPC using both electron beam and Helium ion lithography with a varying constriction width from 250nm down to 8nm. Results from electrical measurements made at 4.2K will be presented and discussed.

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## MWNT-Ovalbumin and MWNT-CpG Interactions in Vaccine Formulation

João P. Coelho[1], Ester F. de Oliveira[1], Paula C.B. de Faria[2], Sara D. da Costa[3], Cristiano F. Leite[3], Marcos A. Pimenta[3], Luiz O. Ladeira[3], Adelina P. Santos [1], Ricardo T. Gazzinelli[3,4], Clascídia A. Furtado[1,*]

*1 Centro de Desenvolvimento da Tecnologia Nuclear – CDTN/CNEN, Brazil (*clas@cdtn.br)*
*2 Universidade Federal de Uberlândia - UFU, Brazil*
*3 Universidade Federal de Minas Gerais - UFMG, Brazil*
*4 Instituto Renê Rachou - Fundação Oswaldo Cruz, Brazil*

Carbon nanotubes (CN) have been considered for a variety of therapeutic and drug delivery applications due to characteristics like internalization capacity by different type of cells, unique ability to incorporate multiple functionalization and intrinsic stability and structural modifiability that allow a long circulation time in the body. However, fundamental questions concerning for example the CN-biomolecules interaction, the mechanism of CN action and toxicological effects need to be answered. Herein, we describe the non-covalent interaction between the protein ovalbumin (OVA) and the oligonucleotide CpG and multi-walled carbon nanotubes (MWNT) by Raman, FTIR and UV-Vis spectroscopies, circular dichroism and transmission electronic microscopy, aiming to understand the hybrid system (MWNT-OVA-CpG) performance in a tested vaccine formulation for cancer. All the hybrids obtained showed high stability in aqueous media and binding site selectivity. While CpG interacts with both MWNT and oxidized MWNT (Ox-MWNT) via $\pi$-stacking, the interaction between the nanotubes and the OVA seems to occur mainly via $\pi$-stacking with MWNT and be dominated by an electrostatic character with Ox-MWNT. The interaction with carbon nanotubes alters the conformational freedom of both biomolecules, mainly OVA, weakening their intramolecular hydrogen bonds and better defining the vibrational bands associated with each one of the protein secondary structure.

**P260**

# Catabolic intracellular compartments enable degradation of carbonaceous nanomaterials

Jennifer Conroy[1,2], Navin K. Verma[1,2], Ronan J. Smith[2], Ehsan Rezavani[2], Georg S Duesberg[2], Jonathan Coleman[2], and Yuri Volkov[1,2]

*1 Institute of Molecular Medicine, Trinity College Dublin, Ireland (conroyje@tcd.ie)*
*2 Centre for Research on Adaptive Nanostructures & Nanodevices, Trinity College Dublin, Ireland.*

Advanced conductive nanomaterials such as, single walled carbon nanotubes (SWCNT), graphene and their derivatives are being used in many cutting-edge electronic, energy and medical devices due to their unique physicochemical properties. However, the potential impact of these new engineered nanomaterials on human health following exposure during manufacture, use or at the end of their lifecycle is uncertain. Here, we investigated the interaction of SWCNT, graphene and their enabled thin films with primary human macrophages isolated from healthy donors. Macrophages are one of the first lines of defense in the body against foreign invaders. High content screening and confocal microscopic analysis indicated no signs of acute cytotoxicity due SWCNT, graphene or their enabled thin films. Further analysis using a real time impedance technique revealed a low level toxic cellular response which is probably due to a reduction in cellular adhesion. Raman spectroscopic mapping confirmed cellular uptake of SWCNT and graphene. Electron microscopy demonstrated SWCNT to be contained within double membrane cytoplasmic vesicles whereas graphene was contained within single walled vesicles. These data suggest the induction of two different catabolic pathways, an autophagic and lysosomal response respectively, which were verified by biochemical and microscopic techniques. This study suggests that in-depth characterisation of possible biological effects of these conductive nanomaterials at the molecular level is required for their safe applications.

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# Tailoring electronic structure of $MoS_2$ by electrostatic doping

Nguyen Thanh Cuong[1,3], Minoru Otani[1,3], Susumu Okada[2,3]

*1 National Institute of Advanced Industrial Science and Technology (AIST), Japan*
*(cuong-nguyen@aist.go.jp)*
*2 University of Tsukuba, Japan*
*3 CREST-JST, Japan*

Transition metal dichalcogenide molybdenum disulfide (MoS2) has been attracted a lot of research interests because of its 2-dimensional layer structure, intrinsic band-gap, and optical properties [1]. Recent experiments observed the superconductivity in this insulator material at a transition temperature of 11 K, by using the electrostatic electron doping technique [2,3]. However, the mechanism of this superconductivity behavior is still unclear. Therefore, in this work, we investigate the electronic structure of few-layer MoS2 under electrostatic electron doping based on the first-principles total-energy calculations. We find that under the electron doping process, the unoccupied nearly free (NFE) states shift downward, and finally crosses the Fermi level at 0.07 electron/cell doping due to the strong electric field induced by accumulated charge near the surface. Because of this shift to lower energy, the NFE state acts as the conducting channel for the injected carrier. On the other hand, the NFE states are not only distributed at atomic sites but also in vacuum region where the atoms are absent. These results suggest that the NFE state plays an important role in the field-induced superconductivity of $MoS_2$ [2,3].

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## Graphene growth on copper using gradients of temperature and carbon concentration

J. Ek-Weis, T. H. R. Cunha, R. G. Lacerda, A. S. Ferlauto

*Department of Physics, ICEx, Universidade Federal de Minas Gerais – Belo Horizonte*
*(ekweis@fisica.ufmg.br)*

Nowadays, one of the main methods to synthesise graphene is by chemical vapour deposition, CVD, of methane on copper, where temperatures in the range 800-1000 °C are typically used. Usually, the optimal growth conditions are found by many trial experiments using different atmospheres and temperatures. However, for a complete understanding of the growth mechanism of graphene on copper a clear picture of the influence of each parameter, such as temperature and pressure, is necessary. To achieve this goal, we present a study on the influence of temperature and carbon concentration on individual samples by using gradients of temperature and/or carbon concentration. This guarantees that all the growth conditions are exactly the same apart from the investigated temperature and carbon concentration.

A cold-wall CVD chamber is used. A temperature gradient is created by forming the copper foil into different geometrical shapes, where the end closest to the heater becomes significantly hotter than the other end. It is found that the size and density of the graphene grains depend on the temperature.

Using a gradient of carbon concentration, samples which are partly fully covered with graphene and partly with sparse growth are synthesised. Raman studies of these samples show that the D/G ratio is minimised for the fully covered growth, where the G'/G ratio is maximised. The G and G' peaks shift along the gradient, showing that there is a strain difference between the individual grains and the fully covering graphene. The results provide insights on graphene grain nucleation and growth that can help the optimisation of graphene CVD synthesis.

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## Carbon nanotubes-based electrodes and their post-functionalization for biosensing applications

Sandra Enriquez Sansaloni[1,2], Alain Penicaud[2], Francesco Paolucci[1]

*1 Department of Chemistry "G. Ciamician", Via Selmi 2, University of Bologna, Italy*
*2 Centre de Recherche Paul Pascal, CNRS, Bordeaux, Université of Bordeaux 1, France*

Due to their small size, high aspect ratio and excellent electrochemical properties, carbon nanotubes continue to attract high interest as components in biosensors. As it is well reported, electrodes made of carbon nanotubes have electrochemical properties that are equal or superior to most other electrodes [1]. They are promising materials for sensing applications due to several intriguing properties. In particular, their large length-to diameter aspect ratios provide for high surface-to-volume ratios. Moreover, they have an outstanding ability to mediate fast electron-transfer kinetics for a wide range of electro active species, such as hydrogen peroxide or NADH. Here we show carbon nanotubes-based electrodes made from solutions of single wall carbon nanotubes in DMSO [2] via formation of polyelectrolyte salts. They allow us to maintain aspect ratio and electrical properties of tubes with no need of surfactant or sonication steps. The transferring of the films on polystyrene or polyethylene terephthalate substrates yields ready-to-use carbon nanotubes-based electrodes.

Their covalent or non-covalent post-functionalization on the surface, allow us to link specific properties –specific functional groups- for further applications; e.g. diazonium chemistry which permits the modification by aryl groups it is used for the covalent modification of carbon nanotubes either by electro grafting or spontaneous grafting [3, 4].

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## Integration of two-dimensional atomic crystal multi-heterostructures for ultrahigh responsivity photodetector

Hua Xu, Juanxia Wu, Yabin Chen, Jin Zhang*

*Center for Nanochemistry, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China (*jinzhang@pku.edu.cn)*

Two-dimensional atomic crystal, such as graphene, h-BN, $MoS_2$, etc. have attracted great attention in recent years because their superior electrical and optical properties make them an excellent candidate for future optoelectronics. However, each material has both spotlight merit and fatal weakness, for example, graphene has high carrier mobility but low band gap, $MoS_2$ has large band gap but low carrier mobility, which limit their potential applications.[1] Here, we take a graphene-$MoS_2$ heterstructure photodetector and a h-BN/$SiO_2$ substrate engineered graphene photodetector as examples to introduce how we tactfully integrate graphene with other materials to complement they merit and weakness.

As we know, graphene based photodetector has high responsive rate for it's high mobility, but low gain due to it's low absorption (2.3%), and no wavelength selectivity. In contrast, $MoS_2$ based photodetector has large absorption and wavelength selectivity for it's large and thickness dependent band gap, but slow responsive rate.[2] For complementing the merit and the weakness of these materials, we constructed a graphene/$MoS_2$ heterstructure device, using $MoS_2$ as sensitizer to absorb light, graphene as expressway for carries transport, the photo carriers are transferred to a graphene transport layer. In this case, light absorption and charge-transport processes are decoupled in one device with two materials. Both the response rate and gain are greatly increased in our graphene-$MoS_2$ heterstructure photodetector. Moreover, benefit from the intrinsic and the p-doping of graphene on h-BN and $SiO_2$ substrate, respectively, h-BN/$SiO_2$ substrate engineered graphene photodetector with high responsivity were obtained. Therefore, integration of two-dimensional atomic crystal multi-heterostructures opens the way to novel and high performance optoelectronics.

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P265

## Electrical and thermal properties of morphology-controlled carbon nanotube/graphene aerogels for energy storage devices

Zeng Fan[1], Daniel Zhi Yong Tng[1], Clarisse Sabrina Lim Xue Ting[1], Pengfei Xiao[1], Son T Nguyen[1], Amy Marconnet[2], Bo Sun[1], Hai M. Duong[1]

*1 Mechanical Engineering Department, National University of Singapore, Singapore*
*2 Mechanical Engineering Department, Purdue University, USA*
*(mpedhm@nus.edu.sg)*

We present a cost effective method to develop graphene aerogels from graphite at low temperature (from 45°C) through the modified Hummers and chemical reduction methods using three reducing agents (L-ascorbic acid, $NaHSO_3$ and HI) without any binder. The nanostructured graphene aerogels have large surface area ($577 m^2/g$) and the morphology is well-controlled by optimizing the graphene oxide concentrations, reaction and annealing conditions. Electrical conductivities of the graphene aerogels measured by a 2-probe method increase by up to a factor of four after annealing at 400°C for 5h under an inert environment. The thermal conductivity of the graphene aerogel is measured with a comparative infrared microscopy technique and is ~0.6W/m. K. The addition of CNTs to the aerogels enhances the electrical conductivity, and by controlling the concentration of CNTs, the optimal morphology for electrical and thermal conduction through the CNT/ graphene aerogels is explored. Electrodes fabricated from the CNT/ graphene aerogels can sustain higher power density than conventional batteries and high energy density than conventional dielectric capacitors, as well as having excellent stability when cycled.

## Investigation of the viability and proliferative activity of nerve cells on the CNT films obtained by vapor deposition

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I.A. Gayduchenko[1], G.E. Fedorov[1], M.Yu. Presnyakov[1], I.A. Suetina[2], M.V. Mezentceva[2], I.I. Bobrinetskii[3]

*1 NRC "Kurchatov Institute", Russia (igorandg@gmail.com)*
*2 The D.I. Ivanovsky Institute of Virology of the Ministry of Health and Social Development of The Russian Federation, Russia*
*3 National Research University of Electronic Technology, Russia*

Functional conjugation of biological systems with electronic systems of information processing and transmission is now attracting attention of developers working on the creation of hybrid nanoelectronic devices, including biosensors. One of the possible interface components are carbon nanotubes (CNT), demonstrating a high biocompatibility, chemical stability and unique electrical properties [1,2]. This work aims at developing methods for the synthesis of CNT films, and clarification of the influence of the synthesis parameters of CNTs on the viability and proliferative activity of the nerve cells grown. Thin CNT films were fabricated by chemical vapor deposition (CVD) technique on silicon oxidized wafers and quartz substrates. We investigated the structural properties of the films, and measured their resistance and transmittance.

The nerve cells were grown on the obtained CNT-films. Viability and proliferative activity of the cells grown, have been studied by MTT method and via visualizing the cultures by optical and electron microscopy. Possible toxic effect of the used catalyst on the cells is also discussed. The results show that the use of CNTs hardly reduces the viability and proliferative activity of cells and don't affect the cell morphology. That means no toxic effect of carbon nanotubes on nerve cells, which, combined with good electrical conductivity of CNTs makes these hybrid systems a promising material for biosensors.

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## Preparation and properties of graphene composite films based on water-soluble organic conjugated systems

P267

Jianxin Geng

*Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, 29 Zhongguancun East Road, Haidian District, Beijing 100190, China (jianxingeng@mail.ipc.ac.cn)*

Owing to the fact that graphene films and graphene composite films have many potentially important applications in the areas of field-effect transistors, sensors, transparent conductive films [1-2], preparation of graphene films is a key goal of research efforts. In our study, we make use of the π-π interactions between graphene and water-soluble organic conjugated systems such as porphyrins and polythiophenes to stabilize the chemically converted graphene (CCG) during chemical reduction of exfoliated graphene oxide, leading to stable suspension of CCG in water. We prepared CCG films of various thicknesses by using the CCG suspension through the vacuum filtration approach [3]. The thickness of the films was readily controlled by varying the volume of the suspension employed for film preparation. Such CCG films also turned out to be applicable as transparent electrode in polymer solar cells [4].

We also prepared CCG composite films using layer-by-layer assembly method, which takes advantage of the π-π and/or electrostatic interactions between negatively charged graphene sheets and positively charged organic conjugated systems. Due to the photoinduced electron transfer from the organic conjugated systems to the CCG sheets, the CCG composite films show applications in areas such as photoelectrochemical cells and photoresponse detection [5-6].

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# Formation of nitrogen-doped graphene nanoscrolls by adsorption of magnetic $\gamma$-$Fe_2O_3$ nanoparticles

Tiva Sharifi[1], Eduardo Gracia-Espino[1,2], Hamid Reza Barzegar[1], Xueen Jia[1], Florian Nitze[1], Guangzhi Hu[1], Thomas Wågberg[1,*]

*1 Department of Physics, Umeå University, 901 87 Umeå, Sweden (*thomas.wagberg@physics.umu.se)*
*2 Department of Chemistry, Umeå University, 901 87 Umeå, Sweden*

Graphene nanoscrolls are Archimedean-type spirals formed by rolling single layer graphene sheets. They are conceptually interesting due to their unique structure and understanding their formation can give important information on the manipulation and characteristics of various carbon nanostructures. Here, we present a 100 % efficient process to transform nitrogen doped reduced graphene oxide sheets into homogeneous nanoscrolls by the decoration with magnetic maghemite, $\gamma$-$Fe_2O_3$, nanoparticles. By performing a large number of control experiments, and extensive *ab initio* calculations we conclude that the rolling is initiated by the strong adsorption of maghemite nanoparticles at nitrogen defects in the graphene lattice, and their mutual magnetic interaction. The formation of the nanoscrolls is fully reversible and upon removal of the maghemite nanoparticles, the nanoscrolls return to open sheets. Besides, supplying information on the rolling mechanism of graphene nanoscrolls, our results also provide important information on the stabilization of iron oxide nanoparticles.

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# Domain structure in graphene islands grown on copper foil by chemical vapor deposition

Kenjiro Hayashi, Ayaka Yamada, Shintaro Sato, Naoki Yokoyama

*Collaborative Research Team Green Nanoelectronics Center (GNC), AIST, Japan*
*(hayashi.kenjiro@aist.go.jp)*

Tailoring large-scale single-crystalline graphene on Cu surface by means of chemical vapor deposition is a crucial issue for its application to electronic devices. Since self-limited graphene growth on a Cu surface is governed by surface diffusion processes, understanding the role of surface is important. Previous studies have made great efforts to enlarge the graphene domain size based on a strategy for suppressing the island density [1] and/or that for controlling the orientation of each graphene island with respect to the atomic arrangement of underlying epitaxial Cu(111) film [2]. However, very few studies have focused on the domain structure within an individual island. It remains unclear whether a graphene island consists of a single domain or multiple domains, which may depend on the surface orientation and growth conditions.

In this study, we investigated the initial stage of graphene growth on poly-crystalline Cu foil under various growth conditions to clarify the correlation between the domain structure of an island and the orientation of an individual Cu grain surface. It has been revealed that the four-lobed and the hexagonal shaped islands were grown on (001) and (111)-oriented Cu surfaces, respectively. Each island was found to align with the specific direction. Moreover, the graphene lattice has a commensurate relationship with the atomic arrangement of the surface for both the four-lobed and the hexagonal shaped islands. The graphene islands grown at lower temperature or at lower partial pressure of $H_2$, however, showed poly-crystalline nature consisting of small domains. This work was supported by JSPS through the FIRST Program, initiated by CSTP, Japan. This work was partly conducted at the Nano-Processing Facility supported by ICAN, AIST, Japan.

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# Nickel sulfides/nitrogen-doped graphene composites: phase-controlled synthesis and high performance anode materials for lithium ion batteries

N. Mahmood, C. Zhang, Y. Hou*

*Department of Materials Science and Engineering, College of Engineering*
*Peking University, Beijing 100871, China (*hou@pku.edu.cn)*

Nickel sulfides have great potential applications in lithium ion batteries (LIBs) due to the peculiar electronic properties and high theoretical capacities. However, the synthesis of pure phase $Ni_3S_4$ is a great challenge due to the presence of mixed-phases, which has become a major obstacle to explore its potential applications. Herein, we report a facile, one-pot, hydrothermal synthesis to produce phase-controlled $Ni_3S_4$ nanoparticles (NPs) grown on nitrogen-doped graphene (NG) sheets. Annealing treatment was further used to achieve the better electrochemical coupling of $Ni_3S_4$/NG composite. Interestingly, we found that the annealing process at 350 °C resulted in the formation of another high temperature stable phase of nickel sulfide, $NiS_{1.03}$/NG. To develop the applications of nickel sulfides in LIBs, nickel sulfides/NG composites were designed as anode materials, which exhibited not only high reversible capacity but also extraordinary cyclic performance and rate capability. It is worth noting that $Ni_3S_4$/NG composites showed 98.87% capacity retention with a discharge capacity of 1323.2 mAh/g at 100th cycle. It is expected that the synthetic methodology developed here would be a general strategy for the phase-controlled synthesis of other metal chalcogenides/NG composites. [1,2]

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P271

# Energy barrier effect on the hysteresis of graphene field-effect transistors

Dong Hoon Hwang[1,3], In Cheol Nam[3,4], Tae Geun Kim[1,3], Chan-Wook Baik[2], Sung Woo Hwang[1,2], and Sangsig Kim[3]

*1 Research Center for Time-domain Nano-functional Device, Samsung Advanced Institute of Technology,Yongin 446-712, Korea (swnano.hwang@samsung.com)*
*2 Frontier Research Laboratory, Samsung Advanced Institute of Technology, Yongin 446-712, Korea*
*3 Department of Electrical Engineering, Korea University, Seoul 136-713, Korea*
*4 DRAM Product Engineering Team, Memory Division, Samsung Electronics Co., Hwaseong 445-701, Korea*

We studied the effect of energy barrier on the hysteresis by observing the position of Dirac point. The graphene field-effect transistors are fabricated by bottom-up process, and measured under various source-to-drain voltages (VSD) in a continuous bidirectional sweep of gate voltage. It is found that the Dirac point depends on VSD as temperature [1], and the difference between the forward and reverse sweep decreases when VSD increases. These results show a hysteresis on VSD in the graphene field-effect transistor. We suggest that the channel carrier is not completely exhausted by the one-directional sweep, assuming the carrier is confined among the energy barriers of metal-to-graphene. In addition, the remaining carrier is thought to be recombined by the tunneling mechanism when the high VSD increases the electric field in the depletion region. The barrier effect is, therefore, regarded as one of origins of the hysteresis. The difference of Dirac Point by the bidirectional sweep of VSD is also similar to the previous reported tunneling current model [2].

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## Enhanced electric double layer capacitance of new poly sodium 4-styrenesulfonate intercalated graphene oxide electrodes

Hae Kyung Jeong

*Department of Physics, Daegu University, Republic of Korea (outron@gmail.com)*

We synthesized a new composite of poly sodium 4-styrenesulfonate intercalated graphene oxide for energy storage devices by controlling oxidation time in the synthesis of graphite oxide. Electrochemical properties of the new composite were investigated in an aqueous electrolyte and compared to those of previous composites, proving high performance of the electric double layer capacitor of the new composite. Specific capacitance was improved from 20 F/g of the previous composites to 88 F/g of the new composite at the current density of 0.3 A/g. The cycle test confirmed that the capacitance retention was 94 % after 3000 cycles, providing excellent cyclic stability. The new composites with high cyclic stability, prominent performance as electric double layer capacitor, and even low resistance could be an excellent carbon based electrode for further energy storage devices.

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## Local investigation of reduction process of graphene oxide using electrostatic force microscopy

Huiseong Jeong, Ji-Yong Park*

*Department of Physics and Division of Energy Systems Research, Ajou University, Korea (*jiyong@ajou.ac.kr)*

Graphene oxide (GO) has been actively studied as a promising nanomaterial due to simple chemical synthesis and large aqueous solubility. GO can be reduced thermally or chemically resulting in similar electrical and optical properties to pristine graphene. The reduction process of GO has been typically studied with XPS, Raman, and electrical transport measurements which require thick films or large flakes of GO. These measurements give information about averaged properties of GO. Changes in local electrical properties of GO with reduction process can help to understand the reduction process better.

In this study, individual GO flakes, synthesized by Hummer's method, are deposited onto 90 nm-thick-$SiO_2$/Si substrates. We utilize electrostatic force microscopy (EFM) with high spatial resolution and capability to probe local electrical properties to monitor local conductance changes in the individual GO flakes at various stages of reduction process by controlling the process temperature and time. We can monitor the changes of local conductance inside each GO flake as it reduces with EFM. We found significant inhomogeneities in original GO flakes and investigated evolution in local electrical characteristics of GO with different kinds of reduction processes with EFM.

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## Surface-area-dependent effects of carbon nanotubes on soil enzyme activity and microbial biomass

Lixia Jin[1], Yowhan Son[2], Tae Kyung Yoon[2], Yu Jin Kang[3], Woong Kim[3], Haegeun Chung[1]

*1 Department of Environmental Engineering, Konkuk University, Seoul 143-701, Republic of Korea (hchung@konkuk.ac.kr)*

*2 Department of Environmental Science and Ecological Engineering, Korea University, Seoul, 136-713, Republic of Korea*

*3 Department of Materials Science and Engineering, Korea University, Seoul, 136-713, Republic of Korea*

Commercial development of single-walled carbon nanotubes (SWCNTs) may lead to the discharge of SWCNTs to the soil environment with unknown consequences. We evaluated the impacts of powder and suspended forms of SWCNTs at 0, 30, 100, 300, 600, and 1000 μg g$^{-1}$ soil on soil enzyme activity and microbial biomass through a 3-week soil incubation experiment. The activities of cellobiohydrolase, β-1,4-xylosidase, β-1,4-N-acetylglucosaminidase, L-leucine aminopeptidase, and acid phosphatase which are involved in decomposition of key compounds in terrestrial ecosystems, and microbial biomass were measured. SWCNTs of concentrations at 300-1000 μg g$^{-1}$ soil significantly lowered the activities of most enzymes and microbial biomass. We found that SWCNTs showed comparable negative effects on soil enzyme activity and biomass at lower concentrations than those of multi-walled carbon nanotubes [1]. Our results also showed that CNT surface area has significant negative relationship with relative enzyme activity and biomass. Thus, we suggest that greater microorganism-CNT interactions could increase the negative effect of CNTs on soil microorganisms [2].

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## Self-assembling graphene grating synthesized directly on a dielectric substrate

Tommi Kaplas, Martti Silvennoinen, Kimmo Päiväsaari, and Yuri Svirko

*University of Eastern Finland, Department of Physics and Mathematics, P.O.Box-111, FI-80101, Finland (tommi.kaplas@uef.fi)*

Graphene has recently found a number of applications in photonic and optoelectronic components including transparent electrodes, saturable absorbers, ultrafast transistors and optical modulators [1]. However, until now, incorporation of graphene into photonic and optoelectronic devices requires its transferring from metallic catalyst used for its synthesis to an insulator or semiconductor substrate. Moreover in order to achieve monolithic integration graphene should be deposited on the prescribed location on e.g. the $SiO_2$ wafer. Here we propose a technique for position-selective graphene growth directly on the pre-patterned dielectric substrate. This transfer free technique can be employed for introducing graphene elements into optical gratings or planar waveguides.

In the experiment, we prepared binary gratings with chancing periodicity (from 400 nm to 4 μm) and height (from 150 nm to 500 nm) by using electron beam lithography and reactive ion etching. This pre-patterned substrate was covered by a 200 nm thick copper film and was employed as a substrate in the chemical vapor deposition (CVD) process (see Ref. [2] for details). During the CVD process the Cu film liquidizes and forms a network prescribed by the morphology of the substrate and the temperature, while a few layer graphene will grow both on copper-vacuum and copper-silica interfaces [2,3]. Thus the graphene network will be "imprinted" on the silica substrate and can be revealed by removing copper by plasma and wet etching. The fabricated graphene network was characterized by scanning electron microscope and Raman spectroscopy.

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**P276**

# Simulation on thermoelectric power of SWNT buckypapers

Teppei Kato[1], Shinji Usui[2], Takahiro Yamamoto[1]

*1 Department of Electrical Engineering, Tokyo University of Science, Japan*
*2 QuantumWise Japan KK, Japan*

An SWNT buckypaper is expected to be a ubiquitous thermoelectric material with large thermoelectric power factor. Recent experiments reported that the temperature dependence and doping dependence of Seebeck coefficient $S$ (or thermoelectric power) of SWNT buckypapers are essentially different from those of an individual SWNT [1,2]. However, such unusual behaviors of $S$ of SWNT buckypapers have not been understood yet. In this study, we clarify the $S$ of SWNT buckypapers by performing the first-principles simulation using the software AtomistixToolKit based on density-functional theory and the none-equilibrium Green's function method [3]. We consider that the above unusual behaviors originate from the contacts between SWNTs, and we set a simulation model consisting of the laterally-contacted two SWNTs. The obtained results are as follows

(i) $S$ exhibit larger value of the order of 100μV/K at room temperature.
(ii) The sign of $S$ can change at low temperature.
(iii) The temperature dependence of $S$ is sensitive to small changes of the chemical potential.

These simulation results are in good agreements with experimental results and can be understood in terms of Mott's formula.

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# Enhancement of integrity of graphene transferred by interface energy modulation

Un Jeong Kim, Jaehyun Hur, Sangmo Cheon, Dae-Young Chung, Yeonsang Park, Young-Geun Roh, Jineun Kihm, Jaesoong Lee, Sang Won Kim, Sungwoo Hwang, and Chang-Won Lee

*Frontier Research Lab, Samsung Advanced Institute of Technology (SAIT), P. O. Box 111, Suwon 440-600, Republic of Korea*

We report on the systematic studies of the parameters governing the integrity of graphene film during general "wet" transfer from a thermodynamic point of view. We chose polystyrene (PS) as a test carrier material and attempted to use seven different solvents to find optimal conditions for the graphene transfer from a catalyst film to a desired substrate without defects. When parameterizing the conventional chemical properties of solvents, the boiling points and surface tension were found to be critical in determining the quality of the transferred graphene. During the formation step of a conformal PS film on a graphene surface before catalyst etching, a solvent with a boiling point over ~130°C was essential. During the following PS film removal step, a solvent with surface tension higher than approximately 30 dyne/cm led to the formation of a continuous graphene film without cracks and holes. In addition, a high spin-coating velocity and lower concentration of PS in the solvent enhanced the quality of a transferred graphene film. The UV treatment of $Si/SiO_2$ (100 nm) was also found to improve the adhesion of the graphene on substrates. By electrical characterization, morphological differences were found to affect the electrical properties markedly.

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## How graphene slides: measurement and theory of strain-dependent frictional forces between graphene and $SiO_2$

Alex Kitt[1], Zenan Qi[2], Sebastian Remi[1], Harold Park[2], Bennett Goldberg[1,3] and Anna Swan[1,3]

*1 Physics, Boston University, USA (alkitt@bu.edu)*
*2 Mechanical Engineering Boston University, USA*
*3 Electrical and Computer Engineering, Boston University, USA*

Graphene exhibits extreme elasticity and impermeability to gases. As a pure two dimensional material, graphene's interactions with its supporting substrate are unique. Amontons' first law states that macroscopic friction is proportional to the applied load, justified by arguing that increasing the load increases the microscopic contact area between two surfaces. Graphene, however, because of its ultrastrong adhesion and low bending rigidity requires no load to achieve nearly perfect conformation to the nanoscale topography of its substrate. Hence, the friction between graphene and the substrate might be expected to exhibit an atypical load dependence.

Using Raman spectroscopy of circular, graphene-sealed microchambers under variable external pressure, we demonstrate that graphene is not firmly anchored to the substrate when pulled. Analyzing Raman G band line scans with a continuum model extended to include sliding, we extract the pressure dependent sliding friction between the $SiO_2$ substrate and mono-, bi-, and trilayer graphene. The sliding friction for trilayer graphene is directly proportional to the applied load, but the friction for monolayer and bilayer graphene is inversely proportional to the strain in the graphene, which is in violation of Amontons' law. We attribute this behavior to the high surface conformation enabled by the low bending rigidity and strong adhesion of few layer graphene.

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## Synthesis of multi-layer graphene on epitaxially-grown metal catalyst film and its electrical properties

Daiyu Kondo, Haruhisa Nakano, Bo Zhou, Ichiro Kubota, Junich Yamaguchi,
Kenjiro Hayashi, Shintaro Sato, and Naoki Yokoyama

*Collaborative Research Team Green Nanoelectronics Center (GNC), AIST (kondo.daiyu@aist.go.jp)*

Nano-carbon materials including graphene are a candidate for new wiring materials for the future LSIs due to their excellent electrical properties [1]. Among nano-carbon materials, we focus on multi-layer graphene, and its application to LSI interconnect is discussed in this study. Recently, results regarding multi-layer graphene wiring obtained by chemical vapor deposition (CVD) or a related growth method have been reported [2, 3]. Although high-quality graphene is necessary for LSI interconnect, the electrical resistivity of graphene obtained by CVD is usually worse than that of highly oriented pyrolytic graphite (HOPG) by more than one order of magnitude due to its poor crystallinity. To solve this problem, we employed an epitaxial cobalt film to grow high-quality multi-layer graphene by thermal CVD method. A cobalt (Co) catalyst film with a thickness of 200 nm was deposited on a sapphire substrate by the conventional sputtering method at 500 degree C. Multi-layer graphene was then grown on the Co film by CVD at 1000 degree C using $CH_4$ diluted by $H_2$/Ar as the source gas. After synthesis, the multi-layer graphene obtained was evaluated by Raman spectroscopy. Raman spectra suggest that high-quality multi-layer graphene with the AB-stacked structure was synthesized. The measurement of electrical properties was then performed at room temperature. It was found that the resistivity of the multi-layer graphene was as good as that of HOPG. This research is granted by JSPS through FIRST Program initiated by CSTP. A part of this work was conducted at the Nano-Processing Facility, supported by IBEC Innovation Platform.

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**P280**

# Peculiarities of CVD graphene synthesis on nickel

Kondrashov Ivan, Rusakov Pavel, Rybin Maxim, Anatoliy Pozharov and Elena Obraztsova

*A.M. Prokhorov General Physics Institute, Vavilov str. 38, Moscow, Russia,119991*
*(navi.soul@gmail.com)*

Graphene is one of the most interesting carbon nanomaterials. It is a two-dimensional hexagonal lattice of carbon atoms. Researches in graphene are very active nowadays because of its unique electrical and optical properties and an immense potential for applications in electronics, sensors, solar cells, and many others. A chemical vapour deposition method for graphene synthesis on metal substrate is a very promising approach for fabrication of large-scale and high quality graphene films. A variety of metals can be used for CVD synthesis of graphene. The most popular of them are copper and nickel. Copper is used for synthesis of the multi-layer graphene films and nickel for synthesis of one-layer and multi-layer graphene. Therefore, it is very important to control the synthesis process for obtaining the desired number of graphene layers.

Thereby in this work we present the detailed investigation of CVD method of synthesis of graphene on polycrystalline nickel foils from the gas mixture of methane, hydrogen and argon[1,2]. We heated the metal foil by Joel effect with a direct input of an electric current. The heating of substrate starts after a methane injection in the chamber. Additionally to standard synthesis parameters as pressure, methane concentration, temperature, we also observed a change in resistance of the nickel foil during the experiment. The final number of graphene layers can be controlled via monitoring the resistance changes during synthesis.

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**P281**

# Poking from both sides – Reshaping the graphene landscape via face-to-face dual-probe microscopy

Franz Eder, Jani Kotakoski, Katharina Holzweber, Clemens Mangler, Viera Skakalova,
and Jannik Meyer

*Department of Physics, Universität Wien, Boltymanngasse 5,1090 Wien, Austria*
*(jani.kotakoski@iki.fi)*

In two-dimensional samples, all atoms are at the surface and thereby exposed for probing and manipulation by physical or chemical means from both sides. Here, we show that we can access the same point on both surfaces of a few-layer graphene membrane simultaneously, using a dual-probe scanning tunneling microscopy (STM) setup. At the closest point, the two probes are separated only by the thickness of the graphene membrane. Our study builds on the previous works on out-of-plane deformations in suspended graphene induced by STM tips and the gate voltage-driven switching between convex and concave forms.

We first demonstrate how an STM probe can impose a similar switch on few-layer graphene, and in both directions. Then, we place another probe at the same position but on the other side of the sample. With varying conditions on the first (stationary) probe, the second (scanning) probe will observe one of two landscapes: either a small point-like feature or a significantly larger mountain. These are identified as two regimes where the initial deformations of the membrane are either maintained or stretched out. Finally, by displacing and retracting the second probe we demonstrate an accurate control over the local height of the membrane. This allows us to directly measure the deformations induced by one STM probe on a free-standing membrane with an independent second probe. We reveal different regimes of stability of few-layer graphene, and show how STM probes can be used as tools to shape the membrane in a controlled manner. Our work opens new avenues for the study of mechanical and electronic properties of two-dimensional materials.

## 2D transition-metal dichalcogenides: doping, alloying and electronic structure engineering using electron beam

**P282**

H.-P. Komsa[1], S. Kurasch[2], J. Kotakoski[3], O. Lehtinen[1,2], U. Kaiser[2], and A.V. Krasheninnikov[1,4]

*1 Department of Physics, University of Helsinki, Finland*
*2. Central Facility for Electron Microscopy, Ulm University, Germany*
*3 Department of Physics, University of Vienn, Austria*
*4 Department of Applied Physics, Aalto University (arkady.krasheninnikov@aalto.fi)*

By combining first-principles simulations with high-resolution transmission electron microscopy experiments, we study the evolution of atomically thin layers of transition metal dichalcogenides (TMDs) under electron irradiation. We show that vacancies produced by the electron beam agglomerate and form line structures, which can be used for engineering materials properties. We also study the radiation hardness of 2D TMD materials [1]. We further show that TMDs can be doped by filling the vacancies with impurity atoms. We also study the stability and electronic properties of single layers of mixed TMDs, such as $MoS_{2x}Se_{2(1-x)}$, which can be referred to as 2D random alloys [2]. We demonstrate that 2D mixed ternary $MoS_2$/$MoSe_2$/$MoTe_2$ compounds are thermodynamically stable at room temperature, so that such materials can be manufactured by CVD or exfoliation techniques. By applying the effective band theory approach we further study the electronic structure of the mixed ternary 2D TMD compounds and show that the direct gap in these material can continuously be tuned. Using GW first-principles calculations for few-layer $MoS_2$, we further study [3] the effects of quantum confinement on the electronic structure of this layered material. By solving the Bethe-Salpeter equation, we evaluate the exciton energy in these systems. Our results are in excellent agreement with the available experimental data. Exciton binding energy is found to dramatically increase from 0.1 eV in the bulk to 1.1 eV in the monolayer. The fundamental band gap increases as well, so that the optical transition energies remain nearly constant.

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## Tailored proteins in graphene biosensors

**P283**

Katri Kurppa[1], Markku Kainlauri[2], Sanna Arpiainen[2], Miika Soikkeli[2], David Gunnarsson[2], Päivi Laaksonen[1], Mika Prunnila[2], Markus Linder[1], Jouni Ahopelto[2]

*1 VTT Technical Research Centre of Finland, Biotechnology, Finland (katri.kurppa@vtt.fi)*
*2 VTT Technical Research Centre of Finland, Microsystems and Nanoelectronics, Finland*

Graphene field-effect transistors are sensitive to any charge variations taking place in the vicinity of the graphene surface. [1] High-sensitivity, label-free detection of specific analytes can be achieved in electric biodevices by the use of functional biomolecules and natural biological interactions. I is necessary that surface-functionalization is achieved without disrputing the electronic properties of graphene by covalent modification. Our approach is based on noncovalent functionalization of graphene by engineered surface binding proteins, the hydrophobins. [2]

The hydrophobin proteins self-assemble into monolayers on hydrophobic surfaces such as graphene or plastics and are therefore ideal candidates for surface modification of nanocarbon based assemblies. [3,4] We have developed a graphene FET biosensor with surface functionalization by a genetically engineered fusion of the hydrophobin protein HFBI and the leucine zipper motif. [5] We demonstrate sensing of specific molecular interactions by measuring the interaction of the analyte $Z_R$ peptide with the immobilized protein scaffold HFBI- $Z_{E.}$ Binding of the analyte molecule can be seen as a shift of the Dirac peak measured against the reference liquid electrode.

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**P284**

## Electron-phonon coupling in suspended graphene

Antti Laitinen, Mika Oksanen, Daniel Cox and Pertti Hakonen

*O.V. Lounasmaa Laboratory, Aalto University, Finland (antti.laitinen@aalto.fi)*

The voltage biased electron system of a graphene monolayer will attain a quasi-equilibrium state where the Joule heat flows from electrons to the supporting substrate both via electronic heat diffusion and through inelastic scattering with the phonons of the graphene lattice. Heat flow from the electron system as a function of the electron temperature is characterized by a specific power law [1] given by $P=\Sigma(T_e^{\delta}-T_p^{\delta})$, where $T_e$ is the electron temperature, $T_p$ the phonon temperature, $\Sigma$ the coupling constant and $\delta$ a characteristic exponent.

We have employed shot noise thermometry in combination with ac conductance measurement for determination of the electron-phonon coupling in high quality suspended graphene monolayers. The substrate, acting as a thermal bath, was kept at 50 mK using a dilution refrigerator while the electrons in our two-terminal graphene devices were heated up to $T_e$ = 100 - 600 K by Joule heating. In the regime $T_e$ > 200 K, we found that the electron-phonon coupling became the most important thermal relaxation channel with only minor contributions by the electronic heat diffusion along the current leads. Moreover, the chemical potential of the sample was varied using a back gate in our experiments.

At $T_e$ < 100 K, we observe power-law behavior characteristic to electronic diffusion with an exponent $\delta\approx 1.5\text{-}2.0$. Around $T_e$ = 200 K, there is a transition to a region with enhanced thermal relaxation. When $T_e$ > 200 K, we observe nearly quartic power-law dependence, $\delta\approx 4$, and the coupling constant increases as $\Sigma\sim\mu^2$, which indicates a crucial role of two-phonon scattering events, reminiscent to the supercollision events analyzed by J. Song et al [2]. Furthermore, our behavior looks similar to the coupling with acoustic phonons having $\delta=4$, but for single phonon scattering there should be linear dependence on the chemical potential.

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**P285**

## Bilayer grahene nanoribbon with zigzag edges: a modulation gap route via external fields

Andrea Latgé and Carlos Léon

*Instituto de Física, Universidade Federal Fluminense, Brazil (andrea.latge@gmail.com)*

Here we discuss the possibility of modulating energy gaps of graphene nanoribbon bilayers, with zigzag edges, by applying electric fields. The system is disposed in the Bernal configuration and is described by a Hubbard Hamiltonian. We follow a Hartree-Fock mean field theory to calculate electronic properties of the system. Second neighbor interactions are taken into account in the model calculation. Similarly to the case of a single graphene nanoribbon, a local magnetization is found mainly at the edge sites of the two layers and it decays exponentially at the center of the ribbons. Under the action of a transversal electric field, half-metallicity is found: one of the spin bands increases the gap energy as the intensity of the field is increases whereas the other decreases until achieving a null gap [1]. For a particular electric field range, the system exhibits metallic and semiconducting features depending on the spin band. On the other hand, an extra effect is found for the bilayer system: the presence of a robust plateau-like in the gap versus field intensity diagram, for an intermediate value of energy gap value, of the semiconducting band. Ribbons of different width present the same feature. The correlation of the gap plateau with local magnetizations and charge numbers in the two layers is investigated. We believe that possible spintronic applications can be driven based on the differential spin band features achieved in this theoretical analysis. We also consider further applied gate voltage on the ribbons to study the possibility of manipulate the physical responses of the nanostructure systems under tilted electric field configurations [2]. Additional magnetic localization effects offer new degrees of freedom to the gap engineering problem, and are under investigations.

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P286

# Aharonov-Bohm effect on the edge states around nanohole in graphene and thin graphite

Yu.I. Latyshev, A. P Orlov, V.A. Volkov

*Kotelnikov Institute of Radio-Engineering and Electronics RAS, Russia (yurilatyshev@yahoo.com)*

We found that thin graphite and graphene samples perforated with nanoholes exhibit field periodic oscillations of magnetoresistance with periodicity of flux quantum *hc/e* per nanohole area. Observation of the Aharonov-Bohm-type oscillations on non-ring-shaped samples is attributed to the existence of the conducting edge states in graphene around a hole. From the experiment we can estimate the depth of the edge state $\lambda$ as being $\lambda \approx 2$ nm. From the temperature dependence of the amplitude of oscillations we can estimate the characteristic energy and velocity of the edge Dirac fermions as being $5x10^6$ cm/s, 20 times less than the Fermi velocity of the bulk Dirac fermions. The experimental results are consistent with a theory of the Tamm-type edge states in graphene.

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# Effect of graphene oxide on thermal stability of cold-adapted esterase at ambient temperatures

ChangWoo Lee[1], Heeyoung Lee[1], Hae Kyung Jeong[2], Jinwoo Han[2], Sei-Heon Jang[1]

*1 Department of Biomedical Science, Daegu University, Gyeongsan 712-714, South Korea*
*(shjang@daegu.ac.kr)*
*2 Department of Physics, Daegu University, Gyeongsan 712-714, South Korea*

Graphene oxide (GO) has large surface area and oxygen-containing functional groups such as alcohols, epoxides, and carboxylic acids. Several studies reported enzyme immobilization on GO via covalent bonding or non-covalent interactions. Enzymes immobilized on GO showed enhanced thermal stability, storage periods, and reusability compared with the properties of free enzymes.

Cold-adapted enzymes exhibit high catalytic activity at low temperatures. To maintain flexibility at low temperatures, cold-adapted enzymes have modifications in structure including less intramolecular hydrogen bonds and salt bridges and reduced hydrophobic interactions. These features have rendered cold-adapted enzymes more susceptible to denaturation by heat than their mesophilic counterparts.

In this study, we sought to investigate whether GO improves thermal stability of cold-adapted enzymes at ambient temperatures. We used a recombinant esterase, rEstKp, cloned from psychrotrophic *Pseudomonas mandelii*. Here, we report that rEstKp that was covalently immobilized on GO maintains its catalytic activity. Surprisingly, the thermal stability of rEstKp at 20°C was higher than its thermal stability at 4°C. The hydrophilic interactions between GO and rEstKp are considered to play an important role in maintaining the active conformation of the enzyme. Our data suggest that the stability of cold-adapted enzymes at ambient temperatures could be enhanced by immobilizing them on GO. The structural changes in cold-adapted enzymes upon attachment on GO need to be further elucidated.

**P288**

## Boron nitride nanoribbons from in-situ unzipping during nanotube growth

Luhua Li, Ying Chen

*Institute for Frontier Materials, Deakin University, Waurn Ponds, Australia*
*(luhua.li@deakin.edu.au)*

Boron nitride nanoribbons (BNNRs) have many interesting properties. They have been produced previously from unzipping boron nitride nanotubes (BNNTs) via two separate steps: BNNT growth and post-synthesis unzipping treatments. Here, we introduce an in-situ unzipping concept that simplifies the two steps into one. That is, unzipping happens during BNNT synthesis so that BNNRs can be directly harvested without the need for post-synthesis treatment. The resultant BNNRs are of high chemical purity and crystallinity according to near edge x-ray absorption fine structure (NEXAFS) spectroscopy, and prefer a zig-zag orientation.

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**P289**

## Near-band edge optical properties of exfoliated h-BN layers

A. Loiseau[1], J. Loayza[1,3], A. Pierret[1], A. Betz[2], B. Plaçais[2], F. Ducastelle[1], J. Barjon[4]

*1 LEM, CNRS-ONERA, Chatillon, France*
*2 LPA, ENS Paris, France*
*3 GEMAC, U. Versailles St Quentin, Versailles, France*

Hexagonal boron nitride is a wide band gap semiconductor (~ 6.5 eV), which meets a growing interest for graphene engineering. It is therefore highly desirable to better know optical and electronic properties of thin BN layers, in correlation with their structural properties. h-BN has been shown to display original optical properties, governed, in the energy range 5.5 – 6 eV, by strong Frenkel-type excitonic effects [1-3]. Furthermore, excitons are highly sensitive to their environment as revealed by combined cathodoluminescence (CL) measurements and transmission electron microscopy (TEM) observations [4].

In this work, we examine how these properties can be further exploited for the characterization of thin BN layers. We carry out optical and structural characterizations of this material by combining CL at 4K in the UV range and TEM. Thin layers are obtained by mechanically exfoliating powders and single crystals and reported on $SiO_2$ substrates for AFM thickness measurements, and then on TEM grids.

Results are detailed in [5]. As for the reference bulk, excitonic emission consists of two series of lines called S and D. Thanks to the imaging capability of the CL, emission, related to D lines, is found to be localized on defects, identified by TEM as grain boundaries. In defect free areas, D lines completely vanish and S lines only are observed. D/S ratio can therefore be used as a qualification parameter of the defect densities present in the layers. Their energies are found to be upshifted as the number of layers decreases, indicating a perturbation in the exciton localization, which will be discussed.

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P290

# Magnetic two-dimensional sp$^2$ carbon sheet of fused pentagons

Mina Maruyama and Susumu Okada

*Graduate School of Pure and Applied Sciences, University of Tsukuba, Japan*
*(mmaruyama@comas.frsc, @tsukuba.ac.jp)*

Carbon molecules are known to form various polygonal conformations owing to flexibility of its bonding angle and length. These polygons can be a constituent unit for the various molecular patchworks with zero-, one-, two-, and three-dimensions by sewing these polygons. In addition to graphene, it is interested in exploring the possibility of the other two dimensional carbon allotropes consisting of carbon polygons. Among the polygons, pentagon (cyclopentadiene: $C_5$) and dodecagon (cyclododecahexaene: $C_{12}$) can completely cover up a 2 dimensional plane with hexagonal network of fused pentagons (acepentalene) . In this study, we explore the possible geometric structures and electronic properties of the 2D network of sp2 C consisting of fused pentagons (polymerized $C_{14}$) with dodecagon pores by using first-principles calculations based on density functional theory with local spin density approximation.

Our calculations show that the fused pentagon sheet is energetically stable, and the calculated total energy is about 0.6 eV/atom higher than that of graphene. Furthermore, the sheet keeps its sp2 bonding 2D network under the elevated temperature up to 800 K. The sheet is metal with flat dispersion band at the Fermi level leading to the ferromagnetic spin ordering.

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# Direct synthesis of graphene on dielectric substrates by “etching-precipitation” method

Kosaka Masaki[1,2], Soichiro Takano[1], Suguru Noda[2,3,*]

*1 Department of Chemical System Engineering, The University of Tokyo, Japan*
*2 Department of Applied Chemistry, Waseda University, Japan (*noda@waseda.jp)*
*3 PRESTO, JST, Japan*

Currently, chemical vapor deposition (CVD) is most promising for the practical fabrication of graphene because of its potential for high scalability and structure controllability [1,2]. For many of the potential applications of graphene such as transistors, transparent electrodes, and patterned electrodes in LSIs, however, we have to fabricate graphene not on the metals but on the desired dielectric substrates. Despite of many efforts, direct synthesis of graphene on dielectric substrates at a large-scale with a good uniformity is still challenging.

In this study, we directly synthesized graphene on dielectric substrates by the novel ”etching precipitation” method. Fe as solvent and C as solute were co-deposited on $SiO_2$ by sputtering, heated to 500-700 °C, and then Fe was etched away from the “hot Fe-C solid solution” by $Cl_2$ gas to precipitate C and growth graphene on $SiO_2$ in 10 min. Contrary to CVD where C segregate during rapid cooling of metal-carbon solid solution [1], the increase in the carbon concentration in the ″hot″ solid solution caused by etching drives carbon precipitation and graphene growth. We fabricated several-layer graphene with fair quality (grain size of a few µm and specific resistivity of 150 µW cm) directly on quartz glass substrates at 600 °C. This graphene on quartz glass had a optical transmittance of 86% and a sheet resistance of 760 Ω/sq. The layer number can be easily controlled linearly with the Fe-C film thickness (i.e. carbon feed), showing the accuracy and simplicity of this process. This process can be applied to dielectric substrates of arbitrary sizes and to the direct formation of patterned graphene by patterning the metal-carbon solid solutions.

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**P292**

# Controlling the functionalization of carbon nanotubes and graphene nanoplatelets

Enzo Menna[1,2], Patrizio Salice[1], Simone Silvestrini[1], Davide Fenaroli[1], Michele Cristofani[1], Enrica Fabris[2], Camillo Sartorio[3], Sebastiano Cataldo[3], Bruno Pignataro[3], Michele Maggini[1,2]

*1 Dipartimento di Scienze Chimiche, Università di Padova, Italy (enzo.menna@unipd.it)*
*2 ITM-CNR Padova, Italy*
*3 Dipartimento di Fisica e Chimica, Università di Palermo, Italy*

The functionalization of carbon nanostructures by diazonium chemistry is a versatile strategy to obtain soluble nanomaterials with degrees of functionalization among the highest ever reported.[1,2] Starting from these premises we have studied the functionalization of single, double and multi-walled carbon nanotubes and graphene nanoplatelets by addition of aryl diazonium salts generated in situ by treatment of 4-substituted anilines with isopentylnitrite. Taking advantage of highly controlled flow synthesis [3-5] and following a thorough purification and characterization protocol (UV-vis, TGA, ATR-IR, AFM and other surface tools), we have investigated the key parameters to obtain both functionalized nanostructures, where the amount of functional groups anchored to the carbon surface is less than a monolayer, and superfunctionalized nanostructures with a carbon core and a multilayered aryl coating. The results outlined provides the basis for the design and controlled processing of novel decorated carbon nanostructures that would be useful for a number of technological applications.

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**P293**

# Formation of advanced carbon nanostructures in controlled induction heating of preceramic silicon-carbon nanoparticles

Mirella Miettinen[1], Jouni Hokkinen[2], Tiina Torvela[1], Tommi Karhunen[1], Carsten Pfüller[3], Manfred Ramsteiner[3], Unto Tapper[2], Jorma Jokiniemi[1,2], Anna Lähde[1]

*1 Fine Particle and Aerosol Technology Laboratory, Dept. of Environmental Science, University of Eastern Finland, Finland (mirella.miettinen@uef.fi)*
*2 VTT Fine Particles, Finland. 3 Paul-Drude-Institut für Festkörperelektronik, Germany*

The post-processing of previously synthesized preceramic Si-C nanoparticles was performed by induction heating under argon flow at atmospheric pressure. Three precursor powders with increasing crystallinity, and induction temperatures between 1900 °C and 2600 °C were used. Three structures were found after induction, i.e. large SiC crystals, spherical carbon particles and carbon sheets.

Transmission electron microscopy (TEM) analysis proved that the spherical particles consisted of curved carbon layers growing from the amorphous Si-C core and forming a so-called nanoflower structure. To our knowledge the formation of this kind of structures has not been reported previously. The core was clearly visible at the induction temperature of 1900 °C, and decreased in size with increasing temperature. Above 2200 °C there was no visible core left. With increasing crystallinity of the precursor material, fewer layers were present in the carbon nanoflowers. In addition, there were more carbon sheets than for precursor particles with lower degree of crystallinity. The ordered nature of these sheets was verified with selected area electron diffraction analysis (SAED). At the highest induction temperature (2600 °C) complete dissociation of the precursor particles occurred and the material left in the crucible was mainly pure carbon. An X-ray diffraction analysis verified the existence of crystalline carbon in that sample and the Raman spectrum showed remarkably narrow G and 2D bands, which may indicate the presence of single layer graphene (SLG) [1]. The intensity of the 2D band was roughly four times that of the G band, which is also typical to SLG.

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# Photoluminescence of 1D-graphene ribbons formed from coronene molecules inside single-wall carbon nanotubes

E.D. Obraztsova[1], A.I. Chernov[1], P.V. Fedotov[1], A.V. Talyzin[2], I.L. Suarez[1], I.V. Anoshkin[3],
A.G. Nasibulin[3], E.I. Kauppinen[3]

*1 A.M. Prokhorov General Physics Institute, RAS, Russia (elobr@mail.ru)*
*2 Department of Physics, Umeå University, Sweden 3 Department of Applied Physics, Aalto University, Finland*

One-dimensional graphene structures – nanoribbons- are interesting both from fundamental and technological (optoelectronics) points of view due to opening the electronic gap with the value inverse proportional to the ribbon width. Under the ribbon widths less than 20 nm the optical gap can be measured, for instance, with photoluminescence (PL) spectroscopy. Many attempts have been made for preparation of such narrow ribbons with different techniques, however, to the best of our knowledge, PL still has not been measured. In this work we report about formation of carbon nanoribbons inside single-wall carbon nanotubes by fusion of coronene molecules. The ribbon existence has been proved by HRTEM [1]. The PL maps have been registered for coronenes and nanotubes before and after the filling procedure. After filling the additional PL peak has appeared in a spectral range between those being characteristics for coronenes (below 500 nm) and nanotubes (longer than 700 nm). The wavelength of this peak changed while the diameter of pristine nanotubes changed and demonstrated a resonance dependence on the light excitation energy. This band was ascribed to graphene nanoribbon inside SWNTs. The Raman spectra of filled nanotubes showed a significant shift of breathing modes due to the mechanical stress arising after incapsulation.

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P295

# Slow Dirac electrons on hexagonal dangling bond networks on hydrogen deposited diamond(111) and Si(111) Surfaces

Junki Sone[1], Susumu Okada[2]

*1 Department of Materials and Engineering, Tokyo Institute of Technology, Japan*
*2 Graduate School of Pure and Applied Sciences, University of Tsukuba, Japan*
*(sokada@comas.frsc.tsukuba.ac.jp)*

In the present work, we aim to investigate the electronic structure of hexagonal networks of dangling bond (DB) on H-terminated diamond (111) and H-terminated Si (111) surfaces by first-principles total-energy calculations within the framework of density functional theory. Our calculations revealed that hexagonal DB networks on these semiconductor surfaces have a pair of linear dispersion bands at the K point, as in the case of graphene. The calculated Fermi velocities for the hexagonal DB networks on both diamond and Si are 10 % slower than that of graphene. Therefore, *slow electrons/holes with zero effective mass* exist in the hexagonal DB network on semiconductor surfaces. The results indicate that DB graphene on semiconductor surfaces allows us to control the velocity of massless electron and the correlation among massless electrons. The liner dispersion bands are robust against surface reconstructions, which are inherent on semiconductor surfaces, for diamond. In contrast, on the Si surfaces, the 2x1 buckling reconstruction disrupts the linear bands.

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## Electrical characterization for graphene film grown by low-temperature microwave plasma CVD

Yuki Okigawa[1,2], Kazuo Tsugawa[2], Takatoshi Yamada[1,2]
Masatou Ishihara[1,2], Masataka Hasegawa[1,2]

*1 Nanotube Research Center, National Institute of Advanced Industrial Science and Technology (AIST), Japan (okigawa.yuki@aist.go.jp)*
*2 Technology Research Association for Single Wall Carbon Nanotubes (TASC), Japan*

We have developed the microwave plasma CVD technique combined with the roll-to-roll process to deposit the graphene film. In this method, a continuous deposition process of graphene film has been demonstrated at low temperature in a few ten seconds [1]. To attain higher electrical conductivity, the details of the electrical properties of the graphene film deposited by plasma CVD technique must be clarified. Hall effect measurement is useful to measure the electrical properties for graphene, which is expected to understand the mechanism of its electrical conductivity. In this study, we discuss the details of the electrical properties of the graphene films deposited by low-temperature plasma CVD based on Hall effect measurements.

The graphene film was deposited by microwave plasma CVD technique on Cu foil typically at 300 – 400 °C. Then, it was transferred to the quartz substrate. After that, the van der Pauw device for Hall effect measurement was fabricated using conventional photolithography, metal deposition and lift-off processes. The fabricated devices show that the mobility is estimated to be from 10 to 100 $cm^2/Vs$. To investigate the mobility dispersion, we quantify defects and disorder for graphene by Raman mapping. The results suggest that the intensity of the D/G ratio could correlate with the mobility. Based on these results, we'll discuss the cause which predominates the present conductivity of the films and how to improve the electrical conductivity of graphene film.

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P297

## Multimode Fabry-Pérot interference in suspended graphene

Mika Oksanen[1], Andreas Uppstu[2], Antti Laitinen[1], Daniel Cox[1], Ari Harju[2], Monica Craciun[3], Saverio Russo[3], Pertti Hakonen[1]

*1 O. V. Lounasmaa Laboratory/LTL, Aalto University, Finland (mika.oksanen@aalto.fi)*
*2 Department of Applied Physics, Aalto University, Finland*
*3 Center for Graphene Science, University of Exeter, UK*

The conditions for Fabry- Pérot resonances in rectangular graphene sheets with nonperfect contacts were recently analyzed by Gunlycke and White [1] who showed that, under certain conditions evenly spaced groups of resonances, separated by $\Delta E \sim hv_F/2L$, can emerge. These collective resonances originate owing to simultaneous participation of modes in nonequivalent channels that are facilitated by transversely quantized states with small energy separation. Such collective resonances should not be confused with the ordinary two-channel Fabry- Pérot resonances observed in single-wall carbon nanotubes.

We report analysis of Fabry- Pérot type interferences in high-mobility suspended graphene using both shot noise and conductance measurements. Differential conductance shows definite Fabry- Pérot patterns emerging, by taking the derivative of the conductance the visibility is improved. The Fourier transform of the data shows three sets of peaks which are identified as resonances of 1) clean suspended part bordered by pn junctions, 2) full length of the sample with scattering from the contacts, and 3) width of the sample.

The Fabry-Pérot pattern is also visible in our shot noise measurements. Their analysis reveals again three sets of Fourier peaks, which nearly coincide with those obtained from our conductance measurements. A correlation analysis between conductance and shot noise, indicates rather weak correlation. This analysis demonstrates that the observed Fabry-Pérot pattern originates from more than two channels in contrast to interference phenomena in single walled carbon nanotubes.

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## Optical properties of twisted trilayer graphene

**P298**

Mónica Pacheco[1], J. D. Correa[2], E. Suárez Morell[1]

*1 Dept. de Física, Universidad Técnica Federico Santa María, Valparaíso, Chile (monica.pacheco@usm.cl)*
*2 Dept. de Ciencias Básicas. Universidad de Medellin, Medellin, Colombia.*

In the last few years the study of opto-electronic properties of multilayer graphene has attracted the interest of the scientific community due to the possibility of modulate its electronic structure by changing its stacking arrangement, applying external fields or adding impurities to the system. Recently many efforts have been focused on the electronic and optical properties of twisted bilayer graphene (TBG) [1-2]. This system has linear dispersion bands like in monolayer graphene but a puzzling behavior occurs for low angles. The flattening of the bands results in Van Hove singularities and optical absorption peaks that depend on the relative rotation angles between the layers, this has been observed experimentally by several groups [3-4]. In this work we study by *ab initio* calculations the optical absorption spectra through the imaginary part of dielectric function of three graphene layers when one or two of the layers are rotated with respect to the others. Our study comprises two sets of structures. The first one consists of three layers, the first and second layers are in Bernal stacking and the third layer is rotated with respect to the other two. We were able to study three of these structures and compare them with the corresponding twisted bilayer graphene. The other kind of structure is composed also of three layers but the RRA between the first and the second layer is different than between the second and the third layer. We found that it is possible to discern the optical absorption spectra of twisted trilayer graphene from the bilayer counterpart, two angle dependent absorption peaks can be found in the trilayer case while there is only one in the bilayer. The position of the two peaks depends on the stacking of the three layers and might serve as a signature to identify the twisted trilayer structure. A tight binding model was also employed to calculate the optical transition matrix to determine the effects of twisting on the optical selection rules of the structures.

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## Fabrication of stretchable $MoS_2$ thin-film transistors using elastic ion-gel gate dielectrics

**P299**

Jiang Pu[1], Yijin Zhang[2], Yoshifumi Wada[1], Jacob Tse-Wei Wang[3], Lain-Jong Li[3], Yoshihiro Iwasa[2], and Taishi Takenobu[1]

*1 Department of Applied Physics, Waseda University, Tokyo 169-8555, Japan (takenobu@waseda.jp)*
*2 Department of Applied Physics, The University of Tokyo, Tokyo 113-8656, Japan*
*3 Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 10617, Taiwan*

Recently, the transition metal dichalcogenide molybdenum disulfide ($MoS_2$) has attracted considerable interest because of its mechanical strength, large intrinsic bandgap and optical properties. Transistors based on mechanically exfoliated $MoS_2$ monolayers have already been reported to exhibit a high current on/off ratio of $1 \times 10^8$ and an electron mobility of 200 $cm^2/(V \cdot s)$. [1] Furthermore, CVD-grown $MoS_2$ thin-film transistors (TFTs) built on a plastic substrate have shown extremely high mechanical bendability, and their transistor properties were stable down to a curvature radius of 0.75 mm. [2] However, the potential for using $MoS_2$ in stretchable electronics has not been explored.

Here, we demonstrate the fabrication of stretchable $MoS_2$ TFTs on rubber substrates using ion-gel films as elastic gate dielectrics. The $MoS_2$ TFTs were directly stretched to investigate the electrical stability under deformation, and they operated at a channel strain of up to 5% without significant degradation of the carrier mobility and on/off current ratio, which might be owing to a relaxation of ripples. Moreover, the optical and spectroscopic characterizations suggest the domain boundaries play an important role of the origin of the electrical resistance increase in CVD-grown polycrystalline $MoS_2$ thin films. These results provide the possibilities for using $MoS_2$ films for stretchable electronics.

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P300

# Topological signatures in the electronic structure of graphene spirals

S.M. Avdoshenko[1], P. Koskinen[2], H. Sevinçli[3], A.A. Popov[4], C.G. Rocha[2]

*1 School of Materials Engineering, Purdue University, West Lafayette, Indiana, USA*
*2 Nanoscience Center, Department of Physics, University of Jyväskylä, Jyväskylä, Finland*
*(claudia.c.gomes-darocha@phys.jyu.fi)*
*3 DTU Nanotech, Department of Micro- and Nanotechnology, Technical University of Denmark, Denmark*
*4 The Leibniz Institute for Solid State and Materials Research in Dresden, Dresden, Germany*

Topology is familiar mostly from mathematics, but also natural sciences have found its concepts useful. Those concepts have been used to explain several natural phenomena in biology and physics, and they are particularly relevant for the electronic structure description of topological insulators and graphene systems. Here, we introduce topologically distinct graphene forms - graphene spirals [1] - and employ density-functional theory to investigate their geometric and electronic properties. We found that the spiral topology gives rise to an intrinsic Rashba spin-orbit splitting. Through a Hamiltonian constrained by space curvature, graphene spirals have topologically protected states due to time-reversal symmetry. This unique electronic feature requires neither an external magnetic field nor spin-orbit interaction to manifest, which is unlike any typical quantum Hall system. Therefore, graphene spirals ought to deserve a prominent role as a fundamental graphene topology, comparable to the topologies of carbon nanotubes and graphene nanoribbons. In addition, we argue that the synthesis of such graphene spirals is feasible and can be achieved through advanced bottom-up experimental routes that we indicate in this work.

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P301

# Graphene films for lasers

Pavel Rusakov, Ivan Kondrashov, Maxim Rybin, Anatoliy Pozharov, Vladimir Sorochenko and Elena Obraztsova

*A.M. Prokhorov General Physics Institute, Vavilov str. 38, Moscow, Russia,119991 (rusakov.@gmail.com)*

Graphene is a two-dimensional hexagonal carbon network with unique physical and chemical properties. Over the past period the efforts of researches were concentrated on experimental formation of single layer or multiple layers of graphene of different scales. One layer samples are useful for nanoelectronics, sensors, solar cells, etc. Multi layers can be used in optics. One layer of graphene absorbs 2.3% of incident light. The working spectral range of graphene is very wide: our measurements show that a flat absorption of 2.3% (per 1 layer) extends from 0.4 μm up to 12 μm (at least). This property opens a possibility to form the saturable absorbers for mid-IR lasers (CO laser – with a working wavelength of 6 μm and $CO_2$ laser - with a wavelength of 10 μm [1]).

In this paper we show features of preparation of samples [2,3] for further use in lasers as saturable absorbers. We will demonstrate the progress made for lasers of different wavelengths from 1.5 to 10.5 microns. We denote the problems and questions coming for further applications.

The work was supported by RFBR projects 12-02-31373, 13-02-01354 and by contract № 14.513.12.003 with Ministry of education and science of Russian Federation.

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P302

# Coating with multi-walled carbon nanotubes accelerates osteoconductivity of the anodized titanium

Saori Inoue[1], Motohiro Uo[2], Masatoshi Sakairi[1], Eri Hirata[1], Min Ho Lee[3], Tae Sung Bae[3], Tsukasa Akasaka[1], Fumio Watari[1], Atsuro Yokoyama[1]

*1 Hokkaido Univ., Sapporo Japan*
*2 Tokyo medical and dental Univ., Tokyo, Japan*
*3 Chonbuk National Univ., South Korea*

Objective: Carbon nanotubes (CNTs) have attracted attention from the viewpoint of biological applications. Excellent osteocompatibility for the CNTs monolith was also reported *in vivo*. The purpose of this study is to coat anodized titanium with multi-walled CNTs (MWCNTs), and to investigate their effects on osteoblastic cell and bone tissue.

Materials and methods: The anodized titanium (Ano-Ti) disks (φ10mm×1mm) were silanized (Si-Ti). They were soaked in the calboxylated MWCNTs (Nanolab, MA, USA) suspension (CNT-Ti). Human osteosarcoma Saos2 cells were cultured on CNT-Ti, Ano-Ti and Si-Ti. The DNA contents and ALP activity were measured at 3 and 7 days. The CNT-Ti and Ano-Ti wire (φ1mm×5mm) were implanted in the bone marrow space in femurs of rats aged 10 weeks. At 2 and 4 weeks after surgery, the rats were sacrificed and histological and histomorphological evaluation was carried out. The CNT-Ti/bone interface was also observed by SEM. The elements at the interfaces were analyzed with energy dispersive spectrometry (EDS) mapping. The analyzing areas were produced using focused ion beam (FIB).

Results: Saos2 cells on CNT-Ti showed excellent proliferation. After 7 days, the DNA contents of the cells of the CNT-Ti were significantly higher than other specimens. Histological investigations revealed that bone tissue formed more extensively on the surface of CNT-Ti compared to Ano-Ti. Bone contact ratio of the CNT-Ti was significantly higher than those on the Ano-Ti at 2 and 4 weeks. EDS analysis revealed that carbon existed between the interface of bone and titanium, and calcium originated bone and carbon contacted densely.

Conclusion: The surface modification of anodized Ti with MWCNTs could be effective for new bone formation.

P303

# Photoluminescence and Raman spectroscopy of free-standing single and bilayer molybdenum disulfide

Nils Scheuschner[1], Anne-Marie Kaulitz[1], Oliver Ochedowski[2], Marika Schleberger[2], Janina Maultzsch[1]

*1 Technische Universität Berlin, Institut für Festkörperphysik, Germany (nils.scheuschner@tu-berlin.de)*
*2 Universität Duisburg-Essen, Fakultät für Physik and CeNIDE, Germany*

Monolayers of molybdenum disulfide ($MoS_2$), unlike the bulk material, have a direct band gap. Therefore their photoluminescence (PL) is strongly enhanced compared to the bulk with indirect band gap [1]. We present spatially resolved PL and Raman microscopy [2] of free-standing single-layer (SL) and bilayer (BL) $MoS_2$ prepared by mechanical exfoliation on $Si/SiO_2$ substrates with holes with a diameter of approximately 3 µm. The µ-Raman mappings show indications of charge transfer effects between the $Si/SiO_2$ substrate and the $MoS_2$. The µ-PL mappings show a blue shift and an intensity increase of more than one order of magnitude for the free standing SL $MoS_2$ compared to the supported SL, while for the free-standing BL the PL intensity is reduced compared to the supported BL. Furthermore we show that the configuration of $MoS_2$ above holes can result in a Fabry-Pérot like oscillation of the PL signal.

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## P304

# Non-linear dissipation in graphene mechanical resonators

M. Tomi, X. Song, A. Laitinen, M. Oksanen, P. Hakonen*

*O. V. Lounasmaa Laboratory, School of Science, P. O. Box 15100, FI-00076 AALTO*
*(*pertti.hakonen@aalto.fi)*

Damping in macroscopic mechanical resonators can generally be described by a linear damping force. Present-day advances in nanofabrication, however, have made it possible to explore damping in systems with atomic-scale dimensions. Recently, damping in graphene mechanical resonators was found to depend non-linearly on the amplitude of motion in measurements using frequency modulated mixing techniques [1]. The drawback of such mixing techniques is that it is hard to know the amplitude of motion for quantitative analysis.

In this work, we have employed capacitive detection methods [2], in which the graphene mechanical resonator, positioned on top of a counter-electrode, acts as part of an electrical cavity (LC) resonator. In our measurements, the change in the resonator capacitance can be calculated quite accurately, which allows precise determination of the amplitude of vibrational motion. Our samples were manufactured using micromanipulation techniques in which the graphene membrane is suspended on top of a PMMA stamp [3]. On one of our single layer graphene resonators, an inclined response curve starts to develop at amplitudes exceeding 10 pm, indicating a stiffening Duffing resonator. At high swings, above 30 pm in this case, the response curve becomes hysteretic as is expected for Duffing-type behavior. The scaled maximum amplitude in the hysteretic regime should remain constant if the response is governed by linear damping [4]. While in our data, clear decrease is observed, which allows us to determine the strength of non-linear damping.

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## P305

# Using ultra-violet exposure to study the effect of chemical vapor deposition growth process on the graphene grain size

Jannatul Susoma, Changfeng Li, Juha Riikonen and Harri Lipsanen

*Department of Micro and Nanosciences, Aalto University, PO Box 0, FI-0007 Aalto, Finland*
*(jannatul.susoma@aalto.fi)*

Grain boundaries of graphene are formed when single grain graphene islands are merged during the chemical vapor deposition (CVD) growth process. These boundaries govern transport properties affecting device performance [1]. Grain size of graphene varies with different growth conditions like temperature, pressure and gas flow [1-2]. Typically, transmission electron microscopy (TEM) is used to observe grain boundaries, which is time consuming and require special sample preparation. Recently, it has been demonstrated that, graphene grain boundaries also can be made visible for optical microscopy when they are exposed under UV light [1]. We utilize this technique to study the grain size under different growth conditions. Exposing UV light under moisture environment, Cu is oxidized underneath the graphene following the grain boundaries. Then the grain boundaries become visible under optical and scanning electron microscopy (SEM).

We demonstrate that, different growth conditions affects grain size of the graphene and that can be easily observed by optical microscopy using UV treatment. This method will be certainly useful to understand graphene grain size depending on different growth conditions which, leads to the direction of high quality graphene synthesizing techniques useful for device applications.

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P306

# Direct growth of hexagonal-domain graphene on $SiO_2$ substrate by rapid heating plasma CVD

Hiroo Suzuki, Toshiaki Kato*, Toshiro Kaneko

*Department of Electronic Engineering, Tohoku University, Sendai 980-8579, Japan*
*(*kato12@ecei.tohoku.ac.jp)*

Graphene is a monolayer carbon sheet including high carrier mobility, flexibility, and high optical transmittance. These properties are advantageous if graphene is to be used as a component in electrical devices such as field effect transistors, solar cells, and various gas and chemical sensors. Chemical vapor deposition (CVD) is one of the most promising methods of growing graphene, which can produce large, relatively high-quality graphene sheets. However, the graphene growth by CVD is limited only to the metal catalyst surfaces such as Ni, Cu, or Co, which is one of the most serious problems for the practical application of graphene as electrical devices. Thus, the development of the method for the direct growth of graphene on the insulating substrate, especially on a $SiO_2$ substrate, is highly required.

Recently, we have established a novel, simple, and scalable method for the direct growth of graphene on the insulating substrate by rapid-heating plasma CVD [1]. It is revealed that by adjusting the growth parameters using plasma CVD, the graphene layer can be grown along the interface of the Ni layer and the $SiO_2$ substrate instead of on top of the Ni layer. After removing the top Ni layer, high-quality single- or few-layer graphene sheets are found to be directly grown on the entire substrate area in large scale. Interestingly, at the initial growth stage, the hexagonal domain structure of graphene can be observed in our method [2]. Since the hexagonal domain graphene structure should appear only when graphene has a single domain structure, it can be possible to realize a direct growth of single domain large scale graphene on a $SiO_2$ substrate with our established novel approach.

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P307

# Raman spectroscopy of carbon nanohoops

Hang Chen[1], M.R. Golder[3], S.K. Doorn[2], R. Jasti[3], A.K. Swan[1]

*1 Department of Electrical and Computer Engineering, and Photonics Center,*
*Boston University, Boston, MA 02215, USA*
*2 MPA-CINT, Los Alamos National Lab, Los Alamos, NM 87545, USA*
*3 Department of Chemistry, Boston University, Boston, MA 02215*

We present Raman analysis for cycloparaphenylenes (CPPs) of different sizes ([6]-, [8-12]CPPs). [n]CPP molecules are carbon nanohoops reminiscent of a single unit of (n, n) armchair carbon nanotubes (CNTs).[1, 2] A plethora of Raman modes are observed in these spectra, including modes that are analogous the G band in CNTs, as well as peaks that are unique for carbon nanohoops. We have calculated the theoretical Raman spectra of [n] CPPs for n= 4~20 using density functional theory (DFT), which are then compared to the experimental spectra for the assignment of different modes. Theoretically, the even-numbered CPPs should have $D_{(n/2)d}$ symmetry, while the odd-numbered hoops have only $C_1$ symmetry. However, for certain Raman bands of the even-numbered CPPs, the experimental results seem to contradict this prediction. To address the problem, we have done further calculations by manipulating the geometry of even-numbered hoops. In addition, the peak positions for almost all Raman modes are found to be dependent on the size of the hoops from both the experimental and the calculated results. The effect of low temperature on the Raman features of the CPPs is also examined.

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**P308**

# Quantum Hall effect in hydrogenated graphene

T. Szkopek[1], J. Guillemette[1], S.S. Sabri[1], B. Wu[1], K. Bennaceur[1], P.E. Gaskell[1], M. Savard[1],
P.L. Lévesque[2], F. Mahvash[1,3], A. Guermoune[1,3], M. Siaj[3], R. Martel[2] and G. Gervais[1]

*1 McGill University, Montréal, Canada (thomas.szkopek@mcgill.ca)*
*2 Université de Montréal, Montréal, Canada*
*3 Université du Québec à Montréal, Montréal, Canada*

The quantum Hall effect (QHE) is observed in a two-dimensional electron gas formed in millimeter-scale hydrogenated graphene [1], with a mobility < 10 cm$^2$/Vs and corresponding Ioffe-Regel disorder parameter $(k_F\lambda)^{-1}$ ~ 500. Our observations push the limit of disorder where the QHE can still be attained in a strong magnetic field, suggesting that the QHE might be robust to arbitrarily large disorder. Disordered graphene samples were prepared from pristine, large-area, monolayer graphene samples grown by chemical vapour deposition (CVD) on Cu foils. Disorder was controllably introduced into the graphene by exposure to a beam of atomic hydrogen in a UHV chamber. *In-situ* measurement shows an exponential growth in graphene sheet resistance versus hydrogen dose. We find hydrogenated graphene to exhibit a strong temperature dependent resistance consistent with variable range hopping. We measured the 2-point resistance of hydrogenated graphene at low temperatures in magnetic fields of up to 45T. A colossal negative magnetoresistance was observed, with a dramatic transition from a highly resistive state of $R_{2pt} = 250\ h/e^2$ at zero field to a quantized resistance $R_{2pt} = 12\,962\ \Omega$ at 45 T, which is within 0.5% of $h/2e^2$. The quantized resistance corresponds to a QHE state with $\nu = -2$ filling factor, $R_{2pt} \approx |R_{xy}| = h/2e^2$, and $R_{xx} = 0$. The high field resistance versus charge carrier density is consistent with the opening of an impurity-induced gap in the density of states of graphene. The mean spacing between point defects induced by hydrogenation was estimated to be $\lambda_D = 4.6 \pm 0.5$ nm via Raman spectroscopy. The rapid collapse of resistance and emergence of a QHE state is observed to occur when the magnetic length $\ell_B = (\hbar/eB)^{1/2}$ is comparable to $\lambda_D$. The interplay between electron localization by defect scattering and magnetic confinement in two-dimensional atomic crystals will be discussed.

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**P309**

# Preparation of single layer graphene and investigation on the graphene-based flexible transparent field-effect transistor

Nyan-Hwa Tai and Li-Wei Tsai

*Department of Materials Science and engineering, National Tsing-Hua University, Taiwan*
*(nhtai@mx.nthu.edu.tw)*

In this work, large-area single graphene was synthesized on a Cu foil using the low pressure chemical vapor deposition process. The graphene flims were then transferred from the Cu foil to polyethylene terephthalate by using PMMA anisole solution for fabricating flexible transparent graphene-based field-effect transistors. The electropolish method was adopted to smooth the surface of the Cu foil. Roughness of the Cu foil surface is an important factor because it not only influences the smoothness of graphene films on arbitrary substrate after transfer but also affects electronic transport property of the graphene-based devices. We investigated the influences of the electropolish process using Raman spectrum, scanning electron microscope, and optical microscope. This study found that adoption of the electropolish process to improve the carrier mobility of the flexible transparent graphene-based field-effect transistors from 90 cm$^2$/Vs to 340 cm$^2$/Vs. In the bending tests, change rate of carrier mobility was smaller than 10% when bending radius of curvature was changed from 1.0 to 6.0 cm.

## Phosphorous-doped reduced graphene oxide

**P310**

Ferdinando Tristan[1], Sofía M. Vega-Diaz[1], Aaron Morelos-Gomez[3], Rodolfo Cruz-Silva[1],
Morinobu Endo[1,3], Mauricio Terrones[1,2,4]

*1 Research Center for Exotic Nanocarbons, Shinshu University, Nagano, Japan*
*2 Department of Physics, Materials Research Institute, The Pennsylvania State University, PA, USA*
*3 Faculty of Engineering, Shinshu University, Nagano, Japan*
*4 Department of Materials Science and Engineering, and Center for 2-Dimensional and Layered Materials, The Pennsylvania State University, PA, USA*

Graphene oxide is a versatile material which could be used to produce bulk quantities of reduced graphene oxide (graphene). Graphene oxide has an additional advantage: it can be easily doped. Since doped-carbon materials with different elements such as boron, nitrogen or other elements have attracted the interest of numerous scientists due to its unique electronic properties that result in exceptional performance for applications in electronics or catalysis. In this work, a simple procedure to dope graphene oxide with phosphorous in bulk quantities, is described. This kind of doping is expected to promote a strong n-type behavior than that of nitrogen doping [1].

The produced samples were mainly characterized by SEM, Raman spectroscopy and XPS in order to confirm the successful doping of graphene oxide with substitutional amounts of phosphorous. Additionally, the effect of temperature during synthesis was studied, and it was found that synthesis temperatures above 800 °C, resulted in graphene doped with less amounts of phosphate.

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## Assembling molecular nano-magnets on a graphene surface

**P311**

Sarah A. Varey[1,2], George F. S. Whitehead[2], Richard E. P. Winpenny[2], Aravind Vijayaraghavan[1]

*1 National Graphene Institute and School of Computer Science, University of Manchester, UK (sarah.varey@manchester.ac.uk)*
*2 School of Chemistry and Photon Science Institute, University of Manchester, UK*

Magnetic molecules or molecular nano-magnets (MNMs) can be complexes with either a high or low total spin. The well-defined ground and excited spin states of particular low-spin MNMs have shown potential for their utilisation in quantum information processing and for spintronics. Assembled into a well-ordered system on the conductive surface of graphene, molecular spins can be addressed and coupled to the graphene, modulating the conductance of the graphene.

Chromium-based rotaxane MNMs with a ground state spin of S=1/2 have been well documented in the bulk as candidates encoding qubits in quantum information processing. In this structure, a molecular core of eight transition metal atoms is templated around an ammonium thread, held together by organic ligands. Pyrene-derivatised threads within this system have been designed and synthesised for favourable attraction to the conjugated $\pi$-system of carbon nano-materials. Solution phase deposition via dip-coating onto exfoliated and CVD graphene flakes is demonstrated. Room-temperature in-air atomic force microscopy measurements show specific adsorption to graphene over the $SiO_2$ substrate, with evidence of $\pi$-stacking taking place. Differential adsorption, with varying levels of coverage of these MNMs on the surface is observed with changing the number of layers of graphene present within the sample.

**P312**

# Functionalization of carbon nanotubes by luminescent $Eu^{3+}$ complex: markers for environmental and health monitoring

E.C.R. Vaz, A.N. Andrade, J.V. dos Anjos, Y.I. Vega-Cantú, F.J. Rodríguez-Macías, and P.A. Santa-Cruz

*DQF, Universidade Federal de Pernambuco, Recife-PE, Brazil*

Carbon nanotube (CNT) functionalization is a well-known way to improve their interaction with complex molecules. In this study we show functionalization with a luminescent marker based in a Eu3+ complex, which could be used for highly sensitive, selective detection via fluorescence allowing tracking of these functionalized CNT in the environment or in the body. We have studied the use of lanthanide complexes as fluorescent labels. These complexes ha ve the advantage of particularly narrow bands in their electronic spectra long fluorescence lifetimes and good resistance to UV irradiation [1]; which makes them suitable for many applications [2]. We used these fluorescent photonic markers to functionalize multi-walled CNT. Carbon nanotube were covalently functionalized by reaction with 4-azidobenzoic acid and then complexed with Eu salts, 1,10-phenantroline and oxadiazole under microwave irradiation for 15 min. SEM showed that this procedure can coat CNT with a layer of crystalline fluorescent complexes. Non covalent functionalization was performed by dispersing the CNT with sodium dodecylsulfate (SDS) and then synthesizing in situ the Eu complex with phenantroline, hydroxybenzoic aci d, and 4,4,4-trifluoro-1-phenyl-1,3- butanedione (BTFA). FT-IR and UV-vis confirmed the formation of the complexes, EDS analysis in the SEM confirmed the presence of Eu over the CNT. We found by fluorometry that these complexes did not show the fluorescence quenching typically produced by CNT, showing 2 ms lifetimes for thehypersensitive 5D0 7F2 Eu3+ transition, while the isolated complex has fluorescence lifetimes of 1.8 ms. This verifies the feasibility of tracking these labeled CNT in aqueous solutions for health and environmental studies, which our group is currently pursuing.

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**P313**

# Signature of the two-dimensional phonon dispersion in graphene probed by double-resonant Raman scattering

Patrick May[1], Michele Lazzeri[2], Pedro Venezuela[3], Felix Herziger[1], Gordon Callsen[1], Juan S. Reparaz[1], Axel Hoffmann[1], Francesco Mauri[2], and Janina Maultzsch[1]

*1 Institut fur Festkorperphysik, Technische Universitat Berlin, Germany,*
*2 IMPMC, Universite Pierre et Marie Curie, France,*
*3 Instituto de Física da Universidade Federal Fluminense, Brazil*

The contributions of the two-dimensional phonon dispersion to the double-resonant Raman scattering process in graphene is determined from the line shape of the two-phonon combination mode around 2450 $cm^{-1}$. This mode is usually referred to as $G^*$ or $D + D''$. By combining Raman experiments with excitation energies up to 2.8 eV and a full two-dimensional calculation of the double-resonant Raman process based on fourth-order perturbation, we can describe in detail the composition of this two-phonon mode and explain the asymmetry on the high-frequency side. The asymmetry directly reflects phonon contributions with wave vectors away from the high-symmetry lines in the Brillouin zone. The main peak of this mode originates from the $\mathbf{K\Gamma}$ high-symmetry line highlighting and supporting two important findings: first, the existence of so-called *inner* processes and, second, the dominant contribution along the high-symmetry line.

## Ultrafast nanomechanical mapping of suspended graphene

**P314**

Nick Clark, Antonios Oikonomou, Aravind Vijayaraghavan

*Centre for Mesoscience and Nanotechnology, The University of Manchester, UK*
*(aravind@manchester.ac.uk)*

I present quantitative nanomechanical maps of suspended graphene membranes, both monolayer and multilayer. Peakforce QNM, a new off resonance tapping AFM mode, allows rapid mapping of force response curves at every pixel, two orders of magnitude faster than conventional force volume mapping. A range of nanomechanical properties, including the adhesion, modulus, dissipation and deformation can then be extracted in real time along with the topographic data. Circular holes were created in silicon nitride membranes on silicon supports via a SF6 etch using a photolithographically defined etch mask. Mechanically exfoliated graphene flakes were then transferred onto the nitride membrane, leaving an array of suspended circular areas suitable for transmission characterization methods as TEM as well as AFM. The adhesion of the flakes to the silicon nitride membrane was also investigated, and compared with previously published results on silicon dioxide substrates.

## An improved technique for aligned transfer of mechanical-exfoliated single layer graphene with low contamination

**P315**

Xuanye Wang[1], Roberto Paiella[1], Bennett Goldberg[1,2], Anna Swan[1,2,*]

*1 Department of Electrical and Computer Engineering, Boston University, Boston MA 02215 USA*
*(swan@bu.edu)*
*2 Department of Physics, Boston University, Boston MA 02215, USA*

We present an improved aligned transfer technique for mechanical exfoliated single layer graphene. The method overcomes the problem of random positioning in graphene exfoliation without potentially contaminating its quality caused by polymers such as poly-(methyl methacrylate) (PMMA), which limits its performance [1]. Here, we avoid using PMMA and instead use a heavier polymer that leaves less residue.

Graphene is first exfoliated on a Si/SiO2 wafer with water soluble polymer layer spun on top to a combined thickness which makes it easy to observe through interference. Transparent Poly-dimethylsiloxane (PDMS) is then attached on top of the graphene as the supporting transfer material. The wafer is released by immersion the sandwich in water so that water soluble layer dissolves. The graphene/PDMS structure is manipulated with a three dimensional micrometer stage and a microscope to place the graphene with micrometer precision on the target surface. Single layer defect-free graphene with size as large as 50 microns are precisely positioned onto silicon dioxide substrates, as well as hexagonal Boron Nitride and hole patterns. The transferred graphene quality is evaluated using atomic force microscope (AFM) data, scanning electron microscope (SEM) picture, Raman spectra comparison and electrical mobility measurement show the perfect flatness and cleanliness of our transferred graphene. Raman spectra of suspended post-transferred graphene show no extra charge is introduced in this transfer process.

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## P316 The effect of CNHs adsorbed simvastatin on bone regeneration

Akiko Yamauchi[1], Sachiko Matsumura[2], Kiyotaka Shiba[2], Masako Yudasaka[3],
Sumio Iijima[3,4] and Atsuro Yokoyama[1]

*1 Hokkaido University, Japan (yama-aki@den.hokudai.ac.jp)*
*2 Cancer Institute, Japanese Foundation for Cancer Research, Japan*
*3 National Institute of Advanced Industrial Science and Technology, Japan*
*4 Meijo University, Japan*

Objectives: Previously we reported that carbon nanohorns (CNHs) had excellent osteoconductivity. Simvastatin well known as a cholesterol-lowering drug is studied as a substance that promotes bone formation. The purpose of this study was to evaluate the effect of CNHs adsorbed simvastatin on bone regeneration.

Materials and Methods: CNHs was dispersed in 50% ethanol solution. Simvastatin was dissolved in the CNHs suspension, and it was fixed on porous polytetrafluoroethylene (PTFE) membrane by vacuum filtration (S-CNHs/PTFE). CNHs without simvastatin were also fixed on PTFE membrane (CNHs/PTFE). Bone defects of 7 mm diameter were created in calvarial bone of rats. The defects were covered with CNHs/PTFE membrane (NH groups) and S-CNHs/PTFE membrane (S-NH groups), or left untreated for control (C groups). The rats were sacrificed after 2 and 8 weeks. Radiographic, histological and histomorphometric evaluation and were carried out. Also, some specimens were observed by TEM and HRTEM.

Results: Simvastatin was adsorbed to CNHs. The amounts of newly formed bone of S-NH groups was significantly extensive than those of the other groups at 8 weeks, while those of NH and S-NH groups were same at 2 weeks. Many osteoclasts were observed along the membrane in S-NH group in comparison with those of the C and NH groups.

Conclusions: These results suggested that CNHs could be an excellent carrier for simvastatin and CNHs absorbed simvastatin would be effective for bone regeneration.

## P317 Electrically driven ultra-high-speed black body emitters based on graphene

Tomoya Yokoi[1], Yusuke Takayama[1], Tatsuya Mori[1], Daiju Tsuya[2], Hideyuki Maki[1]

*1 Department of Applied Physics and Physico-Informatics, Faculty of Science and Technology,*
*Keio University, Japan (maki@appi.keio.ac.jp)*
*2 NIMS Nanofabrication Platform, Japan*

Graphene is an ideal two-dimensional materials with interesting electrical, optical and thermal properties, and these unique properties have been utilized for the novel application in optoelectronics and photonics. In this study, we fabricated a graphene-based emitter, and firstly observed high-speed blackbody emission with the response speed of > 1 GHz, which is > $10^6$ times higher than that of a conventional incandescent emitter with a filament and is higher or comparable to a light-emitting diode and a laser diode. We used mechanical exfoliation technique to deposit graphene onto $SiO_2$/Si substrate, and the Ti/Pd electrodes were deposited on it. We measured emission spectra under DC bias. Since the spectra can be fitted to Planck’s law, these emissions can be explained by the blackbody radiation by Joule heating. The graphene temperature obtained from the fitting increased with increasing bias voltage. The response speed of the emission from this device was evaluated by the time-resolved emission measurement under applying pulsed voltage. The observed emission intensities quickly respond to the applied pulse voltage. In addition, we also experimentally demonstrated 1-ns-width pulsed light generation. This high-speed response in graphene is explained by the extremely short temperature response time dominated by the high heat dissipation to the substrate owing to the direct heat dissipation to the substrate and the small heat capacity per unit area of graphene. This electrically driven, small footprint and ultra-high speed emitter may open novel applications of blackbody emission such as an integrated light source for integrated photonic or optoelectronic circuit, an ultrafast white light source and so on. This work was partially supported by Grants-in-Aid for the Encouragement of Young Scientists from the MEXT, by the A-STEP from JST and by NIMS Nanofabrication Platform in “Nanotechnology Platform Project”.

P318

# The effect of molecular adsorption on single-walled carbon nanotube field-effect transistors

P. Yotprayoonsak[1], K. Hannula[1], A. Johansson[1], T. Lahtinen[2], G. R. Szilvay[3],
P. Laaksonen[3], M. B. Linder[3], M. Ahlskog[1]

*1 Nanoscience Center, Department of Physics, University of Jyvaskyla, Finland,*
*2 Department of Chemistry, University of Jyvaskyla, Finland,*
*3 VTT Technical Research Centre of Finland, Biotechnology, Tietotie 2, Espoo, Finland*
*(peerapong.p.yotprayoonsak@jyu.fi)*

In this study, we have investigated the electrical properties of single SWCNT-FETs before and after exposure to a specific solution consisting of tetrahydrofuran (THF), naphthalene and lithium. Prior exposure to the active solution, carbon nanotubes ordinarily show a p-type semiconducting behavior with strong gate-potential response. After deposition, their electrical property has been switched from p-type to n-type semiconductor. The measurements were carefully carried out in oxygen-free condition inside an argon-filled glove box. The influence of doping is, however, reversible by simply cleaning the devices with deionized water outside glove box, in order to remove the lithium hydroxide attached on nanotube sidewalls. This is the first demonstration on electronic measurement of lithium doping by a solution [1] that has previously been demonstrated on the solubility of SWCNTs [2].

Furthermore, we have studied the effect of protein adsorption on individual SWCNT-FETs by hydrophobin. Hydrophobin is basically a surface active and amphiphilic protein which can be utilized as a surfactant for functionalization and solubilization of CNTs [3]. Our result shows the decrease in electrical conductance after the devices have been exposed to protein solution, instead of changing from p-type to n-type characteristics as previously observed in lithium deposition experiment.

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P319

# Freestanding vs supported graphene – Simulated ion irradiation

E. Harriet Åhlgren[1], Ossi Lehtinen[2], Jani Kotakoski[3], Arkady V. Krasheninnikov[1,4]

*1 University of Helsinki, Finland (harriet.ahlgren@helsinki.fi)*
*2 University of Ulm, Germany*
*3 University of Vienna, Austria*
*4 Aalto University, Finland*

Defects in nanomaterials can have drastic effects on the properties of these materials. This allows, in principle, controlled modification of these materials for example with ion irradiation. While nanomaterials can have a different response to irradiation than their bulk counterparts, existing theories only occasionally apply in their case. Therefore, to answer the question of what are the specific defect production mechanisms in graphene under ion irradiation, we have studied ion irradiation of graphene using molecular dynamics simulations [1,2,3]. We show that the defect types in freestanding graphene depend strongly on the energy of the specific ion, defects occurring at distinct energy ranges that differ from one defect to the next. Our results also indicate, that with growing amount of defects the membrane is stable, even with high defect concentrations up to 35% of the atoms missing. Besides freestanding graphene, we have recently extended our studies for graphene on a Pt(111) surface to analyze the effect of the substrate to the defect production mechanisms in graphene under ion irradiation. We also compare our results with experimental ones obtained by scanning tunneling microscopy.

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# Friday

K5

# Carbon nanotubes and nanocarbon hybrid materials

Hongjie Dai

*Stanford University, USA (hdai1@stanford.edu)*

This talk will cover two topics. The first is a new biological imaging technique based on the intrinsic fluorescence of carbon nanotubes, quantum dots and organic molecules in the so called NIR-II region in the spectral window of 1000-1400nm. *In vivo* real-time epifluorescence imaging of mouse hind limb vasculatures in the second near-infrared region (NIR-II) is performed using in NIR-II. Both high spatial (~30 micron) and temporal (<200 ms per frame) resolution for small-vessel imaging are achieved at 1–3 mm deep in the hind limb owing to the beneficial NIR-II optical window that affords deep anatomical penetration and low scattering. This spatial resolution is unattainable by traditional NIR imaging (NIR-I) or microscopic computed tomography, and the temporal resolution far exceeds scanning microscopic imaging techniques. Chirality sorted SWNTs for biological applications will also be presented.

Secondly, I will present our work on carbon nanotubes, graphene nanoribbons and inorgani-nanocarbon hybrid materials. Graphene nanoribbons obtained by nanotube unzipping will be presented. I will then talk about our recent work on making nanoparticles and nanocrystals on carbon nanotubes and graphene sheets for energy storage and photocatalytic applications. Lastly, for electronics applications, I will talk about our results on enrichment of semiconducting SWNTs with high purity and self-assembly of semiconducting SWNTs high packing density of >100 tubes/µm for device applications.

# The unique chemistry of carbon nanotubes in catalysis

Xiulian Pan*, Xinhe Bao*

*State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China (*xlpan@dicp.ac.cn and xhbao@dicp.ac.cn)*

Carbon materials have properties different from conventional oxides in catalysis, in particular as catalyst supports. Recently, carbon nanotubes (CNTs) interest us with their well defined tubular morphology and their electron structure in the graphene walls, where π electrons shift from the inside to the outside due to the curvature. This provides an intriguing confinement environment for nanocatalysts and catalytic reactions inside such small cavities. In the present talk, the unique effects of the electron confinement with CNT's and the resulted modulating in catalysis will be illustrated. The techniques to introduce metal nanoparticles homogeneously inside the CNT channels have been developed and the effects of confined metal catalysts on their physio-chemical properties, as well as their catalytic activities have been studied systematically. Using Fe as a probe, it is found that the redox properties of iron oxide and metallic iron are modified when they are confined inside the CNT channels. For example, the reduction of the CNT confined iron oxide is facilitated compared to that dispersed on the outer surface of CNTs. In this way, a distinct enhancement of the CNT encapsulated Fe species to the F-T process has also been revealed, which is attributed the favourable formation of the reduced iron species, e.g. iron carbides, inside the channel of CNTs. A striking enhancement of the catalytic activity of Rh particles confined inside nanotubes for the conversion of CO and $H_2$ to ethanol has been found. The overall formation rate of ethanol inside nanotubes exceeds that on the outside of the nanotubes by more than an order of magnitude, although the latter is much better accessible.

Another example will be showed in the present presentation is the effective substitution of CNT-encapsulated metallic iron particles for noble metals as a fuel cell catalyst. We have creatively encapsulated metallic iron nanoparticles within the compartments of pea-pod like carbon nanotubes. Thus direct exposure of metallic iron to oxygen and acid solution, as well as other poisons is prevented, which consequently solve the long lingering stability issue for metallic iron as fuel cell cathode catalysts. However, this physical isolation does not impede the catalytic properties of the encapsulated metals in ORR. We observed for the first time that the active d electrons of iron transfer to (penetrate) the carbon nanotube wall via interaction. The electrons enriched on the carbon surface catalyze directly oxygen reduction. Doping the nanotube wall with heteroatoms such as nitrogen and changing the encapsulated metals can further modulate the performance. In particular, the cell performance remains rather stable even in the presence of 10 ppm $SO_2$ in the air. This research provides a new idea for development and understanding non-noble metal catalysts for fuel cells, and the novel catalyst structure, "chainmail for catalyst", provides a novel concept for designing of efficient and durable catalysts under harsh reaction conditions.

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C27

# Designing nitrogen functionalities on N-doped few-walled carbon nanotubes for the oxygen reduction reaction

Maryam Borghei[1], Toma Susi[1], Jani Sainio[1], Ilya V. Anoshkin[1], Albert G. Nasibulin[1], Esko I. Kauppinen[1], Eeva L. Rautama[2], Tanja Kallio[2], Kaido Tammeveski[3], Virginia Ruiz[4]

*1 Department of Applied Physics, Aalto University, P.O. Box 15100, 00076 Aalto, Finland.*
*(maryam.borghei@aalto.fi)*
*2 Department of Chemistry, Aalto University, P.O. Box 16100, 00076 Aalto, Finland.*
*4 Institute of Chemistry, University of Tartu, Ravila14a, 50411 Tartu, Estonia*
*4 IK4-CIDETEC, Paseo Miramón 196, E-20009 San Sebastián, Spain*

The introduction of nitrogen heteroatoms into the hexagonal lattice of carbon nanotubes and graphene has received tremendous recent attention. This has led to a new class of catalyst materials with remarkable electrocatalytic activity for the oxygen reduction reaction (ORR) comparable to precious metal Pt-catalysts, for the cathode reaction in fuel cells [1]. However, there are still open questions about the intrinsic nature of the active sites for ORR in these materials [2]. In this study, we doped few-walled carbon nanotubes (FWCNTs) with nitrogen by first coating them with polyaniline (PANI) followed by pyrolysis at high temperatures. The synthesis conditions (FWCNTs pretreatment, amount of PANI coating and post-pyrolysis temperature and duration) were varied to investigate the effects of the resulting types of nitrogen functionalities. Despite relatively low nitrogen loadings, remarkable ORR electrocatalytic activity was observed. A comprehensive characterization combining ORR electrochemical measurements, HR-TEM, Raman and XPS on the series of N-FWCNTs with different nitrogen contents, provided deeper knowledge on the role of N-functionalities on the ORR activity, rather than solely focusing on bulk N-loadings.

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C28

# Formation of active sites for oxygen reduction reactions by transformation of nitrogen functionalities in nitrogen-doped carbon nanotubes

Tiva Sharifi, Guangzhi Hu, Xueen Jia, and Thomas Wågberg*

*Department of Physics, Umeå University, S-901 87 Umeå, Sweden (*thomas.wagberg@physics.umu.se)*

Recently, the intrinsic catalytic properties of non-metallic nitrogen-doped carbon nanotubes (N-doped CNTs) have received increasing attention as oxygen reduction reaction (ORR) catalysts. Even though the basic mechanisms of ORR in N-doped CNTs are known there is still a large controversy regarding the catalytic efficiency of different nitrogen functionalities present in the doped carbon nanostructures toward ORR. In our study, instead of trying to control the type of nitrogen functionality in the growth process, we have focused on transforming the nitrogen functionalities into others in the already synthesized samples. By a simple heat treatment, the unstable pyrrolic functionalities transform into pyridinic followed by an immediate transition into quartenary center and valley nitrogen functionalities. By measuring the electrocatalytic oxidation reduction current for the different samples, we achieve information on the catalytic activity connected to each type of nitrogen functionality. Through this, we conclude that quaternary nitrogen valley sites, N-$Q_{valley}$, are the most active sites for ORR in N-doped CNTs. Our study gives both insights on the mechanism of ORR on different nitrogen functionalities in N-doped CNTs and it proposes how to treat samples to maximize the catalytic efficiency of such samples [1].

[1] Sharifi T, Hu G, Jia X, Wågberg T. ACS Nano. 2012;6(10):8904-12

C29

# Controlled substitutional functionalization in single-walled carbon nanotubes: Is it really possible?

Paola Ayala

*Faculty of Physics, University of Vienna, Austria (paola.ayala@univie.ac.at)*

The practical difficulties to produce ultra-clean, nearly defect-free single walled carbon nanotubes (SWCNTs) have constantly appeared as stumbling blocks to have a direct proof of their predicted properties. This is not surprising because the electronic and optical properties SWCNTs are very sensitive to the chemical environments [1]. Whether we have to deal with the inevitable interactions of nanotubes in a bundle, single dopants, encapsulated structures, suspending media or tailored defects, the energies of charge carriers and lattice vibrations are always modified.

I will show our recent progress on establishing the prerequisites for studying the rich low-dimensional physics of functionalized SWCNTs [2,3]. It will be discussed how metallicity-sorting combined with high energy spectroscopy techniques can nicely disentangle the characteristic density of states of functionalized SWCNTs unambiguously. An insight into the influence of doping, chemical interactions on the electronic ground state and the electronic transport properties of SWCNTs will be presented. We will discuss the changes in the site selective electronic structure within various types of metallicity pure SWCNTs (metallicity-sorted and functionalized) and substitutionally doped SWCNTs (with B, N and P).

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C30

# Large-scale synthesis of few-walled small diameter boron nitride nanotubes (sub. 10 nm) by an induction thermal plasma

Keun Su Kim, Christopher Kingston, Amy Hrdina, Mark Plunkett, and Benoit Simard

*Emerging Technologies Division, Security and Disruptive Technologies Portfolio, National Research Council of Canada, Canada (christopher.kingston@nrc-cnrc.gc.ca)*

Few-walled small diameter boron nitride nanotubes (BNNTs) have been attracting much attention due to their intriguing properties [1]. However, unlike the carbon nanotube cases, the absence of an effective method for the large-scale synthesis of ultrafine BNNTs (sub. 10 nm) has still been a prime obstacle to further understanding BNNTs and their real-world applications. Here we report a new method for the hundred-gram-scale synthesis of ultrafine BNNTs at atmospheric pressure. A high temperature plasma technology was employed [2] for the continuous conversion of pure h-BN powder into few-walled BNNTs without catalysts. We have successfully demonstrated that BNNTs can be synthesized continuously in various forms of macroscopic cloth-like sheets, fibrils, and thin transparent films with a relatively high purity (> 50%). In a typical run, the yield rate is ~10 g/h which is ~100 times higher than those of the present state-of-the-art technologies reported in the literature. The diameters and lengths of the BNNTs produced are estimated as ~5 nm and few µm, respectively. The high temperature of the plasma, over 8,000 K, enables us to achieve this high yield rate with a high structural quality. Additionally, the very high quenching rate (~$10^6$ K/s) in this method improves the selectivity towards small diameter BNNTs significantly by facilitating the nucleation of small B nanoparticles. The BNNT growth mechanism in our process is also discussed based on a root-growth mechanism, which has allowed us to understand the effects of the plasma conditions on the nucleation and growth of BNNTs systematically. Lastly, we introduce a cost-effective and scalable purification protocol developed for this new class of BNNTs. Combining the plasma synthesis method and the purification protocols developed here will open up new possibilities for providing high purity small diameter BNNTs at large scales for scientific investigation and practical applications.

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C31

# Interface engineering of nanostructured BN surfaces

Amir Pakdel*, Yoshio Bando, Dmitri Golberg*

*International Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), Tsukuba, Japan (*pakdel.amir@nims.go.jp and golberg.dmitri@nims.go.jp)*

Continuous progress in nanofabrication methods have led to the better understanding of physics and chemistry of the liquid/solid and liquid/gas interfaces at low-dimensional materials and brought the advent of a new area of nanoscale interface engineering. The main goal of this new field is to employ nano- and microscale interfacial features to obtain materials with radically new and previously unattainable properties.[1] A classic example of such systems is hierarchical boron nitride (BN) surfaces, in which nano- and microscale topography gives an unusual rise to their water-repelling properties. That is, the intrinsic hydrophilic BN with water contact angle (CA) of ~50° exhibits superhydrophobic behavior with water CAs larger than 150°.[2]

BN-based hierarchical nanostructures, in particular, vertically aligned and randomly distributed nanotubes and nanosheets, were synthesized and employed as a platform to study the influence of surface nano-morphology on its static and dynamic interaction with water droplets.[3,4] The variation of contact angle in different nano-hierarchical BN surfaces is attributed to the combined effects of surface roughness and partial liquid-solid contact at the interface. Moreover, the impact response of water droplets impinging on BN arrays with different wetting properties is distinct. In the case of superhydrophobic surfaces, the water droplet bounces off several times, while in less hydrophobic surfaces it does not rebound and remains pinned to the surface. These results provide a facile route for the selective preparation of nano-hierarchical BN films and tuning their water-repelling behavior, for which a number of promising applications in microelectronics and optics can be envisaged.

[1] S. Manakasettharn, J.A. Taylor, T. Krupenkin, Comprehensive Nanoscience and Technology: Academic Press (2011) 383–411
[2] A. Pakdel, *et al.*, Mater. Today 15 (2012) 256-265
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[4] A. Pakdel *et al.*, Nanotechnology 23 (2012) 215601

# Saturday

# NT13 Satellite Symposia

As has been a tradition of the NT Conference series for many years, thematically linked Satellite Symposia take place after the main NT13 conference. These will be held during Saturday June 29, 2013 across the bay of Finland in Tallinn, Estonia. Satellite participants travel to Tallinn by ferry on Friday afternoon, which leaves from Länsisatama at 16:30 sharp. *Do not be late!*

The programs and abstracts for the Satellites can be found on the following pages, and the joint schedule on the last page of the abstract book.

The NT13 Satellite Symposia and their Organizers are:

## 9TH INTERNATIONAL SYMPOSIUM ON COMPUTATIONAL CHALLENGES AND TOOLS FOR NANOTUBES (CCTN13)

Arkady Krasheninnikov (Aalto University and University of Helsinki, Finland)
Hisashi Nakamura (RIST, Japan)
David Tomanek (Michigan State University, USA)

## 7TH INTERNATIONAL WORKSHOP ON METROLOGY, STANDARDIZATION AND INDUSTRIAL QUALITY OF NANOTUBES (MSIN13)

Ado Jorio (Universidade Federal de Minas Gerais, Brazil)
Hua Jiang (Aalto University, Finland)

## 5TH CARBON NANOMATERIAL BIOLOGY, MEDICINE AND TOXICOLOGY SATELLITE SYMPOSIUM (CNBMT13)

Markus Ahlskog (University of Jyvaskyla, Finland)
Markus B. Linder (VTT Nanobiotechnology, Finland)

## 4TH GRAPHENE SATELLITE SYMPOSIUM (GSS13)

Pertti Hakonen (Aalto University School of Science, Finland)
Andreas Isacsson (Chalmers University of Technology, Sweden)

## 3RD NANOCARBON COMPOSITES SYMPOSIUM (NCC13)

Albert G. Nasibulin (Aalto University, Finland)
Milo Shaffer (Imperial College London, UK)
Irina Hussainova (Tallinn University of Technology, Estonia)

## 1ST CARBON NANOTUBE THIN FILM APPLICATIONS SYMPOSIUM (CNTFA13)

Yutaka Ohno (Nagoya University, Japan)
Esko I. Kauppinen (Aalto University, Finland)
Young Hee Lee (SungKyunKwan University, Korea)

# CCTN13

| | | |
|---|---|---|
| | **SESSION 1** ***(chair: Oleg Yazyev)*** | |
| 09:00–09:45 | **I1:** Carbon nanotube sensors and electronic properties of carbon chains (J-C. Charlier) | p. 242 |
| 09:45–10:30 | **I2:** Atomic-scale description of electron beam effects in nanotubes and two-dimensional materials (J. Kotakoski) | p. 242 |
| 10:30–10:45 | **POSTERS+** ***(David Tomanek)*** | |
| 10:45–11:45 | **COFFEE + POSTERS** | |
| | **SESSION 2** ***(chair: Jean-Christophe Charlier)*** | |
| 11:45–12:30 | **I3:** Non-equilibrium gaps generated in graphene-based materials: electron-phonon coupling in nanotubes – laser excitation in graphene (S. Roche) | p. 243 |
| 12:30–13:00 | **C1:** Computer simulation study of the CVD synthesis of carbon nanotubes and graphene (C. Bichara) | p. 243 |
| 13:00–13:30 | **C2:** Possibilities for Bose-Einstein condensation in individual carbon nanotubes (I. Bondarev) | p. 244 |
| 13:30–14:30 | **LUNCH** | |
| | **SESSION 3** ***(chair: Somnath Bhattacharyya)*** | |
| 14:30–15:15 | **I3:** A theorist's journey through carbon nanotubes, graphene and other two-dimensional materials (O. Yazyev) | p. 244 |
| 15:15–15:45 | **C3:** Ewald summation on a helix: A route to self-consistent charge density-functional based tight-binding modeling of helical structures (I. Nikiforov) | p. 245 |
| 15:45-16:15 | **C4:** Understanding initial dissociation process of carbon source molecules during nanotubes and graphene synthesis: *Ab initio* molecular dynamics simulations (Y. Shibuta) | p. 245 |
| 16:15–17:15 | **COFFEE + POSTERS** | |
| | **SESSION 4** ***(chair: Jani Kotakoski)*** | |
| 17:15–17:45 | **C5:** Formation of diamond nanowires inside carbon nanotubes: An *ab initio* study (Z. Zhu) | p. 246 |
| 17:45–18:15 | **C6:** Extended Hückel theory for electronic transport in carbon nanotubes with metal contacts (A. Zienert) | p. 246 |
| 18:15–19:00 | **I4:** Understanding high frequency transport in low-dimensional graphitic carbon and superlattice systems (S. Bhattacharyya) | p. 247 |
| 19:00–20:00 | Transport to dinner | |
| 20:00–23:00 | **SATELLITES DINNER** | |

# CCTN13 Posters

# MSIN13

| | | |
|---|---|---|
| | **SESSION 1** ***(chairs: Hua Jiang and Mark Hersam)*** | |
| 09:00–09:45 | **K1:** Preparation and characterization of monodisperse carbon nanomaterials (M.C. Hersam) | p. 254 |
| 09:45–10:15 | **I1:** Search for high $T_c$ in boron-doped single-walled carbon nanotubes (J. Haruyama) | p. 254 |
| 10:15–10:45 | **I2:** Metrology using doped single-wall carbon nanotubes and graphite intercalation compounds (T. Pichler) | p. 255 |
| 10:45–11:30 | **COFFEE + POSTERS** | |
| | **SESSION 2** ***(chair: Francisco Bonaccorso)*** | |
| 11:30–12:00 | **I3:** Optical absorption of single-walled carbon nanotubes in the far-infrared region (T. Okazaki) | p. 255 |
| 12:00–12:30 | **I4:** Individual carbon nanotubes probed by non-linear optical spectroscopy (A. Johansson) | p. 256 |
| 12:30–13:00 | **I5:** Evaluation of carbon nanotube and graphene by absorption and Raman spectroscopy (M.S. Jeong) | p. 256 |
| 13:00–13:30 | **I6:** Carbon nanotube metrology at NIST: A progress report (M. Zheng) | p. 257 |
| 13:30–14:30 | **LUNCH** | |
| | **SESSION 3** ***(chair: Thomas Pichler)*** | |
| 14:30–15:00 | **I7:** Low-cost and high-throughput metal/semiconductor separation of single-wall carbon nanotubes toward industrial production (T. Tanaka) | p. 257 |
| 15:00–15:30 | **I8:** Purification of carbon nanotubes (C. Liu) | p. 258 |
| 15:30-16:00 | **I9:** Single tube to bulk characterisations of carbon nanotubes (D.Roy) | p. 258 |
| 16:00–17:00 | **COFFEE + POSTERS** | |
| | **SESSION 4** ***(chair: Ado Jorio)*** | |
| 17:15–17:45 | **I10:** Production and characterization of graphene dispersions with controlled morphological properties (F. Bonaccorso) | p. 259 |
| 17:45–18:15 | **I11:** Isotopic labeling in metrology of graphene (M. Kalbac) | p. 259 |
| 18:15–19:00 | **I12:** Metrology of focused ion beam patterning on graphene (B.S. Archanjo) | p. 260 |
| 18:30–19:00 | **WRAP UP** (Ado Jorio) | |
| 19:00–20:00 | Transport to dinner | |
| 20:00–23:00 | **SATELLITES DINNER** | |

# MSIN13 Posters

# CNBMT13

| | | |
|---|---|---|
| 10:00–10:45 | **K1:** Carbon nanotube meets plant cell biology: carbon nanotubes as organelle targeting nanocarriers (Y. Baba) | p. 268 |
| 10:45–11:45 | **COFFEE + POSTERS** | |
| 11:45–12:30 | **I1:** Carbon nanotubes and biomembranes: simulation studies (M. Sansom) | p. 268 |
| 12:30–13:00 | **C1:** Multiplexed biomimetic lipid membranes on graphene by dip-pen nanolithography (A. Vijayaraghavan) | p. 269 |
| 13:00–13:30 | **C2:** Catabolic intracellular compartments enable degradation of carbonaceous nanomaterials (J. Conroy) | p. 269 |
| 13:30–14:30 | **LUNCH** | |
| 14:30–15:15 | **C3:** Vertically aligned double- and single- walled carbon nanotubes for electrochemical surfaces (K. Moore) | p. 270 |
| 15:15–15:45 | **I2:** Functionalized carbon nanotubes for targeted drug delivery and magnetic cell labeling (C. Menard-Moyon) | p. 270 |
| 15:45-16:15 | **C4:** Hybrid nanocomposites from graphene, nanocellulose and genetically engineered proteins (P. Laaksonen) | p. 271 |
| 16:15–17:15 | **COFFEE + POSTERS** | |
| 17:15–19:00 | Free time | |
| 19:00–20:00 | Transport to dinner | |
| 20:00–23:00 | **SATELLITES DINNER** | |

# CNBMT13 Posters

# GSS13

**SESSION 1** ***(chair: Pertti Hakonen)***

09:00–09:45 **I1:** Photoconductivity and mid-infrared plasmons in graphene (M. Freitag) ........ p. 276

09:45–10:30 **K1:** Illuminating graphene (A. Ferrari) ........ p. 276

10:30–10:45 **C1:** Photoluminescence of 1D-graphene ribbons formed from coronene molecules inside single-wall carbon nanotubes (E.D. Obraztsova) ........ p. 277

10:45–11:45 **COFFEE + POSTERS**

**SESSION 2** ***(chair: Andreas Isacsson)***

11:45–12:30 **I2:** Thermo-opto-mechanics with graphene resonators (J. Parpia) ........ p. 277

12:30–13:00 **I3:** Electromechanical properties of suspended graphene membranes (E. Mariani) ........ p. 278

13:00–13:15 **C2:** Thermally assisted energy relaxation in nanomechanical graphene resonators (A. Croy) ........ p. 278

13:15–13:30 **C3:** Mechanical nonlinearities in graphene resonators (M. Tomi) ........ p. 279

13:30–14:30 **LUNCH**

**SESSION 3** ***(chair: Elena Obraztsova)***

14:30–15:15 **K2:** Graphene Flagship (J. Kinaret) ........ p. 279

15:15–15:45 **I4:** Graphene devices: from transistor to barristor (H-J. Chung) ........ p. 280

15:45-16:00 **C5:** *Ab initio* study and possible applications in NEMS of double- layer graphene separated by adsorbed molecules (A.M. Popov) ........ p. 280

16:00-16:15 **C6:** Photocurrent imaging of metal-graphene-metal photodevices with few-layer graphene (H. Cheong) ........ p. 281

16:15–17:15 **COFFEE + POSTERS**

**SESSION 4** ***(chair: Alexander Croy)***

17:15–17:45 **I5:** Scanning probe microscopy on graphene nanoribbons and self-assembled molecular layers on graphene (P. Liljeroth) ........ p. 281

17:45–18:00 **C6:** Incoherent interlayer conduction in graphene-graphene cross junction (S.W. Lee) ........ p. 282

18:00–18:15 **C7:** Electronic properties of a covalent GO-$C_{60}$ hybrid (F. Langa) ........ p. 282

18:15–18:30 **C8:** Boron nitride nanoribbons from *in-situ* unzipping during nanotube growth (L. Li) ........ p. 283

18:30–18:45 **C10:** Nitrogen-doped graphene materials as non-precious catalysts for oxygen reduction reaction (Y. Hou) ........ p. 283

18:45–19:00 **C11:** Synthesis of multi-layer graphene on epitaxially-grown metal catalyst film and its electrical properties (D. Kondo) ........ p. 284

19:00–20:00 Transport to dinner

20:00–23:00 **SATELLITES DINNER**

# GSS13 Posters

# NCC13

### SESSION 1 *(chair: Albert G. Nasibulin)*

09:00–09:45 **K1:** Graphene-based composite materials for flexible devices (H-M. Cheng) ........ p. 298

09:45–10:30 **I1:** Optimization of multi-walled carbon nanotube properties for composite production (V. Kuznetsov) ........ p. 298

10:15–10:30 **C1:** Rheology and morphology of pristine graphene/polymer composite gels (M.J. Green) ........ p. 299

10:30–10:45 **C2:** Insight on viscoelastic modeling of carbon nanotube composites (C. de Matos) ........ p. 299

10:45–11:45 **COFFEE + POSTERS**

### SESSION 2 *(chair: Milo Shaffer)*

11:45–12:15 **I2:** Modeling interdependent nano- and micro-structures in fiber reinforced composites (L. Gorbatikh) ........ p. 300

12:15–12:45 **I3:** Nano/micro hybrid structures and their multifunctional composites (J. Bai) ........ p. 300

12:45–13:00 **C3:** Development of a powder based, scalable route for the production of nano and hierarchical thermoset composites (T. Herzeg) ........ p. 301

13:00–13:15 **C4:** Insight on viscoelastic modeling of carbon nanotube composites (M. Giordano) ........ p. 301

13:15–13:30 **C5:** Continuous synthesis of carbon nanotubes on carbon fibre: towards scalable hierarchical composite production (D. Anthony) ........ p. 302

13:30–14:30 **LUNCH**

### SESSION 3 *(chair: Irina Hussainova)*

14:30–15:00 **I4:** Past, current and future applications of carbon nanotubes in composites (J. Amadou) ........ p. 302

15:00–15:30 **I5:** Metal-carbon composite materials (O. Tolochko) ........ p. 303

15:30–15:45 **C6:** Effect of carbon nanotube aqueous dispersion quality on mechanical properties of cement composite (I. Anoshkin) ........ p. 303

15:45-16:00 **C7:** Simple methods to prepare carbon nanotubes-gold nanoparticles hybrid materials for sensing applications (S. Moshkalev) ........ p. 304

16:00-16:15 **C8:** Mechanical reinforcement of a high-performance aluminium alloy AA5083 with homogeneously dispersed multi-walled carbon nanotubes (E. Anglaret) ........ p. 304

16:15–17:15 **COFFEE + POSTERS**

| | | |
|---|---|---|
| | **SESSION 4** ***(chair: Renno Veinthal)*** | |
| 17:15–17:30 | **C9:** Features of carbon nanotube based ceramics compounding on silicon dioxide (M. Simunin) | p. 305 |
| 17:30–17:45 | **C10:** Decoration of carbon nanofillers via flow functionalization and controlled polymerization (P. Salice) | p. 305 |
| 17:45–18:00 | **C11:** Nitrogen functionalization of vertically aligned carbon nanotubes through rf-plasma: tips and side walls photoemission response (M. Scardamaglia) | p. 306 |
| 18:00–18:15 | **C12:** Toughening of epoxy matrices with reduced single-walled carbon nanotubes and the effect of the resin stoichiometry (C. Kingston) | p. 306 |
| 18:15–18:30 | **C13:** Flexible transparent nanotube based coating for electronic applications (I. Komarov) | p. 307 |
| 18:30–19:00 | Free time | |
| 19:00–20:00 | Transport to dinner | |
| 20:00–23:00 | **SATELLITES DINNER** | |

# NCC13 Posters

| | | |
|---|---|---|
| **SP50** | Sensor properties of carbon nanotube/ZnO composites in ammonia presence (I.I. Bobrinetskiy) | p. 308 |
| **SP51** | Synthesis of PANI/$CN_x$ composites by lithium intercalation and exfoliation of carbon nanotube (C.M. Ibanez) | p. 308 |
| **SP52** | A novel alumina – nanocarbon hybrid material (R. Ivanov) | p. 309 |
| **SP53** | Aerosol synthesis of carbon nanotube-interweaved nanostructures for high-power lithium-ion battery applications (X. Jia) | p. 309 |
| **SP54** | Direct synthesis of the carbon nanomaterials on copper particles (T.S. Koltsova) | p. 310 |
| **SP55** | Tuning the localization behavior of CNTs in immiscible polymer blends by a reactive component (P. Potschke) | p. 310 |
| **SP56** | Elaboration of TiC/CNT composites by sol-gel technique (M. Umalas) | p. 311 |
| **SP57** | Application of tungsten dichalcogenide layered nanostructures Li-ion batteries negative electrode (E.S. Vasilyeva) | p. 311 |
| **SP58** | Thermoelectric modules made of p- and n-type single walled carbon nanotube composite films (U. Dettlaff-Weglikowska) | p. 312 |

# CNTFA13

**SESSION 1** ***(chair: Yutaka Ohno)***

09:00–09:45 **K1:** Carbon nanotubes: a road to applications (S. Fan)....... p. 314

09:45–10:00 **C1:** High performance aerosol-CVD SWCNT network electrodes (A. Kaskela)....... p. 314

10:00–10:15 **C2:** Spatially resolved transport properties of pristine and doped single-walled carbon nanotube networks (A. Hassanien)....... p. 315

10:15–10:30 **C3:** Mapping charge transport in chirality-selected carbon nanotube networks by electroluminescence (J. Zaumseil)....... p. 315

10:30–10:45 **C4:** Percolation in realistic hybrid carbon nanostructures networks (L. Simoneau)....... p. 316

10:45–11:45 **COFFEE + POSTERS**

**SESSION 2** ***(chair: Esko I. Kauppinen)***

11:45–12:15 **I1:** Extremely bendable, fully inkjet-printed transistors of carbon-nanotube films (T. Takenobu)....... p. 316

12:15–12:45 **I2:** Nano carbon devices & applications (K. Matsumoto)....... p. 317

12:45–13:15 **C5:** High-mobility carbon nanotube thin-film transistors based on transfer and printing techniques (Y. Ohno)....... p. 317

13:15–13:30 **C6:** Transferred wrinkled $Al_2O_3$ for highly stretchable and transparent graphene–carbon nanotube transistors (S. Chae)....... p. 318

13:30–14:30 **LUNCH**

**SESSION 3** ***(chair: Taishi Takenobu)***

14:30–15:15 **K2:** Carbon nanotube thin films for high-performance logic electronics (Q. Cao)....... p. 318

15:15–15:45 **C7:** Transparent and conductive thin films of both carbon nanotubes- and graphene-based nanocomposites (A. Zarbin)....... p. 319

15:45-16:00 **C8:** Commercially viable SWNT transparent conductive thin films from nanotubide inks (S. Fogden)....... p. 319

16:00-16:15 **C9:** Carbon nanotube transparent conducting films as electrodes for organic light-emitting diodes (H-Z. Geng)....... p. 320

16:15–17:15 **COFFEE + POSTERS**

**SESSION 4** ***(chair: Kazuhiko Matsumoto)***

17:15–17:45 **I3:** Monodisperse carbon nanomaterial thin film applications (M.C. Hersam)....... p. 320

17:45–18:15 **I4:** Self-assembled micro-honeycomb network of single-walled carbon nanotubes for heterojunction solar cell (S. Maruyama)....... p. 321

18:15–18:45 **C10:** Catalysts for controlled growth of single-walled carbon nanotubes (Y. Li)....... p. 321

18:15–18:30 **SUMMARY** ***(Yutaka Ohno and Esko I. Kauppinen)***

19:00–20:00 Transport to dinner
20:00–23:00 **SATELLITES DINNER**

# CNTFA13 Posters

# CCTN13

**I1**

# Carbon nanotube sensors and electronic properties of carbon chains

J.-C. Charlier

*University of Louvain, Institute of Condensed Matter and Nanosciences, Louvain-la-Neuve, Belgium*

The remarkable electronic and transport properties of carbon nanotubes (CNTs) make them very promising for a wide variety of applications in nanoelectronics and spintronics. In particular CNTs could be used as detection element for gas sensing nanodevices thanks to their high surface-to-volume ratio and to the high sensitivity of their physical properties to external perturbations. However, the response of pristine CNTs to gases is weak due to the intrinsically inert $sp^2$ carbon network that characterizes their sidewalls. In this talk, I will show how *ab initio* simulations can help to predict that CNT containing defects and decorated with various metal catalytic particles exhibit an extraordinary sensitivity and selectivity to gas molecules [1-4].

As strings of monoatomic thickness, chains of *sp*-hybridized carbon atoms constitute the logical one-dimensional phase of carbon. These 1D systems have been proposed theoretically for a long time until they were observed in electron microscopy studies. However, electrical measurements on these monoatomic chains have not been feasible. Now, by using a measuring system with an STM tip in a TEM specimen stage, carbon chains are not only produced but their electrical properties are also measured. Ab initio simulations (confirmed by MBPT calculations) reveal that strain has a decisive influence on the bandgap of the chain, thus determining its conductivity [5].

[1] Z. Zanolli, J.-C. Charlier, Phys. Rev. B 80 (2009) 155447
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[3] J.-C. Charlier , *et al.*, Nanotech. 20 (2009) 3755011
[4] Z. Zanolli, J.-C. Charlier, ACS Nano 6 (2012) 10786–10791
[5] O. Cretu, A. R. Botello-Mendez, I. Janowska, C. Pham-Huu, J.-C. Charlier, and F. Banhart (*arXiv* 1302.5207), *submitted* (2013)

**I2**

# Atomic-scale description of electron beam effects in nanotubes and two-dimensional materials

Jani Kotakoski

*Department of Physics, Universität Wien, Boltzmanngasse 5, 1090 Wien, Austria (jani.kotakoski@iki.fi)*

Recent developments in transmission electron microscopy (TEM) and computational resources have allowed quantitative atomic-level analysis of irradiation damage. We combine state-of-the-art TEM experiments with dynamical ab initio simulations to establish a detailed understanding of knock-on events in carbon nanotubes and two-dimensional materials under an electron beam. Irradiation-induced structural changes will be discussed in the context of pristine and doped carbon nanotubes and graphene, hexagonal boron nitride and transition metal dichalcogenide mono-layers, and in two-dimensional silica glass. The presented results have important implications for characterization methods involving energetic electrons, and provide basis for future advances in atomic-level engineering.

[1] Kotakoski *et al.*, Phys. Rev. B 74, 245420 (2006)
[2] Gan *et al.*, New J. Phys. 10, 023022 (2007)
[3] Kotakoski *et al.*, Phys. Rev. B 82, 113404 (2010)
[4] Banhart, Kotakoski, Krasheninnikov, ACS Nano 5, 26-41 (2011)
[5] Kotakoski *et al.*, Phys. Rev. Lett. 106, 105505 (2011)
[6] Kotakoski *et al.*, Phys. Rev. B 83, 245420 (2011)
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[9] Meyer *et al.*, Phys. Rev. Lett. 108, 196102 (2012)
[10] Kurasch *et al.*, Nano Lett. 12, 3168-3173 (2012)
[11] Susi *et al.*, ACS Nano 6, 8837-8846 (2012)
[12] Komsa *et al.*, Phys. Rev. Lett. 109, 035503 (2012)

I3

# Non-equilibrium gaps generated in graphene-based materials: electron-phonon coupling in nanotubes – laser excitation in graphene

Stephan Roche[1], Luis Foa Torres[2]

*1 CIN2 (ICN-CSIC) and Universitat Autonoma de Barcelona, Catalan Institute of Nanotechnology,*
*Campus UAB, Bellaterra, Spain (stephan.roche@icn.cat)*
*2 FaMAF - Universidad Nacional de Córdoba, Cordoba, Argentina (lfoa@famaf.unc.edu.ar)*

The occurrence of non-equilibrium dynamical gaps in transport properties of graphene related materials will be discussed, with a particular focus on inelastic transport in carbon nanotubes under high bias voltage, and graphene nanoribbons and two-dimensional graphene under laser illumination. The transport methodology based on the Landau-Büttiker multichannel methods, and extended in the Fock space or the Floquet space will be shown to be highly convenient to unravel non-perturbative and non-equilibrium phenomena.

[1] H. Calvo *et al.,* J. Phys. C. Matter 1 (2013) 144202
[2] H. Calvo *et al.,* App. Phys. Lett. 101 (2012) 253506
[3] L. E. F. Foa Torres and S. Roche, Phys. Rev. Lett. 97 (2006) 076804

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C1

# Computer simulation study of the CVD synthesis of carbon nanotubes and graphene

M. Diarra[1,2], H. Amara[2], F. Ducastelle[2] and C. Bichara[1]

*1 Centre Interdisciplinaire de Nanoscience de Marseille – CINaM*
*CNRS and Aix Marseille University – France*
*2 Laboratoire d'Etude des Microstructures (LEM) – CNRS and ONERA, France*

Using the tight binding model developed for nickel and carbon [1, 2] we investigate the growth mechanisms of Single Wall Nanotubes or graphene on a metallic catalyst. In both cases, the solubility of carbon in Ni plays an important role. It favors the growth of SWNT by enabling the nucleation and the dewetting of the tube cap from the catalyst nanoparticle [3-5], but seems detrimental in the growth of graphene, since it makes the control of the structure more difficult (number of layers, in particular). We try and understand the differences in growth conditions and mechanisms by making use of the Grand Canonical Monte Carlo method that is a trademark of our approach.

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[3] H. Amara *et al.*, Phys. Rev. Lett., 100, 056105 (2008)
[4] M. Diarra *et al.*, Phys. Stat. Sol. B 249, 12, 2629–2634 (2012)
[5] M. Diarra *et al.*, Phys. Rev. Lett. 109, 185501 (2012)

C2

# Possibilities for Bose-Einstein condensation in individual carbon nanotubes

I.V. Bondarev and A.V. Meliksetyan

*Department of Physics, North Carolina Central University, Durham, NC 27707, USA*

We show that carbon nanotubes (CNs) offer a testing ground to study the fundamentals of condensed matter physics in one dimension (1D). Specifically, we discuss possibilities for the 1D Bose-Einstein condensation (BEC) phenomenon that originates from the strong coupling of excitons and low-energy inter-band plasmons enabled via the quantum confined Stark effect by using an external electrostatic field applied perpendicular to the CN axis. This affects the exciton-plasmon coupling in individual semiconducting CNs [1], mixing excitons and inter-band plasmons of the same band, to result in strongly coupled hybridized excitations – exciton-plasmons in one individual nanotube [2]. Such hybridized excitations are strongly correlated collective Bose-type quasi-particles and, therefore, could likely be condensed under appropriately created external conditions – in spite of the well-known statements of the BEC impossibility in ideal 1D/2D systems [3] and experimental evidence reported earlier for no exciton BEC effect in carbon nanotubes [4]. Possibilities for achieving BEC in 1D/2D systems are theoretically demonstrated earlier in the presence of an extra confinement potential [5]. We show that the strongly correlated exciton-plasmon system in the semiconducting CN presents such a special case. We find the critical BEC temperature, as well as the condensate fraction and its exciton contribution as functions of temperature and electrostatic field applied. We discuss how the effect can be observed experimentally.

IVB acknowledges fruitful discussions with Janet Anders of UCL, UK. IVB is supported by the US DOE grant DE-SC0007117; AVM is supported by the US ARO grant W911NF-11-1-0189.

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I3

# A theorist's journey through carbon nanotubes, graphene and other two-dimensional materials

Oleg V. Yazyev

*Institute of Theoretical Physics, Ecole Polytechnique Fédérale de Lausanne (EPFL),*
*CH-1015 Lausanne, Switzerland*

The purpose of my talk is to reveal some close analogies and contrasting differences between carbon nanotubes, graphene and a few other emerging two-dimensional systems. I will compare the concepts of chirality of carbon nanotubes and graphene edges showing some recent experimental observations [1-3]. The similarities of electronic transport phenomena across carbon nanotube junctions and grain boundaries in polycrystalline graphene will be discussed [4,5]. Finally, I will cover the two-valley physics of two-dimensional semiconductors like $MoS_2$ and the topologically protected Dirac fermion states found at the surfaces of the recently discovered bulk topological insulators.

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# Ewald summation on a helix: A route to self-consistent charge density-functional based tight-binding modeling of helical structures

I. Nikiforov[1], T. Dumitrică[1,*], B. Hourahine[2], B. Aradi[3], Th. Frauenheim[3]

*1 Department of Mechanical Engineering, University of Minnesota, USA (*dtraian@me.umn.edu)*
*2 Department of Physics, University of Strathclyde, United Kingdom*
*3 BCCMS, Universität Bremen, Germany*

We present the generalization to helical case of the classical Ewald method [1], the harbinger of all modern self-consistent treatments of waves in crystals, including ab initio electronic structure methods. The derived formulas for the electrostatic potential and van der Waals energy prove to be numerically tractable and thus capable to provide the crucial component needed for coupling objective molecular dynamics [2] with the machinery of self-consistent charge density-functional based tight-binding [3]. The resultant method is put to work in illustrative simulations on a helical boron nitride nanotube, a screw dislocated zinc oxide nanowire, and an ideal DNA strand.

We will discuss in more depth the case of twisted zinc oxide nanowires and nanotubes, which were recently synthesized by screw-dislocation growth. We show [4] that the existence of these structures can be rationalized in terms of the energetics of surfaces and veritable Eshelby's twist linear elasticity mechanics supplemented by a nonlinear core term.

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# Understanding initial dissociation process of carbon source molecules during nanotubes and graphene synthesis: Ab initio molecular dynamics simulations

Yasushi Shibuta[1], Kohei Shimamura[2], Tomoya Oguri[1], Rizal Arifin[2], Wataru Hashizume[2],
Fuyuki Shimojo[2], and Shu Yamaguchi[1]

*1 Department of Material Engineering, The University of Tokyo, Japan (shibuta@materialt.u-tokyo.ac.jp)*
*2 Department of Physics, Kumamoto University, Japan*

We have investigated the initial dissociation process of carbon source molecules during the carbon nanotubes (CNTs) and graphene growth via a chemical vapor deposition (CVD) process by *ab initio* molecular dynamics (MD) simulation. In particular, we have examined the following three cases: (1) Methane dissociation on Ni(111) surface [1]. (2) Ethylene dissociation on Ni32 cluster [2] and (3) Ethanol dissociation on Ni32 cluster [3].

For example, methane molecules are dissociated into isolated carbon and hydrogen atoms via CH3 and CH fragments with chemisorbing the nickel (111) surface [1]. Dissociated carbon atoms are then buried into the subsurface space between first and second nickel layers via diffusion through hollow sites in the nickel layers.

In the presentation, our recent results will be introduced and then the role of the catalytic metals on the CNTs and graphene growth at the initial stage will be discussed.

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C5

## Formation of diamond nanowires inside carbon nanotubes: An ab initio study

Zhen Zhu[1], David Tománek[1], Yanquan Feng[2]

*1 Physics and Astronomy Department, Michigan State University, USA (zhuzhen@msu.edu)*
*2 School of Physics, Beijing Institute of Technology, P.R. China*

We investigate the possibility of templated growth of diamond nanowires from functionalized diamondoid molecules enclosed in a carbon nanotube (CNT). Our *ab initio* density functional theory studies identify suitable candidate molecules and conditions, under which such molecules may fuse to narrow diamond nanowires with $C_8H_8$ or $C_7H_8$ unit cells inside a CNT. We find that the unique environment inside a narrow carbon nanotube, which can be suitably represented by a cylindrical potential, subjects enclosed molecules to a high pressure, caused by a “capillary” force. The surrounding narrow nanotube orients the enclosed molecules in a suitable way favoring fusion within the constraining volume. Our calculations indicate that $C_{10}H_{16}$ adamantane molecules do not fuse to diamond nanowires in a reaction that requires additional energy, but rather convert to carbon chains [1]. On the other hand, $C_{14}H_{18}(COOH)_2$ diamantane di-acid molecules may fuse in an exothermic reaction to $-C_8H_8-$ diamond nanowires in hydrogen atmosphere [2]. Our canonical molecular dynamics calculations at elevated temperatures indicate likely intermediate products that occur during these reactions and agree with experimental observations [1,2].

Supported by the National Science Foundation Cooperative Agreement No. EEC-0832785, titled “NSEC: Center for High-rate Nanomanufacturing”.

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C6

## Extended Hückel theory for electronic transport in carbon nanotubes with metal contacts

Andreas Zienert[1], Jörg Schuster[2], Thomas Gessner[1,2]

*1 Chemnitz University of Technology, Germany (andreas.zienert@zfm.tu-chemnitz.de)*
*2 Fraunhofer ENAS, Germany*

Extended Hückel theory (EHT) is a well established method for the description of the electronic structure of molecules and solids. Compared to density functional theory (DFT) it provides a good compromise between accuracy and computational burden. In the present work we use a selfconsistent version of the EHT to study the electronic transport in metallic carbon nanotubes (CNTs) with various metallic electrodes (Al, Cu, Pd, Pt, Ag, Au). While the electronic structure of the metals is well described by the extended Hückel (EH) parameters of Cerdá [1], we show that a new parameter set for carbon strongly improves the agreement between EHT and DFT for small-diameter CNTs by taking into account the curvature of the tubes.

The new set of EH parameters for CNTs is developed by fitting the DFT band structure of the $(6,0)$ CNT [2]. Even though the new parameters are created for one unique CNT, they are highly transferable to all types of CNTs. To demonstrate the versatility of the approach, we compare selfconsistent EHT- and DFT-based electron transport calculations of finite length CNTs with metal electrodes. The good agreement between DFT and our new EHT is visible in the transmission spectra of the metal-CNT-metal systems. Furthermore, electronic transport properties of such systems are discussed in general. The conductance of metal-CNT-metal systems shows strong oscillations depending on the CNT length. This is attributed to finite-size effects. We find that the metals Ag and Au have the largest contact resistances to the CNT. Pd and Pt form low-Ohmic contact.

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# Understanding high frequency transport in low-dimensional graphitic carbon and superlattice systems

Somnath Bhattacharyya[1,2], George Chimowa[1,2,] M. V. Katkov[1]

*1 Nano-Scale Transport Physics laboratory, School of Physics, University of the Witwatersrand, Johannesburg, South Africa (somnath.bhattacharyya@wits.ac.za)*
*2 Centre of Excellence in Strong Materials, South Africa*

Developing hybrid super-structures including carbon nanostructures for quantum information science is widely sought after and we show a possible route in carbon superlattice structures based on experimental results as well as theoretical analysis which also incorporates high-speed switching capabilities. We propose a theoretical model of disordered carbon superlattice structures where the local density of electronic states is controlled by changing the $sp^3$-C bond alternation as well as the hopping disorder parameter of the $sp^2$-C regions [1]. In addition the incorporation of nitrogen atoms in carbon networks was modeled as a combination of disorders which vary both in correlated and uncorrelated manners. Resonant peaks associated with C and N sites in these structures show a conductance cross-over under variation of the nitrogen concentration in these structures which can explain the observed negative differential resistance in diamond-like carbon superlattices as well as the conductivity cross-over in nano-crystalline diamond films [2], [3]. Detailed analysis of transport measurements over a wide range of temperatures, magnetic fields and also frequency shows an enhanced characteristic length in these systems that supports switching of complex impedance in the range of 65 GHz. High frequency transport properties of carbon superlattice structures are compared to carbon nanotube and graphene devices which can demonstrate ballistic conductance features.

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**SP1**

# Ab initio molecular dynamics study of liquid water on NaCl(100) surface

Jian-Cheng Chen

*Department of Applied Physics and Department of Chemistry, Aalto University, FI-00076 Aalto, Finland (jian-cheng.chen@aalto.fi)*

By employing *ab initio* molecular dynamics (AIMD), we have simulated the liquid water-solid surface interaction of 256 water water on a (4×4) NaCl(100) unit cell, equilibriumed at a time scale of 50,000 fs. In this system, our AIMD results show that these water molecules occupy approximately in four layers. The liquid water density distribution has a maximum peak of 1.40 g/cm$^3$ in the first layer 2.8 Å above the NaCl surface. The water density decreases to 1.10 g/cm$^3$ in the fourth layer. The first layer water is about 1 ML on NaCl(100) surface, in which the oxygen atoms mainly occupy Na sites statistically. The liquid water structure appears when water is further away from the NaCl(100) surface by about 7.0 Å from oxygen-oxygen radial distribution function. To understand the dissolving process of NaCl into liquid water, we have calculated the dissolve barriers of $Cl^-$ and $Na^+$ ions from flat, vacancies,stepped and the corner of the island on the NaCl(100) surfaces using constraint method.

The barrier heights for producing Cl- or $Na^+$ ions on flat NaCl(100) surface are 0.78 eV and 0.75 eV, respectively. The dissolve barriers for $Cl^-$ and $Na^+$ ions on stepped surface are 0.19 eV and 0.13 eV respectively. The barriers for producing $Cl^-$ or $Na^+$ ions from the corners of island on NaCl(100) surface are 0.12 eV and 0.11 eV, respectively. These results indicate that the dissolving process of NaCl crystal starts from the corners of an island or a step surface. Thus, departure of the $Na^+$ ion has slightly lower barriers than dissolving $Cl^-$ ion at the initial stage. However when more $Na^+$ ions are dissolved, the $Na^+$ and $Cl^-$ ions have approximately the same barrier height as tested on the stepped surface.

**SP2**

# Early stages of Ti-O clusters' growth on SWNTs by ab initio calculations

M.A. Gialampouki, Ch.E. Lekka

*Department of Materials Science and Engineering, University of Ioannina, Greece (mgialab@cc.uoi.gr)*

We performed Density Functional Theory calculations to study the early stages of growth of Ti-O tetrahedral (Th) and octahedral (Oh) clusters, dimmers or trimmers on Single Wall Carbon Nanotubes (SWNT (8,0) and (5,5)). We found that Th may exist in several conformations with well localized electronic states, mainly below -1.5eV, whereas Oh are less stable and may be transformed to Th. In line with experimental suggestions, the Th could be considered as active, due to the localization of charge distribution and the emergence of C dangling bonds at the Fermi level. On the contrary, the Oh retains the pure SWNT $C_{2p}$-$C_{2p}$ $\pi$-like features. Nevertheless, all Ti-O clusters, exhibit new $Ti_{3d}$ states above -3eV revealing the expected $O_{2p}$ - $C_{2p}$ and interestingly $Ti_{3d}$ - $C_{2p}$ hybridizations, thus altering the (8,0) semiconducting character. From all edge-sharing clusters, we found that the linear Rutile-like octahedral trimmer (OhOhOh) favors the parallel to the zigzag alignment, while equiprobable growth for the two Ti-O phases, with small tendency towards spinal anatase-like OhOhOh, is expected for clusters vertically to SWNT. These results are in line with the Ti-O deposition on a multi wall carbon nanotube. These results could enlighten the early stages of growth of Ti-O on SWNT providing useful information in the field of nanoelectronics and nanotechnology.

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**SP3**

# A chirality selective growth of carbon nanotubes via twisted graphene nanoribbons

Hong En Lim[1], Yasumitsu Miyata[1], Ryo Kitaura[1], Yoshifumi Nishimura[1], Yoshio Nishimoto[1], Stephan Irle[1], Jamie H. Warner[2], Hiromichi Kataura[3,4] and Hisanori Shinohara[1,*]

*1 Department of Chemistry & Institute for Advanced Research, Nagoya University, Nagoya 464-8602, Japan*
*(*noris@nagoya-u.jp)*
*2 Department of Materials, University of Oxford, Parks Road, Oxford, OX1 3PH, UK.*
*3 Nanosystem Research Institute, National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki 305-8562, Japan.*
*4 Japan Science and Technology Agency, CREST, Kawaguchi, Saitama 330-0012, Japan.*

CNTs are commonly known as a roll-up graphene sheet which can be cleaved [1] to give strips of different widths, called graphene nanoribbons (GNRs). To date, we have learnt about the different ways by which a CNT can be unwrapped, however, how can these flimsy, strips of carbon be rolled to attain a tubular geometry remains elusive. Not until recently, Kit *et al.* proposed that the CNT can be formed through the twisting of GNR in their theoretical studies [2]. This inspires the study to construct the CNTs via this peculiar means of fabrication.

Herein, we report the first experimental realization of a thermally-induced, self-intertwining of GNRs for the preferential synthesis of CNTs with chiral indices of (7, 2) and (8, 1). The GNRs generated from the PTCDA, a perylene derivative, were transformed into CNTs in the inner space of a host template. Optical measurements performed on the newly grown CNTs revealed a significant enhancement in these two chiralities, matching the predicted chiralites for CNTs formed via the twisting of GNRs with a width of N=5. Our finding adds a radically new aspect to the present understanding of CNT synthesis, shedding much light on the future tuning of not only specific chiral tubes, but also contemporary nanomaterials engineering.

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**SP4**

# 2D transition-metal dichalcogenides: Doping, alloying and electronic structure engineering using electron beam

H.-P. Komsa[1], S. Kurasch[2], J. Kotakoski[3], O. Lehtinen[1,2], U. Kaiser[2], and A.V. Krasheninnikov[1,4]

*1 Department of Physics, University of Helsinki, Finland 2 Central Facility for Electron Microscopy, Ulm University, Germany 3 Department of Physics, University of Vienn, Austria*
*4 Department of Applied Physics, Aalto University (arkady.krasheninnikov@aalto.fi)*

By combining first-principles simulations with high-resolution transmission electron microscopy experiments, we study the evolution of atomically thin layers of transition metal dichalcogenides (TMDs) under electron irradiation. We show that vacancies produced by the electron beam agglomerate and form line structures, which can be used for engineering materials properties. We also study the radiation hardness of 2D TMD materials [1]. We further show that TMDs can be doped by filling the vacancies with impurity atoms. We also study the stability and electronic properties of single layers of mixed TMDs, such as $MoS_{2x}Se_{2(1-x)}$, which can be referred to as 2D random alloys [2]. We demonstrate that 2D mixed ternary $MoS_2/MoSe_2/MoTe_2$ compounds are thermodynamically stable at room temperature, so that such materials can be manufactured by CVD or exfoliation techniques. By applying the effective band theory approach we further study the electronic structure of the mixed ternary 2D TMD compounds and show that the direct gap in these material can continuously be tuned. Using GW first-principles calculations for few-layer $MoS_2$, we further study [3] the effects of quantum confinement on the electronic structure of this layered material. By solving the Bethe-Salpeter equation, we evaluate the exciton energy in these systems. Our results are in excellent agreement with the available experimental data. Exciton binding energy is found to dramatically increase from 0.1 eV in the bulk to 1.1 eV in the monolayer. The fundamental band gap increases as well, so that the optical transition energies remain nearly constant.

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SP5

# LCAO method for finite-temperature systems and self-consistent perturbation scheme beyond the GW approximation

Satoshi Nakamura[1], Syogo Tejima[2], Hisashi Nakamura[1]

*1 Research Organization for Information Technology and Science (RIST) Tokyo, Japan*
*(s.nakamura@rist.or.jp)*
*2 Research Organization for Information Technology and Science (RIST) Kobe, Japan*

The linear combination of atomic orbitals (LCAO) method, which was originally developed for calculating the electronic structure of systems at zero temperature, is extended to treat finite-temperature systems. The new method yields an approximate free energy that is an upper bound to the true free energy of a real system. The approximate free energy is given in the space spanned by an LCAO basis and in a parameterized form. When a mean field approximation is adopted and the approximate free energy is minimized with respect to the parameters, this method includes the conventional LCAO method at zero temperature as a limiting case.

As further development of the above method, we propose a scheme based on a kind of self-consistent perturbation theory, where both the non-interacting Hamiltonian and charge fluctuation are determined self-consistently. The non-interacting Hamiltonian is given within the Hartree-Fock approximation in which the interacting electron density is used instead of the non-interacting one. To describe the charge fluctuation dynamics, we use a functional-integral representation of the free energy [1]. Our main approximation is to replace the exact free energy functional by a variationally chosen quadratic form in the fluctuating field. This procedure leads to the inclusion of electron correlation beyond the GW approximation.

We also mention the application of our scheme to electron transport in carbon nanotubes and superconductivity in carbon-based materials.

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SP6

# Ab initio molecular dynamics study on the role of nickel cluster as catalytic metal in carbon nanotubes synthesis

Tomoya Oguri[1], Kohei Shimamura[2], Yasushi Shibuta[1],
Fuyuki Shimojo[2], and Shu Yamaguchi[1]

*1 Department of Materials Engineering, The University of Tokyo, Japan*
*2 Department of Physics, Kumamoto University, Japan*

The knowledge on the formation mechanism of carbon nanotubes and the role of catalytic metals in the growth of single-walled carbon nanotubes (SWNTs) via a catalytic chemical vapor deposition method has been established over two decades [1,2]. However, the difficulty of direct experimental observation of the dissociation of carbon source molecules has caused unclear understanding of the initial stage of SWNTs formation. In present study, dissociation of ethanol molecules on the nickel cluster has been investigated by *ab initio* molecular dynamics and nudged-elastic-band (NEB) simulations to discuss the initial stage of metal-catalyzed growth process of carbon nanotubes and the role of nickel cluster as catalytic metal through an alcohol catalytic chemical vapor deposition [2]. It has been observed that both C-C and C-O bonds in ethanol molecules are dissociated on the nickel cluster. Subsequently, formations of various reaction products such as hydrogen atoms and molecules, carbon monoxide, oxygen atom, water, ethylene, methane and their fragments have occurred. In addition, the role of nickel cluster as catalytic metal is evident indicated by a decrease of the activation energy of the C-H bond dissociation in the fragment molecules, which is estimated by the NEB analysis to be approximately one-eighth of the bond-dissociation energy of the corresponding C-H bond without the influence of the nickel cluster. In the presentation, the detail catalytic role of nickel cluster will be introduced after the brief review of recent computational works on this topic.

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**SP7**

# Simulation of nanostructures with helical symmetry using helical boundary conditions

David Teich[1], Gotthard Seifert[1], David Tománek[2], Zacharias G. Fthenakis[2]

*1 Physikalische Chemie, Technische Universität Dresden, Germany (david.teich@chemie.tu-dresden.de)*
*2 Physics and Astronomy Department, Michigan State University, USA*

Quantum mechanical calculations of periodic structures are usually performed by using translational periodic boundary conditions. However, ab initio methods formulated in the typical periodic boundary condition context are computationally very time consuming for helical structures consisting of a large unit cell. A more elegant way is to utilize the helical symmetry of helical structures by introducing helical boundary conditions. This leads to a reduction in the system size to an objective domain containing a minimum of atoms. We present the combination of helical boundary conditions with the density functional based tight binding method by using symmetry-adapted Bloch functions. Instead of translational k-points, the orbital symmetry is described with helical quantum numbers. As an example, the calculation of the deformation energy of a twisted carbon nanotube rope is shown [1].

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**SP8**

# Formation and stability of cellular carbon foam structures: An ab initio study

David Tománek and Zhen Zhu

*Physics and Astronomy Department, Michigan State University, USA (tomanek@pa.msu.edu)*

Inspired by the observation of an unusual structure on top of amorphous carbon covered by a thin metal layer [1], we studied the formation and structural as well as thermal stability of cellular foamlike carbon nanostructures using *ab initio* density functional calculations. The postulated structures with a mixed $sp^2/sp^3$ bonding character may be viewed as bundles of carbon nanotubes fused to a rigid contiguous 3D honeycomb lattice that can be compressed rather easily. The foam may accommodate the same type of defects as graphene, and its surface may be stabilized by terminating caps. We postulate that the foam may form under nonequilibrium conditions near grain boundaries of a carbon-saturated metal surface [2].

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SP9

# Single-molecule sensing using carbon nanotubes decorated with magnetic clusters

Zeila Zanolli[1], J.-C. Charlier[2]

*1 PGI-1 and IAS-1, Forschungszentrum Jülich, Germany (z.zanolli@fz-juelich.de)*
*2 IMCN, Université catholique de Louvain (UCL), Belgium*

Since their discovery, Carbon Nanotubes (CNTs) have constantly attracted growing interest in the scientific community due to their remarkable electronic and quantum transport properties that make them potentially useful for applications in nanoelectronics, spintronics and gas sensing devices. Thanks to their high surface-to-volume ratio and being one-dimensional nanosystems, CNTs are considered as exceptional nanodetectors since their properties are extremely sensitive to external perturbations. Moreover, CNTs decorated with transition metal magnetic nanoparticles are also good candidates for spin-dependent transport applications.

In this work, first-principles techniques and non-equilibrium Green's function approaches are used to investigate magnetism and spin-polarized quantum transport in carbon nanotubes (CNT) decorated with transition metal magnetic nanoclusters (NC). For small cluster sizes (< 1 nm), *ab initio* calculations predict a considerable local magnetic moment that induces spin polarization in the host CNT due to a strong mutual interaction with the magnetic NC. Such a huge local magnetic perturbation can be tailored by molecular adsorption on the metallic NC, thus modifying both the magnetization and the spin-dependent conductance of the hybrid CNT–NC system. The adsorption of benzene on Ni- or Pt-decorated metallic CNTs has been investigated as a test case. The *ab initio* simulations demonstrate that the magnetization change due to the absorption of a single benzene molecule should be large enough to be detected experimentally using either magnetic-AFM or SQUID magnetometer. Consequently, the present research suggests a novel approach for single molecule gas detection, based on local magnetic moment measurements in CNT–NC hybrid systems [1].

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# MSIN13

**K1**

## Preparation and characterization of monodisperse carbon nanomaterials

Mark C. Hersam

*Northwestern University, USA (m-hersam@northwestern.edu)*

This talk will highlight our latest efforts to develop strategies for purifying, functionalizing, and characterizing monodisperse carbon nanomaterials [1]. In particular, we have developed and commercialized a scalable technique for sorting surfactant-encapsulated single-walled carbon nanotubes (SWCNTs) by their physical and electronic structure using density gradient ultracentrifugation (DGU). DGU has proven to be compatible with a wide array of raw SWCNT materials, and enables high purity sorting by essentially all structural and electronic parameters including diameter, electronic type (i.e., metal versus semiconducting), and enantiomeric identity. By performing DGU in an iterative, orthogonal manner, nearly arbitrary sorting targets can be efficiently achieved including single chiralities in the small-diameter limit [2] and diameter refinement of electronically pure large-diameter SWCNTs [3]. Importantly, DGU can be generalized to a wide variety of other nanomaterials including double-walled carbon nanotubes [4], graphene [5], and metallic nanoparticles [6], thereby expanding the suite of monodisperse samples. In addition, DGU is compatible with a diverse range of encapsulation chemistries, including biocompatible, nonionic block copolymers (e.g., Pluronics and Tetronics) [7]. This talk will also delineate how two-dimensional diffusion-ordered spectroscopy (2D DOSY) nuclear magnetic resonance (NMR) characterization provides new insights into the underlying mechanisms of DGU and related SWCNT sorting methods [8].

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**I1**

## Search for high $T_c$ in boron-doped single-walled carbon nanotubes

J. Haruyama[1] and A. M. Rao[2]

*1 School of Science and Engineering, Aoyama Gakuin University, Japan*
*2 Department of Physics and Astronomy, and COMSET, Clemson University, USA*

It is highly expected that the small mass of carbon can promote a high transition temperature ($T_c$) in BCS-type superconductors. Recently, new carbon-based superconductors with a $T_c$ of ~10K [1, 2] were discovered, and a search for higher $T_c$ in similar systems has attracted much interest. In particular, superconductivity (SC) in carbon nanotubes (CNTs) is attracting considerable attention. SC in double-walled CNTs has been reported in last year [3]. Previously, we reported a $T_c$ ~ 12K in entirely end-bonded multi-walled CNTs [4] and boron-doped single-walled CNTs (B-SWNTs) [5], wherein the latter discovery was strongly supported by the first-principles electronic-structure study of the B-SWNTs. Interestingly, a $T_c$ ~ 19 K was recorded upon applying a small pressure (20 MPa) to the densely B-SWNT film. However, the following some problems still obstruct high reproducibility of the above results and improvement of $T_c$, e.g., precise control of (1) small amount of the born concentration (< 2 at.%), (2) chirality of the SWNTs (to all-metallic SWNTs), and (3) diameter, and also (4) reduction of the residual catalyst. Implications of these results will be discussed with recent advancement (e.g., doping of other impurities and ionic-liquid gating).

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I2

# Metrology using doped single-wall carbon nanotubes and graphite intercalation compounds

Julio Chacon[1], Markus Sauer[1], Ludger Wirtz[2], Hiromichi Kataura[3], Kazuhiro Yanagi[4], Hidetsugu Shiozawa[1], Paola Ayala[1], Thomas Pichler[1]

*1 University of Vienna, Faculty of Physics, Boltzmanngasse 5, 1090 Vienna Austria*
*2 Physics and Material Sciences Unit, University of Luxembourg, Luxembourg*
*3 NRI, AIST, Central 4, Higashi 1-1-1, Tsukuba, Ibaraki 305-8562, Japan*
*4 Department of Physics, Tokyo Metropolitan University, Japan*

In this contribution I report on our comparative photoemission study of different metallicity sorted SWCNT-bucky papers functionalized by advanced filling reactions and p- and n-type intercalation as well as on a detailed Raman analysis of graphite intercalation compounds (GICs) from stage I to VI. In the first part I focus on the effect of charge transfer between the functional elements and semiconducting and metallic nanotubes yielding novel metallic SWCNT hybrids. From high resolution photoemission we study the complex interplay between charge transfer and hybridisation as well as the nature of the metallic ground state in these SWCNT hybrids regarding a 1D Tomunaga-Luttinger liquid or Fermi liquid behaviour, respectively [1]. In the second part I revisit the Raman response of highly staged GIC. These compounds consist of charged graphene layeres next to the intercalant layers and uncharged graphene layers surrounded by graphene inbetween. From a detailed line-shape analysis the G- and 2D-lines of these charged and uncharged graphene layers are unambiguously identifyed. Concommitant to the in-plane lattice constants determined by x-ray diffraction and ab-initio theory I will correlate these results to the charge transfer and internal strain of graphene layers. This yields a very powerful toolbox to identify local internal strain in single and few-layer graphene and nanotube based devices, and composites [3]. J.C., M.S., H.S. and T.P acknowledge funding by the FWF, P.A. support by the EU.

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[2] J. Chacon, L. Wirtz, T. Pichler, PNAS *submitted* (2013)

I3

# Optical absorption of single-walled carbon nanotubes in the far-infrared region

Toshiya Okazaki[1,2]

*1 Nanotube Research Center, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba 305-8565, Japan (toshi.okazaki@aist.go.jp)*
*2 Technology Research Association for Single Wall Carbon Nanotubes (TASC), c/o Nanotube Research Center, AIST, Tsukuba 305-8565, Japan*

It is well-known that single-walled carbon nanotubes (SWCNTs) show various optical properties in a wide energy region. For example, the absorption in the UV region has been attributed to the π plasmon of the nanotubes. The interband transitions have been observed in the NIR and visible wavelengths. In addition, there is also optical absorption of SWCNTs in the low energy region.

Although the intensity of normal Drude absorption increases to smaller energy region, there is a peak in the infrared (IR) spectrum of SWCNTs. Recently, we have investigated that tube length dependence of the observed IR peak. Depending on the tube length, the peak positions of the IR signals in low-frequency were shifted, whereas those of the S1 interband transitions were not shifted. These behaviors can be reasonably explained by the antenna-effect-induced IR absorption [1].

In this talk, the detailed mechanism for the experimental observations including temperature dependence of the IR spectra will be discussed.

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I4

# Individual carbon nanotubes probed by non-linear optical spectroscopy

A. Johansson[1], J. Aumanen[2], G. Bautista[3], M. J. Huttunen[3], O. Herranen[1], P. Myllyperkiö[2], H. Jiang[4], A. G. Nasibulin[4], E. I. Kauppinen[4], M. Ahlskog[1], M. Kauranen[3], M. Pettersson[2]

*1 Department of Physics, University of Jyväskylä, Finland (andreas.johansson@jyu.fi)*
*2 Department of Chemistry, University of Jyväskylä, Finland*
*3 Department of Physics, Tampere University of Technology, Finland*
*4 Department of Applied Physics, Aalto University, Finland*

Linear optical methods such as fluorescence and Raman spectroscopy have proven to be very powerful as tools for study and characterization of carbon nanotubes (CNTs). Nonlinear methods are in comparison still rarely used, despite their potential to probe different aspects of the CNTs. We are working with nonlinear optical spectroscopy on individual CNTs, developing both time-resolved four-wave mixing (FWM) spectroscopy for probing excitonic states with femtosecond resolution, as well as second harmonic generation (SHG) and third harmonic generation (THG) imaging as a tool for lattice symmetry determination. For all three techniques, we have made to our knowledge the first observations on individual single-walled CNTs with characterized chiral indices.

In FWM spectroscopy we see a temporal broadening of the signal, which we attribute to two reasons; excitonic lifetime broadening in the 100 femtosecond range, and vibrational states at larger probing delays. We will demonstrate that FWM has good potential for mapping out excitonic states and lifetimes of individual CNTs. SHG and THG measurements, on the other hand, are both very sensitive to the symmetry of the crystal lattice. Here we observe significant variations in the SHG and THG signals of the CNTs between left hand circular polarization (LHCP) and right hand circular polarization (RHCP). The variations in the nonlinear signals may be associated to the unique properties of the CNTs such as chirality.

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I5

# Evaluation of carbon nanotube and graphene by absorption and Raman spectroscopy

Mun Seok Jeong[1], Clare C. Byeon[2], Young Hee Lee[1]

*1 Center for Integrated Nanostructure Physics, Institute for Basic Science, Department of Energy Science, Sungkyunkwan University, Suwon, Republic of Korea*
*2 School of Mechanical Engineering, Kyungpook National University, Daegu, Republic of Korea*

Carbon nanostructures such as carbon nanotube and graphene are emerging materials for realization of nanoscale devices in nanoscience and nanotechnology. Even though these materials have peculiar electrical, optical and thermal properties, deficiency of globally accepted evaluation protocols is one of the major bottlenecks for commercialization. For this reason, we have tried to develop reliable protocols for the measurement of purity of carbon nanotubes and semiconducting/metallic ratio of single wall carbon nanotubes by absorption and Raman scattering spectroscopy which provide a relatively confident and fast way of evaluating a large amount of materials. We will also introduce standardization efforts for graphene currently in the ISO and IEC.

**I6**

## Carbon nanotube metrology at NIST: A progress report

Constantine Khripin, Jeffrey Fagan, Angela Hight-Walker, and Ming Zheng

*National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg, MD 20899, USA*
*(ming.zheng@nist.gov)*

In this presentation, we will report a highly efficient and scalable carbon nanotube purification method developed at the US National Institute of Standards and Technology, and application of the method to obtain electronic-grade semiconducting carbon nanotubes. As the purity of the semiconducting nanotubes improves with successive steps of purification, it becomes more and more challenging on the metrology side to accurately quantity the level of metallic impurities. Strategies to overcome this challenge will be presented.

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**I7**

## Low-cost and high-throughput metal/semiconductor separation of single-wall carbon nanotubes toward industrial production

Takeshi Tanaka[1,2], Satoshi Asano[2], Mariko Kubota[2], Kaori Makino[2], Atsushi Hirano[1,2],
Shunjiro Fujii[1,2], Hiromichi Kataura[1,2]

*1 Nanosystem Research Institute, National institute of Advanced Industrial Science and Technology (AIST), Japan (tanaka-t@aist.go.jp)*
*2 Technology Research Association for Single Wall Carbon Nanotubes (TASC), Japan*

There are two electric types of single-wall carbon nanotubes (SWCNTs), metallic (M) ones and semiconducting (S) ones. For their electrical application, it is required that these two types of SWCNTs are separated into the respective type. We have developed various separation methods of M- and S-SWCNTs using agarose gel [1]. In these methods, column separation was superior in terms of simplicity, rapidity, scalability, automation, etc. For the industrial production of M- and S-SWCNTs, however, it is required the higher-throughput and lower-cost of the separation. In this presentation, we report the improvement of the cost and throughput of the separation.

Among the reagents used in the column separation, the cost of the gel (Sepharose, GE healthcare) occupied the greater part of the total cost. We searched alternative gel and newly found an agarose-based gel which cost only about one-fiftieth of Sepharose gel. We also replaced analytical grade, expensive surfactants with industrial grade, low-priced ones. This new separation condition enabled us to save the separation cost drastically. While, the preparation of the SWCNT dispersion was a bottleneck in the throughput of the separation. The processes of dispersion by sonication and purification by ultracentrifugation restricted the throughput, so we changed the dispersion method from sonication to Nanomizer treatment and used continuous ultracentrifugation for the purification. We also scaled up the column size to 8.5 liter and finally achieved 2 g/day production of separated SWCNTs through the whole process including dispersion, purification and separation. The result of large-scale separation of single-chirality S-SWCNTs will be presented.

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I8

## Purification of carbon nanotubes

Chang Liu, Peng-Xiang Hou, Hui-Ming Cheng

*Institute of Metal Research, Chinese Academy of Sciences, 72 Wenhua Road, Shenyang 110016, China*
*(cliu@imr.ac.cn)*

As-prepared carbon nanotubes (CNTs) usually contain impurities like amorphous carbon, graphitic carbon and residue catalyst. To evaluate the intrinsic property of CNTs and to realize their applications [1], it is necessary to have raw CNT samples purified. A principle for CNT purification is to thoroughly remove impurities while well keeping the CNT structure intact. To achieve this objective, quite a few purification techniques have been developed. In this presentation, various purification methods, including gas phase oxidation, liquid phase oxidation, electrochemical oxidation, filtration, centrifugation, solubilization with functional groups, high temperature annealing, and multi-step approaches will be introduced. The advantage and disadvantage of these purification techniques are analyzed [2]. In addition, the challenges remained on purification and characterization of CNTs are also discussed.

Finally, a standard published by Chinese government for the assessment of the purity and quality of multi-walled CNTs will be introduced.

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I9

## Single tube to bulk characterisations of carbon nanotubes

Debdulal Roy

*The National Physical Laboratory, UK*

At the National Physical Laboratory, UK, a number of characterisation techniques have been applied to investigate structure, chemistry and properties of carbon nanotubes in order to assist industrial manufacturers and users to assess quality and safety of carbon nanotubes, and provide input to the regulators. The presence of a variety of carbon nanotubes in a single batch based on number of walls and chirality makes it a challenging task for the manufacturers, users and the standards organisations. Moreover, most of the contaminations in carbon nanotubes are also carbon based that has the same hybridisation as that of carbon atoms in a carbon nanotube. A multi-technique approach has been adopted to characterise bulk carbon nanotubes using XPS, Raman spectroscopy and related optical techniques. A set of dispersion methods in relevant mediums has also been suggested for standardising toxicological tests. High resolution techniques such as tip-enhanced Raman spectroscopy has been utilised to investigate individual tubes. This talk will describe NPL's approach to address the metrology challenges in characterising single and bulk tubes.

## Production and characterization of graphene dispersions with controlled morphological properties

I10

F. Bonaccorso[1,2]

*1 Cambridge Graphene Centre, University of Cambridge, Cambridge, UK (fb296@cam.ac.uk)*
*2 CNR-IPCF V.le Stagno D'Alcontres 37, 98158, Messina, Italy*

We report a method for the production of graphene and few-layer graphene dispersions with controlled lateral sizes and number of layers, and their characterization using Raman spectroscopy and transmission electron microscopy (TEM). Graphene dispersions are prepared by sonication of graphite in sodium deoxycholate aqueous solution followed by ultracentrifugation [1,2,3]. The morphology of the dispersed graphene flakes is tuned using two centrifugation techniques: sedimentation-based separation (SBS) [3] and isopycnic separation in density gradient ultracentrifugation (DGU) [4,5]. The use of surfactants [5] allows us to create a density differences between flakes with different number of layers. Upon centrifugation the flakes are divided in several fractions depending on their thickness.

We use TEM and Raman spectroscopy to characterize our dispersions, assessing the lateral size, number of layers, doping and amount of defects [6]. The analysis of the shape of the Raman 2D peak gives information on the number of stacked layers [7], while the position of the G and 2D peaks and their intensity ratio can be used to estimate doping [6,7]. We show that both SBS and isopycnic separation can be used to obtain dispersions highly enriched in monolayers and demonstrate the ability of isopycnic separation of sorting flakes by number of layers. By analyzing the dispersion of the G peak with excitation energy the width of the G peak, we can assign the presence of D peak to the edges, rather than to a high defect concentration within the flakes [3]. TEM is used to measure the lateral size distribution of the dispersed flakes. We show that SBS allows us to obtain monolayers with ~600nm$^2$ average size, while DGU allows us to obtain larger flakes with ~1 μm$^2$ average size.

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## Isotopic labeling in metrology of graphene

I11

Martin Kalbac[1,2] Jana Vejpravova,[3] Jing Kong,[2] and Mildred S. Dresselhaus[3,4]

*1 J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, v.v.i.,*
*Dolejškova 3, CZ-18223 Prague 8, Czech Republic (kalbac@jh-inst.cas.cz)*
*2 Department of Electrical Engineering and Computer Science, MIT, Cambridge,*
*Massachusetts 02139, USA*
*3 Institute of Physics, Academy of Sciences of the Czech Republic, v.v.i., Na Slovance 2,*
*Czech Republic*
*4 Department of Materials Science and Engineering, MIT, Cambridge, Massachusetts 02139, USA*

Heterostructures based on graphene belong to an important class of new low-dimensional materials with many prospective applications. One of the problem emerging during the studies of these systems is a selective characterization of individual graphene layers. Raman spectroscopy is a frequently used approach to study graphene layers. However, in conventional systems this method does not allow to address individual graphene layers. The solution of this problem offers isotope labeling. $^{12}$C or $^{13}$C graphene can be grown by chemical vapor deposition by a simple exchange of the $^{12}CH_4$ and $^{13}CH_4$ precursor gases. Multi-layer graphene or in general graphene heterostructure can be prepared by a subsequent transfer of single layer graphene sheets or other 2D materials on top of each other. In this study we combined graphene with different isotope composition to make multi-layer graphene nanostructures. Due to a different mass of carbon isotopes the graphene layers can be easily distinguished by Raman spectroscopy and different phenomena can be addressed on particular graphene layers. A review of our results obtained on isotopically labeled graphene layers will include an analysis of effects of the substrate on the bottom layer and the environment on the top layer in 2 and 3-LG, comparison of the effects of the heat treatment on the top and bottom graphene layer in 2-LG, an analysis of the effects of electrochemical doping on 2 and 3-LG including the discussion of charge distribution between the graphene layers and finally a study of defect formation in 2-LG.

I12

# Metrology of focused ion beam patterning on graphene

B. S. Archanjo, B. Fragneaud, C. A. Achete

*Divisão de Metrologia de Materiais, Instituto Nacional de Metrologia, Qualidade e Tecnologia,*
*Duque de Caxias, RJ, Brazil (bsarchanjo@inmetro.gov.br)*

Graphene, a two-dimensional carbon structure, is a model system that comprises exciting possibilities to demonstrate new physics and novel electronic applications, many of which can be appreciated only by means of nanoscale modifications in its structure. The metrology of defects, impurities and spatial confinement in single layer graphene is of great importance to understand the behavior of this material and also tune its properties for different applications. Some promising applications can be found in ballistic room-temperature transistors, carbon-based spintronic devices, and permeation membranes [1]. Graphene nanostructures have already been fabricated by electron beam lithography followed by reactive ion etching, scanning tunneling microscopy lithography, atomic force microscopy anodic oxidation, and chemically derived techniques [1]. Further modification of these structures is mainly performed by electron and ion radiation where focused ion beams have the advantage of achieving well controlled modification at nanometer scale. In this work we present the results we obtained by nanopatterning super structures in graphene using ion beam milling (i.e. Ga (Focused Ion Beam – FIB) [1,2] or He (Helium Ion Microscope – HIM)). The superstructures were studied using micro Raman spectroscopy, atomic force microscopy and electrical transport measurements.

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SP10

## Probing optical transitions in individual carbon nanotubes using polarized photocurrent spectroscopy

Maria Barkelid, Gary A. Steele, Val Zwiller

*Kavli Institute of Nanoscience, Delft University of Technology, The Netherlands. (k.m.barkelid@tudelft.nl)*

Carbon nanotubes show vast potential to be used as building blocks for photodetection applications. Their direct band gap and high mobilities makes them an attractive choice for near-infra red optoelectronic devices. However, measurements of fundamental optical properties, such as the absorption coefficient and the dielectric constant, has not been accurately performed on a single pristine carbon nanotube. Although optical absorption have been previously studied [1], quantitative measurements of the absorption coefficient for an individual carbon nanotube without environmental influence has not been reported.

In this work we show polarization dependent photocurrent spectroscopy from a single suspended semiconducting carbon nanotube p-n junction, bridging a 4 μm wide trench with two local gates. Using the polarization of the incident laser the $E_{11}$ and $E_{22}$ optical transitions could be probed for a polarization parallel to the nanotube axis and quenched for perpendicular polarization.

By studying the photocurrent spectroscopy on and off resonance with the van Hove singularities, we obtain a quantitative number for the quantum efficiency and attribute this to a lower limit for the absorption coefficient. Enhanced absorption on the carbon nanotube optical resonances gives an external quantum efficiency of 12.3 % and 8.7 % for the $E_{11}$ and $E_{22}$ transitions, respectively. In addition we obtain a value for the dielectric constant through measurements of the polarization dependent photocurrent. A dielectric constant of 3.6 ± 0.2 was experimentally determined for this semiconducting carbon nanotube [2].

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SP11

## A novel approach for integrating horizontally aligned carbon nanotubes into devices by photolithography

P. Braeuninger-Weimer, T. Süss, C. Hierold

*Micro and Nanosystems, ETH Zurich, Switzerland (p.b.w@web.de)*

The controlled integration of carbon nanotubes (CNTs) into components such as carbon nanotube field-effect transistors (CNFETs) is one of the major challenges of CNT device fabrication. If randomly grown individual CNTs are to be contacted in a defined way, atomic force microscopy (AFM) or scanning electron microscopy (SEM) is often used to localize the CNTs with respect to a marker system. Then electron beam lithography is employed to define electrical contacts to the CNTs [1]. This is very costly in terms of time and not suitable for batch fabrication, since for each CNT contact an individual mask must be designed.

Here, a novel approach is presented, which allows controlled contacting of individual CNTs by photolithography (Karl Süss MJB4) utilizing a single photo mask. By exploiting the horizontal alignment of CNTs on quartz substrates [2] and a novel system of alignment marks, CNTs can be contacted by serial optical lithography exposure.

The CNT locations relative to a predeposited marker system is determined by AFM. A system of alignment marks on the sample and on the contact mask enables the precise placement of the contacts at the location of the individually selected CNTs. The marker system allows for a shift of +/- 25 μm in x and y direction, respectively. By this novel approach, an average alignment accuracy of 0.2 ± 0.1 μm was measured by AFM. With this approach, CNFETs with single walled carbon nanotubes (SWNTs) were fabricated and measured.

In conclusion, this novel approach enables the fabrication of a large numbers of single nanotube FETs. This process provides an alternative to electron beam lithography for device designs requiring alignment precisions of up to 0.2 ± 0.1 μm.

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**SP12**

## Ultracentrifugal sorting of empty and water-filled carbon nanotubes: in situ 2D fluorescence-excitation and Raman spectroscopy

J. Campo, S. Cambré, P. Muyshondt, R. Federicci, W. Wenseleers

*University of Antwerp, Physics Department, Universiteitsplein 1, 2610 Antwerp (Belgium)*

Since the pioneering work of Arnold *et al.* [1], density gradient ultracentrifugation (DGU) has emerged as an extremely versatile technique for the sorting of carbon nanotubes (CNTs) by diameter/chirality, electronic type (metal/semiconductor), length and even enantiomers, even though the mechanisms are not yet fully understood. For example, counter-intuitively it is found, in nearly all DGU studies, that increasing diameters possess increasing densities. We have recently shown that this is due to the presence of water-filled CNTs.[2] The intact (and therefore empty) CNTs can be isolated from the filled ones and follow the intuitive sorting order, moreover allowing an enhanced structure sorting by DGU.[2] Also the specific surfactant choice can have a significant effect on the diameter sorting.

In this paper we present 2D wavelength-dependent fluorescence-excitation and Raman spectra measured directly after DGU, in situ, as a function of height, in the centrifuge tube. As such, very detailed information on the chirality-density relation is obtained, allowing for studying and optimizing the DGU sorting process. We will in particular discuss the different sorting for two commonly used surfactants, sodium cholate and sodium deoxycholate, [3] which only differ by one hydroxyl group but result in very different diameter-density dependencies.

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**SP13**

## Resonant Raman spectroscopy of nitrogen-doped single-walled carbon nanotubes (N-SWNT)

Sara D. Costa[1], Theerapol Thurakitseree[2], Shigeo Maruyama[2], Cristiano Fantini[1],
Marcos Pimenta[1]

*1 Dept of Physics, Universidade Federal de Minas Gerais, Belo Horizonte, Brazil (sdcosta@fisica.ufmg.br)*
*2 Dept of Mechanical Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo, Japan*

Vertically aligned nitrogen-doped single-walled carbon nanotubes (N-SWNT) were investigated via resonant Raman spectroscopy. In order to have a basis for comparison, two samples were used in the experiments: one grown with pure ethanol (SWNT) and another one grown with a mixture of ethanol/acetonitrile as feedstock (N-SWNT) [1]. Different laser energies in the ultraviolet, infrared and visible ranges (from 1.53 to 3.8 eV), were used to excite the sample and investigate its resonant behaviour. In order to create a map of the transition energy versus the radial breathing mode frequency, tuneable lasers were employed and a Raman spectrum was acquired every 2nm.

The effects of the incorporation of nitrogen on the electronic and phonon structures were studied. Despite the low amount of nitrogen incorporated (0.2%), shifts in the optical transitions of the nanotubes were detected, showing modifications in the electronic properties upon doping. Additionally, the D and G' bands dispersive behaviour was studied.

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SP14

# Self-assembled micro-honeycomb network of single-walled carbon nanotubes for heterojunction solar cells

Kehang Cui, Takaaki Chiba, Erik Einarsson, Shohei Chiashi, Shigeo Maruyama*

*Department of Mechanical Engineering, The University of Tokyo, Japan (*maruyama@photon.t.u-tokyo.ac.jp)*

The gap between the outstanding electrical and optical properties of an individual single-walled carbon nanotube (SWNT) and inferior performance of macro-scale SWNT devices is hindering its widespread applications. The smart assembly is necessary to play SWNT to its full potential. Here, we propose a self-assembled micro-honeycomb network (μ-HN) of SWNTs obtained by water or ethanol vapor treatment of as-synthesized vertically aligned SWNTs (VA-SWNTs) for heterojunction solar cells with higher performance.

The VA-SWNTs was synthesized by the standard alcohol-catalytic CVD method with Co/Mo dip-coated on Si/$SiO_2$ substrate [1]. The fabrication process of the micro-honeycomb structured film was obtained by exposing the as-synthesized VASWNT to water vapor and drying under ambient environment afterwards. Each micro-honeycomb cell consists of capillary-aggregated walls and randomly oriented bottom that contacts the Si substrate. The SWNT film was transferred on top of the substrate which has a 3 mm × 3 mm bare n-type silicon contact window in the center using hot water transfer technique. By the vapor treatment, collapsed spaghetti-like SWNTs contact to the substrate in the middle of each honeycomb cell. Cell walls consist of cross-linked heavily bundled SWNTs. The pristine SWNT-Si heterojunction solar cell fabricated with μ-HN shows a stable fill factor of 72%, which is the highest fill factor reported to date [2, 3]. The improvement is attributed to the hierarchical structure of micro-honeycomb network. A PCE beyond 10% is achieved in the dry state after dilute nitric acid treatment.

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SP15

# Precursor-dependent reversible diameter modulation of vertically aligned single-walled carbon nanotubes

Erik Einarsson[1], Theerapol Thurakitseree[1], Akihito Kumamoto[1],
Christian Kramberger[2], Shohei Chiashi[1], Yuichi Ikuhara[1], Shigeo Maruyama[1,*]

*1 The University of Tokyo, Japan (*maruyama@photon.t.u-tokyo.ac.jp)*
*2 University of Vienna, Austria*

We synthesized vertically aligned single-walled carbon nanotubes (SWNTs) with a mean diameter of approximately 1 nm by chemical vapor deposition (CVD) of an acetonitrile-ethanol mixture [1]. The addition of no more than five volume percent acetonitrile in ethanol results in a dramatic reduction of the mean SWNT diameter. In the absence of acetonitrile, the mean diameter returns to the ~2 nm typical of ethanol-grown vertically aligned SWNTs. We also show the diameter can be modulated on the fly by the addition or absence of acetonitrile in the feedstock, and this diameter change is both reversible and repeatable [2].

We examined the interface between small- and large-diameter SWNTs by scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HR-TEM). Layers having different diameter can be separated from one another, but the separation is not always clear-cut. Further examination by HR-TEM revealed some of the SWNT junctions are actually continuous, whereas most are discontinuous across the interface [2]. Based on these findings, we propose that acetonitrile changes the growth mode from tangential to perpendicular [3], causing a marked reduction in SWNT diameter.

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**SP16**

## Towards the standardization of fullerene nanofibers

Erlon H Martins Ferreira[1], Lingling Ren[2], Guangzhe Piao[3], Kun'ichi Miyazawa[4]

*1 National Institute of Metrology, Quality and Technology (Inmetro), Brazil (ehferreira@inmetro.gov.br)*
*2 National Institute of Metrology (NIM), China*
*3 Qingdao University of Science and Technology, China*
*4 National Institute for Materials Science (NIMS), Japan*

Fullerene nanofibers are defined as the fibers that are composed of fullerene molecules and have diameters less than 1000 nm [1,2]. The fullerene nanofibers can take both the non-tubular and tubular morphologies. The non-tubular fullerene nanofiber with single crystalline structure is called "fullerene nanowhisker", while the tubular fullerene nanofiber is called "fullerene nanotube". The fullerene nanofibers are the new semiconducting materials that are applicable to solar cells, templates for chemical synthesis, MEMS cantilever beams, field-effect transistors, catalysts, composite fillers and so on. The researcher population of fullerene nanofibers is small at the present time. However, it is gradually increasing, and will increase more with the decreasing price of fullerenes. Hence, the pre-standardization is necessary for future popularization of fullerene nanofibers.

In this work we present the results of interlaboratory comparison of Raman spectroscopy data of Fullerene nanofibers carried out inside the TWA 34 of VAMAS (Versailles Project on Advanced Materials and Standards). The goal of the project is to establish the optimum parameters of exposure power density and time, sample preparation protocol, and evaluation of Raman shift uncertainties. Two round-robins have been performed and the Raman profiles have been obtained in different conditions by different laboratories. We relate here the preliminary results and the major difficulties found in the pre-standardization process.

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**SP17**

## Onset of rippling in MWCNTs studied with in situ TEM force measurements

H. Jackman, P. Krakhmalev, K. Svensson

*Department of Engineering and Physics, Karlstad University, Sweden (henrik.jackman@kau.se)*

When carbon nanotubes (CNTs) are bent they can deform in localized buckling or rippling deformations. The force-deflection relation is only linear up to a critical strain, where the rippling or buckling begins, and then the relation becomes non-linear with a concomitant drop in the bending stiffness (for a review see e.g. [1]). These two effects have important implications for the design of future nanoelectromechanical systems (NEMS) that utilize bending of CNTs. Several theoretical studies have investigated this phenomenon but there is still a lack of experimental data to compare with [1]. In a previous study we have measured the critical strain for the rippling onset of CVD-grown MWCNTs using *in situ* SEM force measurements [2]. We found that a large defect density in the MWCNT will shift the critical strains to higher values than theoretically predicted [3-4].

In this study we have performed *in situ* TEM force measurements on individual, arc-discharge grown, MWCNTs. We found values of the critical strain that are lower, compared to the values of the CVD-grown, owing to the high crystallinity of arc-discharge grown tubes. The values are comparable to previous predictions for SWCNTs [3] and thick MWCNTs [4], but there is also an influence from the geometry. We find a dependence of the critical strain on both the number of walls and the nanotube diameter, and we discuss this effect in terms of a radial stiffness that supports the outermost walls in a MWCNT.

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## BN nanotubes structure probed by luminescence properties

SP18

A. Loiseau[1], A. Pierret[1,2], S. Moldovan[3], O. Ersen[3], B. Attal-Trétout[4], F. Ducastelle[1], J. Barjon[5]

*1 LEM, CNRS-ONERA, Chatillon, France*
*2 NPSC, CEA-CNRS, Grenoble, France*
*3 IPCMS, U. Strasbourg, Strasbourg, France*
*4 DMPH, ONERA, Palaiseau, France*
*5 GEMAC, U. Versailles St Quentin, Versailles, France*

Hexagonal boron nitride (h-BN) is a wide band gap semiconductor (~ 6.5 eV), with a layered structure similar to graphite. In contrast to their carbon counterparts, BN nanotubes are all semiconductors. Calculations show that excitonic emission occurs in the same energy range than h-BN bulk. But because of the paucity of high quality BN materials and the need of specific experimental equipments suited to the deep UV range, few optoelectronic experimental studies have been undertaken. Even bulk h-BN, considered as a reference for the optical studies of the nanotubes, is not yet fully understood.

Detailed studies on boron nitride nanotubes mostly concern multi-wall BNNTs with a large number of walls (20-120 walls) [1]. Whatever their diameter, tubes display luminescence between 226 and 234nm and this spectral range has been assigned, in h-BN, to transitions involving structural defects such as grain boundaries. In order to better understand the nature of the luminescence in these tubes, we propose in this contribution to analyse and correlate the structure of the tubes by transmission electron microscopy (TEM) and their luminescence by cathodoluminescence (CL) with high spatial resolution optimized for the detection of the luminescence in the UV range.

We have determined from detailed TEM imaging and tomographic studies that large tubes have an octagonal section and that the resulting facets are twisted along the tube axis [2] Besides, CL emission is not homogeneous but is localized along the tube on specific areas. Its relationship with the tube faceting will be discussed as well as the use of the luminescence properties to probe the crystallinity and the defects in BN structures.

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## In-situ TEM observation of zipper-like wall-to-wall coalescence of double-wall carbon nanotubes with home-made very high temperature compatible heating holder

SP19

Sihan Zhao, Ryo Kitaura*, Yasumitsu Miyata and Hisanori Shinohara*

*Department of Chemistry & Institute for Advanced Research, Nagoya University, Nagoya 464-8602, Japan*
*(*r.kitaura@nagoya-u.jp and noris@cc.nagoya-u.ac.jp)*

We report, for the first time, the detailed *in-situ* TEM observation of wall-to-wall coalescence [1, 2] of Double-wall carbon nanotubes (DWCNTs) at very high temperature (>2000°C). Such observation is enabled by developing a home-made and very high temperature compatible TEM specimen heating holder equipped with a micro-sized carbon nanotubes (CNTs) network heater. This micro-sized CNT heater could reliably meet the necessity of sample heating to sufficiently high temperature (up to 3000°C) while minimizing spatial drift of sample induced by the heating.

We observed that a single larger-diameter DWCNT is formed at the final stage through a zipper-like mechanism of wall-to-wall coalescence between two individual outer shells and two individual inner shells. The time sequential TEM images obtained throughout the reaction suggests the presence of the Stone-Wales type transformation, which provides insight on thermal reconstruction process of the nanocarbon materials.

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# CNBMT13

**K1**

# Carbon nanotube meets plant cell biology: carbon nanotubes as organelle targeting nanocarriers

Yoshinobu Baba[1,2]

*1 Department of Applied Chemistry, School of Engineering, FIRST Research Center for Innovative Nanobiodevices, Synchrotron Radiation Research Center, Nagoya University, Nagoya, Japan*
*2 National Institute of Advanced Industrial Science and Technology (AIST), Japan*

Carbon nanotubes (CNTs) have attracted a significant interest due to their remarkable physicochemical characteristics and applied to biological and medical sciences. During the past few years, there was an extensive interest in applying nanoparticles to plants for agricultural and horticultural use. Indeed, CNTs have attracted the attention of plant cell biologists as potential molecular transporters based on their intrinsic ability of carbon nanotubes to cross the cell membrane of various types of mammalian cells acting as drug and gene delivery vehicles. In this lecture, I will demonstrate its versatility and applicability in plant cell biology studies. Specifically, we discuss the ability of functionalized carbon nanotubes to penetrate the plant cell wall, target specific organelles, probe protein-carriers activity and induce organelle recycling in plant cells. We, also, shed light on prospective applications of carbon nanomaterials in cell biology and plant cell transformation [1-6].

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**I1**

# Carbon Nanotubes and biomembranes: simulation studies

Mark S.P. Sansom[1], Rebeca Garcia-Fandiño[2], Mickael Lelimousin[1]

*1 Department of Biochemistry, University of Oxford, UK (mark.sansom@bioch.ox.ac.uk)*
*2 Universidade de Santiago de Compostela, Spain*

The interactions of carbon nanotubes (CNTs) with biological membranes are of interest both from the perspective of possible drug delivery mechanism, and also in terms of understanding possible toxic effects on cells. Molecular dynamics simulations enable us to study at near-atomic resolution the nature of such interactions. In particular coarse-grained simulations allow characterization of the possible perturbations of lipid bilayers by CNTs, whereas atomistic simulations enable us to explore CNT interactions with lipids, ions and water molecules in more detail. I will focus on two recent studies of CNTs embedded in lipid bilayers: (i) using coarse-grained simulations to study bilayer perturbation by CNTs, revealing mechanisms for nanoencapsulation during penetration of bilayers by CNTs [1]; and (ii) using atomistic simulations to define the energy landscapes for ion permeation of CNTs as models of bimimetic nanopores [2]. These two studies demonstrate how molecular simulation approaches can contribute to understanding the complexities of the interactions of CNTs with simple models of the membranes of cells.

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# Multiplexed biomimetic lipid membranes on graphene by dip-pen nanolithography

Michael Hirtz[1], Antonios Oikonomou[2], Thanasis Georgiou[3], Harald Fuchs[1,4],
Aravind Vijayaraghavan[2]

*1 Institute of Nanotechnology (INT) and Karlsruhe Nano Micro Facility (KNMF),*
*Karlsruhe Institute of Technology (KIT), Germany*
*2 School of Computer Science and Centre for Mesoscience and Nanotechnology,*
*The University of Manchester, UK (aravind@manchester.ac.uk)*
*3 School of Physics and Astronomy, The University of Manchester, UK*
*4 Physical Institute and Center for Nanotechnology (CeNTech), University of Münster, Germany*

The application of graphene in sensor devices or as an interface to biological systems crucially depends on the ability to appropriately functionalize the pristine graphene. Here we show the direct writing of tailored phospholipid membranes on graphene using dip-pen nanolithography (DPN). Phospholipids exhibit higher mobility on graphene compared to the commonly used silicon dioxide substrate, leading to well-spread uniform membranes. DPN allows for multiplexed assembly of phospholipid membranes of different functionalities in close proximity to each other. The membranes are stable in aqueous environments and we observe electronic doping of graphene by charged phospholipids. Based on these results, we propose phospholipid membranes as a route for non-covalent immobilization of various functional groups on the graphene for applications in biosensing and biocatalysis. As proof of principle, we demonstrate the specific binding of streptavidin to biotin functionalized membranes. The combination of atomic force microscopy in air and fluid and binding experiments yields new insights towards a consistent model for the layer organization within phospholipid stacks on graphene.

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# Catabolic intracellular compartments enable degradation of carbonaceous nanomaterials

Jennifer Conroy[1,2], Navin K. Verma[1,2], Ronan J. Smith[2], Ehsan Rezavani[2], Georg S Duesberg[2],
Jonathan Coleman[2], and Yuri Volkov[1,2]

*1 Institute of Molecular Medicine, Trinity College Dublin, Ireland (conroyje@tcd.ie)*
*2 Centre for Research on Adaptive Nanostructures & Nanodevices, Trinity College Dublin, Ireland*

Advanced conductive nanomaterials such as, single walled carbon nanotubes (SWCNT), graphene and their derivatives are being used in many cutting-edge electronic, energy and medical devices due to their unique physicochemical properties. However, the potential impact of these new engineered nanomaterials on human health following exposure during manufacture, use or at the end of their lifecycle is uncertain. Here, we investigated the interaction of SWCNT, graphene and their enabled thin films with primary human macrophages isolated from healthy donors. Macrophages are one of the first lines of defense in the body against foreign invaders. High content screening and confocal microscopic analysis indicated no signs of acute cytotoxicity due SWCNT, graphene or their enabled thin films. Further analysis using a real time impedance technique revealed a low level toxic cellular response which is probably due to a reduction in cellular adhesion. Raman spectroscopic mapping confirmed cellular uptake of SWCNT and graphene. Electron microscopy demonstrated SWCNT to be contained within double membrane cytoplasmic vesicles whereas graphene was contained within single walled vesicles. These data suggest the induction of two different catabolic pathways, an autophagic and lysosomal response respectively, which were verified by biochemical and microscopic techniques. This study suggests that in-depth characterisation of possible biological effects of these conductive nanomaterials at the molecular level is required for their safe applications.

C3

# Vertically aligned double- and single- walled carbon nanotubes for electrochemical surfaces

Katherine E. Moore[1], Jingxian Yu[2], Benjamin S. Flavel[3], Joseph G. Shapter[1]

*1 Flinders Center for Nanoscale Science and Technology, Flinders University, Australia*
*(katherine.moore@flinders.edu.au)*
*2 School of Chemistry and Physics, The University of Adelaide, Australia*
*3 Institute of Nanotechnology, Karlsruhe Institute of Technology, Germany*

Carbon nanotubes (CNTs) are a highly desirable material for incorporation into electrochemical and biological sensing devices, owing to their fast heterogeneous electron transfer, high surface area and electrochemical stability. We have recently shown that double walled CNTs (DWCNTs) demonstrated superior electron transport compared to single walled CNTs (SWCNTs) when electrochemical redox is isolated to the nanotubes only [1-2]. We attribute this to the selective outer-tube functionalisation with the inner tube retaining its undisrupted $sp^2$ network and hence it's intrinsic electronic properties. In this work, vertically aligned single- and double- walled CNT arrays were assembled on gold surfaces forming electrochemical electrodes. The CNTs were subsequently covalently loaded with a ferrocene modified α-aminoisobutyric acid peptide, followed by characterisation with cyclic voltammetry. The CNT electrode comprised of DWCNTs demonstrated significantly higher peak current compared to its single walled counterparts. This is attributed to a higher loading of the ferrocene modified peptide to the outer wall of the DWCNT due to a larger number of defects sites within the $sp^2$ carbon lattice. This indicates that DWCNTs may offer a useful alternative to SWCNTs in future electrochemical sensors and biosensors.

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I2

# Functionalized carbon nanotubes for targeted drug delivery and magnetic cell labeling

Cécilia Ménard-Moyon[1], Delphine Felder-Flesch[2], Sylvie Bégin-Colin[2], Florence Gazeau[3], Kostas Kostarelos[4], Alberto Bianco[1]

*1 CNRS, Institut de Biologie Moléculaire et Cellulaire, Laboratoire d'Immunopathologie et Chimie Thérapeutique, UPR 3572, 67000 Strasbourg, France. (c.menard@ibmc-cnrs.unistra.fr)*
*2 Institut de Physique et Chimie des Matériaux de Strasbourg (IPCMS), Strasbourg, France.*
*3 Laboratoire Matière et Systèmes Complexes (MSC), Paris, France.*
*4 Nanomedicine Laboratory, London, UK*

Carbon nanotubes (CNTs) have emerged as promising tool due to their unique properties, large surface area, and capacity to cross biological barriers, offering a variety of opportunities for applications in nanomedicine, such as diagnosis, disease treatment, imaging, and tissue engineering [1]. Nevertheless, pristine CNTs are insoluble in water and in most organic solvents; thereby functionalization of their surface is necessary to increase biocompatibility. Multi-functionalization allows to impart multiple functionalities to nanotubes that can be used as multimodal drug delivery systems for the treatment of cancer or different types of infections. In this context, we have developed a strategy for the triple covalent functionalization of CNTs with a therapeutic molecule, a targeting ligand, and a fluorophore [2]. Targeting and therapeutic efficiencies have been evaluated *in vitro*. We have also coated CNTs with iron oxide nanoparticles (NPs) and evaluated the potential of the NP/CNT hybrids as contrast agent for magnetic resonance imaging and their interactions with cells [3]. The capacity of the hybrids to magnetically monitor and manipulate cells has also been investigated.

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# Hybrid nanocomposites from graphene, nanocellulose and genetically engineered proteins

Päivi Laaksonen[1], Andreas Walther[2,3], Jani-Markus Malho[1], Markku Kainlauri[1], Olli Ikkala[2], Markus B. Linder[1,2]

*1 VTT Technical Research Centre of Finland, P.O. Box 1000, FI-02044 VTT, Finland*
*(paivi.laaksonen@vtt.fi)*
*2 Aalto University, P.O. Box 15100, FI-00076 AALTO, Finland*
*3 DWI at the RWTH Aachen University, Pauwelstr. 8, D-52056, Aachen, Germany*

Nature shows many examples of composite structures that have extraordinary properties. Compared to their weight, materials such as bone and nacre have impressive mechanical performance. Inspired by these materials, we have built nanocomposites based on graphene, nanocellulose and interfacial components. [1-2] The interplay between the stiff component (graphene) and the tough component (cellulose nanofibrils) *via* the interfacing molecules has a key role in the toughening of such structures. [3] In some seashells, the stiff aragonite platelets are embedded in a matrix containing chitin and a mixture of multifunctional proteins. [4] These proteins have inspired us for designing proteins being able to glue together graphene flakes and nanofibrillated cellulose.[1] The proteins were created by genetic engineering by fusing together amphiphilic hydrophobin protein and cellulose binding domains. We show that embedding graphene into the nanocellulose paper with the cross-linker protein enhances its mechanical properties greatly when compared to material consisting of cellulose alone.

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## SP21 CNT-based bio-compatible matrix for neural culture growth

G.E. Fedorov[1], I.A. Gayduchenko[1], M.Yu. Presnyakov[1], I.A. Suetina[2], R.Ya. Podchernyaeva[2],
I.I. Bobrinetskii[3]

*1 NRC "Kurchatov Institute", Russia (igorandg@gmail.com)*
*2 The D.I. Ivanovsky Institute of Virology of the Ministry of Health and Social Development of The Russian Federation, Russia*
*3 National Research University of Electronic Technology, Russia*

Conjugation of biological systems and electronic systems of information processing and transmission is essential for the creation of hybrid nanoelectronic devices, including biosensors. One of the possible interface components are carbon nanotubes (CNT), demonstrating a high biocompatibility, chemical stability and unique electrical properties [1, 2]. This work aims at exploring CVD-grown CNT films, and clarification of the influence of the synthesis parameters of CNTs on the viability and proliferative activity of the nerve cells grown. Thin CNT films were fabricated by chemical vapor deposition (CVD) technique on silicon oxidized wafers and quartz substrates.

The nerve cells were grown on the obtained CNT-films. Viability and proliferative activity of the cells grown, have been studied by MTT method and via visualizing the cultures by optical and electron microscopy. Possible toxic effect of the used catalyst on the cells is also discussed. The results show that the use of CNTs hardly reduces the viability and proliferative activity of cells and don't affect the cell morphology. That means no toxic effect of carbon nanotubes on nerve cells, which, combined with good electrical conductivity of CNTs makes these hybrid systems a promising material for biosensors.

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## SP22 The effect of carbon nanotubes functionalized with fibroblast glowth factor on bone marrow-derived stromal cells and bone formation

Eri Hirata[1], Cécilia Ménard-Moyon[2], Enrica Venturelli[2], Hiroko Takita[1], Fumio Watari[1],
Alberto Bianco[2], Atsuro Yokoyama[1]

*1 Graduate School of Dental Medicine, Japan (erieri@den.hokudai.ac.jp)*
*2 CNRS, Institut de Biologie Moléculaire et Cellulaire, Laboratoire d'Immunopathologie et Chimie Thérapeutique, France*

Multi-walled carbon nanotubes (MWCNTs) were functionalized with the fibroblast growth factor (FGF) and the advantages for their use as scaffolds for bone formation were evaluated in vitro and in vivo.

The activity of FGF was assessed measuring the effect on the proliferation of rat bone marrow stromal cells (RBMSCs). The presence of FGF enhanced the proliferation of RBMSCs and the different conjugates tested showed the same effect as FGF alone. We have also observed that an inhibitor of fibroblast growth factor receptors decreased cell proliferation in the presence of FGF covalently conjugated to the nanotubes. In addition, FGF-CNT coated sponges were implanted between the parietal bone and the periosteum of mice and the formation of new bone was investigated. At day 14 after implantation, larger amount of newly formed bone was observed around the sponges coated with functionalized carbon nanotubes.

Covalent conjugation of FGF tailors CNTs with the appropriate function in the proliferation of BMSCs. Scaffolds coated with these conjugates could be considered as promising novel substituting materials for bone regeneration in future tissue engineering applications.

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## Composite nanobiomaterials for compounds biological tissues

**SP23**

A. Gerasimenko, L. Ichkitidze, V. Podgaetsky, S. Selishchev

*National Research University of Electronic Technology (MIET), 124498, Moscow, Russia*
*(leo852@inbox.ru)*

The interest is the possibility of laser welding with using a laser solder based on bovine serum albumin (BSA), and multi-walled carbon nanotubes (MWCNTs) or single-walled carbon nanotubes (SWCNTs). In this case, we can expect a rapid structuring conjugating composite nanobiomaterials and increase strength of compound biological tissues.

In our experiments we used the laser solder based on the aqueous dispersion: 28 wt.%BSA+0.1 wt.%MWCNT and 28 wt.%BSA+0.1 wt.%SWCNT. We investigated the laser solder on the pig skin and bovine cartilage. At the junction of the tissue (cartilage, skin) deposited thin layers of liquid (laser solder) and in the continuous mode made laser welding (laser irradiation - power 1 W/cm$^2$, wavelength 970 nm). Laser welding process ended for 5-20 seconds. After that, we measured the tensile strength $\sigma$ the seam and tensile strength $\sigma_s$ the solid (uncut) tissue. The results obtained were: pig skin, $\sigma_s \approx 15 \pm 5$ MPa, $\sigma/\sigma_s \approx 8$ %; bovine cartilage, $\sigma_s \approx 6 \pm 2$ MPa, $\sigma/\sigma_s \approx 25\%$. The introduction of carbon black or activated carbon in laser solder reduces the strength of welded joints compared to laser solder based on the pure BSA ($\sigma \approx 0.05$ MPa, $\sigma/\sigma_s \approx 0.3\%$).

Thus, the laser solders based on the SWCNT or MWCNT could increase the strength ($\sigma \approx$ ~1–2 MPa, $\sigma/\sigma_s \approx$ 8–25 %) of laser welds by 1–2 orders of magnitude compared with laser soldering on pure BSA. The results of work demonstrate the potential of laser solders on the base composite nanobiomaterials with carbon nanotubes for welding of biological tissues.

This work was partly funded by Russian Ministry of Education (Government contract №16.426.11.0043 from 12.09.2011), by The Russian Foundation for Basic Research (project №12-08-12014/12 from 15.11.2012) and by the Foundation for Promotion of Small Enterprises in Science and Technology (contract 10678№/19537).

## Carbon nanotubes-based electrodes and their post-functionalization for biosensing applications

**SP24**

Sandra Enriquez Sansaloni[1,2], Alain Penicaud[2], Francesco Paolucci[1]

*1 Department of Chemistry "G. Ciamician", Via Selmi 2, University of Bologna, Italy*
*2 Centre de Recherche Paul Pascal, CNRS, Bordeaux, Université of Bordeaux 1, France*

Due to their small size, high aspect ratio and excellent electrochemical properties, carbon nanotubes continue to attract high interest as components in biosensors. As it is well reported, electrodes made of carbon nanotubes have electrochemical properties that are equal or superior to most other electrodes [1]. They are promising materials for sensing applications due to several intriguing properties. In particular, their large length-to diameter aspect ratios provide for high surface-to-volume ratios. Moreover, they have an outstanding ability to mediate fast electron-transfer kinetics for a wide range of electro active species, such as hydrogen peroxide or NADH. Here we show carbon nanotubes-based electrodes made from solutions of single wall carbon nanotubes in DMSO [2] via formation of polyelectrolyte salts. They allow us to maintain aspect ratio and electrical properties of tubes with no need of surfactant or sonication steps. The transferring of the films on polystyrene or polyethylene terephthalate substrates yields ready-to-use carbon nanotubes-based electrodes.

Their covalent or non-covalent post-functionalization on the surface, allow us to link specific properties –specific functional groups- for further applications; e.g. diazonium chemistry which permits the modification by aryl groups it is used for the covalent modification of carbon nanotubes either by electro grafting or spontaneous grafting [3, 4].

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## SP25

# Functionalization of carbon nanotubes by luminescent $Eu^{3+}$ complex: markers for environmental and health monitoring

E. C. R. Vaz, A. N. Andrade, J. V. dos Anjos, Y.I. Vega-Cantú, F.J. Rodríguez-Macías
and P. A. Santa-Cruz*

*DQF, Universidade Federal de Pernambuco, Recife-PE, Brazil (*petrus@inct-inami.com.br)*

Carbon nanotube (CNT) functionalization is a well-known way to improve their interaction with complex molecules. In this study we show functionalization with a luminescent marker based in a $Eu^{3+}$ complex, which could be used for highly sensitive, selective detection via fluorescence allowing tracking of these functionalized CNT in the environment or in the body. We have studied the use of lanthanide complexes as fluorescent labels. These complexes have the advantage of particularly narrow bands in their electronic spectra long fluorescence lifetimes and good resistance to UV irradiation [1]; which makes them suitable for many applications [2]. We used these fluorescent photonic markers to functionalize multi-walled CNT. Carbon nanotube were covalently functionalized by reaction with 4-azidobenzoic acid and then complexed with Eu salts, 1,10-phenantroline and oxadiazole under microwave irradiation for 15 min. SEM showed that this procedure can coat CNT with a layer of crystalline fluorescent complexes. Non covalent functionalization was performed by dispersing the CNT with sodium dodecylsulfate (SDS) and then synthesizing *in situ* the Eu complex with phenantroline, hydroxybenzoic acid, and 4,4,4-trifluoro-1-phenyl-1,3-butanedione (BTFA). FT-IR and UV-vis confirmed the formation of the complexes, EDS analysis in the SEM confirmed the presence of Eu over the CNT. We found by fluorometry that these complexes did not show the fluorescence quenching typically produced by CNT, showing 2 ms lifetimes for thehypersensitive $^5D_0 \rightarrow {}^7F_2$ $Eu^{3+}$ transition, while the isolated complex has fluorescence lifetimes of 1.8 ms. This verifies the feasibility of tracking these labeled CNT in aqueous solutions for health and environmental studies, which our group is currently pursuing.

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## SP26

# The effect of molecular adsorption on single-walled carbon nanotube field-effect transistors

P. Yotprayoonsak[1], K. Hannula[1], A. Johansson[1], T. Lahtinen[2], G. R. Szilvay[3],
P. Laaksonen[3], M. B. Linder[3], M. Ahlskog[1]

*1 Nanoscience Center, Department of Physics, University of Jyvaskyla, Finland,*
*2 Department of Chemistry, University of Jyvaskyla, Finland (peerapong.p.yotprayoonsak@jyu.fi)*
*3 VTT Technical Research Centre of Finland, Biotechnology, Tietotie 2, Espoo, Finland*

In this study, we have investigated the electrical properties of single SWCNT-FETs before and after exposure to a specific solution consisting of tetrahydrofuran (THF), naphthalene and lithium. Prior exposure to the active solution, carbon nanotubes ordinarily show a p-type semiconducting behavior with strong gate-potential response. After deposition, their electrical property has been switched from p-type to n-type semiconductor. The measurements were carefully carried out in oxygen-free condition inside an argon-filled glove box. The influence of doping is, however, reversible by simply cleaning the devices with deionized water outside glove box, in order to remove the lithium hydroxide attached on nanotube sidewalls. This is the first demonstration on electronic measurement of lithium doping by a solution [1] that has previously been demonstrated on the solubility of SWCNTs [2].

Furthermore, we have studied the effect of protein adsorption on individual SWCNT-FETs by hydrophobin. Hydrophobin is basically a surface active and amphiphilic protein which can be utilized as a surfactant for functionalization and solubilization of CNTs [3]. Our result shows the decrease in electrical conductance after the devices have been exposed to protein solution, instead of changing from p-type to n-type characteristics as previously observed in lithium deposition experiment.

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# GSS13

**I1**

# Photoconductivity and mid-infrared plasmons in graphene

Marcus Freitag

*IBM T. J. Watson Research Center, Yorktown Heights, NY, USA (mfreitag@us.ibm.com)*

Photoconductivity can arise in graphene due to Photovoltaic, Thermoelectric, Bolometric, or Phototransistor effects, and the relative importance of each depends on the experimental conditions. Here we measure homogeneous graphene under bias, where photocurrent generation mechanisms can be switched, and the sign of the photocurrent inverted, by gating the graphene in the vicinity of the Dirac point and away from it. [1]

By patterning the graphene into arrays of nanoribbons its optical properties are changed profoundly due to the excitation of standing plasmons (collective electron density oscillations). [2-3] This allows for strong absorption in a narrow band in the mid-IR with dual tunability: First, the plasmon resonance can be tuned by adjusting the width of the nanoribbons, which selects the momentum of the standing plasmon resonance. Second, the plasmon energy can be further tuned by chemical doping or electrostatic interaction with a gate voltage. In addition, interactions of the intrinsic graphene plasmon with surface polar phonons of the $SiO_2$ dielectric lead to hybrid plasmon-phonon modes with increased lifetime. Tunable photodetectors utilizing these hybrid plasmon-phonon modes are demonstrated.

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**K1**

# Illuminating graphene

Andrea C. Ferrari

*Cambridge Graphene Centre, University of Cambridge, Cambridge, CB3 OFA, UK (acf26@hermes.cam.ac.uk)*

The rise of graphene in photonics and optoelectronics is shown by several recent results, ranging from solar cells and light emitting devices, to touch screens, photodetectors and ultrafast lasers [1]. Despite being a single atom thick, graphene can be optically visualized [2]. Its transmittance can be expressed in terms of the fine structure constant [3]. The linear dispersion of the Dirac electrons enables broadband applications. Saturable absorption is observed as a consequence of Pauli blocking [4-6]. Chemical and physical treatments enable luminescence [1,7]. Graphene-polymer composites prepared using wet chemistry [4-5] can be integrated in a fiber laser cavity, to generate ultrafast pulses, and enable broadband tunability [4,5]. By combining graphene with plasmonic nanostructures, the efficiency of graphene-based photodetectors can be increased [8]. Additionally, wavelength and polarization selectivity can be achieved by employing nanostructures of different geometries [8]. Light-graphene interaction can be tailored by using microcavities [9].

Photodetection of far-infrared radiation (from hundreds of GHz to a few THz) is important for a variety of potential applications, ranging from medical diagnostics to process control, and homeland security. THz radiation penetrates numerous commonly used dielectric materials, otherwise opaque for visible and mid-IR light. At the same time, it allows spectroscopic identification of hazardous substances and compounds, through their characteristic molecular fingerprints. In this spectral region, due to the unavoidable doping, Pauli blocking does not allow detection exploiting the common photon-induced creation of charge carriers. Efficient THz detection in graphene can be achieved exploiting the oscillating fields in a graphene field effect transistor [10]. This enables high-sensitivity, room temperature, large-area operation, not limited to a specific region of the THz range [10].

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C1

# Photoluminescence of 1D-graphene ribbons formed from coronene molecules inside single-wall carbon nanotubes

E.D. Obraztsova[1], A.I. Chernov[1], P.V. Fedotov[1], A.V. Talyzin[2], I.L. Suarez[1], I.V. Anoshkin[3], A.G. Nasibulin[3], E.I. Kauppinen[3]

*1 A.M. Prokhorov General Physics Institute, RAS, Russia (elobr@mail.ru)*
*2 Department of Physics, Umeå University, Sweden*
*3 Department of Applied Physics, Aalto University, Finland*

One-dimensional graphene structures – nanoribbons- are interesting both from fundamental and technological (optoelectronics) points of view due to opening the electronic gap with the value inverse proportional to the ribbon width. Under the ribbon widths less than 20 nm the optical gap can be measured, for instance, with photoluminescence (PL) spectroscopy. Many attempts have been made for preparation of such narrow ribbons with different techniques, however, to the best of our knowledge, PL still has not been measured. In this work we report about formation of carbon nanoribbons inside single-wall carbon nanotubes by fusion of coronene molecules. The ribbon existence has been proved by HRTEM [1]. The PL maps have been registered for coronenes and nanotubes before and after the filling procedure. After filling the additional PL peak has appeared in a spectral range between those being characteristics for coronenes (below 500 nm) and nanotubes (longer than 700 nm). The wavelength of this peak changed while the diameter of pristine nanotubes changed and demonstrated a resonance dependence on the light excitation energy. This band was ascribed to graphene nanoribbon inside SWNTs. The Raman spectra of filled nanotubes showed a significant shift of breathing modes due to the mechanical stress arising after incapsulation.

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I2

# Thermo-opto-mechanics with graphene resonators

Jeevak Parpia[1], Roberto DeAlba[1], Vivek Adiga[2], Robert Barton[2], Isaac Storch[1], Paul McEuen[1], Harold Craighead[2]

*1 Department of Physics, Cornell University Ithaca NY 14853, USA (jmp9@cornell.edu)*
*2 Applied and Engineering Physics, Cornell University, Ithaca NY 14853 USA*

By virtue of their low mass and stiffness, atomically thin mechanical resonators are attractive candidates for use in optomechanics applications. We demonstrate two applications where free-standing monolayer graphene resonators interact with light. In one [1] the graphene resonator and silicon backplane form a Fabry-Perot cavity. The graphene's mechanical motion is tunable by a gate voltage tuning and by interaction with the laser light. Interaction with laser light results in either the "cooling" of the fundamental mode of vibration or driving the resonator into a self resonant mode. Owing to graphene's high thermal conductivity and optical absorption, photothermal optomechanics is efficient in graphene and could ultimately enable laser cooling to the quantum ground state or applications such as photonic signal processing. In the second demonstration, monolayer graphene is applied to the surface of a high stress silicon nitride "drum". The graphene's conductivity is used to electrically actuate the resonant motion of the drums. A custom built optical interferometric setup equipped with a piezo controlled mirror is used to tune the Fabry-Perot cavity formed by resonator and mirror. Motion transduction is demonstrated by both optical and electrical means. Optical absorption by graphene-on-silicon-nitride drums in a tunable cavity leads to position dependent damping and resonant frequency control of the devices. Experimental results provide insight into optomechanical coupling in these composite structures and present technology for a new class of hybrid optoelectronic devices. [2]

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I3

# Electromechanical properties of suspended graphene membranes

Eros Mariani

*Centre for Graphene Science, University of Exeter, Stocker Rd EX4 4QL Exeter, UK (e.mariani@exeter.ac.uk)*

In this talk I will discuss theoretically the effects of elastic deformations on the electronic properties of monolayer and bilayer suspended graphene membranes. Distortions of the lattice translate into fictitious gauge fields in the electronic Dirac Hamiltonian that are explicitly derived for arbitrary elastic deformations [1,2]. In the bilayer case I include gauge fields associated to intra- as well as inter-layer hopping terms and discuss their effects on the strain-induced Lifshitz transitions [2]. In parallel, I analyse the temperature dependent resistivity due to electron-phonon coupling [1,2,3] as well as the ballistic transport in bilayer devices close to the neutrality point where the strain-induced reconstruction of the electronic spectrum is most prominent [4].

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C2

# Thermally assisted energy relaxation in nanomechanical graphene resonators

Daniel Midtvedt[1], Alexander Croy[1], Zenan Qi[2], Harold S. Park[2], Andreas Isacsson[1]

*1 Chalmers University of Technology, Sweden (croy@chalmers.se)*
*2 Boston University, Boston, MA, United States*

Nanomechanical graphene resonators display strong nonlinear behavior, which implies, in general, coupling between all normal modes. This allows for an energy transfer between the modes, and may lead to a redistribution of energy initially localized in a single mode. Therefore, the mode-coupling provides a dissipation channel for the fundamental mode dynamics, which is a limiting factor for most applications of graphene resonators. Here, we theoretically investigate the dependence of the energy-decay rate on excitation energy and temperature. To this end we use molecular dynamics simulations and complement them with a continuum mechanics model [2]. Mimicking a ring-down setup, the fundamental mode is excited with a given energy, and the time-evolution of this energy is computed. We find that initially high frequency flexural modes transfer energy to in-plane modes. Then the energy is redistributed from the fundamental to other flexural modes on a time-scale much longer than the fundamental oscillation period. Similar to the Fermi-Pasta-Ulam problem [1] we initially observe a metastable state where only very few modes are excited and whose lifetime decreases with increasing initial energy. Eventually, the system approaches a state with equipartition of energy. At finite temperatures, we observe thermally assisted energy relaxation of the fundamental mode, i.e., an increasing relaxation rate with temperature. In a realistic setting, energy redistribution competes with other dissipation mechanisms [3,4], which makes, in particular, the thermally assisted relaxation relevant for experimental investigations. We report the scaling of the respective time scales with parameters such as temperature, initial energy and size of the resonator.

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# Mechanical nonlinearities in graphene resonators

C3

M. Tomi, X. Song, A. Laitinen, M. Oksanen, P. Hakonen

*O.V. Lounasmaa Laboratory, Aalto University, P.O. Box 15100, FI-00076 AALTO, Finland*
*(matti.tomi@aalto.fi)*

Damping in macroscopic mechanical resonators can generally be described by a linear damping force. Present-day advances in nanofabrication, however, have made it possible to explore damping in systems with one or more atomic-scale dimensions. Recently, damping in graphene mechanical resonators was found to depend non-linearly on the amplitude of motion in measurements using frequency-modulated mixing techniques [1]. The drawback of such mixing techniques is that it is hard to know the amplitude of motion for quantitative analysis. In this work, we have employed capacitive detection methods, in which the graphene mechanical resonator, positioned on top of a counter-electrode, acts as part of an electrical cavity (*LC*) resonator. In our measurements, the change in the resonator capacitance can be calculated quite accurately, which allows precise determination of the amplitude of vibrational motion [2].

At large vibration amplitudes, we observe both softening and hardening Duffing behavior on different single layer graphene resonators. These effects are typically caused by nonlinear external potentials and geometric effects, and can be modeled by a force that is proportional to the cube of the resonator displacement $x^3$. At large amplitudes, we also observe the effect of nonlinear damping (force proportional to $x^2 \cdot \mathrm{d}x/\mathrm{d}t$). From the response amplitude curve, it is difficult to distinguish between linear and nonlinear damping, but when we look at the responsivity (amplitude divided by driving force) of the resonator, we can clearly see a decrease for large amplitudes. As linear damping does not cause any change in responsivity, we can use this to determine the strength of nonlinear damping in our resonators.

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# Graphene Flagship

K2

Jari Kinaret

*Chalmers University of Technology, Gothenburg, Sweden (kinaret@fy.chalmers.se)*

I will describe the Graphene Flagship project which was recently selected a flagship of European research in the area of future and emerging technologies. I will briefly review the route to the one billion euro project, its present status and future, both in terms of implementation and the research program.

I4

# Graphene devices: from transistor to barristor

Hyun-Jong Chung[1,2]

*1 Konkuk University, Korea (hjchung@konkuk.ac.kr)*
*2 Samsung Advanced Institute of Technology, Korea*

Graphene has been considered as one of the potential post Si-materials due to its high mobility. [1] However, since graphene has no band gap, it is difficult to achieve high $I_{on}/I_{off}$ ratio, one of the most important requirements for commercial devices. There have been many attempts to open its band gap for high $I_{on}/I_{off}$ ratio, but most of them end up lowering the mobility. [2] Thus, I proposed and demonstrated a new device structure for graphene transistor based on one of the unique properties of graphene for high $I_{on}/I_{off}$: using this approach, the ratio over $10^5$ is achieved [3]. The device has several major advantages over previously proposed graphene based electronic devices: first, since it does not alter the given properties of graphene, such as opening the band gap, the device has no fundamental issues on mobility degradations. Second, it is fully compatible with current Si technology. In this talk, graphene barristor and graphene transistor will be compared each other especially for working mechanism based on the detailed understanding. Device characteristics including $I$-$V$ curves with $10^5$ on/off ratio will be presented. Finally, the current issues and their potential solutions will be mentioned.

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C5

# Ab initio study and possible applications in NEMS of double-layer graphene separated by adsorbed molecules

Andrei M. Popov[1], Irina V. Lebedeva[2], Andrei A. Knizhnik[2,3], Yurii E. Lozovik[1,4], Boris V. Potapkin[2,3]

*1 Institute of Spectroscopy Russian Academy of Science, Troitsk, Moscow, Russia (popov-isan@mail.ru)*
*2 Kintech Lab Ltd., Moscow, Russia*
*3 NRC “Kurchatov Institute”, Moscow, Russia*
*4 Moscow Institute of Physics and Technology, Dolgoprudny, Russia*

The electronic properties of heterostructures consisting of graphene layers separated by sub-nanometer dielectric spacers have lately attracted fundamental and practical interest. These properties can considerably depend on the relative position, orientation and distance between graphene layers. The possibility to control the commensurability and distance between graphene layers separated by dielectric spacer is considered by the example of recently implemented [1] double-layer graphene separated by layers of adsorbed molecules. Van der Waals corrected density functional theory is applied to study structural, energetic and tribological characteristics of this heterostructure with argon and krypton spacers. It is found that in the ground state, monolayer and bilayer argon spacers are incommensurate with the graphene layers, whereas submonolayer argon spacers which are commensurate with the graphene layers can exist only as metastable states. On the contrary, the graphene layers separated by monolayer krypton spacer are commensurate in the ground state and have the AA stacking. The calculations show that the incommensurability between graphene layers separated by monolayer argon spacer lead to negligibly small static friction for relative motion of graphene layers and therefore offers promise for applications in nanoelectromechanical systems. These applications can include variable nanocapacitors or nanoresistors depending on the conductivity between graphene layers and nanorelays based on relative motion or rotation of the layers. A scheme and operational principles of such a nanorelay are proposed.

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C6

# Photocurrent imaging of metal-graphene-metal photodevices with few-layer graphene

Minjung Kim[1], Sun Keum Choi[1], Jung Cheol Kim[1], Ho Ang Yoon[2], Sang Wook Lee[2], Hyeonsik Cheong[1]

*1 Department of physics, Sogang University, Seoul, Korea (hcheong@sogang.ac.kr)*
*2 Division of Quantum Phases and Devices, School of Physics, Konkuk University, Seoul, Korea*

Electronic and optoelectronic devices based on the unique physical properties of graphene are attracting much attention recently. For optoelectronic applications, high-speed, broad-band photodetectors based on metal-graphene-metal junctions have been demonstrated. Because graphene has a linear electronic band dispersion with no bandgap, light absorption is uniform over a wide range of the spectrum. We have studied the photocurrent and its polarization dependence in metal-graphene-metal devices with single-, bi-, and tri-layer graphene channels. Palladium (Pd) and titanium (Ti) were used as the electrodes. A special measurement system allowed us to image the photocurrent and the Raman spectrum simultaneously, so as to determine the exact positions of the photocurrent generation. The photocurrent in devices made with single layer graphene exhibited photocurrent near the graphene-metal junction and show strong polarization dependence, which could be interpreted in terms of anisotropic electron-photon interaction in graphene. [1] Devices made with trilayer graphene samples showed photocurrent patterns different from that of a device with single-layer channel. Furthermore, trilayer devices with different stacking orders (ABA vs ABC) exhibit photocurrent patterns that depend on the stacking order. This could be interpreted as the manifestation of different band structures.

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I5

# Scanning probe microscopy on graphene nanoribbons and self-assembled molecular layers on graphene

Peter Liljeroth

*Department of Applied Physics, Aalto University, Finland (peter.liljeroth@aalto.fi)*

Control over the graphene band structure is required to realize the full potential of graphene-based electronic devices. Many approaches have been used to attack this problem; I will focus here on quantum confinement in graphene nanoribbons (GNRs) and using periodic potential modulation on graphene. I will discuss our low-temperature STM and AFM experiments aimed at investigating these effects. We have synthesized atomically well-defined GNRs through on-surface polymerization that have armchair edges along the long axis of the ribbon and zigzag ends along the short axis. The electronic states of the GNRs close to the Dirac point are located at the zigzag ends of the nanoribbons, whereas the states away from the Dirac point are more delocalized over the entire ribbon. In addition to the electronic structure of the GNRs, I will discuss contacting the GNR to a metallic lead by a single chemical bond by controllably removing individual hydrogen atoms from the zigzag ends of the GNR.

In the second part of the talk, I will focus on self-assembly of ordered cobalt phthalocyanine (CoPc) lattices on graphene (G) on $SiO_2$ and hexagonal boron nitride (h-BN) substrates. This is an attractive model system for studying the effect of ordered molecular layers on the graphene band structure as the strength and the period of the potential modulation can be tuned by altering the side groups and the metal center in the Pc molecule. On G/$SiO_2$, the long range order is limited by the surface corrugation, whereas on h-BN, the CoPc orders in a perfect square lattice. STM shows that CoPc molecules are doped by the substrate, and that the level of doping varies from molecule to molecule. This variation is larger on G/$SiO_2$ compared to G/h-BN. Analysis of the tunneling spectra yields the tunneling coupling of the molecular orbitals with the graphene substrate. These results suggest that graphene on h-BN is an ideal substrate for the study of molecular self-assembly towards engineered potential landscapes on graphene.

C6

## Incoherent interlayer conduction in graphene-graphene cross junction

Youngwook Kim[1], Hoyeol Yun[2], Seung-Geol Nam[1], Minhyeok Son[3], Dong Su Lee[4], Dong Chul Kim[5], S. Seo[6], Hee Cheul Choi[3], Hu-Jong Lee[1], Sang Wook Lee[2], and Jun Sung Kim[1]

*1 Department of Physics, Pohang University of Science and Technology, Pohang 790-784, Korea*
*2 Division of Quantum Phases and Devices, School of Physics, Konkuk University Seoul, 143-701, Korea (leesw@konkuk.ac.kr)*
*3 Department of Chemistry and Division of Advanced Materials Science, Pohang University of Science and Technology, Pohang 790-784, Korea*
*4 Institute of Advanced Composite Materials, Korea Institute of Science and Technology, Wanju-gun 565-902, Korea*
*5 Department of Electronics and Telecommunications, Norwegian University of Science and Technology, NO-7491 Trondheim, Norway*
*6 Department of Physics, Sejong University, Seoul 143-747, Korea*

Interlayer coherences in twisted bilayer structures were studied. The twisted bilayer graphene structure was realized using micro contact transfer technique. Temperature and gate voltage dependences of resistivity and I-V characteristics were conducted to investigate the interlayer coupling of twisted bilayer graphene. A complete suppression of coherent conduction was observed from the transport measurements even in an atomic length scale of layer separation in twisted bilayer graphene. Fabrication method, Raman and AFM characterization, and transport measurement result with analysis of the twisted bilayer graphene structures will be discussed in this presentation.

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C7

## Electronic properties of a covalent GO-$C_{60}$ hybrid

Myriam Barrejón, María Vizuete, María José Gómez-Escalonilla, Fernando Langa

*Institute for Nanoscience and Molecular Materials, Univ. Castilla-La Mancha, Spain (fernando.langa@uclm.es)*

Graphene (GS) and graphene oxide (GO) have attracted great interest for its superior physical, chemical, mechanical, and electrical properties that enable a wide range of applications from electronics to nanoelectromechanical systems [1]. Functionalization of these materials can allow to modulate their electronic, optical and electrical properties, and due to and the relatively inert surface of the GS and GO are new methods for functionalization are being explored [2]. As precedent, hybrid materials between Carbon Nanotubes (CNTs) and fullerenes have generated intense attention, driven by the possibility of combining some of the outstanding properties of the CNTs with those of fullerenes, rising new properties of the hybrid.[3]

In this sense, the preparation of hybrids involving graphene and fullerenes will permit to explore the potentials applications of these materials. Based on this consideration, we present the synthesis, by means of *"click chemistry"*, and the characterization of a soluble hybrid material, GO-$C_{60}$ that combines fullerene and graphene oxide (GO) into a single structure. Transient absorption spectroscopy of the GO-$C_{60}$ conjugate show photoinduced electron transfer process PET from the GO to the $C_{60}$ cage, suggesting that should be possible to develop an efficient all-carbon system undergoing photoinduced charge separation with potential for solar energy conversion.

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C8

# Boron nitride nanoribbons from in-situ unzipping during nanotube growth

Ling Li,[1,2] Luhua Li,[1] Ying Chen,[1] Xiujuan Dai,[1] Peter Lamb,[1] Bing-Ming Cheng,[3] Meng-Yeh Lin[3]

*1 Institute for Frontier Materials, Deakin University, Waurn Ponds, Australia (luhua.li@deakin.edu.au)*
*2 MEMS Center, Harbin Institute of Technology, Harbin, China*
*3 National Synchrotron Radiation Research Center, 101 Hsin Ann Road, Hsinchu Science Park, Hsinchu, Taiwan*

Boron nitride nanoribbons (BNNRs) have many interesting properties. They have been produced previously from unzipping boron nitride nanotubes (BNNTs) via two separate steps: BNNT growth and post-synthesis unzipping treatments. Here, we introduce an in-situ unzipping concept that simplifies the two steps into one. That is, unzipping happens during BNNT synthesis so that BNNRs can be directly harvested without the need for post-synthesis treatment. The resultant BNNRs are of high chemical purity and crystallinity according to near edge x-ray absorption fine structure (NEXAFS) spectroscopy, and prefer a zig-zag orientation.

[1] Ling Li, Lu Hua Li, Ying Chen, Xiujuan J. Dai, Peter R. Lamb, Bing-Ming Cheng, Meng-Yeh Lin and Xiaowei Liu, Angewandte Chemie International Edition 52(15) 4212–4216 (2013)

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C10

# Nitrogen-doped graphene materials as non-precious catalysts for oxygen reduction reaction

C. Zhang, R. Hao, H. Yin, Y. Hou

*Department of Materials Science and Engineering, College of Engineering, Peking University, Beijing 100871, China (hou@pku.edu.cn)*

Nitrogen-containing graphene is a promising candidate for oxygen reduction reaction (ORR) in fuel cells. However, there are still some challenges in synthesis and further application of nitrogen-doped graphene and in understanding the roles of various nitrogen states on electrocatalysis. Herein, we design a simple and effective solvothermal method to synthesize amino-functionalized nitrogen-doped graphene from graphite oxide only in the presence of ammonia solution. Having a remarkable doping concentration of nitrogen atoms up to 10.6 % (atom %), the resultant product can act as an efficient non-precious catalyst, exhibiting enhanced electrocatalytic properties for ORR. A combination of X-ray photoelectron spectroscopy (XPS) and electrochemical measurements was then used to investigate the roles of various nitrogen states in ORR. The experimental results show that the graphitic- and amino-type of nitrogen components determine the onset potential and electron transfer number, while the total content of graphitic and pyridinic nitrogen atoms is the key factor to enhance the current density in the electrocatalytic activity for ORR. [1] Furthermore, iron phthalocyanine (FePc) and nitrogen-doped graphene composite was also prepared as a novel non-precious catalyst in ORR. The resulting composite exhibits superior ORR catalytic activity, excellent tolerance to methanol crossover, and comparable stability compared to commercial Pt/C. [2] These works could lead to the invention of new non-precious catalysts for ORR in fuel cells.

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C11

# Synthesis of multi-layer graphene on epitaxially-grown metal catalyst film and its electrical properties

Daiyu Kondo, Haruhisa Nakano, Bo Zhou, Ichiro Kubota, Junich Yamaguchi, Kenjiro Hayashi,
Shintaro Sato, and Naoki Yokoyama

*Collaborative Research Team Green Nanoelectronics Center (GNC), AIST (kondo.daiyu@aist.go.jp)*

Nano-carbon materials including graphene are a candidate for new wiring materials for the future LSIs due to their excellent electrical properties [1]. Among nano-carbon materials, we focus on multi-layer graphene, and its application to LSI interconnect is discussed in this study. Recently, results regarding multi-layer graphene wiring obtained by chemical vapor deposition (CVD) or a related growth method have been reported [2, 3]. Although high-quality graphene is necessary for LSI interconnect, the electrical resistivity of graphene obtained by CVD is usually worse than that of highly oriented pyrolytic graphite (HOPG) by more than one order of magnitude due to its poor crystallinity. To solve this problem, we employed an epitaxial cobalt film to grow high-quality multi-layer graphene by thermal CVD method. A cobalt (Co) catalyst film with a thickness of 200 nm was deposited on a sapphire substrate by the conventional sputtering method at 500 degree C. Multi-layer graphene was then grown on the Co film by CVD at 1000 degree C using $CH_4$ diluted by $H_2$/Ar as the source gas. After synthesis, the multi-layer graphene obtained was evaluated by Raman spectroscopy. Raman spectra suggest that high-quality multi-layer graphene with the AB-stacked structure was synthesized. The measurement of electrical properties was then performed at room temperature. It was found that the resistivity of the multi-layer graphene was as good as that of HOPG. This research is granted by JSPS through FIRST Program initiated by CSTP. A part of this work was conducted at the Nano-Processing Facility, supported by IBEC Innovation Platform.

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## Electron-phonon coupling in suspended bilayer graphene

SP26

Antti Laitinen[1], Mika Oksanen[1], Daniel Cox[1], S. Russo[2], P. Hakonen[1]

*1 O.V. Lounasmaa Laboratory, School of Science, FI-00076 AALTO, Finland (daniel.cox@aalto.fi)*
*2 Centre for Graphene Science, CEMPS, University of Exeter, Exeter, EX4 4QF, UK*

Under Joule heating in a graphene bilayer, heat flows via electronic diffusion and inelastic collisions with the lattice phonons. The flow through the phonon system as a function of electronic temperature is given by $P=\sum(T_e^\delta-T_p^\delta)$ where $\sum$ is a coupling constant, $T_e$ the electronic temperature, $T_p$ the phonon temperature, and $\delta$ is a characteristic exponent [1].

We have measured a high quality suspended graphene bilayer using AC conductance measurements and shot noise thermometry to determine the electronic temperature. The sample substrate acted as a thermal bath and was cooled to 20 mK in a dilution refrigerator. Using DC voltage bias the electrons were heated up to 500 K. We observe a quadratic dependence ($\delta$=2) on the electron temperature below 10 K which corresponds to thermal relaxation via electronic diffusion. Above 200 K electron-phonon coupling becomes the dominant method of thermal relaxation with electronic diffusion playing only a minor role. Here we observe a nearly quartic dependence ($\delta$=4) on the electronic temperature and quadratic dependence of the coupling constant on chemical potential $\sum\sim\mu^2$. This indicates the role of two-phonon scattering events, reminiscent of the supercollision events analysed by J. Song et al [2] and is the same as our monolayer case. The results look similar to acoustic phonon coupling ($\delta$=4) but lacks the signature of single-phonon scattering events which yield a linear dependence on the chemical potential ($\sum\sim\mu$).

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## Is graphene chemical vapor deposition (CVD) growth epitaxial

SP27

Feng Ding, Lu Wang, Xiuyun Zhang, Qinghong Yuan

*Institute of Textile and Clothing, Hong Kong Polytechnic University, Hong Kong, PR China*

Chemical vapor deposition (CVD) is broadly recognized as a flexible and economic method of large area and high quality graphene synthesis, while our understanding on the mechanism of graphene CVD growth is very limited. [1-6] Here we present our theoretical study regarding on the epitaxy of graphene CVD growth.By considering the completion between graohene edge-catalyst (GE-C) and graphene wall-catalyst (GW-C) interactions and the barrier of graphene rotation on catalyst surface, we will show that the orientation of a graphene island may inherit that of its infant age but no registry between graphene lattice and catalyst surface. [7]

By considering the three modes of graphene CVD growth, on terrace, near metal step, and the embedded growth, we have revealed that CVD graphene tends to be embedded on soft catalyst surfaces (e.g., Cu and Au) while the on terrace growth dominates the growth on the rigid catalyst surface (e.g., Ru, Ir, Rh). The graphene grown via on terrace mode may align along with different orientations while the graphene grown via the embedded mode or near metal step mode has only two potential orientations. [8]

Based on this understanding, many experimental puzzles are well understood and the strategies of growing high quality graphene on various catalyst surfaces are proposed.

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SP28

## Graphene nanosheets: synthesis, chemical functionalization, and applications

Qi Dong, Yan Zhao, Yan Wang

*Beihang University, China (jennyzhaoyan@buaa.edu.cn)*

Interest in graphene and its derivative materials centers on their excellent mechanical, electrical, thermal and optical properties, their very high specific surface area, and our ability to influence these properties through chemical functionalization [1]. There are a number of methods for generating graphene and graphene oxide nanosheets [2]. In this report, the synthesis of large pieces of graphene oxide (GO) nanosheets by modified Hummers method and the characterization results of the as-obtained GO nanosheets are illustrated. We then use a mild reduction condition to prepare partially reduced graphene oxide (RGO) nanosheets with different reduction degrees. Both GO and RGO have promising applications in the field of composite materials.

An application of the as-obtained GO nanosheets which could enhance the dispersion quality of multiwalled carbon nanotubes (MWCNTs) in tetrahydrofuran (THF) solution is demonstrated. Moreover, the as-prepared GO nanosheets can be further functionalized by chemical methods to achieve improved properties: the nanosheets can be modified by 2,4-Diisocyanatotoluene (TDI) to prepare chemically functionalized filler which serves to enhance the mechanical properties of the epoxy composites. At last, another application using partially reduced graphene oxide nanosheets as the filler in the resin to improve the electromagnetic properties of the composites is also reported.

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SP29

## Graphene growth on copper using gradients of temperature and carbon concentration

J. Ek-Weis, T. H. R. Cunha, R. G. Lacerda, A. S. Ferlauto

*Department of Physics, ICEx, Universidade Federal de Minas Gerais – Belo Horizonte, Brazil*
*(ekweis@fisica.ufmg.br)*

Nowadays, one of the main methods to synthesise graphene is by chemical vapour deposition, CVD, of methane on copper, where temperatures in the range 800-1000 °C are typically used. Usually, the optimal growth conditions are found by many trial experiments using different atmospheres and temperatures. However, for a complete understanding of the growth mechanism of graphene on copper a clear picture of the influence of each parameter, such as temperature and pressure, is necessary. To achieve this goal, we present a study on the influence of temperature and carbon concentration on individual samples by using gradients of temperature and/or carbon concentration. This guarantees that all the growth conditions are exactly the same apart from the investigated temperature and carbon concentration.

A cold-wall CVD chamber is used. A temperature gradient is created by forming the copper foil into different geometrical shapes, where the end closest to the heater becomes significantly hotter than the other end. It is found that the size and density of the graphene grains depend on the temperature.

Using a gradient of carbon concentration, samples which are partly fully covered with graphene and partly with sparse growth are synthesised. Raman studies of these samples show that the D/G ratio is minimised for the fully covered growth, where the G'/G ratio is maximised. The G and G' peaks shift along the gradient, showing that there is a strain difference between the individual grains and the fully covering graphene. The results provide insights on graphene grain nucleation and growth that can help the optimisation of graphene CVD synthesis.

# Domain structure in graphene islands grown on copper foil by chemical vapor deposition

SP30

Kenjiro Hayashi, Ayaka Yamada, Shintaro Sato, Naoki Yokoyama

*Collaborative Research Team Green Nanoelectronics Center (GNC), AIST, Japan*
*(hayashi.kenjiro@aist.go.jp)*

Tailoring large-scale single-crystalline graphene on Cu surface by means of chemical vapor deposition is a crucial issue for its application to electronic devices. Since self-limited graphene growth on a Cu surface is governed by surface diffusion processes, understanding the role of surface is important. Previous studies have made great efforts to enlarge the graphene domain size based on a strategy for suppressing the island density [1] and/or that for controlling the orientation of each graphene island with respect to the atomic arrangement of underlying epitaxial Cu(111) film [2]. However, very few studies have focused on the domain structure within an individual island. It remains unclear whether a graphene island consists of a single domain or multiple domains, which may depend on the surface orientation and growth conditions.

In this study, we investigated the initial stage of graphene growth on poly-crystalline Cu foil under various growth conditions to clarify the correlation between the domain structure of an island and the orientation of an individual Cu grain surface. It has been revealed that the four-lobed and the hexagonal shaped islands were grown on (001) and (111)-oriented Cu surfaces, respectively. Each island was found to align with the specific direction. Moreover, the graphene lattice has a commensurate relationship with the atomic arrangement of the surface for both the four-lobed and the hexagonal shaped islands. The graphene islands grown at lower temperature or at lower partial pressure of $H_2$, however, showed poly-crystalline nature consisting of small domains. This work was supported by JSPS through the FIRST Program, initiated by CSTP, Japan. This work was partly conducted at the Nano-Processing Facility supported by ICAN, AIST, Japan.

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# Synthesis and characterization of layer-patterned graphene film

SP31

Daesung Jung[1], Wooseok Song[2], Yooseok Kim[2], Jumi Cho[2], Chong-Yun Park[1,2,*]

*1 Department of Energy Science, SungKyunkwan university, Suwon 440-746, Republic of Korea*
*2 Department of Physics, SungKyunkwan university, Suwon 440-746, Republic of Korea*

Layer-patterned graphene (composite construction consisted of mono- and multi-layer graphene selectively) was synthesized on Ni-embedded Cu catalytic substrate by using single-step thermal chemical vapor deposition. This composite construction having continuative layer from multi-layer graphene to mono-layer graphene could be controlled by the thickness of deposited Ni layer, the gas ratio methane to hydrogen, the temperature synthesizing graphene and the moment introducing methane gas. In our research, this controllable layer-pattered graphene was observed by Raman spectroscope, surface profiler and transmission electron microscope. Through analysis of electric properties as various bending radiuses, this composite construction could show the possibility for transparent and flexible all-carbon field effect transistors.

## SP32 Growing of a thin layer of $TiO_2$ dielectric on CVD graphene

Tauno Kahro[1], Aarne Kasikov[1], Aivar Tarre[1], Alar Gerst[1], Ahti Niilisk[1], Arvo Tõnisoo[1], Kristel Möldre[1], Jekaterina Kozlova[1], Jaan Aarik[1], Harry Alles[1], Väino Sammelselg[1,2]

*1 Institute of Physics, University of Tartu, Estonia (tauno.kahro@ut.ee)*
*2 Institute of Chemistry, University of Tartu, Estonia*

Successful integration of graphene, single atomic layer carbon, with high k-dielectrics is important for future developments of graphene-based applications. In this work we prepared graphene samples on copper foils with chemical vapor deposition (CVD) method using methane as a carbon source and transferred them onto $SiO_2$/Si substrates. Raman spectroscopy measurements revealed that obtained CVD graphene sheets were primarily monolayers. After that $TiO_2$ layers with thicknesses of ~10 nm were synthesized on graphene by atomic layer deposition (ALD) using $TiCl_4$ and $H_2O$ as precursors at temperatures of 150 °C and 300 °C. Growth of $TiO_2$ at lower temperature turned out to be faster and more successful than at higher temperature.

## SP33 Self-assembling graphene grating synthesized directly on a dielectric substrate

Tommi Kaplas, Martti Silvennoinen, Kimmo Päiväsaari, and Yuri Svirko

*University of Eastern Finland, Department of Physics and Mathematics, P.O.Box-111, FI-80101, Finland (tommi.kaplas@uef.fi)*

Graphene has recently found a number of applications in photonic and optoelectronic components including transparent electrodes, saturable absorbers, ultrafast transistors and optical modulators [1]. However, until now, incorporation of graphene into photonic and optoelectronic devices requires its transferring from metallic catalyst used for its synthesis to an insulator or semiconductor substrate. Moreover in order to achieve monolithic integration graphene should be deposited on the prescribed location on e.g. the $SiO_2$ wafer. Here we propose a technique for position-selective graphene growth directly on the pre-patterned dielectric substrate. This transfer free technique can be employed for introducing graphene elements into optical gratings or planar waveguides.

In the experiment, we prepared binary gratings with chancing periodicity (from 400 nm to 4 μm) and height (from 150 nm to 500 nm) by using electron beam lithography and reactive ion etching. This pre-patterned substrate was covered by a 200 nm thick copper film and was employed as a substrate in the chemical vapor deposition (CVD) process (see Ref. [2] for details). During the CVD process the Cu film liquidizes and forms a network prescribed by the morphology of the substrate and the temperature, while a few layer graphene will grow both on copper-vacuum and copper-silica interfaces [2,3]. Thus the graphene network will be "imprinted" on the silica substrate and can be revealed by removing copper by plasma and wet etching. The fabricated graphene network was characterized by scanning electron microscope and Raman spectroscopy.

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SP34

## Controlled growth of large-area mono-, bi-, and few-layer graphene by chemical vapor deposition on copper substrate

Yooseok Kim[1], Su-il Lee[1], Dae Sung Jung[2], Myoung-Jun Cha[1], Ji Sun Kim[1], Seung-Ho Park[1], and Chong-Yun Park[1,2,*]

*1 Department of Physics, Sungkyunkwan University, Suwon 440-746, Republic of Korea*
*2 Department of Energy Science, Sungkyunkwan University, Suwon 440-746, Republic of Korea*
*(*cypark@skku.edu)*

Direct synthesis of graphene using a chemical vapor deposition (CVD) has been considered a facile way to produce large-area and uniform graphene film, which is an accessible method from an application standpoint. Hence, their fundamental understanding is highly required. Unfortunately, the CVD growth mechanism of graphene on Cu remains elusive and controversial.

Here, we present the effect of graphene growth parameters on the number of graphene layers were systematically studied and growth mechanism on copper substrate was proposed. Parameters that could affect the thickness of graphene growth include the pressure in the system, gas flow rate, growth pressure, growth temperature, and cooling rate. We hypothesis that the partial pressure of both the carbon sources and hydrogen gas in the growth process, which is set by the total pressure and the mole fraction of the feedstock, could be the factor that controls the thickness of the graphene. The graphene on Cu was grown by the diffusion and precipitation mode not by the surface adsorption mode, because similar results were observed in graphene/Ni system. The carbon-diffused Cu layer was also observed after graphene growth under high CH4 pressure. Our findings may facilitate both the large-area synthesis of well-controlled graphene features and wide range of applications of graphene.

SP35

## Raman study of adlayer flakes on single-layer CVD graphene on copper

Wonjae Kim, Juha Riikonen, Changfeng Li, Harri Lipsanen

*Department of Micro- and Nanosciences, Aalto University, Tietotie 3, 02150 Espoo, Finland*
*(wonjae.kim@aalto.fi)*

Chemical vapor deposition (CVD) is well known as the most favorable method to produce the high quality large scale graphene films. Copper is widely used as a catalytic substrate because the growth process is self-terminated after the surface is covered by single-layer graphene. This behavior originates from the low solubility of carbon species into copper substrate. However, the flakes (adlayer domains) are commonly found in single-layer graphene grown on copper [1]. Detail characterization of the flakes, including, e.g., identification of the stacking order, will promote the understanding of growth mechanisms related to the synthesis of graphene.

Using micro-Raman spectroscopy, adlayer flakes appearing in CVD graphene on copper have been characterized. Raman analysis which is well known as a straightforward and non-destructive probing method can provide structural information including stacking configuration related to the misorientation between two graphene layers. In this experiment, the graphene layers were grown in a gas mixture of $CH_4/H_2$ (12/3 sccm) at 935 °C in low pressure (~ 7 mbar) using photo-thermal CVD. From the Raman analysis, it was found that the flakes (multi-layer areas) had a misorientation in respect to the initial single-layer (background) graphene. The misoriented angles between two layers were also identified based on the behavior of double resonance scattering [2-3]. Moreover, detailed Raman mapping reveals that the adlayer flakes which would have been considered as individual grains by scanning electron microscopy consist of merged graphene grains.

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SP36

# Peculiarities of CVD graphene synthesis on nickel

Ivan Kondrashov, Pavel Rusakov, Maxim Rybin, Pozharov Anatoliy and Elena Obraztsova

*A.M. Prokhorov General Physics Institute, Vavilov str. 38, Moscow, Russia,119991 (navi.soul@gmail.com)*

Graphene is one of the most interesting carbon nanomaterials. It is a two-dimensional hexagonal lattice of carbon atoms. Researches in graphene are very active nowadays because of its unique electrical and optical properties and an immense potential for applications in electronics, sensors, solar cells, and many others. A chemical vapour deposition method for graphene synthesis on metal substrate is a very promising approach for fabrication of large-scale and high quality graphene films. A variety of metals can be used for CVD synthesis of graphene. The most popular of them are copper and nickel. Copper is used for synthesis of the multi-layer graphene films and nickel for synthesis of one-layer and multi-layer graphene. Therefore, it is very important to control the synthesis process for obtaining the desired number of graphene layers.

Thereby in this work we present the detailed investigation of CVD method of synthesis of graphene on polycrystalline nickel foils from the gas mixture of methane, hydrogen and argon[1,2]. We heated the metal foil by Joel effect with a direct input of an electric current. The heating of substrate starts after a methane injection in the chamber. Additionally to standard synthesis parameters as pressure, methane concentration, temperature, we also observed a change in resistance of the nickel foil during the experiment. The final number of graphene layers can be controlled via monitoring the resistance changes during synthesis.

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SP37

# Quality of graphene prepared by CVD method on nickel

Jekaterina Kozlova[1], Ahti Niilisk[1], Aarne Kasikov[1], Alar Gerst[1], Tauno Kahro[1], Harry Alles[1],
Väino Sammelselg[1,2]

*1 University of Tartu, Institute of Physics, Riia 142, 51014, Estonia (jekaterina.kozlova@ut.ee)*
*2 Institute of Physical Chemistry, University of Tartu, Ravila 14a, 50011, Estonia*

Chemical Vapor Deposition (CVD) on transition metals is one of the most promising routes to the production of large-scale graphene. Nickel is one of the most suitable catalysts for the synthesis of high quality graphene due to the smallest lattice mismatch with graphene among other catalysts. In addition, nickel does not introduce rotational disorder to graphene, which allows to avoid defective domain boundaries during coalescence of differently oriented graphene domains. Thus, higher quality graphene can be obtained. However, graphene growth on nickel is not self-limiting process which typically results in the growth of inhomogeneous few-layer graphene. In this work the effect of different nickel substrates, film thickness and growth parameters on the graphene quality and thickness were examined. Graphene was synthesized on different nickel substrates (thin films and foils). The synthesis of graphene onto Ni films was carried out in a home-made quartz-tube CVD reactor at low pressure using methane in argon gas as a precursor. Following the synthesis, graphene was covered with PMMA, and nickel was etched away with chemicals. PMMA coated graphene sheets were transferred to 100 nm thick $SiO_2$ coated Si substrates having e-beam evaporated Pt contacts. The quality and uniformity of graphene samples were characterized using Raman spectroscopy and HR-SEM techniques. Electrical parameters of the graphene were determined and compared to values obtained with copper catalyst.

SP38

## Fabry-Pérot interference and shot noise in suspended graphene

Antti Laitinen[1], Mika Oksanen[1], Andreas Uppstu[2], Daniel Cox[1], Ari Harju[2], Monica Craciun[3], Saverio Russo[3], Pertti Hakonen[1]

*1 O.V. Lounasmaa Laboratory / LTL, Aalto University, Finland (antti.laitinen@aalto.fi)*
*2 Department of Applied Physics, Aalto University, Finland*
*3 Center for Graphene Science, University of Exeter, UK*

The conditions for Fabry- Pérot resonances in rectangular graphene sheets with nonperfect contacts were recently analyzed by Gunlycke and White [1] who showed that, under certain conditions evenly spaced groups of resonances, separated by $\Delta E \sim hv_F/2L$, can emerge. These collective resonances originate owing to simultaneous participation of modes in nonequivalent channels that are facilitated by transversely quantized states with small energy separation. Such collective resonances should not be confused with the ordinary two-channel Fabry- Pérot resonances observed in single-wall carbon nanotubes.

We report analysis of Fabry-Pérot type interferences in high-mobility suspended graphene using both shot noise and conductance measurements. Differential conductance shows definite Fabry-Pérot patterns emerging, by taking the derivative of the conductance the visibility is improved. The Fourier transform of the data shows three sets of peaks which are identified as resonances of 1) clean suspended part bordered by pn junctions, 2) full length of the sample with scattering from the contacts, and 3) width of the sample.

The Fabry-Pérot interferences in our shot noise measurements are best visible in the derivatives of the data. Fourier analysis reveals again three sets of peaks, which nearly coincide with those obtained from our conductance measurements. A correlation analysis between conductance and shot noise, indicates rather weak correlation. This analysis demonstrates that the observed Fabry-Pérot pattern originates from more than two channels in contrast to interference phenomena in single walled carbon nanotubes.

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SP39

## Photo-thermal chemical vapor deposition of graphene on copper

Changfeng Li, Wonjae Kim, Juha Riikonen, and Harri Lipsanen

*Aalto University, Department of Micro- and Nanosciences, Micronova, FI-00076 AALTO, Espoo, Finland*

Chemical vapor deposition (CVD) using metal catalyst as a target substrate is an effective way to produce large-area high-quality graphene [1]. An alternative for typically used CVD with resistive heating is photo-thermal chemical vapor deposition (PTCVD) utilizing halogen lamps as a heat source. PTCVD demonstrates a very high growth rate of high-quality single-layer graphene on copper, achieving a short growth time of 20-60 s to complete a continuous graphene film compared to 20-30 minutes using typical tubular furnaces [2].

The growth temperature is the most important factor due to hydrocarbon dissociation on the surface of the copper catalyst. In this study, graphene was synthesized under different PTCVD process parameters. It was found that PTCVD can produce high-quality single-layer graphene, which has high intensity ratio of the 2D and G bands ($I_{2D}/I_G$), at 935 - 950 °C using a growth time of 60 s with a gas ratio ($CH_4$: $H_2$) of 4 : 1 in low pressure (~ 10 mbar). The annealing prior to the growth was varied from 5 to 15 minutes. The influence of the heating rate and the cooling rate from growth temperature were studied. Typically, Raman histograms show intensity ratio of the D and G bands ($I_D/I_G$) lower than 0.1, which corresponds to very low defect density [3, 4].

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**SP40**

# Localized deoxygenation of graphene oxide films by focused ion beams: structural evolution and direct writing of conductive structures

Derrek E. Lobo and Mainak Majumder

*Nanoscale Science and Engineering Laboratory (NSEL), Department of Mechanical and Aerospace Engineering, Monash University, Clayton, VIC 3168, Australia (mainak.majumder@monash.edu)*

Structural modifications to graphene during exposure to energetic particles that includes ion-beams, e-beams has been the subject of extensive theoretical research [1]. We have experimentally studied the effect of ion-beams on films of graphene oxide and observe that the films undergo preferential deoxygenation at low dosages of ion fluence. Areas of GO films unexposed to ion beams had a carbon content of 64±2 % and an oxygen content of 36±2%, which changed to 74.5±2.5% for carbon and 25.5±2.5% for oxygen in the exposed regions demonstrating deoxygenation. A concomitant increase in electrical conductivity by over 2-3 decades was also observed indicating the ability to produce carbon structures analogous to chemically reduced graphene oxide. [2] Progressive increase of ion beam exposure then leads to amorphization, as evidenced by Raman Spectroscopy studies, followed by rupture of the graphene sheets. The phenomena of deoxygenation under controlled dosages can be utilized for direct writing of conductive rGO structures in the length scale of tens of nanometers to hundreds of microns.

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**SP41**

# Electrical characterization for graphene film grown by low-temperature microwave plasma CVD

Yuki Okigawa[1,2], Kazuo Tsugawa[2], Takatoshi Yamada[1,2]
Masatou Ishihara[1,2], Masataka Hasegawa[1,2]

*1 Nanotube Research Center, National Institute of Advanced Industrial Science and Technology (AIST), Japan (okigawa.yuki@aist.go.jp)*
*2 Technology Research Association for Single Wall Carbon Nanotubes (TASC), Japan*

We have developed the microwave plasma CVD technique combined with the roll-to-roll process to deposit the graphene film. In this method, a continuous deposition process of graphene film has been demonstrated at low temperature in a few ten seconds [1]. To attain higher electrical conductivity, the details of the electrical properties of the graphene film deposited by plasma CVD technique must be clarified. Hall effect measurement is useful to measure the electrical properties for graphene, which is expected to understand the mechanism of its electrical conductivity. In this study, we discuss the details of the electrical properties of the graphene films deposited by low-temperature plasma CVD based on Hall effect measurements.

The graphene film was deposited by microwave plasma CVD technique on Cu foil typically at 300 – 400 degC. Then, it was transferred to the quartz substrate. After that, the van der Pauw device for Hall effect measurement was fabricated using conventional photolithography, metal deposition and lift-off processes. The fabricated devices show that the mobility is estimated to be from 10 to 100 $cm^2$/Vs. To investigate the mobility dispersion, we quantify defects and disorder for graphene by Raman mapping. The results suggest that the intensity of the D/G ratio could correlate with the mobility. Based on these results, we'll discuss the cause which predominates the present conductivity of the films and how to improve the electrical conductivity of graphene film.

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# Graphene films for lasers

SP42

Pavel Rusakov, Ivan Kondrashov, Maxim Rybin, Pozharov Anatoliy, Vladimir Sorochenko
and Elena Obraztsova

*A.M. Prokhorov General Physics Institute, Vavilov str. 38, Moscow, Russia,119991 (rusakov.@gmail.com)*

Graphene is a two-dimensional hexagonal carbon network with unique physical and chemical properties. Over the past period the efforts of researches were concentrated on experimental formation of single layer or multiple layers of graphene of different scales. One layer samples are useful for nanoelectronics, sensors, solar cells, etc. Multi layers can be used in optics. One layer of graphene absorbs 2.3% of incident light. The working spectral range of graphene is very wide: our measurements show that a flat absorption of 2.3% (per 1 layer) extends from 0.4 μm up to 12 μm (at least). This property opens a possibility to form the saturable absorbers for mid-IR lasers (CO laser – with a working wavelength of 6 μm and $CO_2$ laser - with a wavelength of 10 μm [1]).

In this paper we show features of preparation of samples [2,3] for further use in lasers as saturable absorbers. We will demonstrate the progress made for lasers of different wavelengths from 1.5 to 10.5 microns. We denote the problems and questions coming for further applications.

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# Low synthesis of magnetic nanoparticles-loaded multiwall-carbon nanotubes

SP43

Liis Seinberg[1,3], Shinpei Yamamoto[2], Hiroshi Kageyama[1] and Mikio Takano[2]

*1 Graduate School of Engineering, Kyoto University, Japan*
*2 Institute for Integrated Cell-Material Sciences, Japan*
*3 The National Institute of Chemical Physics and Biophysics, Estonia (liis.seinberg@kbfi.ee)*

Reaction temperatures as high as 700 °C are typically necessary in order to produce MWCNTs. Although MWCNT synthesis at 650 °C is reported, this includes multi-staged procedure and external pressure [1]. The additional drawbacks of CVD and arc discharge method are the necessity of an external carbon source or a catalyst feedstock during the synthesis. Highly crystalline MWCNTs loaded with metallic Ni and Fe nanoparticle can be prepared by pyrolyzing nickel stearate or ferrocene under a flow of acetylene, respectively, at 800 - 1100 °C [2,3]. However, the pyrolysis is also suffering from high reaction temperature synthesis drawbacks since the reducing agents necessary to form metallic NPs, i.e., decomposed organic ligands and hydrocarbon feedstock, have poor reducing ability at low temperatures.

We have successfully synthesized multi-wall carbon nanotubes (MWCNTs) loaded with Ni or Fe nanoparticles by pyrolyzing metal organic salts with $CaH_2$. The use of $CaH_2$ enables formation of MWCNTs at temperatures as low as 400 °C, which is about half of the lowest reported temperature in the pyrolysis method and is even 100 °C lower than the lowest reported temperature in the CVD procedure [1]. The developed method also enables synthesis of metal NP-loaded MWCNTs without using any catalyst support or external carbon source. The extraordinary strong reducing ability of $CaH_2$ opens a new path to preparation of MWCNTs with loaded NP, not only Ni and Fe but possibly for Co and their metal alloys. The method is not limited to less-carbon rich metal organic salts.

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**SP44**

# Molecular theory about hidden problems in graphene material science

Elena F. Sheka

*Peoples' Friendship University of Russia, Moscow, 117198 Russia (sheka@icp.ac.ru)*

Graphene material science only slightly depends on the uniqueness of a regular one-atom- thick planar sheet, while is mainly governed by peculiarities of electronic structure of 'sp$^2$-bonded carbon atoms that are densely packed in a honeycomb crystal'. The peculiarities are provided by odd electrons of benzenoid units with the smallest separations between them lying in the interval of 1.41-1.47Å. Both interval limits exceed a critical interatomic distance $R_{crit}$ at which and below which the odd electrons are covalently bound and form the classical π non-correlated electrons. Above $R_{crit}$ odd electrons become correlated, which causes their withdrawing from the covalent coupling and, consequently, radicalization of a graphene sample. That is why any pristine graphene sample is a radical of the $N_D$ multiplicity, where $N_D$ marks a total number of unpaired electrons. Regardless the size of the graphene sample, $N_D$ constitutes ~30% of the odd electron number $N_{odd}=N_{at}+N_{edge}$. Here, $N_{at}$ and $N_{edge}$ are numbers of atoms in the entire sample and at its edges, respectively. The odd electrons correlation turns out to be an exceptionally strong factor that significantly influences structural, chemical, magnetic, and mechanic properties of graphene and graphene-derived materials. The correlation is responsible for a highly sensitive topological behavior of graphene, as well. Not taking it into account generates numerous 'underwater stones'. Those are illustrated in the paper by a number of unrealistic predictions and explanations concerning graphene and its applications which are widely discussed by the scientific community. Outside carbonaceous graphene science, the apotheosis of the misconceptions generated by ignoring the fundamental properties of sp$^2$ electronic systems is achieved in the case of silicene. In contrast, boron-nitride analogues of sp$^2$ nanocarbons are free from complications due to complete saturation of their valence ability by covalent bonding.

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**SP45**

# Using ultra-violet exposure to study the effect of chemical vapor deposition growth process on the graphene grain size

Jannatul Susoma, Changfeng Li, Juha Riikonen and Harri Lipsanen

*Department of Micro and Nanosciences, Aalto University, FI-0007 Aalto, Finland (jannatul.susoma@aalto.fi)*

Grain boundaries of graphene are formed when single grain graphene islands are merged during the chemical vapor deposition (CVD) growth process. These boundaries govern transport properties affecting device performance [1]. Grain size of graphene varies with different growth conditions like temperature, pressure and gas flow [1-2]. Typically, transmission electron microscopy (TEM) is used to observe grain boundaries, which is time consuming and require special sample preparation. Recently, it has been demonstrated that, graphene grain boundaries also can be made visible for optical microscopy when they are exposed under UV light [1]. We utilize this technique to study the grain size under different growth conditions. Exposing UV light under moisture environment, Cu is oxidized underneath the graphene following the grain boundaries. Then the grain boundaries become visible under optical and scanning electron microscopy (SEM).

We demonstrate that, different growth conditions affects grain size of the graphene and that can be easily observed by optical microscopy using UV treatment. This method will be certainly useful to understand graphene grain size depending on different growth conditions which, leads to the direction of high quality graphene synthesizing techniques useful for device applications.

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## Cross correlation experiments in multiterminal graphene devices

SP46

Zhenbing Tan[1], Antti Puska[1], Fabian Dürr[2], Charles Gould[2], Laurens W. Molenkamp[2], Pertti Hakonen[1]

*1 O.V. Lounasmaa Laboratory, Aalto University School of Science, P.O. Box 15100, FI-00076 AALTO, Espoo, Finland*

*2 Physikalisches Institut (EP3), University of Würzburg, Am Hubland, D-97074, Würzburg, Germany*

Shot noise and cross correlation measurements were studied in a 50 nm wide graphene cross sample. Shot noise measurements show that the Fano factor decreases with the current bias just as early experimental results in graphene [1]. Shot noise of $S_{11}$ and $S_{33}$ and cross correlation of $S_{13}$ were measured to compare with the theoretical results [2,3]. The Hanbury-Brown–Twiss exchange factor was studied in our sample as a function of charge density. Due to non-linearity and asymmetry of the resistances of all 4 arms in our cross sample, we employed fluctuation analysis at equivalent currents in different bias configurations. We evaluated the exchange factor as $\Delta S = 2S_C(\mu) - S_A(\mu) - S_B(\mu)$, where $\mu$ is the chemical potential in the center of the cross sample. The exchange factor is found to be nearly zero in our experiments, which is in accordance with the theoretical results of diffusive wire.

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## Synthesis and applications of multifunctional graphene sheets decorated with bimetallic transition metal nanoparticles

SP47

Yan Wang[1], Yan Zhao[1], Qi Dong[1], Shumin Li[2]

*1 Beihang University, China (jennyzhaoyan@buaa.edu.cn)*

*2 Aviation Industry Corporation of China, China*

Graphene, a nanostructured carbon material with a one-atom-thick planar sheet of $sp^2$ bonded carbon atoms, is of great current scientific interests because of its unique electronic and geometric properties. It is regarded as a significant substitute in fabrication of transistors, integrated circuits, solar cells, chemical sensors and others [1]. We outline herein a process for preparing bimetallic transition metal nanoparticles (Ni, Co or Fe coated on Pd) supported on reduced graphene oxide sheets by a rapid reducing method, using sodium hypophosphite as reducing agent [2]. A uniform deposition of nanoparticles with an average diameter of 10-20 nm was achieved, and at the same time graphene oxide sheets, the substrates, were also reduced. By keeping the same loading of Pd while varying the initial amount of the other metal (Ni, Co or Fe) precursor and reducing agent proportionally we can alter the content of metals in the shell and particularly the crystalline phase of cobalt (from fcc-Co to hcp-Co). It is confirmed that these magnetic and conductive metal-graphene hybrids exhibit superior electromagnetic properties and catalytic performance, which hold great promise in a wide range of fields.

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SP49

# Graphene-based aerogels: syntheses, properties & performance

Xuetong Zhang, Yongyi Zhang, Hongbo Li, Qingwen Li

*Division of Advanced Materials, Suzhou Institute of Nano-Tech & Nano-Bionics, Chinese Academy of Science, Suzhou 215123, PR China (zhangxtchina@yahoo.com)*

Aerogels, generally prepared from molecular precursors by sol-gel processing and subsequently by supercritical fluid drying or by freeze drying to replace the solvents in the wet gels with air, are highly porous solid nanomaterials with unique characteristics including large pore volumes, high surface areas and tunable porosity. This poster will focus on some novel $sp^2$ hybridized carbon materials (including graphene oxide, graphene and carbon nanotube) used as building blocks of the aerogel 3D frameworks and versatile applications of these new aerogels in the field of energy storage, catalysis, drug carrier, purification of water, etc.

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# NCC13

K1

## Graphene-based composite materials for flexible devices

Zongping Chen, Dawei Wang, Na Li, Zhe Weng, Feng Li, Wencai Ren, Hui-Ming Cheng

*Advanced Carbon Division, Shenyang National Laboratory for Materials Science, Institute of Metal Research, CAS, Shenyang 110016, China (cheng@imr.ac.cn)*

Graphene, which can be fabricated by chemical exfoliation and chemical vapor deposition, has high specific surface area, good chemical stability, high electrical and thermal conductivity, and excellent flexibility [1]. Compared to the individual constituents, graphene-based composites has great potential for many applications in flexible devices such as flexible sensors, conducting elastomers, electromagnetic interference shielding materials, lithium ion batteries and supercapacitors.

First, from the chemically derived graphene materials, flexible graphene/polyaniline paper was prepared by *in situ* anodic electropolymerization of polyaniline on a reduced graphene oxide membrane, and it shows a stable large electrochemical capacitance and excellent cyclibility [2]. Then graphene-cellulose paper membranes were fabricated and used as freestanding and binder-free electrodes for flexible supercapacitors with good performance [3]. Second, we developed template-directed CVD to synthesize a three-dimensional interconnected graphene framework (GF) [4]. This porous graphene bulk material consists of an interconnected network of graphene, is flexible, and has outstanding electrical and mechanical properties. Using this unique network structure, we demonstrate the great potential of GF/PDMS composites for flexible, foldable and stretchable conductors [4]. By using the GF as a current collector, loaded with $Li_4Ti_5O_{12}$ and $LiFePO_4$, for use as anode and cathode, respectively, we fabricated a thin, lightweight, and flexible full lithium ion battery, with a high-rate performance and energy density that can be repeatedly bent to a radius of 5 mm without structural failure and performance loss [5]. Finally, an ultra-lightweight and grapheme foam/PDMS composite with high EMI shielding performance was prepared. The grapheme foam/PDMS composite shows excellent flexibility, and its shielding effectiveness is almost unchanged after repeatedly being bent to a radius of ~2.5 mm for 10,000 times [6].

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I1

## Optimization of multi-walled carbon nanotube properties for composite production

Vladimir Kuznetsov[1,2]

*1 Boreskov Institute of catalysis SBRAS, 630090 Russia (kuznet@catalysis.ru)*
*2 Novosibirsk State University, 630090 Russia*

Multi-walled carbon nanotubes (MWCNTs) are known as the most perspective components for numerical composite materials because their remarkable mechanical, chemical, and electronic properties. At the same time, properties of MWCNTs significantly depend on their structure (defectiveness, diameter distribution, morphology of agglomerates, concentration of impurities etc.), which in turn depends on the type of process and on reaction parameters used for the production. For synthesis of MWCNTs by catalytic CVD techniques the nature of catalysts (metals, supports, metal-support interaction, and the effect of promoters), are the most important factors. Production of effective composites requires fulfillment of conditions of uniform distribution of MWCNTs in polymer, metal or ceramic matrix, which in turn require the formation of specific interfaces between nanotube surface and composite matrix. The optimization of nanotube concentration in composite depending on MWCNT diameter distribution influencing percolation threshold are also crucially important to provide desirable properties. The analysis of the properties of MWCNT based composites leads to conclusion that for every type of composite specific optimal type of nanotubes is required. This paper reviews the synthesis of MWCNTs using different methods especially focusing on their structure and properties (mechanical, electrical and chemical). Various parameters influencing the MWCNT growth and properties along with post synthesis treatments influencing the nanotube structure and surface composition are also discussed.

C1

# Rheology and morphology of pristine graphene/polymer composite gels

Sriya Das, Fahmida Irin, Micah J. Green

*Department of Chemical Engineering, Texas Tech University, USA (micah.green@ttu.edu)*

Pristine graphene/polyacrylamide (PAM) hydrogels are synthesized via in-situ polymerization of dissolved monomer in a PAM-stabilized graphene dispersion. This in-situ polymerization leads to the incorporation of the graphene sheets into the skeleton of the polymeric hydrogel. The graphene sheets interact with the polymer chains of the hydrogel through physisorption and allow for hydrogel formation in the absence of any chemical cross-linker. This is the first report of pristine graphene as a physical cross-linker in a hydrogel. We then measure the viscoelastic properties of graphene-loaded physical hydrogels and observe an increase in the storage modulus of the hydrogels compared to the graphene-free baseline. These hydrogels may then be converted to conductive aerogels. The morphology and elastic chain concentration of the hydrogels is then related to aerogel density and morphology. We also aim to create ultralow percolation threshold graphene composites through monomer infusion into the aerogel scaffold. The aerogels become electrically conductive when graphene sheets form an interconnected network inside the network of the aerogel skeleton. The backfilling of the additives does not disrupt the continuity of graphene sheets and allows for a conductive nanocomposite with an exceptionally low filler loading.

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C2

# Multifunctional and environmentally friendly nanocomposites between graphene or graphene oxide and natural rubber

C.F. de Matos[1], Fernando Galembeck[2], Aldo J.G Zarbin[1]

*1 Universidade Federal do Paraná- UFPR, PR, Brazil (carola@ufpr.br)*
*2 Universidade Estadual de Campinas - UNICAMP, SP, Brazil*

This work describes a green route to multifunctional nanocomposites materials obtained between natural rubber latex (NR) and both i) graphene (rGO) and ii) graphene oxide (GO). The graphene structures used in this study were obtained by a modified Hummers method. Aqueous solution with different concentration of GO and aqueous dispersion of rGO (prepared with surfactant cetyl trimethylammonium bromide - CTAB) were mixed with natural rubber latex under magnetic stirring followed by sonication. The slurries obtained were cast onto a flat plastic mold (10×5×5 cm) and dried in an oven under air at 70 °C for 24 h. The nanocomposites were characterized by TEM, SEM, AFM, X-ray diffraction, Raman and infrared spectroscopies. The thermal, electrical and mechanical properties were evaluated by thermogravimetric analysis, resistivity measurements (four-points) and dynamical mechanical analysis (DMA). Spectroscopic data, XRD and DMA indicated an increase in structural organization of the polymer, which means that the carbon nanostructures induce crystallization in the polymer (proportional to the amount of carbon nanostructures). The occurrence of fillers networks in the polymeric matrices provided significant improvements in the electrical, chemical and mechanical properties, in comparison to the unfilled polymer. For example, the electrical resistivity varied from $10^7$ (NR) to $10^3$ $\Omega cm^{-1}$ after the addition of 2 wt% of rGO and the storage modulus increased from 3.8 (NR) to 6.49 MPa (~73%) with only 2wt% of GO.

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I2

# Modeling interdependent nano- and micro-structures in fiber reinforced composites

Larissa Gorbatikh, Valentin Romanov, Stepan V. Lomov, Ignaas Verpoest

*Department of Metallurgy and Materials Engineering, KU Leuven, Kasteelpark Arenberg 44 B-3001, Leuven, Belgium*

The next level of toughness improvement in fiber reinforced composites is envisioned with the help of modifications on the nano-scale. Carbon nanotubes (CNTs), which have exceptional mechanical properties, are identified as promising reinforcing components in structural composites. The dimensions of these new reinforcements are, however, immensely different from the ones we are used to. The diameters of conventional fibers typically range from 5 to 20 μm whereas those of carbon nanotubes are from 1 to 100 nm. The use of reinforcements of different scales in a single composite raises a series of fundamental questions about interactions between the microstructure and the nanostructure and how to tune these interactions to control failure processes in the composite.

Modeling approaches are expected to play an important role in addressing these questions. They are to help to optimize the multi-scale structure of the composite and to reduce the large number of parameters to be investigated experimentally. Three-dimensional models that simultaneously combine micro-scale and nano-scale reinforcements are virtually non-existent. Even in the two-dimensional formulation the availability of such models is very limited. The present work introduces a new model of a nano-engineered composite where fibers and nanotubes are considered in a single simulation. Any intermediate homogenization of properties or transfer of parameters from one scale to another is avoided. The model in such formulation was inspired by interdependent nano- and microstructures of naturally occurring composites. The model is applied to investigate the effect of CNTs on the stress distribution in carbon fiber/epoxy composites, where CNTs are grown on fibers or added in the matrix.

I3

# Nano/micro hybrid structures and their multifunctional composites

Delong He, Weikang Li, Jinkai Yuan, Anthony Dichiara, Jinbo Bai

*Laboratoire de Mécanique des Sols, Structures et Matériaux (MSSMat), CNRS UMR 8579, Ecole Centrale Paris, Grande Voie des Vignes, 92290 Châtenay-Malabry, France (jinbo.bai@ecp.fr)*

In this presentation, we will show various nano/micrometer hybrid structures and their applications in developing multifunctional polymer composites. The multiscale hybrids are synthesized by in situ growing CNTs on the micrometer materials using a floating chemical vapor deposition (CVD) method. The microsubstrates used include ceramic particles ($Al_2O_3$, SiC, $TiO_2$...), graphene nanoplatelets, or various long fibers. The CNT length, diameter and number density on the microsubstrates can be varied by modulating the CVD conditions like temperature, carbon source, catalyst precursor ratio, hydrogen ratio and gas flow rate. The formation mechanism of these hybrid structures are investigated using various experimental and theoretical techniques. The CNTs/microparticle hybrids show higher reinforcing efficiency than CNTs or micro substrates alone, including the mechanical, (di)electric and thermal properties and self-sensing behaviors. CNT/SiC microplate hybrids can have vertically aligned CNTs on them to form efficient microcapacitors when incorporated into ferroelectric polyvinylidene fluoride matrix. The resultant dielectric composites could afford a much low percolation threshold (1.47vol %) as well as a giant dielectric permittivity (8700). Furthermore, the unique geometry of CNT/SiC hybrids can also make them capable of serving as self-sensing agent in structural epoxy composites. The CNTs/fiber hybrids reinforced composites show improved interfacial connection between fiber and polymer matrix, as well as improved mechanical properties, and electrical and thermal conductivities in transversal and through-thickness directions.

C3

# Development of a powder based, scalable route for the production of nano and hierarchical thermoset composites

T.M. Herceg[1], M.S. Zainol Abidin[2], A. Bismarck[1], E.S. Greenhalgh[2], M.S.P. Shaffer[3,*]

*1 Department of Chemical Engineering*
*2 Department of Aeronautics*
*3 Department of Chemistry, Imperial College London, UK (*m.shaffer@imperial.ac.uk)*

One of the major challenges in the field of nanocomposites has been to distribute and disperse high loading fractions of carbon nanotubes (CNT) in epoxy resins through a route that is scalable to high throughput and still yields a nanocomposite material that has improved properties compared to the parent resin. Furthermore, attempts to produce epoxy based hierarchical composites (HC) with high CNT loadings by introducing nanoreinforcement in the resin have been plagued by processing difficulties related to matrix viscosity and infiltration.

We report the development of a readily scalable powder based processing route to produce epoxy based nanocomposites with a maximum CNT loading of 18.4wt%. The excellent CNT distribution and dispersion allowed the Young's modulus and strength to increase monotonically throughout the range of CNT loadings, and by as much as 82% and 30%, respectively. The electrical conductivity of the nanocomposite makes it suitable for applications requiring electromagnetic interference (EMI) shielding, while the thermal conductivity improved by as much as 166%. The nanocomposite powder was also employed as a constituent in a wet powder impregnation process to produce carbon fibre based HCs containing as much as 5.5vol% CNTs. The processing parameters were optimised to yield a laminate with 55% fibre volume fraction, making it suitable for structural applications. The interlaminar fracture toughness of the laminates improved by as much as 30% with the addition of CNTs with extensive fractographic evidence of toughening mechanisms. Perhaps most interestingly, both nanocomposite and HC properties could be tuned by varying the powder particle size, which, in turn, influenced the homogeneity of the microstructure and material properties.

C4

# Insight on viscoelastic modeling of carbon nanotube composites

A. Martone[1], A. Petriccione[2], M. Zarrelli[1], V. Antonucci[1], M. Giordano[1]

*1 IMCB-CNR, Institute for Composite and Biomedical Materials, National Research Councyl, Italy (gmichele@unina.it)*
*2 UNINA, University of Naples "Federico II", Italy*

Carbon nanotube (CNT) gathered great attention by an heterogeneous community of scientists since their composites exhibits astonishing properties. Available experimental data[1,2] show that special combination of filler and hosting matrix allows to achieve significant and simultaneous improvement in stiffness, fracture toughness, energy adsorption. Final properties of the nanocomposite depend not only on constituents properties but also on processing parameters affecting dispersion state of filler. Nevertheless many attempt, an universal modeling approach for prediction of viscoelastic properties of nanocomposites has not recognized yet.

In this work, dynamical mechanical behavior of carbon nanotube-based composites have been investigated, with the aim of developing an effective and accurate analytical model, which can be used for predict viscoelastic properties of such materials. The structural damping of the nanocomposite is evaluated as ratio between the dissipated energy for cycle within the material and the stored strain energy[3]. The basic shear lag approach has been considered as framework to introduce the decrease of stress transfer efficiency due to contact between nanotubes; the Philipse's model of random contacting rods[4] has been introduced to allow the evaluation of the average reduction of the effective tube aspect ratio by means of reinforcing particle excluded volume computation. The reliability of the micromechanical model for nanocomposite stiffness prediction has been verified by reproducing available mechanical data from open literature. The proposed model has been found able to predict elastic modulus and loss factor data for different filler content and aspect ratio.

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C5

## Continuous synthesis of carbon nanotubes on carbon fibre: towards scalable hierarchical composite production

David B. Anthony[1], Hui Qian[1], Emile S. Greenhalgh[1], Alexander Bismarck[1,2], Milo S. P. Shaffer[1,*]

*1 Imperial College London, UK (*m.shaffer@ic.ac.uk)*
*2 Universität Wien, Austria*

We have developed a bespoke continuous CVD reactor which has synthesised carbon nanotubes (CNTs) from pre-deposited catalyst precursor loaded carbon fibre (CF) tow. In this presentation, reactor design, challenges with catalyst precursor deposition and methodologies are discussed with mechanical characterisation of the CNT grafted CF [1].

Grafting CNTs onto reinforcing fibre surfaces has been shown to improve composite structural performance [2], through improved interfacial bonding of the matrix and reinforcement [3]. Sourcing a suitable amount of CNT grafted fibre has currently limited test coupon geometry and development in the area. Scaling current synthesis procedures for grafting CNTs onto CF surface, using mild processing techniques, compatible with industrial practices has yet to be reported. CNT growth from CF surface without damaging the parent fibre mechanical properties is a challenge as chemical vapour deposition (CVD) CNT growth typically results in catalyst pitting and surface defects. Only recently, retention of original fibre properties has been shown to be controlled under stringent conditions at low temperatures.

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I4

## Past, current and future applications of carbon nanotubes in composites

Julien Amadou

*Nanocyl SA, R&D Department, Belgium (julien.amadou@Nanocyl.com)*

Since their observation by Iijima in 1991, carbon nanotubes have been extensively characterized and studied raising promising interest for key applications. Some of these applications have already been aborted, some have been developed and some new are now expected. In the meantime, upscale of production combined with industrial competitions have led to a decrease of cost (mainly for Multiwall CNTs) by a factor of 1000. Almost 25 years after this observation, the use and production of Singlewall CNTs remain marginal whereas worldwide production capacity for MWCNTs is above 1000 tons per year and graphene is the current research-to-industry focus.

As CNT and CNT-based solution manufacturer, Nanocyl participates to development and use of CNT in today and tomorrow applications by providing efficient products and/or supports to community. Nanocyl also investigates potential of CNTs in unexpected applications such as flame/fire retardancy, eco-friendly fouling release marine coating, heating devices...In this presentation, an overview of past, current and future applications (commercially available and used) will be given trying to answer the major questions: What is CNT potential (theory vs. real)? And for what and where CNTs are used today and tomorrow?

For further information, please visit www.nanocyl.com or email to Julien.Amadou@Nanocyl.com.

I5

## Metal-carbon composite materials

O.V. Tolochko[1], T.S. Koltsova[1], E.S. Vasilyeva[1], A.G. Nasibulin[2], A.I. Rudskoi[1]

*1 Material Science Department, State Polytechnical University, Polytechnicheskaya, St.29,*
*Saint-Petersburg, 195251, Russia*
*2 Department of Applied Physics, Aalto University School of Science and Technology, P.O. Box 15100*
*Puumiehenkuja 2, FIN-02150 Espoo, Finland*

Metal-carbon composite materials have a long history and wide spectra of applications. Starting from the last decade of the 20th century new composites containing carbon nanostructures such as fullerens, carbon nanofibers (CNFs) and nanotubes (CNTs), nanodiamonds, graphenes have been extensively studied. Due to their unique physical and chemical properties carbon nanostructures can be utilized to produce strong and electrically conductive composite materials.

Good dispersion of carbon structures was achieved by the synthesis of nanofibers directly on the surface of copper or iron particles and aluminium particles by adding nickel catalyst. We investigated the effect of carbon-hydrogen ratio and powder surface roughness influence on the morphology of carbon product synthesized. The mechanisms of the carbon nanostructures growth on a copper catalyst are discussed.

Hybrid composite materials of full density strengthened by carbon nanostructures including CNF and CNT, detonation nanodiamonds were produced by powder metallurgy route. Mechanical, electrical and tribological properties of composites were studied and compared.

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C6

## Effect of carbon nanotube aqueous dispersion quality on mechanical properties of cement composite

Ilya V. Anoshkin[1], Larisa I. Nasibulina[1], Albert G. Nasibulin[1], Andrzej Cwirzen[2], Vesa Penttala[2]
and Esko I. Kauppinen[1]

*1 Department of Applied Physics, Aalto University School of Science and Technology, Puumiehenkuja 2, 02150,*
*Espoo, Finland (ilya.anoshkin@aalto.fi)*
*2 Department of Civil and Structural Engineering, Aalto University School of Science and Technology,*
*Rakentajanaukio 4 A, 02150 Espoo, Finland*

An effect of the quality of carbon nanotube (CNT) dispersions added to cement on paste mechanical properties has been studied. High-quality dispersions of few-walled CNT (FWCNTs) were produced in two steps. First, FWCNTs were functionalized in a mixture of nitric and sulfuric acids (70 wt.% and 96 wt.%, resp.) at 80 °C. Second, functionalized FWCNTs were washed out by acetone to remove carboxylated carbonaceous fragments (CCFs) formed during CNT oxidation. Mechanical test results showed 2-fold increase in the compressive strength of the cement paste prepared from the dispersion of acetone-washed functionalized FWCNTs, which is believed to occur due to the chemical interaction between cement matrix and functional groups (–COOH and –OH). Utilisation of unwashed FWCNTs led to a marginal improvement of mechanical properties of the cement pastes, whereas surfactant-treated functionalized FWCNT dispersions only worsened the mechanical properties. [1]

[1] L. Nasibulina, I. Anoshkin, A. Nasibulin, A. Cwirzen, *et al.,* J. Nanomaterials, 169262 (2012)

C7

## Simple methods to prepare carbon nanotubes-gold nanoparticles hybrid materials for sensing applications

S. A. Moshkalev[1], J. V. Silveira[1,2], R. Savu[1], D. S. Lara[1], O. L. Alves[1], J. Mendes Filho[2], A. G. Souza Filho[2]

*1 UNICAMP, Campinas, Brazil (stanisla@ccs.unicamp.br) 2 UFC, Fortaleza, Brazil*

Carbon nanotubes (CNTs) are increasingly used in novel nanoscale devices such as chemical or biosensors. Pristine CNTs exhibit low sensitivity to gases, and to enhance their gas sensing sensitivity and selectivity, decoration by metallic nanoparticles is frequently used. Gold nanoparticles (Au-NPs) are the most stable metal nanoparticles and their composites with nanotubes have numerous applications in photonics, catalysis and biology. For decoration of CNTs by nanoparticles, hydrothermal processes with gold salts as precursors or electrochemical reduction are commonly employed. Here, a simple method for obtaining hybrid structures (carbon nanotubes-gold nanoparticles) that can be used as sensing elements for gas detection and other applications, is presented. Single-step and double-step processes for deposition and decoration of nanotubes with gold nanoparticles through dielectrophoresis (DEP) and electrochemical reduction, respectively, were investigated. In both processes, patterned gold electrodes, working as a two-electrode electrochemical cell, were used for generating and depositing NPs. Gold films (thickness of ~150nm) were first sputtered over oxidized silicon substrates and then electrochemical deposition, photolithography and wet chemical etching were employed to obtain thick patterned electrodes. Gaps between electrodes with a ~1 um width were milled by a focused ion beam. Nanotubes were dispersed in alcohol and deposited over gaps between the electrodes using DEP process. During the process of nanotubes deposition, at a high bias potential (>2 V) applied between the electrodes, formation of gold nanoparticles was also observed. These particles with a few nm diameters were found to decorate the surface of nanotubes bridging the electrodes, in a single-step deposition-decoration process. In another version of the method we used previously deposited nanotubes. Then, an electrodeposition process was induced between the electrodes using a deionized water instead of alcohol. The latter method thus can be called a two-step deposition-decoration process. The advantage of this method is the ability to control independently the densities of nanotubes and nanoparticles.

C8

## Mechanical reinforcement of a high-performance aluminium alloy AA5083 with homogeneously dispersed multi-walled carbon nanotubes

Julien Stein[1], Blanka Lenczowski[2], Nicole Fréty[3], E. Anglaret[4]

*1 Eurocopter Deutschland GmbH, 86609 Donauwörth, Germany*
*2 EADS Innovation Works, 81663 Munich, Germany*
*3 Institut Charles Gerhardt, Univ. Montpellier 2 and CNRS, 34095 Montpellier, France*
*4 Laboratoire Charles Coulomb, Univ. Montpellier 2 and CNRS, 34095 Montpellier, France*

Dense and homogeneous multi-walled carbon nanotube/metal composites are prepared by powder metallurgy [1,2]. The distribution of the nano-reinforcements in the matrix is studied by scanning electron microscopy and Raman spectroscopy, and the mechanical properties of the composites are determined by means of static tensile tests and Vickers micro-hardness measurements.

We show that a homogeneous dispersion of the nanotubes at the micron scale is required in order to improve the mechanical properties of the metal matrix composite [1]. This can be achieved using ball-milling through the mechanisms of plastic deformation and cold-welding. Accordingly, we report significant improvements to the mechanical properties of composites prepared with a high-performance aluminium alloy AA5083 matrix. From the evolution of the composite Young's modulus and yield strength as a function of carbon nanotube concentration, we get an estimate of the nanotubes Young's modulus and aspect ratio [2]. We compare the results for single-walled and multi-walled carbon nanotubes, and discuss how to optimise the mechanical properties of carbon nanotube-reinforced aluminium alloy composites.

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[2] J. Stein *et al.,* Mat. Sci. Eng. A, *to be published*

C9

## Features of carbon nanotube based ceramics compounding on silicon dioxide

Simunin Mikhail, Bobrinetskiy Ivan

*National Research University of Electronic Technology, Russia (vkn@miee.ru)*

The unique properties of carbon nanotubes, such as their strength and chemical resistance [1] causes the interest to use them as an additive to various materials for the production of composites. In carbon nanotubes obtained from ethanol [2] precursor $[Ni(NH_3)_6]Cl_2$ at 600 °C. As a model of ceramics in a quartz ceramics obtained by hydrolysis of tetraethoxysilane. The structure of such a ceramic nanoballs are amorphous $SiO_2$ with carbon nanotubes.

When equal amounts of matter absolutely different volumes of material. It should be noted that the density of the resulting ceramic on carbon nanotubes less than without nanotubes (or carbon nanotubes grown in the pores). This loss of density is determined by adding the carbon nanotubes in the synthesis of ceramics and due to the fact that carbon nanotubes, having a high surface area, lower free energy of formation of ceramics on the surface. Thus, they are the catalyst for the ceramics. Hardness of ceramic composites clearly indicate hardening of ceramics obtained on carbon nanotubes, compared to the original, at the same time the process of growth of carbon nanotubes reduced the strength of carbon nanotubes. A significant increase in the hardness of ceramics grown on carbon nanotubes due to more dense structure of original ceramic grain, which was created by the matrix of carbon nanotubes. Reducing the hardness of ceramics with grown carbon nanotubes compared to the original strains can be explained in ceramics arise in the growth of carbon nanotubes.

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[2] I. Bobrinetskii, V. Nevolin, M. Simunin, Theor. Found. Chem. Eng. 41(5) (2007) 639–643

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C10

## Decoration of carbon nanofillers via flow functionalization and controlled polymerization

Patrizio Salice[1], Michele Mauri[2], Micaela Castellino[3], Alberto Tagliaferro[3], Roberto Simonutti[2], Enzo Menna[1]

*1 Dipartimento di Scienze Chimiche, Università di Padova, Italy (patrizio.salice@unipd.it)*
*2 Dipartimento di Scienza dei Materiali, Università di Milano-Bicocca, Italy*
*3 Dipartimento Scienza Applicata e Tecnologia, Politecnico di Torino, Italy*

While the remarkable properties of isolated carbon nanostructures (CNSs) such as individual carbon nanotubes (CNTs), single layer of graphene, buckyballs and nanodiamonds, have kindled the imagination of researchers, their incorporation as functional fillers in composite materials often falls short on conveying the anticipated mechanical, optical, thermal and electrical properties to the final specimen due to aggregation, poor interfacial stress-transfer and lack of structural order. In this regard, new chemical processes for the controlled compatibilization of CNSs in polymers are in demand. Herein we report an approach which combines the functionalization of CNSs in continuous flow reactors [1-2] with a living radical polymerization to obtain CNSs with controlled decoration. The synthesis of a reversible addition-fragmentation chain transfer (RAFT) agent 1 is reported and its reactivity towards sp2 surfaces is confirmed with a set of subsidiary techniques (UV-vis and Raman spectroscopy, TGA, DLS, XPS) which show that our products have improved processability and can be tailored for specific applications. CNSs functionalized with the novel RAFT agent have been exploited in the preparation of covalently decorated nanofillers with enhanced processability and compatibility for applications in organic photovoltaics, [3] polymer membranes, and plastic piezoelectrics.

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## C11

# Nitrogen functionalization of vertically aligned carbon nanotubes through rf-plasma: tips and side walls photoemission response.

M. Scardamaglia[1], F. J. Aparicio Rebollo[1], B. Aleman Llorente[2], M. Amati[2], L. Gregoratti[2],
P. Mudimela[3], J.-F. Colomer[3], R. Snyders[1] and C. Bittencourt[1]

*1 Chemistry of Interaction Plasma Surface (ChIPS), University of Mons, Belgium*
*(mattia.scardamaglia@umons.ac.be)*
*2 Elettra Sincrotrone Trieste S.C.p.A., AREA Science Park, Italy*
*3 Research Centre in Physics of Matter and Radiation, University of Namur, Belgium*

Chemical functionalization is a promising method to exploit and tailor the extraordinary properties of $sp^2$ carbon nanostructures [1]. The electronic properties of these materials are very sensitive to local perturbations, such as surface charges and adsorbed gas molecules, so that the grafting of functional groups in a controllable way has been proposed as a feasible reproducible solution for band gap engineering and controllable doping. Plasma-based functionalization methods have the advantage to be solvent-free, time efficient and flexible; in particular nitrogen is a natural choice of dopant for carbon nanostructures since its atomic radius is similar to that of carbon [2]. Within this context, we present core level X-ray photoelectron spectroscopy (XPS) and scanning X-ray photoelectron spectromicroscopy (SPEM) measurements on nitrogen functionalized vertically aligned carbon nanotubes (v-CNTs) through nitrogen rf-plasma. The creation of defects induced by ions generated during the plasma treatment, drives the grafting of nitrogen-groups at the CNT surface. A depth of functionalization of about 4 um was evaluated by SPEM, beyond which the properties of the v-CNTs remain unperturbe. Furthermore, an intriguing different behavior of the grafting at the CNT tips with respect to the sidewall, was observed. These differences indicate a different reactivity of the CNT tip, directly exposed to plasma, where the presence of natural defects (pentagons) may be involved in different possible bonding formations between carbon and nitrogen.

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## C12

# Toughening of epoxy matrices with reduced single-walled carbon nanotubes and the effect of the resin stoichiometry

Yadienka Martinez-Rubi, Behnam Ashrafi, Jingwen Guan, Michael B. Jakubinek,
Christopher T. Kingston, Andrew Johnston, Benoit Simard

*National Research Council Canada, Canada (Chris.Kingston@nrc-cnrc.gc.ca)*

Negatively charged (*reduced*) SWCNTs (r-SWCNTs) obtained upon reduction with alkali metal naphthalides react readily at room temperature with epoxide-containing moieties. This surface modification allows better SWCNT dispersion and improves affinity with epoxies. The physical properties of a tridentate epoxy (MY0510, triglycidyl p-aminophenol) were evaluated upon addition of r-SWCNTs. Direct integration of r-SWCNTs by solution processing can improve the toughness and fracture toughness ($K_{IC}$) by 118 % and 40 %, respectively, without compromising important properties like modulus and glass transition temperature ($T_g$) [1], and with smaller reduction of electrical conductivity compared to similar, indirect covalent integration. Raman spectroscopy, imaging, and dynamic mechanical analyses indicate that the reaction of r-SWCNTs with epoxy produces a covalently bonded cross-linked shell on the SWCNT surface, resulting in a soft interface, which acts as a toughener. Special care must be paid to preparation protocols as the introduction of SWCNTs modifies the mixing and curing behavior. The toughness enhancement and other physical properties of the composites depend on the stoichiometry of the epoxy network. Our studies with stoichiometric and off-stoichiometric ratios of epoxide to amine hydrogen (1:0.8, 1:1 and 1:1.1 molar ratios) showed that the $K_{IC}$ values of the unmodified resin increased with the amount of hardener. As expected, $T_g$ decreases and a slightly lower storage modulus is obtained by the addition of more hardener. The molar ratio 1:0.8 provides the best overall properties for the unmodified resin in agreement with the manufacturer's recommended ratio of epoxy to hardener. However, the SWCNT modified nanocomposites showed a different trend, with the 1:1 molar ratio considerably outperforming the other two stoichiometries studied and showing a larger improvement in mechanical properties and $T_g$ with the incorporation of r-SWCNT. The results obtained for composites prepared at different stoichiometric ratios suggest that the formation and structure of the softer interface depends on the stoichiometry of the epoxy.

[1] Y. Martinez-Rubi, *et al.,* ACS Applied Materials and Interfaces (2011), 3 (7), 2309-2317

# Flexible transparent nanotube based coating for electronic applications

K.F. Ahmadishina, I.I. Bobrinetskiy, I.A. Komarov, A.M. Malovichko, V.A. Petuhov, R.A. Ibragimov

*National Research University of Electronic technology, Russian Federation (master_kom@mail.ru)*

Transparent electrodes which most based on indium tin oxide are used in many modern devices such as displays, mobile phones etc. But one of the main problems of indium tin oxide is fragility, so flexible devices can't be based on it. One of the possible alternatives for flexible transparent conductive electrodes creation are carbon nanomaterials [1].

In this work we proposed a method of conductive flexible transparent nanotube based films creation. As a flexible transparent substrate we used polyethylene naphthalate due to its good mechanical properties and good thermal stability. To deposit nanotubes we used surfactant water solution. We investigated the dependence of structure conductivity and transmittance on the carbon nanotube layer number. We found that resistance of structures decrease to about 0,4 – 0,2 MOhm when the number of layers is about 20. The transmittance of structures is about 50 %. Also we focused on the electronic properties of bended substrates. Main investigation was the resistance dependence on cyclic bending on 90°. We found that compression of conducting layer results in 8% structure resistance change and tension results in 10% change. Besides we investigated the effect of nanotube concentration on the electronic properties of structures and found out that nanotube concentration should be about 0,02 mg/ml.

Thus we made a complex investigation of the carbon nanotube based transparent flexible coatings for electronic applications.

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SP50

# Sensor properties of carbon nanotube/ZnO composites in ammonia presence

I.I. Bobrinetskiy[1], I.A. Komarov, A.M. Malovichko, V.K. Nevolin, A.V. Bessonova

*National Research University of Electronic Technology, Russia (vkn@nanotube.ru)*

The combination in a single device of nanowire sensors with different electrical properties in the presence of gases is one of the systems of the "electronic nose" on a single chip [1]. However the development of individual semiconductor devices involves technical difficulties in holding identical properties from crystal to crystal. The development of composites from different nanowires with different electrochemical properties is more promising to ensure stability and reproducibility [2]. The properties of a composite consisting of percolate networks based on carbon nanotubes and ZnO nanorods investigated in this work for ammonia vapor sensor production.

In this work we suggest method of nanowire based sensor structures sensitivity improvement. We developed heterogenic composite of carbon nanotubes and semiconductor nanorods. Structure with composite based sensing area was developed. A dependence of sensor resistance and response on ammonia vaporous, composite specific surface on carbon nanotube and ZnO proportion in composite was investigated. The specific surface of CNT/ZnO composite grows from 30 to 300 $m^2/g$ while resistance drops from 80 to 2 kOhm when CNT concentration changes from 40% to 80%. It was shown that sensitivity decrease by an order of magnitude when nanotube concentration changes from 60 to 80%. Moreover the relative response decreases by an half order of magnitude under sensor heating up to 200 °C. This result can be used in "electronic nose" systems development.

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[2] H. Huang, Q. Yu, Y. Ye *et al.*, Cryst.Eng.Comm 14 (2012) 7294-7300

SP51

# Synthesis of PANI/$CN_x$ composites by lithium intercalation and exfoliation of carbon nanotube

Cristal M. Ibañez[1], André Galembeck[1,2], Humberto Terrones[3], Celso P. De Melo[1,4],
Yadira I. Vega-Cantú[1,2,5,*]

*1 Programa de Ciências de Materiais, Universidade Federal de Pernambuco, Brazil*
*2 Departamento de Química Fundamental, Universidade Federal de Pernambuco, Brazil*
*3 Department of Physics, Penn State University, United States*
*4 Departamento de Física, Universidade Federal de Pernambuco, Brazil*
*5 Advanced Materials Department, IPICYT, México (*yivega.work@gmail.com)*

This work presents the synthesis of nanocomposites with nitrogen-doped mutiwalled carbon nanotube ($CN_x$) and polyaniline (PANI). Exfoliation of $CN_x$ was carried out by lithium-ammonia intercalation followed by a thermal treatment to obtain unzipped $CN_x$ (ex-$CN_x$), using the method developed by Cano *et al.*, [1]. In this work, two different kinds of $CN_x$ were used: (i) intercalated and exfoliated $CN_x$ without acid treatment; (ii) $CN_x$ (without acid treatment) functionalized with aniline monomers in lithium-ammonia solution. The preparation of ex-$CN_x$/PANI composites was carried out by *in situ* by interfacial polymerization of aniline [2]. For the synthesis of ex-$CN_x$/PAni various weight percentages of $CN_x$ (1, 5, 10 and 20 wt. % based on the aniline monomer content) were dispersed in the monomer solution 0.97 g. All the samples were characterized by X-ray powder diffraction, Raman spectroscopy analysis showed increases in the D band intensity for ex-$CN_x$ and $CN_x$ functionalized with aniline monomer. Scanning electron microscope (SEM) and transmission electron microscopy (HRTEM) were used to observe the coating and morphology. The samples ex-$CN_x$/PANI composites were characterized by cyclic voltammetry (CV) and impedance spectroscopy to analyze the electronic properties.

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# A novel alumina – nanocarbon hybrid material

SP52

Roman Ivanov[1], Ilya V. Anoshkin[2], Albert G. Nasibulin[2], Irina Hussainova[1] and Esko I. Kauppinen[2]

*1 Department of Materials Engineering, Tallinn University of Technology, Ehitajate tee 5, 19086 Tallinn, Estonia (roman.ivanov@ttu.ee)*

*2 Department of Applied Physics, Aalto University School of Science and Technology, Puumiehenkuja 2, 02150, Espoo, Finland (ilya.anoshkin@aalto.fi)*

Carbon nanotubes (CNTs) and graphene are promising components for next-generation high-performance structural and multifunctional composite materials. Recently developed industrial scale technology of alumina nanofibers (ANFs) production allows creating brand new hybrid carbon-ceramic nanomaterials combining the properties of constituents.

It was found that morphology, quality and quantity of CNTs/graphene on the ANF surface essentially depends on the pyrolysis of carbon source conditions such as gas flow, duration, temperature and the composition of the gas mixture. After ferrocene vapour pre-treatment and carbonization at 900 – 1100 °C (in the ethylene-hydrogen system), SWCNT formation was confirmed by transmission electron microscopy and Raman spectroscopy. Thickness of graphene layer on ANF surface was found to depend on pyrolysis time. After a few hours treatment time formation of continuous carbon network was confirmed by scanning electron microscopy. Optimum for the CNT formation ratio of total hydrogen [H] to the total carbon [C] in the range [H]/[C] = 20 - 45. Electrical conductivity of ANFs/nano-carbon hybrids increases up to $10^6$ times. Nonconductive ANFs in combination with CNTs can be utilized for monitoring the conductivity change under certain conditions. For instance, as pressure sensors (e.g., in construction for monitoring the crack formation in the construction elements) or as temperature or humidity. Moreover, sintered ANF/CNT material is expected to possess enhanced mechanical properties. The orientation of CNTs is of particular interest, such materials can have anisotropic heating and electrical conductivity and can be used, for instance, as heating elements in highly loaded constructions.

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# Aerosol synthesis of carbon nanotube-interweaved nanostructures for high-power lithium-ion battery applications

SP53

Xilai Jia[1], Yunfeng Lu[2], Fei Wei[1,*]

*1 Beijing Key Laboratory of Green Chemical Reaction Engineering and Technology, Department of Chemical Engineering, Tsinghua University, Beijing 100084, P. R. China (wf-dce@mail.tsinghua.edu.cn)*

*2 Department of Chemical and Biomolecular Engineering, University of California Los Angeles, CA 90095, USA*

Nanosize carbon nanotubes (CNTs) show unique properties. However, creating macroscopic materials that benefit from their unique properties is always a challenge in nanoscience and nanotechnology. Toward more effective preparation of CNT nanocomposites, we proposed to construct micron-level CNT nanostructures to building the gap between nanoscale CNTs and their macroscopic composites for better utilization of CNT properties. A scalable process based on aerosol spray drying process was developed as an versatile platform to produce carbon nanotube (CNT) interweaved nanostructures consisting of conductive CNTs and electrochemical active materials for electrochemical energy storage applications. The aerosol process realized rapid gelatination and transformation of sol-like CNT dispersions into their solid particles.

To demonstrate its efficiency, CNT-interweaved lithiated transmition metal phosphate and metal oxide nanostructures [1], have been synthesized as model materials. We dispersed CNTs into their aerosol spraying precursor, and prepared a class of CNT-interpenetrating active material nanostructures. Then, based on bottom-up principle for preparing nanocomposites, we demonstrated the aerosol-assistant self-assembly of nanoscale functional units and prepared homogeneous CNT-interweaved-nanocrytal architectures. As-fabricated nanostructures performed high performance for energy storage applications.

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**SP54**

## Direct synthesis of the carbon nanomaterials on copper particles

T.S. Koltsova[1,2], I.V. Anoshkin[2], E.I.Kauppinen[2], O.V. Tolochko[1], A.G. Nasibulin[2]

*1 Material Science Faculty, State Polytechnical University, Polytechnicheskaya, 29, 195251 Saint-Petersburg, Russia (annelet@yandex.ru)*

*2 NanoMaterials Group, Department of Applied Physics, Aalto University School of Science and Technology, P.O. Box 15100 Puumiehenkuja 2, FIN-02150 Espoo, Finland*

In the present work we investigated the growth of carbon nanomaterials (nanofibers and graphene) on the surface of copper nano- and micro particles. The synthesis was carried out by chemical vapor deposition technique. Acetylene and ethylene were examined as carbon sources. Acetylene led to the formation of carbon nanofibers, whereas ethylene resulted in multilayer graphene appeared on the copper. Formation kinetics and mechanism of carbon nanostructures on the surface of copper particles were studied. The influence of hydrogen - carbon ratio in the gas phase on the structure and quantity of carbon product were examined. The structures of the synthesized fibers were analyzed. The mechanical tests of compacted copper - carbon composite materials showed significant increase in the hardness.

**SP55**

## Tuning the localization behavior of CNTs in immiscible polymer blends by a reactive component

Petra Pötschke, Marén Gültner, Andreas Göldel

*Leibniz Institute of Polymer Research Dresden (IPF), Germany (poe@ipfdd.de)*

Polymer blends combine the characteristics of the specific polymers and in some cases even synergistic property effects are created. Hereby, in immiscible blends their morphology significantly influences the property profile of the materials. In many cases, co-continuous morphologies are found to be especially advantageous. Adding functional fillers into polymeric matrices is another possibility to generated materials with improved properties. Combining both, blending and filling, can create blend composites with outstanding properties, e.g. the incorporation of carbon nanotubes (CNTs) in insulating polymer blends can improve their electrical, mechanical and thermal properties. Interestingly, in immiscible polymer blends in most cases a selective localization of CNTs in one of the phases is observed which is mainly due to thermodynamic reasons and was found to be very fast and complete.

In the contribution it is shown that chemical reactions or strong interactions between functional groups on the nanotube surface and one of the polymer phases may also influence the localization behavior. By adding a reactive substance miscible with one blend component and able to react with functional groups of CNTs the localization behavior can be tuned, which will be shown on the example of PC-SAN with a reactive component (RC) containing maleic anhydride groups. Thereby, the localization behavior of $NH_2$ modified multiwalled CNTs (MWCNT) will be compared with that of unmodified MWCNTs and singlewalled CNTs (SWCNTs). Due to thermodynamic reasons, in absence of RC all types of CNTs localize in the PC phase of the blends, whereas after addition of the MA containing RC, which is fully miscible with SAN, the MWCNTs show a localization change towards SAN, depending on the RC content, which was not found for the used HiPCO SWCNTs.

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## Elaboration of TiC/CNT composites by sol-gel technique

SP56

Madis Umalas[1,2], Maarja Pohl[1], Ants Lõhmus[1], Rünno Lõhmus[1,2] and, Irina Hussainova[3]

*1 Institute of Physics, University of Tartu, Estonia (madis.umalas@gmail.com)*
*2 Estonian Nanotechnology Competence Centre,*
*3 Department of Materials Engineering, Tallinn University of Technology, Estonia*

Carbon nanotubes possess exceptionally high stiffness and strength combined with high electrical and thermal conductivities. Due to their exceptional characteristics is a new promising reinforcement for ceramic matrix composites (CMCs). CNT-reinforced CMCs possess a unique microstructure, nanoscale objects dispersed throughout ceramic matrix grain boundaries, which allows tailoring physical properties with an unprecedented combination of remarkable engineered transport properties as well as superior mechanical properties [1].

In our work we use combination of sol-gel method and conventional carbothermal reduction to synthesize TiC/CNT composites. Combination of these offers some advantages compared to conventional powder processing, such as the lower reaction temperatures/ shorter reaction times due to the intimate contact of the reactants and CNT is homogeneously dispersed in TiC matrix. TiC/CNT composite were synthesized by carbothermal reduction from of metal alkoxide/CNT polymer blend at 1350 °C in an argon atmosphere and the resulting products had small TiC crystallite size 92 +/-25 nm covered with CNTs .

The structure of TiC/CNT composites were characterized by SEM and by X-ray diffraction (XRD) analysis, energy dispersive X-ray spectroscopy (EDS or EDX) method. The mechanism of the carbothermal reduction of the pyrolysed TiC/CNT precursors were characterized by rate of CO generation in effluent gas.

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## Application of tungsten dichalcogenide layered nanostructures Li-ion batteries negative electrode

SP57

E.S. Vasilyeva[1,2], M.Y. Maximov[1], A.D. Sachdev[3]

*1 Saint-Petersburg State Polytechnic University, Russia (katrinfr@inbox.ru)*
*2 Aalto University School of Science, Department of Applied Physics, Aalto Espoo, FINLAND*
*3 Chemical Sciences and Material Systems Lab., General Motors Global Research and Development Center, Warren, MI 48090- 9055, USA*

Oxides and chalcogenides of transition metals widely used materials for electrodes in Li- ion batteries. Due to grapheme- like open structure but naturally versus 2 time higher interlayer distance tungsten diselenide can be applied of effective lithium ions intercalation. Low-agglomerated layered nanostructures of tungsten diselenide were synthesized by Chemical Vapor Condensation method (CVC) with flat or spherical shape and layered fullerene- like structure.

Experimentally was found dependence of process parameters like tungsten precursor concentration, residential time and reactions temperature, on number of layers per particle, chemical composition and morphology. A nanopowder with the different structure was applied as active material in composite anode with content in range of 70- 80 wt. %.

Experimentally was investigated cell capacity and efficiency as well as at constant current density 50 mAh/g as at variable and voltage in interval 0,001 - 3,0 V at the room temperature. Specific capacity most of prepared cells varied in range of 500- 750 mAh/g for more than 30 cycles with further degradation. Physical- mechanical properties of electrode coating and degradation mechanism of active material were studied by SEM, TEM, EDX and in-situ X-ray diffraction methods. Experimentally were carried out optimal nanoparticles structural parameters.

SP58

# Thermoelectric modules made of p- and n-type single walled carbon nanotube composite films

Urszula Dettlaff-Weglikowska[1], Mingxing Piao[1], Gyutae Kim[1], Siegmar Roth[2]

*1 Korea University, School of Electrical Engineering, South Korea (udettlaff.w@gmail.com)*
*2 Sineurop Nanotech GmbH, Germany*

Single walled carbon nanotube (SWCNT) networks, composed of semiconducting and metallic nanotubes forming free standing mats (buckypaper) are known for high electrical conductivity and a reasonable value of the Seebeck coefficient. SWNT composites with polymers still show a high electrical conductivity, whereas their thermal conductivity is low due to blocked heat flow across the composite structure. We prepared and characterized thermoelectric materials based on thin films of SWCNT composites with polyvinylalcohol. Pristine SWCNTs incorporated in polymer matrix generated positive value of the thermopower and were used as a p-doped thermoelectric material. Polyethyleneimine (PEI) was studied as an n-type dopant for SWCNTs. Simultaneous change of majority charge carriers from holes to electrons upon addition of PEI caused the Seebeck coefficient to change sign from positive to negative providing an n-type thermoelectric material. A single p/n couple made of two composite strips containing 20 wt% of SWCNTs - pristine p-type and n-type PEI doped nanotubes - generated a TEP voltage of 92 μV per 1 K temperature gradient. By comparison, a single p/n couple made of two films made of polyvinylidene fluoride with 95 or 20 wt % of multi-walled carbon nanotubs conducting layers produced ~15 μV per 1 K temperature gradient, as recently reported for the multilayered carbon nanotube/polymer composite based thermoelectric fabrics [1]. In our study, the thermoelectric voltage generated by a single p/n polymer couple per 1 K was improved by factor of 6 through chemical functionalization of SWCNTs loaded to 20 wt%. A module composed of 5 electrically connected p/n junctions demonstrated a 25 mV voltage output by a temperature gradient of 50 K. The module generated 4.5 nW power, when a load resistance matched the internal module resistance of 30 kΩ.

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# CNTFA13

**K1**

# Carbon nanotubes: a road to applications

Shoushan Fan, Kaili Jiang, Jiaping Wang, Qunqing Li, Liang Liu, Changhong Liu

*Department of Physics, Tsinghua University, Beijing 100084, China*
*(fss-dmp@mail.tsinghua.edu.cn)*

A superaligned carbon nanotube (CNT) array is a special kind of vertically aligned CNT array with the capability of being converted into continuous films and yarns. The as-produced CNT films are transparent and highly conductive, with aligned CNTs parallel to the direction of drawing. After passing through volatile solutions or being twisted, CNT films can be further condensed into shrunk yarns. These shrunk yarns possess high tensile strengths and Young's moduli, and are good conductors. Many applications of CNT films and shrunk yarns have been demonstrated, such as TEM grids, loudspeakers, touch screens, etc.

**C1**

# High performance aerosol-CVD SWCNT network electrodes

Antti Kaskela[1], Patrik Laiho[1], Albert G. Nasibulin[1], Yutaka Ohno[2], Esko I. Kauppinen[1]

*1 Nanomaterials Group, Department of Applied Physics, School of Science, Aalto University, P.O. Box 15100, 00076, Finland (antti.kaskela@aalto.fi)*
*2 Department of Quantum Engineering, Nagoya University, Japan.*

Single-walled carbon nanotube networks are a potential material for thin film electronics, including transparent conductive films (TCF) and thin-film transistors (TFT). The common TCF materials are metal oxides with rare and expensive raw materials, they require complex vacuum processing and have limited flexibility. Therefore alternative materials are needed for future thin and flexible electronics. SWCNT networks with low sheet resistance and high transparency are desired, and they should be manufacturable using scalable and affordable methods. To reach these goals, the understanding of fundamental physics of the SWCNT networks should improved along with more technical issues such as SWCNT growth, network formation and deposition method development.

We have used aerosol-CVD process, based on catalytic decomposition of carbon monoxide, for synthesis of high purity SWCNTs with controllable bundle length, transmittance and sheet resistance, demonstrating high performance TCFs. Gas filtration is used to form the SWCNT networks, which can be processed to wide range of substrates by dry press transfer method. The networks can be modified by post-deposition densification and doping, while eliminating the need for harsh pre-deposition dispersion or cleaning steps. The developed synthesis and processing techniques are used to demonstrate applications such as touch sensors, solar cells and thin-film transistor channels. Recently we have studied low density SWCNT samples with conductive-AFM technique to estimate the contact and length resistance and to study the impact of acid doping to both contact and length resistance of SWCNTs.

C2

## Spatially resolved transport properties of pristine and doped single-walled carbon nanotube networks

Andrej Znidarsic[1], Antti Kaskela[2], Patrik Laiho[2], Miran Gaberscek[1], Yutaka Ohno[3],
Albert G. Nasibulin[2], Esko I. Kauppinen[2] and Abdou Hassanien[1]

*[1] National Institute of Chemistry, Slovenia (abdou.hassanien@ki.si)*
*[2] Aalto University, Finland*
*[3] Nagoya University, Japan*

We use a noninvasive atomic force microscopy to probe the spatial electrical conductivity of isolated junctions of pristine and nitric acid treated single-walled carbon nanotube networks (SWCNT-N). By analyzing the local IV-curves of SWCNTs and bundles with various diameters, the resistance per unit length and the contact resistance of their junctions are estimated to be 3 to 16 kΩ/µm and 29 to 532 kΩ respectively. We find that the contact resistance decreases with increasing SWCNT or bundle diameter and is dependent on the contact morphology, reaching a value of 29 kΩ at a diameter of 10 nm. A nitric acid treatment moderately dopes SWCNTs and reduces their average contact resistance by a factor of 3 while the resistance of the nanotubes remains largely unaltered. Remarkably the same treatment on a SWCNT-N shows similar reduction in the sheet resistance by a factor of 4. These results suggest that the resistance reduction mechanism is related to the contact modulation with no major impact on conductance of SWCNTs.

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C3

## Mapping charge transport in chirality-selected carbon nanotube networks by electroluminescence

F. Jakubka[1], C. Backes[2], U. Mundloch[2], F. Hauke[2], A. Hirsch[2], J. Zaumseil[1]

*[1] Institute of Polymer Materials, Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen, Germany (jana.zaumseil@fau.de)*
*[2] Institute of Advanced Materials and Processes (ZMP), Friedrich-Alexander-Universität Erlangen-Nürnberg, Fürth, Germany*

Field-effect transistors (FET) based on networks of semiconducting single-walled carbon nanotubes (s-SWNT) are promising building blocks for future electronics. An interesting aspect of charge transport in a network of s-SWNTs with different bandgap, orientation and mobility is the number of current paths that are available. Previously current paths in such networks have been simulated using percolation models with metallic and semiconducting nanotubes. But even within networks of only semiconducting SWNTs the current paths are likely to be non-homogeneous. Here we show that such current paths can be mapped and visualized by near-infrared electroluminescence (EL) from ambipolar s-SWNT network FETs.

We use networks of chirality-selected s-SWNT comprising only five different nanotube species. These were extracted by dispersion with the conjugated polymer poly(9,9-dioctylfluorene) [1]. Excess polymer was subsequently removed. Top-gate FETs produced with spincoated films of these s-SWNTs show balanced ambipolar transport and efficient near-infrared electroluminescence. The EL spectra show narrow peaks (FWHM<50 nm) with a significant shift of intensity to SWNTs with larger diameters, compared to photo-luminescence spectra of the same area. Mapping the emission from these networks during a gate voltage sweep allows us to visualize preferential current paths, which also depend on the source-drain electrode assignment. These experimental data should enable more realistic percolation models for purely semiconducting nanotube networks.

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C4

## Percolation in realistic hybrid carbon nanostructures networks

Louis-Philippe Simoneau, Alain Rochefort

*École Polytechnique de Montréal, Engineering Physics Department and Regroupement québécois sur les matériaux de pointe (RQMP), Montréal, Canada (louis-philippe.simoneau@polymtl.ca)*

Most transparent electrodes used today in electronic displays and photovoltaic devices are rigid, brittle and expensive. Carbon nanotubes (CNT) or graphene nanoribbons (GNR) networks do not show such drawbacks, and they exhibit very appealing structural, mechanical and electron structure properties. However, due to the complex internal structure of these networks, very few fundamental properties are well known. We have developed a Monte Carlo (MC) method to generate and to study the percolation of charge in such networks. Our model includes several variables that allow us to control the characteristics of the networks, and possibly to optimize the performance of the resulting device.

Our MC algorithms generate random 2D or 3D networks that can be tuned to simulate very realistic networks by directly using experimental data (size, junction resistance) in conjunction with relevant case-specific conditions: hardcore overlap, curliness, preferential distributed orientation, partial local crystallization, or heterogeneous mixture of materials. We have evaluated the total conductance of different CNT networks on the basis of individual contacts conductance represented by numerous specific statistical distributions. Our results show that the length, diameter, orientation and chirality distributions within the percolative network of the CNT networks have a great importance on the resulting electrical performances. Although we observed that low resistance percolation paths dominate the electrical transport, the conductivity of the networks weakly depends on the statistical distribution of the junction resistance. In contrast, the type of distribution for the structural parameters such as a preferential orientation of CNT in the network has a drastic effect on the resulting electrical properties. Our most recent developments using hardcore interpenetration allow us to better evaluate the sensitivity of the percolation threshold and to explore the importance of the network thickness. We also examine the effects of the presence of well-organized bundle of CNTs or other heterogeneous elements such as GNRs on the overall electrical properties of the network.

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I1

## Extremely bendable, fully inkjet-printed transistors of carbon-nanotube films

Taishi Takenobu

*Department of Applied Physics, Waseda University, Tokyo 169-8555, Japan (takenobu@waseda.jp)*

Flexible, printed, and stretchable electronics are attracting considerable attention as the next-generation functional electronics because it is believed that in future many electronic assemblies on rigid substrates will be replaced by mechanically flexible or even stretchable alternatives. Although organic materials have been playing the main role in these research fields, in this study, we would like to show you the considerable potential in single-walled carbon-nanotube (SWCNT) films.

As the first step for carbon-nanotube flexible, printed, and stretchable electronics, we found the simple method to fabricate high-performance SWCNT film transistors using the enriched semiconductor SWCNT and one of the solid electrolyte dielectric materials, ion gel. These semiconducting SWCNT transistors hold carrier mobility of more than 100 cm$^2$/Vs and on/off ratio of $10^4$-$10^5$. Based on this method, we fabricated SWCNT transistors on flexible plastic substrates, and, during the bending test, both on- and off-current of SWCNT transistors were almost constant, and transistor kept high performance without degradation under the curvature radius of less than 300 μm.

Because we have already performed the ink-jet printing of SWCNT transistors [1,2], the fully ink-jet printed all-carbon SWCNT transistors were fabricated on flexible plastic films. We ink-jet printed the enriched metallic SWCNT, enriched semiconducting SWCNT, and ion gel as electrodes, active layer, and dielectric layer, respectively. These printed SWCNT transistors also revealed high performance and excellent flexibility. We also applied our SWCNT films into a stretchable poly(dimethylsiloxane) (PDMS) substrates and successfully fabricated stretchable SWCNT transistors.

I2

# Nano carbon devices & applications

Kazuhiko Matsumoto, Takafumi Kamimura, Kenzo Maehashi, Yasuhide Ohno

*Institute of Scientific and Industrial Research, Osaka University, Japan (k-matsumoto@sanken.osaka-u.ac.jp)*

In this paper, we will present the nano carbon devices and its applications, i.e., 1) carbon nanotube (CNT) single charge nano memory, 2) CNT net bio sensor, 3) Graphene selective bio sensor. These devices and applications are detailed below.

1) A single charge nano memory operated at room temperature is one of the candidates for the device beyond CMOS. The device was realized by the all arounded carbon nanotube channel FET, i.e., CNT was wrapped by the double layered insulator of $Al_2O_3$ (3nm) and $SiN_x$ (27nm), and by the top gate metal. When the top gate bias was applied, the charge in the CNT channel was injected into the interface of $Al_2O_3/SiN_x$ and trapped there. When one charge was trapped, the next charge was stopped for the injection because of Coulomb blockade phenomena. By one charge injection and storage, the threshold of the memory shift and works as a single charge memory at room temperature.

2) Multi-channel CNT FET was fabricated on the quartz substrate. About 100 CNT's were used as a channel of the FET and was applied as a biosensor. Compared to the single CNT channel FET, the trans-conductance of 100CNT FET improved more than 100 times, current fluctuation improved two orders of magnitudes, and the yield of the device improved from 21% to 100%. The detection limit of the pH was improved about 10 times from 0.65 to 0.073. Using the multi channel CNT FET, the bio molecule of the IgE was succeeded in selectively detected, and also the stochastic resonance device was formed and succeeded in detecting the small pH change by adding the noise to the gate signal.

3) Graphene bio sensor was first demonstrated by our group. The mono layer graphene was used as the channel of the FET. In order to detect the bio molecule selectively, we used the antigen/antibody reaction. Therefore the surface of the graphene was modulated by the fragment antibody, which is the head part of the antibody and size is smaller than Deby length. As the normal antibody was larger than Deby length in the solution, it is difficult to detect the charge of the antigen which combines with the antibody in the solution. Also the concentration of the fragment antibody on the graphene surface was controlled. Using these technologies, we have detected the heat shock protein with the highest sensitivity of 7pM.

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C5

# High-mobility carbon nanotube thin-film transistors based on transfer and printing techniques

K. Higuchi[1], S. Kishimoto[1], Y. Nakajima[2], T. Tomura[2], M. Takesue[2], K. Hata[2],
A. Kaskela[3], A. G. Nasibulin[3], E. I. Kauppinen[3], and Y. Ohno[1,4]

*1 Dept. of Quantum Eng., Nagoya Univ., Japan (yohno@nuee.nagoya-u.ac.jp)*
*2 Research and Development Center, Bando Chemical Industries, Japan*
*3 Dept. of Applied Physics, Aalto Univ., Finland*
*4 MIDE, Aalto Univ., Finland*

Among many kinds of thin-film transistors, carbon nanotube (CNT) thin-film transistors (TFTs) have attractive features such as high mobility, flexibility, and transparency. CNT thin films also have a good processability. In this work, we introduce high-speed flexographic printing technique in the device fabrication process. The devices are fabricated by fully lithography-free and ambient-pressure processes.

We fabricated bottom-gate CNT TFTs on a polyethylene naphthalate (PEN) film with the flexographic printing technique, which is a kind of high-speed typographic prints with a flexible relief plate made of photopolymer. The inks of silver nanoparticles and polyimide were respectively used for the electrodes and insulator. A CNT thin film grown by the floating-catalyst CVD was transferred as our previous work [1]. CNTs outside the channel region were etched by the ambient pressure $Ar/O_2$ plasma. The device with a channel length of 115 μm showed a high mobility of 157 $cm^2/Vs$ for the rigorous model [2] (112 $cm^2/Vs$ for parallel plate model) with on/off ratio of about $10^4$.

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**C8**

## Transferred wrinkled $Al_2O_3$ for highly stretchable and transparent graphene–carbonnanotube transistors

Sang Hoon Chae, Young Hee Lee

*Centre for Integrated Nanostructure Physics (CINAP), Institute of Basic Science (IBS), Department of Energy Science, Department of Physics, Sungkyunkwan University, Suwon 440-746, Republic of Korea*

Despite recent progress in producing transparent and bendable thin-film transistors using graphene and carbon nanotubes[1,2], the development of stretchable devices remains limited either by fragile inorganic oxides or polymer dielectrics with high leakage current[3,4]. Therefore, to maximize the performance of the oxide without compromising the ability to stretch and bend, we propose a new approach for preparing a wrinkled gate dielectric using a transfer method.

Here we report the fabrication of highly stretchable and transparent field-effect transistors combining graphene/single-walledcarbon nanotube (SWCNT) electrodes and a SWCNT-network channel with a geometrically wrinkled inorganic dielectric layer. The wrinkled $Al_2O_3$ layer contained effective built-in air gaps with a small gate leakage current of $10^{-13}$ A. The resulting devices exhibited an excellent on/off ratio of ~$10^5$, a high mobility of ~40 $cm^2\,V^{-1}\,s^{-1}$ and a low operating voltage of less than 1 V. Importantly, because of the wrinkled dielectric layer, the transistors retained performance under strains as high as 20% without appreciable leakage current increases or physical degradation. No significant performance loss was observed after stretching and releasing the devices for over 1,000 times. The sustainability and performance advances demonstrated here are promising for the adoption of stretchable electronics in a wide variety of future applications.

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**K2**

## Carbon nanotube thin films for high-performance logic electronics

Qing Cao

*IBM T.J. Watson Research Center, USA (qcao@us.ibm.com)*

The scaling of transistor technology is expected to continue for the next 15 years, with the adoption of novel device structures, e.g. 3D Fin-FET and ETSOI devices, and the adoption of new materials, e.g. SiGe/SiC stressors, HfSiON/$La_2O_3$ gate dielectrics, TiSi contacts, and SiBCN spacers. The ultimate challenge is to replace the silicon channel with new materials such as single-walled carbon nanotube (SWNT) thin films. Experimental results on devices based on individual nanotubes directly demonstrate the superior performance, i.e. capability to delivers higher current and requires lower operating voltage, than most advanced silicon technologies at an extreme dimension of 9 nm. However, it is still a daunting challenge to realize practical devices and systems, mainly limited by manufacturability issues related with material processing. Here we show our latest progress on achieving scalable separation of nanotubes based on their electronic type,[1] assembling nanotubes with Langmuir-Schaefer method to form full surface coverage nanotube arrays with tube density well above 500 tubes/um,[2] and forming highly efficient end-bonded point contact between nanotubes and electrodes, together with new understandings on the channel length scaling behavior of solution-processed nanotubes and contact length scaling of nanotube transistors.[3] These results show great promise for nanotube based high-performance logic electronics. Further optimization of the nanotube electronic type and diameter separation techniques, reduction of interface traps for better device consistency, together with CMOS compatible circuit and system level implementation, represent some most important directions for future work, where major challenges come from the requirement of extreme engineering control rather than intrinsic limitations of the material or processes.

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C7

# Transparent and conductive thin films of both carbon nanotubes- and graphene-based nanocomposites

Edson Nossol[1], Rodrigo V. Salvatierra[1], Sergio H. Domingues[1], Hiany Mehl[1], Vitor Hugo R. Souza[1], Samantha Hussman[1], Eduardo G.C. Neiva[1], Marcela M. Oliveira[2], Aldo J.G. Zarbin[1]

*1 Department of Chemistry, Federal University of Parana (UFPR), Brazil (aldozarbin@ufpr.br)*
*2 Dep. of Chemistry & Biology, Technological Federal University of Parana (UTFPR), Brazil*

We will present here a summary of the main results obtained in the last 5 years in our research group, related to the synthesis, characterization, study of properties and applications of different nanocomposites based on graphene or carbon nanotubes (CNTs), prepared directly as thin and transparent films. Specifically, we will discuss the following systems: i) films of carbon nanotubes/Prussian blue (and analogues) nanocomposites, and their application as electrochemical sensor, in electrochromic device, and as catalyst to water treatment; ii) films of CNTs/conducting polymers, and their application as ITO substitutes and in flexible organic solar cells; iii) films of neat graphene or graphene/conducting polymers, and their application as ITO substitutes; iv) films of graphene/silver nanoparticles, and their application as SERS substrates.

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C8

# Commercially viable SWNT transparent conductive thin films from nanotubide inks

Siân Fogden, Ce Ma, Kee-Chan Kim, Kathleen Ligsay, Graham McFarlane

*Linde Nanomaterials, 1970 Diamond St, San Marcos, CA, USA (sian.fogden@linde.com)*

Although commercial interest has been growing into alternatives to doped metal oxides for transparent conductive thin films (TCFs), none have been able to achieve the required resistivity and transparency for commercial viability, commonly quoted in the literature as 100 ohms/sq at 90% transparency, without affecting other critical properties such as haze, environment stability, flexibility, hardness, adhesion and of course, cost. Single Walled Carbon Nanotubes (SWNTs) have shown great promise as an alternative material due to their outstanding electrical, optical and mechanical properties. However, up until now the resistivity and transparency requirements have not been met.

Using reduction dissolution technology to produce nanotubide inks, Linde Nanomaterials has been able to produce TCFs which exceed the resistivity and transparency requirements without affecting the other critical properties.

This reductive dissolution technology begins by reducing SWNTs in liquid ammonia followed by dissolution in a polar aprotic organic solvent without the need for additional mechanical energy. This mild dissolution technique results in solutions of long, undamaged, individualized SWNTs which can be deposited using spin or spray coating to make TCFs. This technique directly addresses the critical SWNT conductivity scaling factors of purity, length and bundle size to produce commercially viable TCFs. At the lab scale, photovoltaic devices made using these TCFs have been successfully produced. The developments presented here will pave the way for the mainstream use of SWNT based TCFs in both the touch and display markets.

C9

## Carbon nanotube transparent conducting films as electrodes for organic light-emitting diodes

Jing Gao, Yan Meng, Xiao-Bing Xu, Li-Ting Chen, Yan Wang, Hong-Zhang Geng

*State Key Laboratory of Hollow Fiber Membrane Materials & Membrane Processing, School of Materials Science and Engineering, Tianjin Polytechnic University, Tianjin 300387, P. R. China (genghz@tjpu.edu.cn)*

Purified single-walled carbon nanotubes (SWCNTs) were dispersed in water using sodium dodecyl benzene sulfonate (SDBS) as dispersant for SWCNT transparent conducting films (TCFs). The optimal ratio of SWCNT/SDBS was found according to the film resistance of before and after post-treatment by nitric acid [1]. The TCFs were then further treated with thionyl chloride to improve their conductivity. Low sheet resistance and the high transmittance TCFs were achieved [2]. The TCFs were selected for electrodes of organic light-emitting diodes (OLEDs). The as prepared SWCNT-TCFs displayed a rather large surface roughness of 30 nm. The TCFs was top-coated with poly (3, 4-ethylenedioxythiophene): poly (styrene sulfonate) (PEDOT:PSS) to achieve PEDOT:PSS coated TCFs and the surface roughness decreased to 12 nm. The SWCNT-TCFs mixed with PEDOT:PSS (PM-TCFs) achieving high conductivity, low surface roughness (3 nm). Flexible OLEDs were fabricated on TCFs with the same structure using 4,4′-bis(2,2′-diphen ylvinyl)-1,1′-biphenyl as emitting layer to evaluate the performance of different types of SWCNT films for OLEDs. Among these types of OLEDs, the PM-TCF devices showed the optimal performance with high luminance and current efficiency. The result was explored in details to further explore the mechanism involved for better applying SWCNT films to OLED devices [3].

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I3

## Monodisperse carbon nanomaterial thin film applications

Mark C. Hersam

*Northwestern University, USA (m-hersam@northwestern.edu)*

Recent years have seen substantial improvements in the structural, chemical, and electronic monodispersity of carbon nanomaterials, leading to improved performance in a variety of thin film applications [1]. For example, high purity semiconducting single-walled carbon nanotubes (SWCNTs) allow the fabrication of thin-film field-effect transistors with concurrently high transconductance, mobility, and on/off ratio [2] and/or high frequency operation exceeding 150 GHz [3]. Using dielectrophoretic assembly, arrays of individual SWCNT transistors can also be realized with high yield [4]. Similarly, high performance digital circuits can be fabricated from semiconducting SWCNT inks via aerosol jet printing [5]. Beyond transistors, semiconducting SWCNTs have been utilized for light-emitting optoelectronic devices [6] or chemical sensors [7], while metallic SWCNTs are well-suited as transparent conductors [8] in organic photovoltaics [9]. This talk will also explore the utility of chemically functionalized graphene for high-frequency transistors [10], metal-oxide-graphene capacitors [11], charge blocking layers in organic photovoltaics [12], and supports for photocatalytic production of solar fuels [13].

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I4

# Self-assembled micro-honeycomb network of single-walled carbon nanotubes for heterojunction solar cell

Shigeo Maruyama, Kehang Cui, Takaaki Chiba, Erik Einarsson, Shohei Chiashi

*Department of Mechanical Engineering, The University of Tokyo, Tokyo 113-8656, Japan*
*(maruyama@photon.t.u-tokyo.ac.jp)*

Various forms of nano-carbon films such as random network of single-walled carbon nanotubes (SWNTs), vertically aligned SWNT (VA-SWNTs) and graphene have been examined for SWNT/Si heterojunction solar cells. Here, we propose a self-organized micro-honeycomb network structure of SWNTs obtained by water or ethanol vapor treatment of as-synthesized VA-SWNTs for such devices with higher performance. VA-SWNTs were synthesized by the standard alcohol-catalytic CVD (ACCVD) method with Co/Mo dip-coated on Si/$SiO_2$ substrates [1]. The VA-SWNT film was then exposed to water vapor by hanging over heated water. By drying the film, quasi-regular honeycomb cell structure was obtained. Honeycomb cell walls consist of capillary-aggregated vertically aligned SWNTs with heavily bundled top part. Within each cell, collapsed spaghetti-like SWNTs make contact to the substrate.

The SWNT/n-Si heterojunction solar cell was built by placing the micro-honeycomb SWNT network film on top of the substrate which had a 3 mm x 3 mm bare n-type silicon contact window in the center. Our preliminary test showed that the photovoltaic conversion efficiency (PCE) under AM1.5 was over 6 %, with the fill factor of 72% without any doping. The fill factor of 72 % is the highest record for such SWNT/n-Si heterojuction solar cells without doping. The PCE should be further increased by adjusting the transparency of the SWNT film, reducing contact resistances and reducing the sheet resistance of film. A PCE beyond 10% is achieved in the dry state after dilute nitric acid treatment. Furthermore, by modifying the vapor treatment condition, micro-honeycomb skeleton structure without the collapsed spaghetti-like SWNTs can be made. This structure is ideal for transparent and conductive film.

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C10

# Catalysts for controlled growth of single-walled carbon nanotubes

Yan Li

*Beijing National Laboratory for Molecular Science, Key Laboratory for the Physics and Chemistry of Nanodevices, State Key Laboratory of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China*
*(yanli@pku.edu.cn)*

Catalysts play crucial roles in the chemical vapor deposition (CVD) of single-walled carbon nanotubes (SWNTs). In the past dozen years, we have worked on the catalyst design for the controlled growth of SWNTs. We studied the relation between the diameter of the SWNTs with the size and composition of catalyst nanoparticles. We developed catalysts for the growth of pure semiconducting SWNTs. By carefully designing the composition and structure of catalyst nanoparticles, we even realized the structure-specific growth of SWNTs. The chirality purities of such produced SWNTs are higher than 90%.

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## SP60

# Identification of doping heteroatoms in single-walled carbon nanotube films: The ultra-low doping case

Paola Ayala

*Faculty of Physics, University of Vienna, Austria (paola.ayala@univie.ac.at)*

The identification of heteroatoms in doped single-walled carbon nanotubes has always been a challenging task. The practical difficulties to produce ultra-clean, nearly defect-free SWCNTs have constantly appeared as stumbling blocks to have a direct proof of their predicted properties. This is not surprising because the electronic and optical properties SWCNTs are very sensitive to the chemical environments [1]. Whether we have to deal with the inevitable interactions of nanotubes in a bundle, single dopants, encapsulated structures, suspending media or tailored defects, the energies of charge carriers and lattice vibrations are always modified. Focusing on the case of "single dopants", I will show our recent progress on establishing the prerequisites for studying the rich low-dimensional physics of these functionalized SWCNTs [2,3]. We will discuss on the preparation of films of doped nanotubes.

It will be discussed how metallicity-sorting combined with high energy spectroscopy techniques can nicely disentangle the characteristic density of states of these doped SWCNT-films unambiguously. An insight into the influence of doping, chemical interactions on the electronic ground state and the electronic transport properties will be presented. We will discuss the changes in the site selective electronic structure of substitutionally B doped SWCNT films.

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[3] R. Nakanishi, R. Kitaura, P. Ayala, H. Shiozawa, K. de Blauwe, P. Hoffmann,. D. Choi,Y. Miyata, T. Pichler, H.Shinohara., Phys Rev B 86 (2012) 115445

## SP61

# Rapid and easy patterning of carbon nanotube films and its application to transparent conductive films

Norihiro Fukaya[1], Dong Young Kim[2], Shigeru Kishimoto[1],
Suguru Noda[2], and Yutaka Ohno[1]

*1 Department of Quantum Engineering, Nagoya University, Japan (yohno@nuee.nagoya-u.ac.jp)*
*2 Department Applied Chemistry, Waseda University, Japan*

Carbon nanotubes (CNTs) are quite promising material for transparent conductive films (TCFs) and interconnections of flexible devices without resource problems. For the formation of CNT interconnections, patterning of a thick CNT film on a plastic substrate is one of key processes. In this study, we propose the filtration and transfer process with patterned membrane filter to fabricate CNT patterns on a transparent plastic substrate on the basis of the floating-catalyst chemical vapor deposition technique (FC-CVD) [1]. We also apply this technique to produce CNT TCFs that consists of double layers of a uniform film and a grid of single-walled CNTs. By adding the grid, the performance of CNT TCFs were fairly improved over the tradeoff between transmittance and sheet resistance of conventional CNT TCFs with single layer CNT film. The sheet resistance at a transmittance of 80 % was reduced by 46 % from 95 Ω/sq to 53 Ω/sq by adding the grid.

Acknowledgment: This work was supported by JST/ALCA.

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## Collective optical resonances in networks of metallic carbon nanotubes

**SP62**

Tommi Isoniemi[1], Andreas Johansson[1], J. Jussi Toppari[1], Henrik Kunttu[2]

*1 Nanoscience Center, Department of Physics, University of Jyväskylä, Finland (tommi.isoniemi@jyu.fi)*
*2 Nanoscience Center, Department of Chemistry, University of Jyväskylä, Finland*

In carbon materials, actual optical plasmonics have this far been restricted to graphene, but the experiments we have performed provide novel evidence of plasmonic functionality in a different form of pure carbon [1]. We demonstrate optical resonances in thin films of single walled carbon nanotubes (SWCNTs) with a highly enriched (98 %) proportion of metallic chiralities. These resonances are measured in the Kretschmann configuration, and can be seen as intensity dips of up to 90 % in reflection spectra beginning at 360 and 650 nm at the critical angle for total internal reflection and moving to longer wavelengths for higher angles of incidence. Unexpectedly, they are only visible when the sample is excited with s-polarized light, the opposite of surface plasmon polaritons on thin metal films. The resonances are dispersive and intense only when the layer thickness is close to 100 nm, implying that a collective excitation might be responsible for the resonance. They are also sensitive to the dielectric environment, clearly distinguishing the data from normal total internal reflection absorption spectra. The length of the CNTs seems to be irrelevant, ruling out localized surface plasmon resonance, and increasing the amount of amorphous carbon only decreases the intensity of the resonance. Corresponding materials of semiconducting and unsorted SWCNTs with similar diameters (1.4 nm) do not display noticeable dispersive resonances. Although additional experimental and theoretical studies are needed to confirm the underlying mechanism, a magnetic plasmon resonance [2] due to intertube effects, possibly within bundles, is a possible explanation. A probable coupling to excitons can also be pointed out, as the resonances are found close to $M_{11}$ and $M_{22}$ transition energies of the SWCNTs. If the fundamental reason for the observed phenomenon is connected to a magnetic resonance, metallic SWCNTs might find applications in plasmonic metamaterials.

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[2] A. Sarychev, G. Shvets, V. Shalaev, Phys. Rev. E 73 (2006) 036609-18

## Periodically patterned porous thin films of carbon nanotubes fabricated by polystyrene-nanosphere templating

**SP63**

Yuki Kuwahara[1], Takayoshi Hirai[2], Takeshi Saito[1]

*1 Nanotube Research Center, National Institute of Advanced Industrial Science and Technology (AIST), Japan (takeshi-saito@aist.go.jp)*
*2 Technology Research Association for Single Wall Carbon Nanotubes (TASC), Japan*

Carbon nanotubes (CNTs) have been studied as one of emerging conductive materials for the application to transparent conductive films (TCFs) due to their unique properties such as high electrical conductivity, and transparency, accompanied by the mechanical strength and chemical stability. As for CNT-TCFs, the optimal film morphology for the high optical transparency and low electrical resistivity is one of the controversial issues. Therefore, the studies on the film fabrication techniques with controllability of their morphology are highly important. Such investigations will contribute to further improvements in conductivity and transparency of CNT-TCFs. It is well-known that the close-packed layer of ordered latex particles forms a hexagonal pattern that is frequently used as a template. In this study, we have fabricated periodically patterned CNT thin films with different pore-sizes by the templating method using polystyrene spheres (PSs), and investigated the relationship between the performance as CNT-TCFs and the film morphology. For the fabrication of the porous patterned CNT thin films, we combined PS template and filtration methods. At first, the PSs latex solution was filtered through membrane filter to form self-assembled close-packed layers on the membrane. Then, the CNT dispersion was poured on it and washed with ample amounts of Millipore water. After removing PSs, CNT films were transfer to glass substrates according to the method described by Wu *et al.* [1]. Patterned CNT films were observed by using SEM, AFM, and optical microscopy. The surface resistance and transparency of CNT films were also characterized. The study has been supported by the New Energy and Industrial Technology Development Organization (NEDO).

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**SP64**

# Carbon nanotube thin film transistors: towards all-printed devices

F. Cheng, J. Ding, N. Du, G. Dubey, J. Dunford, P. Finnie, C. Homenick, A. Hrdina, R. James‡, M. Jakubinek, C. Kingston, J. Lefebvre, Z. Li, G. Lopinski, P. Malenfant, B. Simard, S. Zou

*National Research Council Canada, Ottawa, Ontario, K1A 0R. (jacques.lefebvre@nrc.ca)*
*‡Communications Research Centre Canada, Ottawa, Ontario, K2H 8S2*

In this presentation, I will cover our recent activities related to carbon nanotube transistors for applications in printable electronics. Aspects currently addressed include source and drain contacts, gate dielectric and transistor channel. For the dielectric, we selected one with high dielectric constant, good capacitance, and importantly, compatible with a printing process. For the transistor channel, two aspects are being addressed: ink formulation with an important focus on semiconductor enrichment (chromatography & conjugated polymer extraction), and ink deposition using three methods, drop-cast, inkjet and aerosol. I will highlight mobility numbers in excess of > 20 cm$^2$/Vs and current On/Off ratio >10$^4$ for transistors obtained using semiconductor enriched carbon nanotubes with a diameter distribution centered at 1.3 nm.

**SP65**

# In-situ Raman spectroscopy applied to SWNT growth kinetics

Benji Maruyama[1], Boris Yakobson[3], Rahul Rao[1,2], Stefano Curatolo[4], Daylond Hooper[1], Neal Pierce, and Pavel Nikolaev[1]

*1 Air Force Research Laboratory, Wright-Patterson AFB, OH, USA*
*2 Currently, Honda Research Institute, Columbus, OH, USA*
*3 Rice University, Houston, TX, USA*
*4 Duke University, Durham, NC, USA*

We report progress on our study of SWNT growth using our Adaptive Rapid Experimentation an *in-situ* Spectroscopy system (ARES). Initially we used our system to link the initial growth rate of a SWNT to its chirality [1]. We showed experimentally that higher chiral angle nanotubes grew faster than lower chiral angle nanotubes. This was predicted in a theoretical treatment by Ding and Yakobson [2]. Our discovery was enabled by the ARES system's unique ability is to probe the growth kinetics of individual SWNTs.

We extended this to a comparison of iron and nickel catalysts over a range of temperature (750–1200 °C) [3]. Here we found that, while for nickel the lifetime of the catalyst decayed as temperature increased, the iron catalyst underwent a discontinuous increase in catalyst lifetime. We explain this using the binary Fe-C and Ni-C phase diagrams, showing that the jump in lifetime around 1000 °C correlates well the Fe-C eutectic temperature modified for the nano-size of the catalyst. In contrast, no jump is seen for nickel, which is explained by the higher eutectic temperature in the Ni-C phase diagram.

[1] R. Rao *et al.*, Nature Materials 11, pp. 212-216 (2012) doi:10.1038/nmat3231
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[3] R. Rao *et al.*, ACS Nano, Article ASAP (Web: 1/24/2013) DOI: 10.1021/nn304064u

## Multifunctional material based on carbon nanotube/Prussian blue nanocomposite film

**SP66**

Edson Nossol[1], Arlene B.S. Nossol[1], Alan M. Bond,[2] Aldo J.G. Zarbin[1]

*1 Federal University of Paraná, Brazil (edsonnossol@ufpr.br)*
*2 Monash University, Australia*

Prussian Blue (PB), $Fe_4[Fe(CN)_6]_3.xH_2O$ ($x$=14-16), has an open framework structure constituted by alternating face centered cubic lattices of $Fe^{3+}$ and $Fe^{2+}$ cations, distinguishable by their different coordination to the $CN^-$ ligand. Electrodeposited thin films with this structure show the simultaneous presence of two redox couples, semiconductor characteristics and have the capability to reversibly intercalate different cations. Based on the exceptional electrochemical properties of carbon nanotubes (CNTs) such as high current density and heterogeneous electron transfer rate, mechanical stability and electrocatalytic effect on redox process of different compounds, the preparation of carbon nanotube/Prussian blue (CNT/PB) nanocomposites has attracted a great interest of the scientific literature. A new methodology to prepare PB nanostructures based on an in situ electrochemical reaction between the iron-based compounds present in the cavities of CNTs and the ferricyanide ions in solution was developed in our group [1]. This work reports the preparation of homogeneous, transparent and electroactive films of CNT/PB nanocomposites using this new method. PB electrosynthesized as nanocubes over the CNTs walls showed intimate contact between PB and CNTs, which improved the stability and redox properties of PB. The electrodeposition of PB and the chemical interaction between PB and CNTs were attested by cyclic voltammetry, X-ray diffraction, UV-Vis and Raman spectroelectrochemistry and *in situ* electrochemical techniques. The CNT/PB composite film presented as a multifunctional material, showing its application as $H_2O_2$ sensor with a very high sensitivity and low detection limits [1]; as a new electrode material for environmental treatment of water samples using different Fenton processes [2]; and as a eletrochromic device [3], with a good response time and excellent stability upon the application of several double potential cycles.

[1] E. Nossol, A. J. G. Zarbin, J. Mater. Chem. 22 (2012) 1824-1833 [2] E. Nossol, A. B. S. Nossol, A. J. G. Zarbin, A. M. Bond, RSC Advances (2013) [3] E. Nossol, A. J. G. Zarbin, Sol. Energy Mater. Sol. Cells. 109 (2013) 40-46

## Carbon nanotube thin film transistors for printed electronics

**SP67**

Kimmo Ojanperä[1], Patrik Laiho[2], Antti Kaskela[2], Toma Susi[2], Ari Alastalo[1], Esko Kauppinen[2]

*1 VTT, Printed Functional Solutions, Finland (kimmo.ojanpera@vtt.fi)*
*2 Department of Applied Physics, Aalto University School of Science, Finland*

We present single-walled carbon-nanotube (SWCNT) thin-film transistors (TFT) fabricated on a plastic substrate using a hybrid manufacturing method. The device structure is a bottom-gate top-contact (BGTC) configuration. The SWCNT network for the TFT channel was collected onto a nitrocellulose membrane filter directly from a floating catalyst CVD reactor [1], and press transferred onto a plastic PEN substrate followed by the dissolution of the filter in acetone. Before the press transfer, the gate electrode was shadow-evaporated and a polyimide dielectric layer spun-cast on the substrate. Finally, the source and drain electrodes were inkjet-printed on top of the percolating SWCNT network.

The TFTs were characterized in ambient conditions by transfer curve measurements using a Keithley 4200 Semiconductor Characterization System. The TFTs had mobilities on the order of 4 $cm^2/Vs$ and on/off-ratios over $10^3$, with the measurement voltage ranging from -10 V to +5 V. The TFT performance was limited by the combination of materials, impurities, statistical variation of the deposition processes, and the roughness of the substrate and the solution-processed surfaces. The demonstrated process can be used to fabricate, for example, backplane circuits of flexible displays.

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**SP68**

# Filtration-wet transferred transparent conducting films of mm long CNTs grown using water-assisted chemical vapor deposition

Shashikant P. Patole[1,2,*], Dong Wook Shin[1], Bunshi Fugetsu[3] and Ji-Beom Yoo[1,2,*]

*1 SKKU Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan University, Suwon 440746, Republic of Korea (*sppatole@skku.edu and jbyoo@skku.edu)*
*2 School of Advanced Materials Science & Engineering, Sungkyunkwan University, Suwon 440746, Republic of Korea*
*3 Graduate School of Environmental Science, Hokkaido University, Sapporo 0600810, Japan*

Transparent conducting films (TCF) made up from carbon nanotubes (CNTs) have a tremendous potential in replacing the indium tin oxide films. Compare to single wall CNTs, multiwall CNTs are more metallic and are more suitable candidate for the TCF. In this letter we report the use of selectively grown mm-scale, few-wall, vertically aligned CNTs for the fabrication of TCF. Water-assisted chemical vapor deposition was used to grow the mm-scale CNTs within short growth time. A special post-growth water-vapor treatment allowed us to remove the catalyst-free CNT forest very easily from the substrate and use it for the further process. A filtration-wet transfer process was used to form the TCF. The TCF shows sheet resistance of 228 Ω/sq. at 72% transparency (at 550 nm). The ratio of optical conductivity to dc conductivity was observed in between 0.21 to 0.25 for below 80% transmission.

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**SP69**

# Effect of visible light and air exposure on CNT films

Olivier Reynaud[1], Albert G. Nasibulin[1], Jani Sainio[2], Sergey D. Shandakov[3], Ilya V. Anoshkin[1], Ying Tian[1], Esko I. Kauppinen[1]

*1 Nanomaterials Group, Aalto University, Finland (olivier.reynaud@aalto.fi)*
*2 Surface Science Group, Aalto University, Finland*
*3 Kemerovo State University, Russia*

Single-walled carbon nanotubes (SWCNTs) are promised to a great future as key component in optoelectronic devices such as thin and flexible displays or light sources, solar cells, touch sensors or printable and flexible electronic devices like thin films transistors [1]. What make SWCNT so interesting are its unique optical and electrical properties. However, changes in optical and electronic properties of SWCNTs can be observed when they are exposed to light and oxygen [2]. Any device that is not a sensor, fabricated from SWCNTs, is expected to be as stable as possible and not to be perturbed by its surroundings. This can be a problem, and raises the question SWCNT-made devices reliability.

In this contribution, we present results of SWCNT optical absorption spectra measurement before and after air and light exposure, and changes in Van Hove transitions intensity. We also performed XPS analysis to study the surface state of SWCNT after air and light exposure.
We show that CNT samples exposed to light are no longer “pristine”: the history of UV/light exposure of a sample is important, not only the synthesis method. We present the difference of sensitivity with light and oxygen exposure between “fresh” samples and older samples. There is almost no change in absorbance spectra for fresh samples: samples with less exposure history are more stable. The absorbance spectrum of an old sample that has been previously exposed to light is more sensitive to exposure and can change with time without any further exposition.

[1] A. Kaskela, A. G. Nasibulin, M. Y.Timmermans, *et al.*, Nano Lett. 10 (2010) 4349-4355
[2] M.E. Itkis, S. Niyogi, M.E. Meng, M. A. Hamon, H. Hu, and R. C. Haddon, Nano Lett. 2 (2002) 155-159

SP70

## Hybrid thin films of unsubstituted polythiophene and in situ synthesized carbon nanostructures

Rodrigo V. Salvatierra[1], Carlos E. Cava[1,2], Marcela M. Oliveira[3], Lucimara S. Roman[2],
Aldo J. G. Zarbin[1]

*1 Department of Chemistry – Universidade Federal do Paraná (UFPR), Curitiba, Brazil (rodrigovs@ufpr.br)*
*2 Department of Physics - Universidade Federal do Paraná (UFPR), Curitiba, Brazil*
*3 Department of Chemistry and Biology, Universidade Tecnológica Federal do Paraná (UTFPR), Curitiba, Brazil*

Polythiophenes (PT) are the most studied in the class of conjugated polymers. However, the simplest form – the unsubstituted PT – is limited by its improcessability whereby thin films cannot be produced, thus not utilizing its properties (like stability, charge transport), which are potentially superior related to its soluble counterparts (e.g., P3HT). In a previous work, we developed a liquid-liquid interfacial (water/oil interface) route to obtain self-assembled thin films of polyaniline and carbon nanotubes [1,2]. Adapting this route to the interfacial polymerization of thiophene, we observed a dramatic effect of solvents used in the polymerization of thiophene with solid iron chloride ($FeCl_3$). Testing four different solvents (benzene, toluene, chloroform and *n*-hexane), we found that hybrid thin films were synthesized with the aromatic solvents – toluene and benzene – in which the iron chloride promotes the polymerization and crosslinking of benzene or toluene, producing small graphene nanostructures along with the PT [3], leading to distinct properties of the polymer, like more conjugated samples, different absorption characteristics and significant hole mobilities (~$10^{-3}$ $cm^2.V^{-1}.s^{-1}$). Also, the effect of adding external carbon nanotubes was evaluated and its interaction with the polymer and *in situ* generated graphene structures.

[1] Salvatierra, R. V., Oliveira, M. M., Zarbin, A. J. G., Chem. Mater. 22 (2010), 5222-5234
[2]Salvatierra, R. V., Cava, C. E., Roman, L. S., Zarbin, A. J. G., Adv. Funct. Mater. 23 (2013) 1490-1499
[3] Kovacic, P., Kyriakis, A., J. Am. Chem. Soc., 85 (1963), 454-458

SP71

## Growth of single-walled carbon nanotubes thin film with controlled diameters and lengths by an aerosol method

Ying Tian, Marina Y. Timmermans, Matti Partanen, Albert G. Nasibulin,
Hua Jiang, Zhen Zhu, Esko I. Kauppinen

*NanoMaterials Group, Department of Applied Physics and Center for New Materials, Aalto University,*
*Puumiehenkuja 2, 00076 AALTO, Finland (ying.tian@aalto.fi)*

Single-walled carbon nanotubes (SWCNTs) with desirable diameter are required for various applications particularly in electronics and photonics, since the diameter is an essential characteristic to determine their electronic and optical properties. In this work, we demonstrate an effective and simple approach for diameter-controlled growth of SWCNTs in an aerosol chemical vapor deposition (CVD) reactor based on ferrocene vapour decomposition in an atmosphere of CO [1]. The wide range modulation of SWCNT diameters from 1.1 to 1.9 nm gives possibility to effectively adjust the properties of SWCNTs to meet the needs for specific applications.

A detailed investigation of SWCNT products and related growth mechanism is presented as a function of the synthesis reactor temperature, water-cooled probe position and addition of a small amount of $CO_2$ during growth on the basis of combined analyses of transmission electron microscopy (TEM), scanning electron microscopy (SEM), Raman and ultraviolet-visible-near infrared (UV-Vis-NIR) absorption spectroscopy. The results show that increasing the temperature gives rise to the formation of high quality and large diameter SWCNTs. By monitoring the water-cooled probe position, both the bundle length and the diameter of the SWCNTs are effectively tuned due to the variation of the residence time and temperature profile in the reactor. An introduction of a small amount of $CO_2$ suppresses the growth of small diameter nanotubes and enlarges the mean diameter of SWCNT samples.

[1] Tian.Y, Timmermas, M.Y., Partanen, M., Nasibulin, *et al.*, Carbon 49 (2011)

## SP72 Electrical and optical properties of SWNTs-based composites

Fernando Torres-Canas[1,2], Manuel Perez[2], Christophe Blanc[2], Camilo Zamora-Ledezma[1,3],
Pedro Silva[1], Eric Anglaret[2]

*1 Laboratorio Física de la Materia Condensada, Centro de Física, IVIC,*
*Altos de Pipe, AP 21827, 1204 Caracas, Venezuela*
*2 Laboratoire Charles Coulomb, Univ. Montpellier 2 and CNRS, 34095 Montpellier, France*
*3 Centro de Investigaciones de Astronomía Francisco J. Duarte, 5101 Mérida, Venezuela*

Most of the current SWNTs production today is used to process bulk composite materials and thin films for exploiting their intrinsic properties at the macroscopic scale. However, the poor control of their distribution and orientation lead to unorganized architectures and limited properties [1]. Besides mechanical properties, electrical and optical properties are the most widely studied. However, various kinds of photoluminescent (PL) nanotube-based composites can be prepared only when the tubes are well dispersed as individuals in the composites [2-4]. Indeed, contacts between nanotubes quench the PL intensity. On the other hand, contacts are required to obtain some electrically conductive materials.

In this work we propose and compare different strategies to sort and control the number and nature of contacts in order to control both the PL and electrical (conductivity) properties of SWNTs-based composites [2-4]. These approaches include the control of the quantity of SWNTs, the quantity and nature of the dispersing agents used to disperse them, and their orientational order. We especially work on thin films and thin layers of polymer composites, as well as inorganic gels. Different optical spectroscopy techniques, i.e. absorption, Raman and photoluminescence spectroscopies, are used to study the dispersion and orientation of the nanotubes [2-4]. Electrical measurements are achieved using two and four point probes.

[1] Michael F. L. De Volder *et al.,* Science 339, (2013) 535 [2] C. Zamora-Ledezma *et al.,* J. Phys. Chem. C, 116 (25), (2012) 13760 [3] C. Zamora-Ledezma *et al.,* Phys. Rev. E 84, (2011) 062701 [4] C. Zamora-Ledezma *et al.,* Carbon 46, (2008) 1253-1269

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## SP73 Study on stability of chemically-doped n-type carbon nanotube thin film transistors

Tomohiro Yasunishi, Shigeru Kishimoto, and Yutaka Ohno*

*Dependent of Quantum Engineering, Nagoya University, Japan*
*(*yohno@nuee.nagoya-u.ac.jp)*

The networks of single-walled carbon nanotubes (CNTs) have attracted much attention as an active layer of thin-film transistors (TFTs). Techniques for p/n control have been proposed by utilizing chemical doping; however, the mobility of the n-type devices reported so far are still much lower than those expected for CNT-TFTs, ranging from 1 to 10 cm$^2$/Vs. In this study, we realized n-type CNT-TFTs with high mobility as 70 cm$^2$/Vs (on/off: ~$10^5$) by the transfer process [1] and solution-based chemical doping technique with PEI. The stability of the device will also be discussed.

Acknowledgments: This work was partially supported by ’08 NEDO Grant, NICT, ALCA/JST, and Grant-in-Aid for Scientific Research of JSPS.

[1] D. -M. Sun, M. Y. Timmermans, Y. Tian, A. G. Nasibulin, E. I. Kauppinen, S. Kishimoto, T. Mizutani, and Y. Ohno, Nature Nanotech, 6 (2011) 156
[2] M. Shim, A. Javey, N. W. S. Kam, and H. Dai, J. Am. Chem. Soc. 123 (2001) 11512

## Legend

1. Tallink ferry terminal
2. Tallink Spa & Conference hotel
3. Tallink Express hotel
4. Mustpeade maja (Satellites dinner)

# Satellites venue

The venue of the Symposia is the 2nd floor Conference center of the

**TALLINK SPA & CONFERENCE HOTEL**

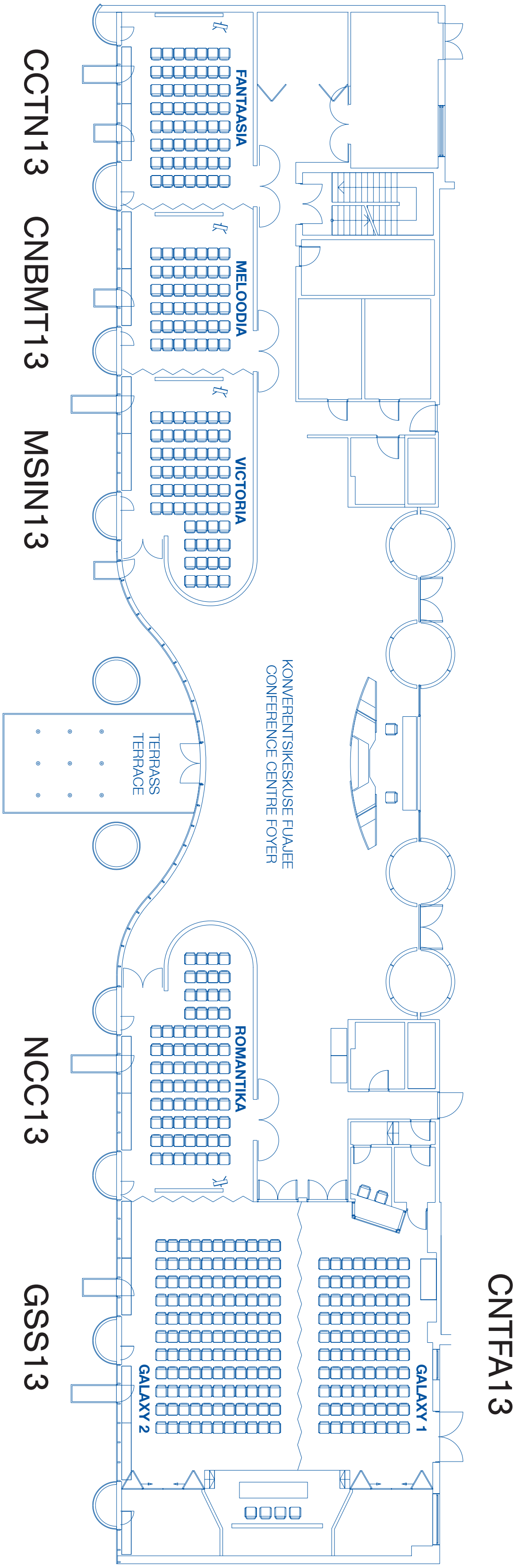
Address: Sadama 11a, 10111 Tallinn
Tel: +372 630 1000
Fax: +372 630 1010
E-mail: spahotel@tallink.ee

The Satellites dinner will be held on Saturday evening starting from 8 pm at

**MUSTPEADE MAJA (HOUSE OF THE BLACKHEADS)**

Address: Pikk str. 26, 10133 Tallinn
Tel: +372 631 3199
E-mail: info@mustpeademaja.ee

Dinner entertainment will be provided by the *Engineers' Male Choir* and the folk dance group *Kuljus*.



# Satellite support

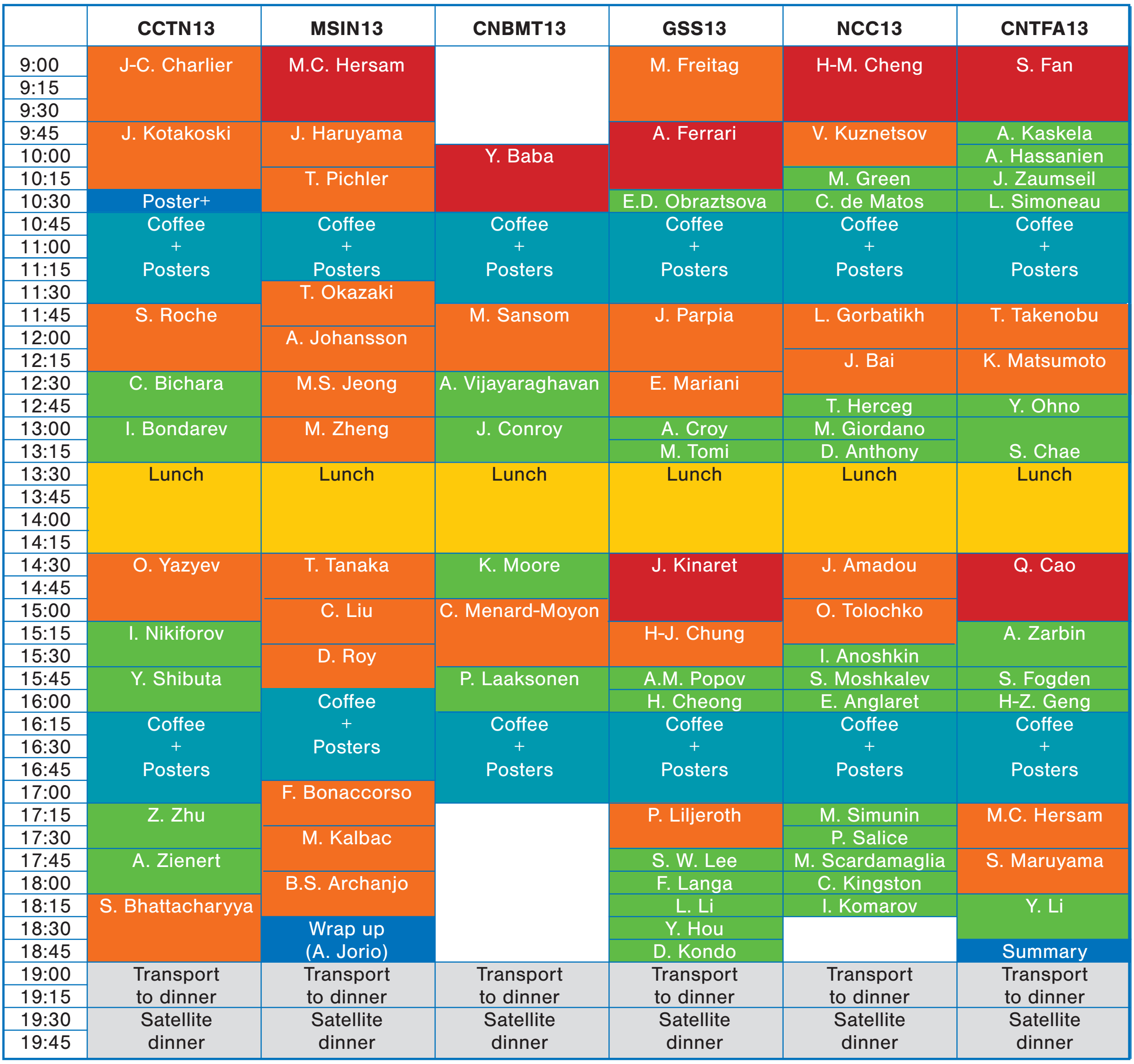
The satellites have been organized in cooperation with the Tallinn University of Technology.

The organizers gratefully acknowledge the financial support of the City of Tallinn.

Tallinna Ettevõtlusamet

# Notes

# Program



| | CCTN13 | MSIN13 | CNBMT13 | GSS13 | NCC13 | CNTFA13 |
|---|---|---|---|---|---|---|
| 9:00 | J-C. Charlier | M.C. Hersam | | M. Freitag | H-M. Cheng | S. Fan |
| 9:15 | | | | | | |
| 9:30 | | | | | | |
| 9:45 | J. Kotakoski | J. Haruyama | | A. Ferrari | V. Kuznetsov | A. Kaskela |
| 10:00 | | | Y. Baba | | | A. Hassanien |
| 10:15 | | T. Pichler | | | M. Green | J. Zaumseil |
| 10:30 | Poster+ | | | E.D. Obraztsova | C. de Matos | L. Simoneau |
| 10:45 | Coffee + Posters | Coffee + Posters | Coffee + Posters | Coffee + Posters | Coffee + Posters | Coffee + Posters |
| 11:00 | | | | | | |
| 11:15 | | | | | | |
| 11:30 | | T. Okazaki | | | | |
| 11:45 | S. Roche | | M. Sansom | J. Parpia | L. Gorbatikh | T. Takenobu |
| 12:00 | | A. Johansson | | | | |
| 12:15 | | | | | J. Bai | K. Matsumoto |
| 12:30 | C. Bichara | M.S. Jeong | A. Vijayaraghavan | E. Mariani | | |
| 12:45 | | | | | T. Herceg | Y. Ohno |
| 13:00 | I. Bondarev | M. Zheng | J. Conroy | A. Croy | M. Giordano | S. Chae |
| 13:15 | | | | M. Tomi | D. Anthony | |
| 13:30 | Lunch | Lunch | Lunch | Lunch | Lunch | Lunch |
| 13:45 | | | | | | |
| 14:00 | | | | | | |
| 14:15 | | | | | | |
| 14:30 | O. Yazyev | T. Tanaka | K. Moore | J. Kinaret | J. Amadou | Q. Cao |
| 14:45 | | | | | | |
| 15:00 | | C. Liu | C. Menard-Moyon | | O. Tolochko | |
| 15:15 | I. Nikiforov | | | H-J. Chung | | A. Zarbin |
| 15:30 | | D. Roy | | | I. Anoshkin | |
| 15:45 | Y. Shibuta | | P. Laaksonen | A.M. Popov | S. Moshkalev | S. Fogden |
| 16:00 | | Coffee + Posters | | H. Cheong | E. Anglaret | H-Z. Geng |
| 16:15 | Coffee + Posters | | Coffee + Posters | Coffee + Posters | Coffee + Posters | Coffee + Posters |
| 16:30 | | | | | | |
| 16:45 | | | | | | |
| 17:00 | | F. Bonaccorso | | | | |
| 17:15 | Z. Zhu | | | P. Liljeroth | M. Simunin | M.C. Hersam |
| 17:30 | | M. Kalbac | | | P. Salice | |
| 17:45 | A. Zienert | | | S. W. Lee | M. Scardamaglia | S. Maruyama |
| 18:00 | | B.S. Archanjo | | F. Langa | C. Kingston | |
| 18:15 | S. Bhattacharyya | | | L. Li | I. Komarov | Y. Li |
| 18:30 | | Wrap up (A. Jorio) | | Y. Hou | | |
| 18:45 | | | | D. Kondo | | Summary |
| 19:00 | Transport to dinner | Transport to dinner | Transport to dinner | Transport to dinner | Transport to dinner | Transport to dinner |
| 19:15 | | | | | | |
| 19:30 | Satellite dinner | Satellite dinner | Satellite dinner | Satellite dinner | Satellite dinner | Satellite dinner |
| 19:45 | | | | | | |

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|---|---|
| 🟥 Keynote talk | 🟦 Summaries |
| 🟧 Invited talk | 🟦 Coffee + Posters |
| 🟩 Contributed talk | ⬜ Evening event |
| 🟨 Lunch | |

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