

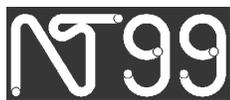
## The Nanotube (NT) Conference Series

Since their conception in 1999, the NT Conferences attempt to provide an informal setting to exchange the most current information in the rapidly evolving nanotube research field.

During the initial years, the number of registered participants exceeded the planned capacity by a factor of two. This was manageable at NT'99 in East Lansing, with 120 instead of the planned 60 participants. The following conference, NT'01, was planned to accommodate 140 participants at a beautiful location in Potsdam. The large number of applications, close to 300, turned from a blessing to a headache for the organizers. Only half of the applicants could be admitted due to the hard limit imposed by the hotel capacity at the somewhat remote location. The strong interest in the topic and the conference format held on at NT'02 at Boston College. Since then, the number of participants has equilibrated in the range between 200 and 300. To reflect the international nature of the research field, the NT'03 conference was held at Seoul National University in Korea. By that time the Asia-Europe-Americas "continent swapping mode" emerged as a pattern. The NT'04 conference was held in San Luis Potosi, Mexico and the NT'05 conference has returned to Europe.

Common to all conferences is a venue located close to a strong centre of nanotube research, and a local organization team active in nanotube research. Contributions, primarily presented as posters, have traditionally been treated with a high priority, taking up about half of the total conference time, with no parallel sessions. Other features common to the conferences include an emphasis on quality, originality, and informality.

### Previous NT conferences:



Michigan, USA



Potsdam, Germany



Boston, USA



Seoul, South Korea



San Luis Potosi, Mexico

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## NT'05 SCIENTIFIC PROGRAM

Time	Sun 26	Mon 27	Tues 28	Wed 29	Thurs 30	Fri 1		
08:30-09:00		registration	registration					
09:00-09:45			Maurizio Prato	Morinobu Endo	David Tomanek	Paul L. McEuen		
09:45-10:15		Welcoming address (09:30-10)	Alan Windle	Susumu Katagiri	Jean-Louis Sauvajol	Nadine Kam		
10:15-10:45		Sumio Iijima (10-10:45)	Jerry Tersoff	Jean Dijon	Junichiro Kono	Cheol Jin Lee		
10:45-11:15		Steven G. Louie	Coffee	Coffee	Coffee	Coffee		
11:15-11:45		Coffee	Young Hee Lee	Jong-Min Kim	Tony Heinz	Brian LeRoy		
11:45-12:05		Humberto Terrones (11.45-12.15)	Yoshinori Sato	Atsuko Nagataki	A.V. Krashennnikov	S. W. Lee		
12:05-12:25		Lars Samuelson (12.15-12.45)	lunch	A. K. Swan	lunch	lunch		
12:25-14:00		lunch (12.45-14.20)		lunch				
14:00-14:20			Pavel Nikolaev	Boat trip and conference dinner	G. Seifert	Perti Hakonen		
14:20-14:40		Feng Ding	Vincent Jourdain		B. Gao	A. Wall		
14:40-16:00		Masahiko Ishida (14.40-15)					Poster Session B	
16:00-18:00	registration	Poster Session A	Poster Session A	conference dinner	Poster Session B			
18:00-19:00	Welcome party							Snacks 19:00
19:00-21:00		Göteborg reception						Concluding Remarks 20.00

Welcoming address at 09:30 on Monday by the Chancellor of Göteborg University.

Welcome party, welcoming address, registration, talks, posters, lunch and Friday evening snacks are in the Chalmers University Student Union Building, located at the main entrance to Chalmers University of Technology.

Göteborg Reception is on Monday evening at 'Börsen' in the heart of Göteborg, about 30 minutes walk from the Student Union. Guides (if needed) leave the Student Union at 18:15.

On Wednesday buses leave from the Student Union to the boat trip at 14:00.

Poster sessions include reports by the poster chairs

## NT'05 contributions

In the spirit of the NT Conference series, oral presentations will consist of plenary, keynote and contributed talks. However, most contributions are presented as posters, and over half of the conference is dedicated to the poster exhibitions. Due to the large number of poster presentations, the NT'05 program does not include the two minute 'poster+' presentations that were a feature of preceding NT conferences. Instead, posters will be introduced by poster 'chairs', which leaves most of the time for discussion at the individual posters.

There are two poster sessions.

- Session A is on Monday and Tuesday and includes posters I.1 – VIII.12.
- Session B is on Thursday and Friday and includes posters IX.1 – XXI.30

These two sessions are divided into sub-sessions that will be introduced by the chairs. In addition, it is expected that contributors are available at their posters after the presentation of their sub-session.

<b>Sub-session</b>	<b>Posters</b>	<b>Poster chair</b>	<b>Presentation by chair</b>
A.1	I.1-I.40	Annick Loiseau	Monday, June 27
A.2	I.41-I.81	Esko I. Kauppinen	Tuesday, June 28
A.3	II-IV	Marcos Pimenta	Tuesday, June 28
A.4	V-VIII	Jack Fischer	Tuesday, June 28
B.1	IX-X	Pavel Nikolaev	Thursday, June 30
B.2	XI-XIII	Apparao Rao	Thursday, June 30
B.3	XIV	Tony Heinz	Thursday, June 30
B.4	XV-XVIII	Gianaurelio Cuniberti	Friday, July 1
B.5	XIX-XXI	Yoshiyuki Miyamoto	Friday, July 1

## Chairs for NT'05 oral contributions

Chair	Session	
Kim Bolton	Monday	10:15-11:15
Yoshikazu Nakayama		11:45-12:25
Shigeo Maruyama		14:20-16:00
Eleanor Campbell	Tuesday	09:00-10:45
Takuya Hayashi		11:15-12:05
Yung Woo Park		14:00-14:40
Mats Jonson	Wednesday	09:00-10:45
Hirokichi Kataura		11:15-12:25
Jari Kinaret	Thursday	09:00-10:45
Gotthard Seifert		11:15-12:05
Jean-Christophe Charlier		14:00-14:40
Mildred Dresselhaus	Friday	09:00-10:45
Philip Collins		11:15-12:05
Dmitri Golberg		14:00-14:40

# *NT'05 Abstracts*

## Growth and structures of Carbon Nanotubes

*Sumio Iijima*

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Research Center for Advanced Carbon Materials/ AIST, and NEC Special Research  
Fellow  
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Last year, our group at AIST has developed super-growth CNTs (1) that grow as high as 3mm under highly controlled CVD method and also are available in a patterned form on a substrate. The growth mechanism has been discussed in a quantitative way (2). Regarding the SG nanotubes some of new developments will be presented. Another effort going on in our group is structural characterization of SWCNTs and their modifications using modern electron microscope techniques, e.g., HRTEM and STEM equipped with electron energy loss spectroscopy. We have reported already chiral determination of single or double walled CNTs by analyzing TEM images as well as electron diffraction patterns. Our specialty is to use dynamic observation at the atomic level resolution, that is, individual carbon atoms and their vacancies on a single graphene sheet that are generated by electron beam irradiation are visualized in video pictures (3). Their stability will be discussed in terms of temperature (4). One of problems with double-wall CNTs is to know chirality for the inner tube including handedness of which determination has been attempted. Other topics include structure determination of endohedral metalfullerenes and ion transport through SWCNTs.

- (1) D. Futaba et al., Science 306, 1362-1364 (2004).
- (2) D. Futaba et al., PRL (2005) in press.
- (3) A. Hashimoto, et al., Nature, 430, 870-873 (2004).
- (4) K. Urita, et al., PRL, 94, 155502(2005).

## Excitonic Effects and Optical Response of Nanotubes

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Owing to their symmetry and reduced dimensionality, electron-electron Coulomb interaction often strongly influences the behavior of quasi-one-dimensional systems. We show, through first-principles excited-state calculations, that the optical response of carbon nanotubes is qualitatively altered by many-electron interaction effects.[1, 2] It is discovered that exciton states in the semiconducting tubes have binding energies that are orders of magnitude larger than bulk semiconductors and hence they dominate the optical spectrum at all temperature, and that bound excitons can exist even in metallic carbon nanotubes. These predictions demonstrate the crucial importance of an exciton picture in interpreting experimental data. Similar studies show that excitonic effects are even stronger in the BN nanotubes. For both carbon and BN nanotubes, in addition to the optically active (bright) exciton states, theory predicts a number of optically inactive or very weak oscillator strength (dark) exciton states. We have further performed analysis and modeling of the exciton properties (symmetry, binding energy, exciton size, oscillator strength, and radiative lifetime) as a function of factors such as tube diameter, chirality, temperature, and screening due to external medium. The physics behind these phenomena is discussed.

1. C. D. Spataru, S. Ismail-Beigi, L. X. Benedict, and S. G. Louie, Phys. Rev. Lett. 92, 077402 (2004).
2. C. D. Spataru, S. Ismail-Beigi, L. X. Benedict, and S. G. Louie, Appl. Phys. A78, 1129 (2004).

## **Geometry and the Electronic and Magnetic Properties of Curved Carbons**

*Humberto Terrones*

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In a 3-D space there are just three geometries possible: Euclidean, spherical and hyperbolic and all the forms we find in nature are realizations of these geometries. At the atomic scale, there are layered materials which can acquire different curvatures contained in the three geometries mentioned above. In this work we study the electromagnetic properties of several curved carbon nanostructures showing that by having control on the curvature, we would be able to generate new materials with new shapes and amazing electronic and magnetic behaviours. In particular, the possibility of having magnetism in curved carbons is analyzed. In this context, a possible explanation of the magnetism found in the rhombohedral phase of C<sub>60</sub> is given.

## **Materials and device physics aspects of semiconductor nanowires**

*Lars Samuelson*

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One-dimensional materials structures, such as carbon nanotubes and semiconductor nanowires, attract much attention for their promise to extend the miniaturization of electronic devices and circuits. Top-down fabricated nano-devices tend to have their properties dominated by process-induced damage, rendering ultra-small devices not so useful, while bottom-up fabrication methods may allow dimensions on the scale even below 10 nm, still with superb device properties. I will in this talk describe our research on catalytically induced growth of semiconductor nanowires. Our method uses catalytic gold nanoparticles, allowing tight control of diameter as well as position of where the nanowire grows, with our work completely focused on epitaxially nucleated nanowires in which the nanowire structure can be seen as a coherent, monolithic extension of the crystalline substrate material. One of the most important achievements in this field of research is the realization of atomically abrupt heterostructures within nanowires, in which the material composition can be altered within only one or a few monolayers, thus allowing 1D heterostructure devices to be realized. This has allowed a variety of quantum devices to be realized, such as single-electron transistors, resonant tunneling devices as well as memory storage devices. Another recent field of progress has been the realization of ideally nucleated III-V nanowires on Si substrates, cases where we have also been able to report functioning III-V heterostructure device structures grown on Si. Finally, I will describe opportunities to form new kinds of materials based on this technique, such as 3D complex, tree-like nanowire structures.

## Nucleation of single-walled carbon nanotubes on catalyst particles: MD and electronic structure calculations

*Feng Ding<sup>1</sup>, Arne Rosén<sup>1</sup>, Kim Bolton<sup>1,2</sup>*

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Metal catalyzed single-walled carbon nanotube (SWNT) nucleation was studied by classical molecular dynamics (MD) and electronic structure theory. The simulations revealed the atomic-level mechanism for SWNT nucleation on metal catalyst particles. The SWNTs nucleate between 800 K and 1400 K, [1] which is the same temperature interval used for chemical vapor deposition (CCVD) experiments. Also, in agreement with experimental results the nucleated SWNT has same diameter with the catalyst particle [2]. The studies also show that a highly supersaturated carbon concentration in the catalyst particle is needed to initiate the nucleation process. [1] Based on the simulations a detailed Vapor-Liquid-Solid (VLS) growth model was developed for both liquid and solid catalyst particles. [1, 3] Furthermore, MD and electronic structure theory studies indicate that the catalyst particle must be able to maintain an open end of the growing SWNT in order to be suitable for growth.

### References:

- [1] F. Ding, K. Bolton and A. Rosén, J. Phys. Chem. B, 108, 17369-17377 (2004).
- [2] F. Ding, A. Rosén, and K. Bolton, J. Chem. Phys., 121, 2775-2779 (2004).
- [3] F. Ding, A. Rosen, and K. Bolton, Chem. Phys. Lett., 393, 309-313 (2004).

## Single walled carbon nanotube growth from lithographically defined nanoparticle

*Masahiko Ishida, Hiroo Hongo, Fumiyuki Nihey, and Yukinori Ochiai*

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A semiconducting single walled carbon nanotube (SWNT) is an indispensable component of a carbon-nanotube (CNT)-based field-effect transistor (FET). However, for the high-density and high-yield integration of CNTs in devices, many technological issues still remain in obtaining only semiconducting SWNTs and in controlling their individual position, orientation, diameter, length, and chirality etc. One feasible approach is chemical vapor deposition (CVD) from custom-designed catalyst particles because the catalysts are thought to determine the characteristics of CNTs. We demonstrated the top-down control of diameter and position of Fe catalysts by means of "lithographically anchored nanoparticle synthesis (LANS\*)", and the CNT growth from the patterned particles. LANS was able to control the average diameter of Fe particles less than 2nm with the positioning error less than  $\pm 10$ nm. CNTs were grown by the CVD using ethanol and methane. Yield of the CNTs was strongly dependent on the particle size, CVD temperature, preparation procedure of the particle etc. However, we confirmed that SWNTs were grown from the particles with the root-growth mode and that their diameters were directly influenced by the particle size. These results showed the possibility of top-down control of SWNT characteristics.

\*M. Ishida et. al., Jpn. J. Appl. Phys. 43 (2004) L1356.

## Organic Functionalization of Carbon Nanotubes: Synthesis and Applications

*Maurizio Prato*

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Carbon nanotubes (CNT) are of great interest due to their unique electronic, chemical, and mechanical properties for creating new generation electronic devices and networks. Advances in production processes have resulted in obtaining CNT with high structural perfection: relatively large amounts can now be produced of either single-walled carbon nanotubes (SWNT), or multi-walled carbon nanotubes (MWNTs). However, high molecular weights and strong intertube forces keep CNT together in bundles, making their manipulation, characterization and analytical investigation very difficult. The organic functionalization offers the great advantage of producing soluble and easy-to-handle CNT. As a consequence, compatibility of CNT with other materials, such as polymers, is expected to improve. In addition, once properly functionalized, CNT become soluble in many solvents, so that their solution properties can be studied. Many functionalized carbon nanotubes may find useful applications in the field of materials science and technology. Also in medicinal chemistry carbon nanotubes are set to play an important role. Their use as drug delivery scaffolds and substrates for vaccines has been already demonstrated. Within this contribution, we will review our most recent achievements in the field of synthesis of functionalized carbon nanotubes and their applications in materials science and medicinal chemistry.

**Tues. Invited talk**

*Alan Windl* (abstract not received)

## Optical and Transport Properties of Carbon Nanotubes

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Carbon nanotubes (CNTs) have remarkable optical and transport properties, with important implications for technology. They have extraordinarily high electron and hole mobilities at low fields, although the mobility saturates at high fields. We calculate the electron-phonon scattering and binding in CNTs, within a tight binding model, and calculate mobility using a multi-band Boltzmann treatment [1]. Our results for mobility as a function of temperature, electric field, and nanotube chirality can be captured by a few simple equations, to provide a broad overview of the transport. The optical properties are also unusual, being dominated by excitons even at room temperature, with binding energies and oscillator strengths that are orders of magnitude larger than those in conventional semiconductors. We find simple scaling relationships for the exciton size, oscillator strength, and binding energy as a function of the tube radius, chirality, and the dielectric constant of the embedding material [2]. For the optical absorption, we find a phonon sideband 200 meV about the zero-phonon line, which provides a signature of the excitonic character [3]. Finally, we calculate the exciton radiative lifetime, which in turn determines the efficiency. We predict an unusual nonmonotonic temperature dependence, due to optically inactive exciton bands below the optically active exciton.

### References

- [1] V. Perebeinos, J. Tersoff, and Ph. Avouris, Phys. Rev. Lett. 94, 086802 (2005).
- [2] V. Perebeinos, J. Tersoff, and Ph. Avouris, Phys. Rev. Lett. 92, 257402 (2004).
- [3] V. Perebeinos, J. Tersoff, and Ph. Avouris, Phys. Rev. Lett. 94, 027402 (2005).

## A Strategy to Select Metallic or Semiconducting Carbon Nanotubes from Their Mixtures

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Carbon nanotubes have played an important role in leading the nanoscience and nanotechnology due to their peculiar one-dimensional characteristics and potential applicabilities in various areas. One important feature is its peculiar electronic structure that can be metallic and semiconducting depending on the chirality and diameter of nanotubes. Up to now, it has not been possible to control the chirality of nanotubes systematically by the conventional synthesis approaches such as arc discharge, laser ablation, and (high-pressure) chemical vapor deposition methods. Both metallic and semiconducting nanotubes coexist in the grown sample, which often hinders device applications with high performance. For instance, application to nanoscale transistors and memories requires nanotubes to be semiconducting for clear gate modulation. Therefore, tailoring the metallicity of nanotubes is highly desired.

One approach is to transform the electronic structures by functionalization using gas adsorbates. We will introduce simple gases such as fluorine and hydrogen gases to transform electronic structures from metallic to semiconducting.[1,2]

Another approach is to select either metallic or semiconducting nanotubes from their mixtures. Several methods of selecting semiconducting nanotubes from metallic ones or vice versa using dielectrophoresis, octadecylamine (ODA), bromination, and DNA have been reported. Our aim is to select semiconducting nanotubes from metallic ones in large quantity with high yield and more importantly without affecting nanotube properties so that the separated nanotubes could be used directly for various applications.

We have found a method for a selective removal of metallic single-walled carbon nanotubes from semiconducting ones by stirring SWNT powder in tetramethylene sulfone (TMS)/chloroform solution with nitronium hexafluoro-antimonate ( $\text{NO}_2\text{SbF}_6$ : NHFA) and tetrafluoroborate ( $\text{NO}_2\text{BF}_4$ : NTFB). Positively charged nitronium ions ( $\text{NO}_2^+$ ) were intercalated into nanotube bundles, where the intercalation was promoted also by the counter ions. Nitronium ions selectively attacked the sidewall of the metallic SWNTs due to the abundant presence of electron density at the Fermi level, thus yielding stronger binding energy compared to the counterpart semiconducting SWNTs. The semiconducting SWNTs were left on the filter after filtration, whereas the metallic SWNTs were disintegrated and drained away as amorphous carbons. The effectiveness of selectivity was confirmed by the resonant Raman spectra and absorption spectra.[3] Some other ideas of removing zigzag nanotubes by carbon dioxide gas will be also discussed.[4]

[1] K. H. An et al., Amer. Chem. Soc. 125, 3507 (2003); K. H. An et al., Appl. Phys. Lett. 80, 4235; K. A. Park et al., Phys. Rev. B 68, 045429 (2003).

[2] K. S. Kim et al. Adv. Mat. 14, 181 (2002); K. A. Park et al., . Phys. Chem.B, to be published.

[3] K. H. An et al. J. Amer. Chem. Soc. 127, 5196 (2005).

[4] K. Y. Seo et al., J. Amer. Chem. Soc. Comm. 125, 13946 (2003).

## **Influence of Length on Cytotoxicity of Multi-Walled Carbon Nanotubes against Human Acute Monocytic Leukemia Cell Line THP-1 *in Vitro* and Subcutaneous Tissue of Rats *in Vivo***

Yoshinori Sato<sup>1</sup>, Atsuro Yokoyama<sup>2</sup>, Ken-ichiro Shibata<sup>2</sup>, Yuki Akimoto<sup>1</sup>, Shin-ichi Ogino<sup>1</sup>, Yoshinobu Nodasaka<sup>2</sup>, Takao Kohgo<sup>2</sup>, Kazuchika Tamura<sup>2</sup>, Tsukasa Akasaka<sup>2</sup>, Motohiro Uo<sup>2</sup>, Kenich Motomiya<sup>1</sup>, Balachandran Jeyadevan<sup>1</sup>, Mikio Ishiguro<sup>3</sup>, Rikizo Hatakeyama<sup>4</sup>, Fumio Watar<sup>2</sup>, and Kazuyuki Tohji<sup>1</sup>

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Carbon nanotubes (CNTs) are single- or multi-cylindrical graphene structures that possess diameters of a few nanometers, while the length can be up to a few micrometers. These could have unusual toxicological properties, in that they share intermediate morphological characteristics of both fibers and nanoparticles. Here, we investigated the activation of the human acute monocytic leukemia cell line THP-1 *in vitro* and the response in subcutaneous tissue *in vivo* to CNTs of different lengths. We used 220 nm and 825 nm long CNT samples for testing, referred to as "220-CNTs" and "825-CNTs", respectively. 220-CNTs and 825-CNTs induced human monocytes *in vitro*, although the activity was significantly lower than that of microbial lipopeptide and lipopolysaccharide, and no activity appeared following variation in the length of CNTs. On the other hand, the degree of inflammatory response in subcutaneous tissue in rats around the 220-CNTs was slight in comparison with that around the 825-CNTs. These results indicated that the degree of inflammation around 825-CNTs was stronger than that around 220-CNTs since macrophages could envelop 220-CNTs more readily than 825-CNTs. However, no severe inflammatory response such as necrosis, degeneration or neutrophil infiltration *in vivo* was observed around both CNTs examined throughout the experimental period.

## Reference standard for carbonaceous impurity measurements in carbon nanotubes

*Pavel Nikolaev, Sivaram Arepalli*

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Near-infrared spectroscopy is a convenient tool for measuring nanotube / non-tubular carbon impurities ratios in carbon nanotube samples<sup>1</sup>. These measurements are based on separation of contributions from nanotubes and impurities to the near-infrared absorption. In the current work we produced a reference standard for NIR measurements using purified laser nanotubes. The sample was oxidized slowly in a thermal gravimetry analyzer (TGA) in 2 % oxygen atmosphere. In these conditions, the sample oxidized in several steps, which were attributed to carbonaceous impurities, nanotubes and graphitic shells based on TEM and Raman observations. Stopping oxidation at 625 °C (this temperature is sample-specific) allowed us to produce a sample with well-defined ratio of nanotubes, graphite and metal catalyst. Since carbonaceous impurities no longer glue nanotubes and particles together, further dispersion and centrifuging allowed us to remove particles (verified by IC P-MS) and produce pure nanotube sample. This sample was used as a reference standard to determine relative contributions of nanotubes and impurities to NIR absorption in p-plasmon background and Van-Hove peak areas. We will also discuss a refinement of this technique for samples with varying diameter distributions, that takes into account energy dependence of absorption.

1. M. E. Itkis, et al. Nano Lett, 3, 309 (2003)

## **Magnetic properties of metal phosphide nanoparticles periodically inserted in carbon nanotubes**

*Vincent Jourdain (a), John Robertson (a), Ed Simpson (b), Takeshi Kasama (b), Rafal Dunin-Borkowski (b), Matthieu Paillet (c), Philippe Poncharal (c), Ahmed Zahab (c), Patrick Bernier (c), Etienne Snoeck (d), Annick Loiseau (e)*

- (a) Department of Engineering, University of Cambridge,
  - (b) Department of Materials Science, University of Cambridge,
  - (c) GDPC, Université Montpellier II,
  - (d) CEMES, Toulouse, France,
  - (e) LEM, CNRS-ONERA, Châtillon, France
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Understanding the growth mechanism of carbon nanotubes and controlling their morphology and insertion still remain important challenges. The possibility to fill their inner channel with foreign materials also opens the way to the design of new hybrid materials with novel or enhanced properties, in terms of electron charge/spin transport or magnetic storage. We showed that the use of phosphorus as a co-catalyst enables to modify the kinetic equilibrium between the growth elementary steps of multiwall nanotubes (MWNT) and to induce a mechanism of sequential catalytic growth. Such a mechanism produces nanotube-based filaments periodically inserted with catalyst nanoparticles. The periodically inserted nanoparticles are nickel, cobalt or iron phosphides. We will present our work devoted to the control of the magnetic properties of the inserted metal phosphide nanoparticles and their characterisation by local techniques (MFM and electron holography).

## **Mass Production, Applications and Structural Controllability of Carbon Nanotubes by Catalytic CVD (CCVD) Method**

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Multi walled carbon nanotubes (MWNTs) have been successfully produced by large-scale production system based on CVD method using Fe catalyst [1,2]. The diameters are in the range of several 10 nm or less and have provided different mechanical as well as electronic properties than those of conventional carbons. The commercially available NT's have been applied and contributing to lithium ion battery technology, sporting goods, NT based carbon composite for advanced audio speaker cones. It is also expected to be applied as a micro-catheter (inner diameter 0.43mm, outer diameter 0.53mm) made by resin/high-purity NT composite with enhanced mechanical properties (easier to handle) and extremely reduced thrombogenicity [3]. Based on the present CCVD process, controllable growth of double-walled carbon nanotubes (DWNTs) has been established, because it is expected that DWNTs are expected to have striking new electronic and mechanical properties, which is also very promising for specified applications. Here, we fabricate a paper-like material that consists of hexagonally packed bundles of clean, coaxial carbon nanotubes whose double walls vary little in diameter [1,2,4]. Also demonstrated are the coalescence of DWNTs [5], and a novel structure consisting of flattened tubules containing two SWNTs (bicable) [5].

It is envisaged that carbon nanotubes will take an important place in the development of emerging technologies in near future.

The author would like to thank Prof. M.S.Dresselhaus, Prof. M.Terrones, Prof. H.W.Kroto and Drs. Hayashi, Y.A.Kim for their helpful discussion and collaboration.

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Wed. Invited talk

## **The Nano Carbon ; Potential and Practical applications with business models**

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Since back in 1993, I have been working on various types of nano carbons' commercialization from mass production to applications. In NT05, several types of nano carbons shall be introduced with world producers, capacities, target applications etc. Out of these nano carbons, Endo-Tube (Multi wall carbon nano tube) is my main focus for industrial applications. Metal composites, rubber composites, resins, ceramics and so on with Endo-Tube shall be introduced with the properties improved by Endo-Tube. Also business models shall be introduced. Several key factors to succeed in business will be discussed. People, products, money and IP strategies must be well balanced, and how to expand network are introduced. I do hope my introduction focusing on nano carbon application development in NT05 rings your bell to come up with new ideas, that leads us to contribute to our society.

## Field Emission Display: a good application for carbon nano tubes

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The exceptional properties of CNT as electron emitters [1] have triggered since the end of the nineties a growing interest to use it in devices like field emission displays (FED). Considering the other leading display technologies, the large size (40 inches diagonal) flat TV market is the most attractive one to introduce a new technology. Thus as a requirement the emerging CNT FED technology must be better in quality and at a lower cost than existing technologies. To handle such requirements most of the leading display companies develop a low cost approach which is based on printing techniques [2]. In that case, CNT are localised after growth onto the device by using some paste which allows to localise and to connect the CNT with the device structure. While attractive this technology leads to limited display performances.

At LETI direct growth of the CNT onto the device is done by using a CVD process [3]. This kind of technology prefigures future integration of CNT for more complex electronic applications.

The purpose of this paper is to discuss why this approach which uses bottom up and self organisation is able to meet both the cost and quality requirements. Our last results will help to present how far from the target we are and to outline the directions where more basic work is needed in order that our future TV display will integrate few milligrams of this dreaming CNT material.

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[3] J. Dijon, C. Bridoux, A. Fournier, F. Geffraye, T. Goislard De Monsabert, B. Montmayeul, M. Levis, D. Sarrasin, R. Meyer, K. A Dean, B. F. Coll, S. Johnson, C. Hagen, J. Jaskie. Journal of the SID 12/4 2004, 373-378

## Application of carbon nanotubes to the field emission display

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Field emission display (FED) having carbon nanotube (CNT) emitters has been fabricated for several years in Samsung [1]. The phase shift from metal electron emitter to CNT has given us great success not only in the business field, but also in the academic field. In this presentation, the parameters to enhance field emission property of CNT will be discussed. We will also describe secondary electron emission and photoemission property of CNT incorporated with MgO and CsI.

The study and precise control of CNTs in the form of paste and CVD grown thin films gave us much information to use CNTs as a better electron emitter. Four components in CNT paste are CNT, frit, filler, and vehicle [2]. The pretreatment of CNT, using proper frit and vehicle, and modifying frit resulted in 10 times larger emission current and half value of operating bias. The CNTs are also directly grown on the FED structure by CVD method. The emission properties of CVD grown multiwalled CNT are similar with those of physically synthesized single wall CNTs.

### References:

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- [2] W.A. De Heer, A. Chatelain, and D. Ugarte, Science **270**, 1179 (1995).

## Current-Induced Permanent Bend in Carbon Nanotubes

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Carbon nanotubes are nanometer wide cylinders with extraordinary mechanical properties and unique electronic properties, and thus promising building blocks for nanosized electronic and electromechanical devices. For realization of these nanotube devices, a well-controlled process of plastic deformation of individual nanotubes is crucial. Substitution of hexagons by pentagons and heptagons is known to cause a permanent bend in the tube. We have explored a process for inducing the permanent bend in a straight nanotube by adopting a current flow as the energetic perturbation. Nanotubes examined were double-walled ones. An individual nanotube was manipulated using a nanomanipulator system installed in a transmission electron microscope. By introducing current to a nanotube elastically bent under mechanical duress we achieved to induce a permanent bend of plastic deformation in the originally straight nanotube. The most bending angles are between 20° and 30°, which are formed by the insertion of pentagon-heptagon pairs in a nanotube. The onset of the plastic deformation, which is measured by the circumference-density of current, is more than twenty times smaller than that of the sublimation. The onset decreases with increasing the diameter of nanotubes and the energy of the electron beam used in the transmission electron microscope.

## Unperturbed Optical Transition Energies in Carbon Nanotubes

*Yan Yin<sup>1</sup>, Stephen Cronin<sup>2</sup>, Andrew Walsh<sup>1</sup>, Alexander Stolyarov<sup>2</sup>, Michael Tinkham<sup>2</sup>, Anthony Vamivakas<sup>3</sup>, Wolfgang Bacsa<sup>3,4</sup>, M. Selim Ünlü<sup>3,1</sup>, Bennett B Goldberg<sup>1,3</sup> and Anna K. Swan<sup>3</sup>,*

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We have measured the resonance Raman excitation profiles on individual and isolated semiconducting single wall carbon nanotubes suspended in air. We find that the previously measured ES<sub>22</sub> optical transitions from nanotubes in surfactants are blue shifted 70-90 meV with respects to our measurements of nanotubes in air, despite the larger surrounding dielectric constant in solution. This surprising result implies that the energy contribution from exciton binding is larger than from band-gap renormalization, in contradiction to current theoretical understanding, which predicts that the Coulomb driven exchange interaction gives rise to a large increase of the band gap energy counteracted by a somewhat smaller exciton binding energy shift (1,2).

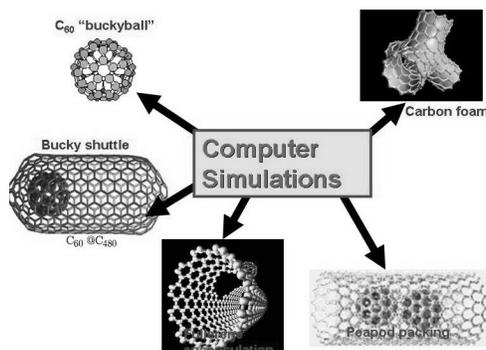
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## Solving Nanotube Puzzles on a Supercomputer

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The quantum nature of phenomena, which underlies the behavior of nanotubes and other nanostructures, raises new challenges when trying to predict their physical behavior. Due to the unavoidable influence of the measurement process on the result in the quantum regime, predictive calculations on high-performance computers have emerged as a powerful research tool complementing experimental observations.

In this presentation, I will review recent computer simulations, which shed light onto some of the puzzling behavior observed in nanotubes and related carbon nanostructures [1]. Due to the stability of the  $sp^2$  bond, carbon fullerenes and nanotubes are thermally and mechanically extremely stable and chemically inert. They contract rather than expand at high temperatures, and are unparalleled thermal conductors. Nanotubes may turn into ballistic electron conductors or semiconductors, and even acquire a permanent magnetic moment. In nanostructures that form during a hierarchical self-assembly process, even defects may play a different, often helpful role.  $sp^2$  bonded nanostructures may change their shape globally by a sequence of bond rotations, which turn out to be intriguing multi-step processes. At elevated temperatures or following photo-excitation, efficient self-healing processes may repair defects, thus answering an important concern of molecular electronics.



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## Structure and vibrations of the same individual single-walled carbon nanotube

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Despite the large number of prior works devoted to Raman scattering in nanotubes, there are still answers about the Raman response of individual metallic and semiconducting isolated single-walled carbon nanotubes (SWNT). Up to now, the Raman response of an isolated SWNT has been mainly understood in the framework of different modelizations of the electronic and vibrational features. By contrast, the ultimate goal of our "complete experimental" approach is to relate the Raman response of an individual SWNT to its (n,m) structure determined from an independent way. In this aim a procedure including the preparation of substrates, the sample preparation, atomic force microscopy imaging (AFM), transmission electronic microscopy (TEM), electronic diffraction and Raman spectroscopy experiments has been developed. The following results can be pointed out:

1) A comparison between the Raman spectra measured on well characterized thin bundles and isolated tubes clearly highlights the dependence of the profile of the TM of metallic tubes with the size of the bundles. We state that the observation of a Breit-Wigner-Fano component in the profile of the the tangential modes is an intrinsic feature of metallic SWNT bundles, this latter component vanishing in the Raman response of an individual metallic tube.

2) We demonstrate the determination of the structural indices (n,m) by electron diffraction and of the frequencies of the vibrational modes by Raman spectroscopy on the very same single nanotube. The precise and independent determination of both structure and frequencies allows for direct and unambiguous verification of molecular dynamical calculations. The relation between diameter (d) and the radial breathing mode frequency (nRBM) is thus determined in a direct way. It is found to be close of  $nRBM = 273 \text{ (cm}^{-1} \text{ nm)}/d$ . The pre-factor of this expression is significantly higher than that predicted in different modelizations. The accuracy of this relation is discussed. On the other hand, the profile of the tangential modes with the respect to the structure of the tube is reported and discussed in relation with previous modelizations. Finally, some clarifications of the resonant process involved in the Raman scattering from SWNTs are shown.

**Acknowledgements:** This study has been performed in complete and tight collaboration with M. Paillet (Laboratoire des Colloïdes, Verres et Nanomatériaux, Montpellier) and J.C. Meyer (Max Plank Institut of Stuttgart).

## **Optical Detection of the Aharonov-Bohm Phase in Carbon Nanotubes in Ultrahigh Magnetic Fields**

*Junichiro Kono*

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Abstract: This talk will describe our recent magneto-optical studies of micelle-suspended single-walled carbon nanotubes in aqueous solutions. Using magneto-absorption, magneto-photoluminescence, and magneto-photoluminescence-excitation spectroscopies in ultrahigh magnetic fields, we have detected optical signatures of the Aharonov-Bohm effect [1] (predicted more than 10 years ago by Ajiki and Ando [2]) and determined the magnetic susceptibility anisotropy of semiconducting nanotubes [3].

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3. S. Zaric et al., Nano Lett. 4, 2219 (2004).

## **New Approaches to Optical Characterization of Single-Walled Carbon Nanotubes**

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Two recent advances in the application of laser-based techniques to characterize the fundamental optical properties of single-walled carbon nanotubes (SWNTs) will be presented. The first concerns the determination of the strength of the excitonic interactions in SWNTs. Recent theoretical treatments of the excited states in SWNTs predict that strong electron-hole interactions yield excitons with large binding energies and that the optical resonances in absorption and emission correspond to excitonic transitions. A direct determination of the exciton binding energy has, however, been lacking. Here we show how the distinct selection rules for two-photon spectroscopy allow us to identify the excited states of the SWNT excitons and to deduce thereby exciton binding energies [1]. Values as large as 400 meV are obtained, corresponding to a significant appreciable fraction of the SWNT band-gap energy. The second topic involves a new and general approach to the optical spectroscopy of individual SWNTs. The method is that of elastic or Rayleigh light scattering [2]. The scattering cross-section as a function of photon energy exhibits resonances for any optical transition, whether in a metallic or semiconducting tube. Applications to examine tube-tube interactions, polarization effects, and changes in SWNT structure along the tube axis will be presented.

[1] F. Wang, G. Dukovic, L. E. Brus, and T. F. Heinz, *Science* 308, 838 (2005).

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## Mobility of native and electron-irradiation-induced point defects in carbon nanotubes

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Understanding the mechanism of point defect production and migration in carbon nanotubes is important for the complete comprehension of the nanotube growth and electron irradiation-stimulated transformations in nanotubes, e.g., welding and coalescence. We study the behavior of carbon nanotubes under high-energy (300 keV) electron irradiation both experimentally and theoretically. We show that multi-walled nanotubes shrink by a loss of atoms from the inner shells of the tube and by diffusion of interstitials in the axial direction through the inner hollow of the tube. Thus, experimental evidence is given that nanotubes can act as nanoscale pipes for the transport of atoms. We further study the details of defect production under electron irradiation and the annealing of single vacancies and interstitials via migration and mutual annihilation. We demonstrate that the electron threshold energy for displacing carbon atoms and the defect production rate strongly depend on the diameter of the nanotubes. We also address the effect of nanotube atomic network curvature on the defect migration.

## **Molecular Dynamics Simulations of the mechanical and electronic properties of nanotubes**

*G. Seifert, V. Ivanovskaya, N. Ranjan, Th. Heine*

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Density Functional based (DFTB) Molecular Dynamics (MD) simulations were carried out to examine the mechanical and electronic properties of nanotubes under axial elongation. The mechanism of breaking tubes at finite temperatures were studied. Likewise, the electronic properties, including electronic transport, during the stretching process were investigated. As examples, armchair and zigzag Carbon and molybdenum disulfide nanotubes were chosen. The results are compared with corresponding experimental data.

## Evidence for Luttinger-Liquid Behavior in Crossed Metallic Single-Wall Nanotubes

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Transport measurements through crossed metallic single-wall nanotubes are presented. We observe a zero-bias anomaly in one tube which is suppressed by a current flowing through the other nanotube. These results are compared with a Luttinger-liquid model which takes into account electrostatic tube-tube coupling together with crossing-induced backscattering processes. Explicit solution of a simplified model is able to describe qualitatively the observed experimental data with only one adjustable parameter.

**Fri. Keynote talk**

*Paul L. McEuen* (abstract not received)

## **Single-walled Carbon Nanotubes Transporters: Generality, Mechanism, Functionality and Exploitation of Intrinsic Properties**

*Nadine Wong Shi Kam and Hongjie Dai*

Department of Chemistry, Stanford University, Stanford, CA.

The ability of single walled carbon nanotubes (SWNTs) to act as molecular transporters that are able to cross the cellular membrane is reported. Covalent and non-covalent techniques are employed to yield SWNTs conjugates with a variety of proteins. It is observed that SWNTs are able to carry proteins (MW <80 kD) across the cellular membrane. Once released from the endosomal compartments, the functionality of the internalized cargo is assessed. We report that cytochrome-c transported inside cells via the SWNT transporter induces apoptosis, a cell death pathway. Cells that are exposed to the cytochrome-c itself (no SWNTs) do not exhibit any significant decline in cell viability. The cytotoxicity of the SWNTs themselves is minimal, with cell viability and proliferation observed in cells exposed to SWNT conjugate being comparable to control, untreated cells. Current studies are underway to verify endocytosis as the internalization pathway in order to pinpoint the mechanism of entry as either through clathrin-coated pits or lipid rafts. SWNTs are emerging as a new class of molecular transporters for various biological cargos, with no apparent cytotoxic effects or disruption of the inherent biological functionality of the cargo after internalization. Exploiting the intrinsic physical properties of SWNTs in-vitro and the development of novel functionalization schemes to achieve selective internalization are also of interest and hold many promises for the application of SWNTs in drug delivery, protein delivery and gene therapy.

## **Large-scale synthesis of DWCNTs and their high field emission properties**

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We have studied large-scale synthesis and characterization of high-quality double-walled carbon nanotubes (DWCNTs) using a catalytic chemical vapor deposition method and a hydrogen arc discharge method. For the synthesis of DWCNTs using a catalytic CVD method, we used various carbon containing molecules such as methane, THF and propanol over Fe-Mo embedded MgO support material. The produced carbon filaments indicated high-purity DWCNTs free of amorphous carbon on the surface. The diameters of DWCNTs were dependent on process conditions, carbon sources and support materials. In this work, DWCNTs by methane indicated smaller diameters compared with DWCNTs by THF or propanol. By adopting a hydrogen arc discharge method, we could obtain high-purity DWCNTs in large-scale. In this work, we used FeS promoter and Fe catalyst to synthesize DWCNTs effectively. The purity and yield of produced DWCNTs by arc discharge were mainly dependent on catalyst concentration and reaction pressure. Transmission electron microscopy, Raman analysis and TGA showed that produced carbon materials had low defect level in the atomic carbon structure, indicating the synthesis of high-quality DWCNTs. We have evaluated field emission from DWCNTs. According to our experimental results, DWCNTs showed low turn-on voltage similar to SWCNTs and higher emission stability than that of SWCNTs. Interestingly, field emission performance from DWCNTs largely was dependent on the diameter of nanotube.

## Electrical generation and absorption of phonons in carbon nanotubes using STM

*Brian LeRoy*

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We have performed low temperature scanning tunneling spectroscopy on individual single-wall carbon nanotubes freely suspended over trenches. Spatially resolved spectroscopy shows a Coulomb-staircase behavior superimposed on the local density of states [1]. In addition to the Coulomb peaks from the addition of electrons, side peaks appear due to phonon-assisted tunneling [2]. Electrons inelastically tunneling into the nanotube cause a non-equilibrium phonon occupation, leading to both emission and absorption of phonons by successive tunneling electrons. The addition of a gate electrode into our STM configuration[3] allows further validation of this interpretation. These observations represent a new class of electrical transport phenomena, namely a current induced non-equilibrium phonon distribution and its influence on transport through a molecule.

### References:

- [1] LeRoy et al., Appl. Phys. Lett. 84, 4280 (2004)
- [2] LeRoy et al., Nature 432, 371 (2004)
- [3] Kong et al., Appl. Phys. Lett. 86, 112106 (2005)

## A Three Terminal Carbon Nanotube Relay

*S.W. Lee*<sub>1</sub>, *M. Sveningsson*<sub>2</sub>, *Y.W. Park*<sub>1</sub>, *E.E.B. Campbell*<sub>2</sub>

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A carbon nanotube nanorelay has been fabricated. A freely hanging MWNT is attached to a source electrode. By applying a voltage to a gate electrode situated below the nanotube, the nanotube is induced to bend until it makes contact with a drain electrode [1]. The operating characteristics will be described and compared with theoretical predictions. Two operating modes have been studied. The first, "contact mode", requires physical contact between the nanotube and the drain electrode and shows hysteretic behaviour. The second "non-contact" mode uses field emission to make electrical contact between the nanotube and the drain. In this case we observe a self-annealing behaviour at the source electrode on operation and the hysteresis is suppressed.

## Shot noise and electron-phonon coupling in carbon nanotubes

*Fan Wu<sup>1</sup>, Taku Tsuneta<sup>1</sup>, Mikko Paalanen<sup>1</sup>, Taihong Wang<sup>2</sup>, and Pertti Hakonen<sup>1</sup>*

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We have investigated shot noise in individual SWNTs and MWNTs at 4.2 K over the frequency range 650 - 850 MHz. At small currents, our SWNT samples display a Fano-factor of  $F \sim 1$ , reminiscent of a single tunnel junction behavior. At large bias, we observe a strong reduction in the Fano factor both in SWNTs and MWNTs. Using the theory by Nagaev, we may interpret this noise suppression as originating from inelastic processes caused by electron-phonon scattering, both due to acoustic and optical phonons. We find that the electron-phonon scattering length in a SWNT decreases rapidly above 0.1 V and it is about 5 nm at a bias of 0.5 V. In disordered MWNTs, we observe a Fano-factor of  $\sim 0.1$ , clearly less than expected for diffusive conductors.

## **Physical mechanism for the mechanical reinforcement in nanotube-polymer composite materials**

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The significant increase in the Young's modulus of nanotube-polymer composites is often correlated with the formation of a crystalline layer of polymers surrounding the nanotubes. Although the improved stress transfer between the stiffer nanotube and the softer polymer matrix has been attributed to the presence of this ordered polymeric layer, the actual mechanism for this stress transfer is unclear. To clarify this matter, we model the polymer-nanotube composite by harmonic chains interacting with a rigid periodic potential, an extension of the so-called Frenkel-Kontorova model. We identify the origin of the reinforcement with the occurrence of a templating transition, in which polymers are constrained by the periodic potential of the underlying nanotube. The model points to the existence of a suitable combination of polymers and nanotube diameters to maximally enhance the mechanical properties of composite structures. The model is tested against experimental data.

# *Abstracts for Poster Session*

## Posters

Poster abstracts are listed from page XX, and are identified according to a sorting category given below.

Posters in categories I-VIII will be presented in Session A (Monday and Tuesday).

Posters in categories IX-XXI will be presented in Session B (Thursday and Friday).

- I. CVD Synthesis of Carbon Nanotubes
- II. Non-CVD Synthesis of Nanotubes
- III. Formation and Characterization of Unusual Nanostructures
- IV. Raman Characterization of Nanotubes
- V. Other Characterization of Nanotubes
- VI. Nanotube Dispersion and Purification
- VII. Chemical Modification of Nanotubes
- VIII. Non-Carbon Nanotubes
- IX. Nanotube-Based Composites
- X. Morphology and Application of Modified Nanotubes
- XI. Photo-Induced Reactions in Nanotubes
- XII. Thermal and Mechanical Properties of Nanotubes
- XIII. Atomic Structure of Carbon Nanotubes
- XIV. Transport in Nanotubes
- XV. Field Electron Emission
- XVI. Optical Properties and Optoelectronics
- XVII. Transport in Complex Nanostructures
- XVIII. Electron-Phonon Coupling in Complex Nanostructures
- XIX. Nanotube-Based Transistors
- XX. Magneto-Transport and Magnetism
- XXI. General Studies of Carbon Nanostructures

## Nucleation of single-walled carbon nanotubes on catalyst particles: MD and electronic structure calculations

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Metal catalyzed single-walled carbon nanotube (SWNT) nucleation was studied by classical molecular dynamics (MD) and electronic structure theory. The simulations revealed the atomic-level mechanism for SWNT nucleation on metal catalyst particles. The SWNTs nucleate between 800 K and 1400 K, [1] which is the same temperature interval used for chemical vapor deposition (CCVD) experiments. Also, in agreement with experimental results the nucleated SWNT has same diameter with the catalyst particle [2]. The studies also show that a highly supersaturated carbon concentration in the catalyst particle is needed to initiate the nucleation process. [1] Based on the simulations a detailed Vapor-Liquid-Solid (VLS) growth model was developed for both liquid and solid catalyst particles. [1, 3] Furthermore, MD and electronic structure theory studies indicate that the catalyst particle must be able to maintain an open end of the growing SWNT in order to be suitable for growth.

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## The influence of different metal underlayers on vertically aligned carbon nanofibers grown from Ni dots by PE-CVD

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Growth of carbon nanotubes on metal electrodes constitutes one of the important issues for electronic devices manufacturing. The future development of such technology will rely to a large extent on the ability to grow the nanotubes directly on devices and to achieve good electrical contact between the nanotube and electrodes. Vertically aligned carbon nanofibers (VACNFs) represent a kind of carbon nanotubes whose growth can be very easily controlled by plasma enhanced chemical vapor deposition. Therefore they represent good candidates for developing CNT-based nanodevice production. This work is focused on growing these nanostructures on nickel (Ni) patterned substrates where metal underlayers were pre-deposited on SiO<sub>2</sub>. Recently, we have performed a thorough study [1] of VACNFs growth on unpatterned substrates when a thin intermediate Si layer was deposited between the Ni catalyst layer and the metal underlayer film. We observed that the Si/metal interaction occurring during growth plays a vital role in nanostructure formation for metals such as: W, Mo, Pt, Pd. The growth of VACNF on metal underlayers such as Ti, Cr is still under investigation.

Electron beam lithography was used to fabricate Ni dots. Preliminary results show that individual VACNFs grew from 50 nm dots and their diameter changed depending on the dose modulation of the electron beam used at the initial stage of pattern fabrication. For 100 nm dots, the Ni catalyst tends to split into several islands resulting in the growth of more than one nanofiber. The growth of VACNFs was also investigated for smaller dot sizes (10 and 20nm). Samples were characterized with SEM, TEM and EDX.

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## **Study of encapsulated mechanism of N<sub>2</sub> into central hollow of multiwall carbon nanotube**

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Recent studies have revealed that gaseous molecules can be stored in carbon nanotube (CNT). In the typical process of gas molecule storage, high-pressure gas was introduced after growing nanotube. However, nitrogen molecules could be encapsulated directly in the hollow of carbon nanotube core during the growth procedure. For studying the encapsulated mechanism of nitrogen molecules, we synthesized the tip growth CNT and bottom growth CNT by dc plasma-enhanced chemical vapor deposition and microwave enhanced plasma chemical deposition, respectively. Crystal structure, composition, and electronic structure of nanotubes were investigated using SEM, XPS, and HRTEM equipped with GATAN image filter (GIF). The diagnosis of plasma was carried out with OES. In the case of dc PECVD, Well-crystalline N-CNTs were grown. The distributions of nitrogen atoms and molecules on CNTs were investigated by elementary mapping using GIF and near-edge x-ray absorption fine structure. Based on experimental measurements, we will suggest the direct encapsulation mechanism of nitrogen molecules into the hollows of CNT during the growth process.

## Nanostructure of Boron and Nitrogen incorporated multiwall carbon nanotube

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Boron- and nitrogen-incorporated multiwall carbon nanotubes (BN-MWCNTs) synthesized with the mixture of C<sub>2</sub>H<sub>2</sub>, NH<sub>3</sub>, N<sub>2</sub> and B<sub>2</sub>H<sub>6</sub> by dc plasma-enhanced chemical vapor deposition for 30 min. BN-MWCNTs were vertically aligned on substrate with diameter of ~100 nm and length of ~3 mm. The ratio of components for BN-MWCNT was investigated by x-ray photoelectron spectroscopy (XPS) and by elementary mapping of transmission electron microscopy (TEM) equipped with Gatan image filter (GIF). The estimated ratio of each element from XPS was 0.31 (boron) : 1.0 (carbon) : 0.34 (nitrogen). The images of elementary mapping observed with GIF showed that nitrogen and boron into BN-MWCNTs were uniformly distributed. Typically suggested hexagonally bonded nanostructures such as BCN-I (13B, 21C and 14N) and BCN-II (11B, 24C and 13N) did not coincided with our observations. We suggest the simple model of BC<sub>3</sub>N nanotube, which is deduced by the ratio of elements from core level spectra and fitted spectra and by the distribution of elements from mapping images with GIF. However, suggested model of BCN nanotube needs investigation of theoretical calculation.

## **Growth Mechanism of Carbon Single-Walled Nanotubes on Liquefied Metal Particles**

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There has been much discussion of whether the active catalytic species are in liquid or solid phase during carbon single-walled nanotube (SWNTs) growth. However, the actual phase and its evolution over time still have to be experimentally verified for furthering our understanding on the growth of these fascinating materials. The evolution of a series of Fe and Fe/Mo catalysts during carbon SWNTs growth have been studied using calorimetry, temperature programmed oxidation and Raman measurements. Carbon induced solid-liquid and solid-liquid-solid phase transitions of the nanocatalyst during the synthesis were observed. We found that liquid phase is favourable for the growth of nanotubes, while solidification because of the formation of stable iron carbides, along with the poisoning of the catalyst surface by amorphous carbon, nearly terminates the growth. No growth of SWNTs was observed below the eutectic point, when the catalyst is in solid phase. In the meantime, the presence of Mo decreases the eutectic point of the catalyst and preserves it from the formation of stable carbides during the growth, thereby increasing the yield and quality of the SWNTs. Our results support a growth mechanism of single-walled carbon nanotubes on liquefied catalyst particles.

## **Industrial-Scale Production of Single-Walled Carbon Nanotubes by Catalytic Decomposition Method**

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In order to exploit the unique properties of carbon single-walled nanotubes (SWNTs), it is necessary to realize their large-scale production. Current methods for continuous production of SWNTs allow rates of less than 1 g h<sup>-1</sup>, after purification. We have developed a new technique for industrial production of SWNTs by chemical vapor deposition, with a vertical configuration, using for the first time continual injection of pre-prepared alumina supported iron catalyst powders. The system can run continuously for days at a time. Remarkable high injection rates, up to 30 g h<sup>-1</sup>, with a corresponding production of ~ 6 g h<sup>-1</sup> of high purity (~ 95 wt%) SWNTs, have been achieved even using a small laboratory model. Further, the product has been accumulated in several cyclones connected in series, which appear to separate in situ the SWNTs by synthesis duration. This unique feature of our process opens the opportunity to study SWNTs at an early stage of the growth. The method allows pursuing industrial production rate, up to ~250g/h, after purification, by scaling up the powder injector with the corresponding adjustments of other parameters. The samples were characterized by scanning and transmission electron microscopy, temperature programmed oxidation, and Raman spectroscopy.

## Temperature dependence growth of carbon nanotubes monitored by TEOM

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The most common process of fabrication of carbon nanotubes at industrial scale is chemical vapor deposition (CVD) using metallic catalysts and hydrocarbon as a carbon source. However, the major obstacle confronting the field is being the lack of the detailed understanding of the nanotubes growth mechanism at the very early stage of the process. It is though that such understanding could help for the scaling up of the process. In this contribution, we show that the early growth stage of the multi-walled carbon nanotubes (MWCNTs) can be accurately monitored with Tapered Element Oscillating Microbalance (TEOM). The TEOM setup simulates a packed bed reactor in which the reactive gas flows through the entire length of the sample bed and permits to continuously monitor of the growing process within a very short synthesis duration. The CVD process was done with iron as catalyst supported on a high surface area alumina (40-80 nm size). After impregnation, the solid was oven-dried at 100 °C and then calcined in air at 350 °C for 2 h in order to obtain the oxidic form of the catalyst. The catalyst was placed in weighting pan of the TEOM setup between quartz cotton. The reduction was carried out in situ in flowing hydrogen at 400°C. The CVD was carried out with a mixture of ethane and hydrogen while pure He was used as a contra gas. The influence of the synthesis temperatures on the growth rate and the quality of the carbon nanotubes will be investigated. The structural properties of the as-growth MWCNTS are checked by TEM, SEM and Raman spectroscopy. Preliminary results show that when the temperature increases up to ~ 700 °C, the TEM and SEM micrographs show the microstructure of MWCNTs with the diameter about 5 to 50 nm. In summary TEOM setup seems to be a very efficient setup which allows the continuous and accurate monitoring of the carbon nanotubes growth in a very early stage of the synthesis. The obtained results could allow the greater understanding of the growth stage which was extremely useful for the carbon nanotubes synthesis scaling up.

## **Multi-walled carbon nanotubes growth from silicon- and zeolite-based catalysts for optoelectronic applications**

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During the last decade, an increasing scientific interest was devoted to the study of silicon-based nanodevices for optical applications. The most important properties of these Si-nc was linked to the fact that they are able to exhibit bright photoluminescence at room temperature. However, the well separation and manipulation of these Si-nc remain the great challenge due to their high ability to form aggregates. In the proposed contribution, a new wiring method of Si-nc by multi-walled carbon nanotubes (MWCNTs) is presented and discussed. The MWCNTs were directly grown from the Si-nc catalysts previously coated with different metals such as iron, cobalt and nickel. The Si-nc were synthesized by electrochemical etching as described elsewhere (Cz silicon, p-type boron doped, <111>, 1 Ohm.cm) 3,4. After coating of these Si-nc with a metal salt precursor, the solid was calcined and reduced in situ before starting the CVD process in the presence of a mixture of ethane and hydrogen. The CVD process was followed in an early growth stage using a Tapered Element Oscillating Microbalance (TEOM) allowing the continuous monitoring of the very small weight change as a function of the synthesis duration. This instrument allows us precisely control the MWCNTs deposition on the Si-nc based catalyst. Electron microscopy characterizations (SEM and TEM) carried out on the as-grown samples reveal the formation of a well separated Si-nc wired with MWCNTs. Observations proofs that by using the present synthesis method we are able to establish strong mechanical contacts between the Si-nc and the MWCNTs which in principle can assure proper contacts for optoelectronic applications. The strong mechanical contacts are due to the formation of a thin layer of graphene on the surface of the Si-nc support which significantly improves the manipulation of these nanoparticles. The diameter of the synthesized MWCNTs from the Si-based catalyst was compared with that of MWCNTs grown from the same metallic phase deposited inside the zeolite channel. Results obtained indicate that the MWCNTs grown from the zeolite-based catalysts have a smaller diameter compared to those observed on the Si-based catalysts along with a narrow diameter distribution. Works are ongoing to wire Si-nc on such narrow size MWCNTs for photoluminescence applications.

## Thermophoretic deposition of catalyst clusters for substrate CVD growth of carbon nanotubes

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An efficient thermophoretic precipitator (TP) has been designed, built and utilised for collection of nanometer-sized catalyst particles to grow CNT via the substrate CVD method. Using thermophoretic forces for particle collection the size distribution on substrates may be preserved as in the gas phase. The precipitator employs an electrically heated and water cooling plates. Two different temperature gradients of 2220 K/cm and 2419 K/cm were fixed between plates by changing the applied voltage to the hot element. Fe particles with a mean diameter and a geometric standard deviation of 3.57 nm and 1.40, respectively, were synthesized by physical vapour nucleation method using a hot wire generator. Particles were then used to estimate the thermophoretic deposition efficiency as well as the uniformity of the collection along the TP. A high thermophoretic deposition efficiency of 100 % was attained when the aerosol flow rate was 10 cm<sup>3</sup>/min. When particle collection was carried out on microscope support grids, a gentle and homogeneous deposition of clusters at ambient temperature was achieved. For the synthesis of CNT, Fe particles were deposited thermophoretically on SiO<sub>2</sub> substrates and CO was used as carbon source in the presence of H<sub>2</sub>.

## **Predictions of Preformed Catalyst Cluster Dynamics during SWCNT Nucleation in a Novel Floating Catalyst Method Using a Combined CFD-Aerosol Population Balance Model**

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A Computational Fluid Dynamics (CFD) based polydisperse aerosol population balance model for the behavior of iron catalyst particles up to the initiation of SWCNTs is used to understand cluster dynamics in a novel floating catalyst synthesis method [1]. In the method, preformed catalyst particles are introduced near the centerline of a heated tubular reactor into conditions leading to CNT nucleation and growth. It is found that introduced catalyst particles with diameters capable of catalyzing SWCNTs are stable until CNT initiation under all studied reactor conditions. In particular, it is found that the level of wall and inlet iron vapor concentration does not significantly affect the catalyst particle stability. More rapid diffusion of smaller catalyst particles leads to a radial distribution in mean particle size and a narrowing of the particle size distribution in the reactor core. In conjunction with longer residence times in the CNT growth zone near the reactor walls, smaller diameter but longer CNTs are predicted near the walls than at the centerline. [1] Nasibulin, A. G., Moisala, A., Brown, D. P., Jiang, H. and Kauppinen, E.I. (2005) "A novel aerosol method for single walled carbon nanotube synthesis". *Chemical Physics Letters* 402, 227 - 232.

## Aligned ultralong carbon nanotubes by a novel CVD method on smooth and grooved SiO<sub>2</sub>/Si substrates

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A novel method to synthesize cm long and horizontally aligned carbon nanotubes (CNTs) on SiO<sub>2</sub> is developed by using a chemical vapor deposition (CVD) process. Fe catalyst particles were produced by vaporization with a hot wire generator [1] and deposited on smooth and grooved Si/SiO<sub>2</sub> substrates using a thermophoretic precipitator. Subsequently, the substrates were positioned in the hot zone of the reactor. Before introducing the carbon source (CO), the catalyst particles were heated at 880 °C under H<sub>2</sub> flow for their reduction. In this method, the type of the SiO<sub>2</sub> substrate used has no effect on the synthesis and ultralong CNTs, up to 1 cm, were grown at growth rates as high as 8 μm s<sup>-1</sup>.

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## Large diameter SWCNTs grown on thin holey SiO<sub>2</sub> substrates

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Single walled carbon nanotubes (SWCNT) were synthesized on holey SiO<sub>2</sub> films supported on Ni TEM grids by chemical vapour deposition (CVD). Unlike conventional CVD methods, Fe catalyst particles were formed by physical vapour nucleation [1] and directly deposited on the grids by diffusion inside the reactor or outside using an electrostatic precipitator. In the former case, the substrates were placed in two different zones of the reactor for cluster collection and subsequent growth of the nanotubes. CO was used as carbon source at the furnace temperature of 880 °C. Isolated SWCNTs were produced, with lengths ranging from 10 to 20 µm and diameters around 4-6 nm, as observed directly on the substrates by TEM. Image analysis revealed sudden sharp bends in otherwise straight individual SWCNTs and collisions between SWCNTs (inherent to 2D geometry of the substrate) such that parts of SWCNTs stuck together in a Y-junction manner. This finding implies that the catalyst particle sustains a large mechanical force to the growing SWCNT and that the growth of long SWCNTs can be controlled by the interaction between the catalyst particle and the substrate.

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## DWNTs: Gram-scale Synthesis, Characterisation, Purification and Applications

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Double-walled carbon nanotubes (DWNTs) are at the frontier between single (SWNTs) and multi-walled CNTs (MWNTs). Because they are the MWNTs with the lowest possible number of walls, their structure and properties are both still very similar to those of SWNTs. Any functionalisation, often required to improve the compatibility of CNTs with their external environment (composites) or bring them new properties (solubility, sensors), will partially damage the external wall, resulting in drastic modifications in terms of both electrical and mechanical properties. This is a serious drawback for SWNTs. In the case of DWNTs, the outer wall can be modified (functionalised) while retaining the structure of the inner tube. We report here the gram-scale synthesis of high-quality DWNTs by CCVD [1]. The DWNTs are produced by the catalytic decomposition of methane over a CoMo-MgO catalyst. They are free of amorphous carbon contamination and the use of a MgO support allows its easy removal [2] without damaging the DWNTs. The high purity of the DWNTs has been characterised by different techniques including HRTEM [1], Raman spectroscopy [1, 3], TGA, photoluminescence [4], electron-diffraction [5] and the electrical properties of individual DWNTs have been investigated with or without applied magnetic field (up to 35T) [6, 7]. Further purification by air oxidation has been investigated by in-situ Raman spectroscopy and the results will be presented. These DWNTs being available at the gram-scale, they have been already applied into supercapacitors [8], processing into fibres and composite materials (ceramic or polymer matrix [9-10]). The toxicological aspects of DWNTs have also been investigated recently [11].

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## **LIQUID SOURCE CVD OF FERROMAGNETIC FILLED CARBON NANOTUBES IN A CONTINUOUS PROCESS**

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Carbon nanotubes (CNT) filled with ferromagnetic metals like Fe, Co or Ni represent a very interesting material with different possible uses because of their fascinating properties for example as data storage [1] and also for biomedical applications [2]. For the synthesis of ferromagnetic filled carbon nanotubes the liquid source CVD (LSCVD) [3] is applied. The LSCVD is an optimal method to synthesize ferromagnetic filled carbon nanotubes with defined properties. In addition this deposition method can be realised as a continuous process and is so favourable for a high scale production. In dependence on the deposition conditions vary the length, thickness, structure, filling grade and in terms of the filling grade the magnetic properties of the CNTs. The nanotube material was investigated by transmission electron microscopy (TEM) and Raman spectroscopy especially to characterise the crystalline perfection of the tube-shells. The filling grade was determined by thermal gravimetric analysis (TGA), the ferromagnetic behaviour of the filled nanotube-ensembles on Si-substrates by alternating gradient magnetometry (AGM).

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## Direct evidence for base-growth of carbon nanotubes in multilayer carpets formed by aerosol-assisted Catalytic CVD

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Samples of well aligned multiwall carbon nanotubes (MWNTs) can be formed by aerosol-assisted Catalytic Chemical Vapor Deposition (CCVD) [1,2]. Growth mechanisms of aligned MWNTs in liquid-assisted CVD methods are still discussed [3-5], and no definitive experimental evidence has been carried out. In this study, we demonstrate that sequential synthesis (multi step process) is an effective way to evidence the growth mechanisms. In a given step, the aerosol (toluene/ferrocene) injection in the CVD reactor is controlled through parameters such as duration and composition of precursors. Thus, multilayered carpets of aligned MWNTs were obtained and analysed by SEM and X-Ray scattering to identify the chronology of the growth. Our results demonstrate that nanotubes grow through a base-growth mechanism: any new injection sequence leads to the growth of a new layer directly at the substrate surface, under the pre-existing one by lifting it up. It is confirmed by nuclear microprobe analysis of multilayered carpets obtained from alternative injection of benzene enriched in <sup>13</sup>C isotope labels. We also demonstrate the absolute need of the catalyst source (ferrocene in our study) for the continuous growth of the carpet as well as for the growth of a new carpet at the base of a pre-existing one.

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## **Synthesis of Carbon Nanofibers on the Surface and in the Pores of Modified Activated Carbon**

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Carbon nanotubes or nanofibers have attracted the interest of many researchers because of their extraordinary properties, in particular in chemistry, physics and the area of nanotechnology. Activated carbon is widely used to absorb some unwanted species from drinking water (Mn, As, Hg, Fe). In this work, carbon nanofibers were synthesized successfully on activated carbon by means of chemical vapour decomposition of ethylene. Both TEM and SEM images show that carbon nanofibers were nested inside and immobilized onto the activated carbon. The preliminary results of adsorption dichromate and heteropolymolybdate indicate that the concept that deliberate nanostructuring of a carbon surface can create novel functions of carbon that cannot be achieved alone by providing the adequate surface functional groups to the reactive medium.

## **Single-wall carbon nanotubes synthesized on islanded catalytic film by a single burst of acetylene**

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Carbon nanotubes are considered to be perspective objects to create devices of molecular electronics. Direct synthesis of nanotubes at desirable sites of a sample seems preferable in comparison with deposition of preliminary prepared nanotubes at these sites. Only the chemical vapour deposition (CVD) technique allows to implement it. In our work the technique is developed for a rapid CVD synthesis of carbon nanotubes in a low-pressure atmosphere created by a single short burst of carbon-containing gas. Nanotubes were grown on thin membranes with through-slits to ensure possibilities of the study of nanotube structure in transmission electron microscope. Islanded Fe film consisting from nanoparticles was used as catalyst. The technique ensures the growth of high quality single-wall nanotubes (up to 20  $\mu\text{m}$  in length) in a broad range of synthesis conditions. It is essential that the synthesised nanotubes were very weakly contaminated by amorphous carbon. The influence of the synthesis parameters (temperature, gas pressure, content and thickness of the catalyst and buffer layer) on the concentration and parameters of the nanotubes were studied with the transmission and scanning electron microscopy. Nanotube growth on sub-micron areas patterned by electron beam lithography is demonstrated.

## **Study of Temperature, Time and Catalyst Role in the Fabrication of PECVD Grown Carbon Nanotubes**

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We have successfully grown carbon nanotubes on cobalt coated silicon substrates at a temperature below 800°C Using PECVD method. In this experiment ethylene and nitrogen gases are used as carbon source and diluting gas respectively. A thin film of cobalt layer is used as the catalyst and its critical role in the growth of carbon nanotubes has been studied. Also, the role of temperature is studied as another important factor. SEM micrographs indicate the evolution of nanotubes at a DC-plasma current of 8 mA. At lower currents, however, growth is insignificant. The length of nanotubes depends on the time of deposition and increases with time. Also, the diameter of tubes is a function of the size of the catalyst islands.

## **Influence of the catalyst composition on the growth rate of isolated SWCNTs**

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CVD on patterned surfaces offers the possible advantages in growth of self-organised nanotubes at specific locations. The length mastering of SWCNTs is one of the key stages that it is essential to control, to develop systems containing carbon nanotubes. It is usually observed the growth of SWCNTs by thermal CVD reaches some micrometers per second. This fast growth rate can make very difficult the realization short SWCNTs. Here, we show that, on the base of the same catalytic system, the length of isolated SWCNTs can be easily controlled from a few tens of nanometer up to a millimetre for the same thermodynamic parameters, only by tailoring the catalyst composition. 3 nm-thick nanocomposite films deposited on silicon wafers were prepared by co-evaporation of silicon oxide and iron, or cobalt or nickel. After an appropriate thermal process either pure metal or metal-silicide nanoparticles are precipitated in silica and act as catalyst for the thermal decomposition of methane. Whatever the catalyst composition is, most of the CNTs obtained are single walled, generally isolated and free of amorphous carbon over-coatings. The apparent growth rate of SWCNTS observed on a silicide is smaller of two magnitude orders than the one on a pure metal.

## Effect of particle size in Co-Fe supported on alumina catalyst on the multi-walled carbon nanotubes production

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The influence of the catalyst particle sizes on the multi-walled carbon nanotubes production is here investigated. A cobalt-iron oxide supported on alumina catalyst, having different particle sizes distribution and constant metal loading was prepared. The alumina used as starting material contained the following particle sizes distribution: 48 % of particles showed sizes higher than 63  $\mu\text{m}$ , 44% between 20-63  $\mu\text{m}$  and 8 % lower than 20  $\mu\text{m}$ . The impregnated samples were characterised by X-ray photoelectron spectroscopy (XPS) and X-ray diffraction. (XRD). The MWNT synthesis was carried out in a horizontal quartz reactor at different temperatures (600-800°C), ethylene space time (W/F) of 0.9 g.h/mole and reaction time of 20 minutes. Results show that the optimal reaction temperature for the MWNT production corresponds to 700 °C. Both, MWNTs yield and the reaction effectiveness factor are optimal for the 0-63  $\mu\text{m}$  particle sizes range and decrease for the catalyst contained particle sizes higher than 63  $\mu\text{m}$ . The relative MWNTs yield and reaction effectiveness factors increase in about 2.7 and 2.4, respectively, with respect the catalyst prepared with all particle sizes. XPS measurements indicated that the smaller particles present better Fe surface dispersion than the bigger ones while the Co dispersion increases when increasing particle sizes. Our results suggest that the carbon nanotube formation reaction is highly sensitive to the catalyst particle sizes as well as the metallic surface dispersion and phase composition.

## Freestanding single-walled carbon nanotube formation via diffusion-plasma chemical vapor deposition

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The as grown state control of single-walled carbon nanotubes (SWNTs) is one of the critical issues for full use of their potential abilities in the wide application fields. Especially for the individual SWNTs, the as grown state control is an inevitable factor in order to avoid the bundle-forming caused by the van der Waals attraction. Based on these backgrounds, we attempt the three-dimensional as grown state control for individual SWNTs, i.e. freestanding SWNTs formation using a plasma-enhanced chemical vapor deposition (PECVD) [1]. The PECVD has been known as a powerful method for the individually-, and vertically-aligned multi-walled carbon nanotube formation [2]. When we apply this outstanding benefit to the SWNT production stage, however, high-energy particles in a plasma core region cause the serious damage for tube structure. In order to overcome this disadvantage of the general PECVD, we utilize a plasma diffusion region, where the particle motion is less energetic compared with that in the core region. By using this modified PECVD technique, damage-free and high-purity SWNTs have been successfully produced. Furthermore, most of all the SWNTs grow with freestanding form based on the plasma sheath effect. We also investigate the dependence of the sheath electric field strength on the tube alignment and their metallicity. The details will be presented at the meeting.

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## **MOCVD synthesis, purification and structural characterization of Fe-filled multi-walled carbon nanotubes**

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The vertically aligned Fe-filled multiwall carbon nanotubes (MWCNTs) films 2-3 mm in length are grown on quartz substrates at temperatures ranging from 750 to 9000C by employing the mixture of ferrocene-benzene or ferrocene-toluene in an Ar atmosphere. MWCNTs with outer diameter of 20-120 nm have a metal particle inside and in the tip of the tubes. The purification method consists in several steps including milling, oxidation in air (5000C, during 0,5-1,5 hour) and finally the acid treatment in a concentrated sulfuric acid/nitric acid mixture (3:1 v/v) under refluxing at 1400C during 0,5-1,0 hour. In this work, each step of the purification process was followed by X-ray diffraction, high resolution transmission electron microscopy, Raman spectroscopy and thermogravimetric analysis studies. These analysis methods showed that the MWCNTs had changed appearance after purification. The intershell spacing in MWCNTs increases from 3.41 Å to 3.73 Å as a result of intercalation into the carbon nanotube without breaking the tubular structure. The resulting material are stable in air. The reaction mechanism, structure and morphology of these nanomaterials are discussed. This work was supported by the ISTC project No.2511 and Programs of RAS.

## Control of diameter distribution of SWNTs using the zeolite-CCVD method

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Single-walled carbon nanotubes (SWNTs) have been synthesized on zeolite powder with Fe/Co catalysts by a catalytic chemical alcohol-vapor deposition (CCAVD). We used a cold wall reactor [1] at atmospheric pressure. The reactor system was then modified: radio-frequency heating was used for zeolite CCAVD [2]. The G/D ratio (~25), estimated by analysis of Raman spectroscopy, obtained here is equivalent to that by the conventional CCAVD method under reduced pressure [3], indicating the high purity of the present specimen. The estimated diameter distributions of the SWNTs obtained at synthesis temperatures of 1173, 1273 K and constant ethanol temperature of 273 K are 0.9-1.8 and 1.2-2.2 nm, respectively, whereas that of synthesized at synthesis temperature of 1173 K and ethanol temperatures of 313 K ranges from 0.8 to 1.4 nm. The diameter distribution shifts towards larger diameters as the synthesis temperature is increased and the carbon supply rate (ethanol temperature) decreases, from which we suggest a selective growth model due to a competition between deposition and etching of carbon atoms.

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## **Laser-Irradiated Chemical Vapor Deposition for Position- and Chirality-Controlled Growth of Single-Walled Carbon Nanotubes**

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We have proposed the laser-irradiated CVD (LICVD) method using laser irradiation as a source of heat to grow single-walled carbon nanotubes (SWNTs). The circular area corresponding to the position of the laser spot in the growing process was characterized by Raman scattering spectroscopy and scanning electron microscopy. The results revealed that SWNTs were synthesized at selective localized region on the catalysts in room-temperature chamber, and the regions of SWNT growth strongly depended on the laser power. By decreasing the laser power and the irradiation time, the regions of SWNT growth were narrowed and the amount of SWNT was decreased. Furthermore, depending on the wavelength of the laser in the LICVD process, the distribution of the intensity in the radial breathing mode (RBM) signals was exceedingly changed. Comparing the Raman spectra of SWNTs grown by 325- and 514.5-nm lasers, almost the same RBM signals were obtained by 457.9-nm Raman spectroscopy. However, when they were measured by 514.5-nm Raman spectroscopy, two large intensities of RBM signals were clearly observed from the SWNTs grown by the 325-nm laser. This result indicates that the chirality of SWNTs grown by LICVD process depended on the wavelength of the laser.

## High Yield, Selective Growth of Millimeter Long, Vertically Aligned Single-Walled Carbon Nanotubes at Low Temperatures

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We will demonstrate the controlled growth of SWNTs on Si substrates coated with a sandwich-like structure  $\text{Al}_2\text{O}_3$  /Fe / $\text{Al}_2\text{O}_3$  (/Si) at low temperatures by point-arc microwave plasma CVD,[1,2] which overcomes all the disadvantages such as high growth temperature (800-1200oC), low production yield (the mass ratio of SWNTs to catalyst, usually <100%) and out of control of the as-grown SWNTs (randomly entangled bundles or ropes) by other methods. The as-grown SWNTs are neat, extremely dense and vertically aligned. The lifetime of the catalyst is almost unlimited, and thus, on one hand, the thickness of SWNTs can be easily controlled; and on the other hand, millimeter long SWNTs with a production yield over 2 500 000% can be easily achieved. The volume density of the as-grown SWNTs is as higher as 66 kg·m<sup>-3</sup>. Up to now, the growth temperature about 6000C is the lowest, while both the volume density and the production yield are the highest for the synthesis of aligned SWNTs. We have also succeeded in selective growth of SWNTs, showing a very promising future for applied researches using our as-grown neat, vertically aligned SWNTs without further purification.

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## **Is plasma assistant CVD unfavorable for the growth of single-walled carbon nanotubes?**

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As we know, plasma assistant chemical vapor deposition (CVD) is good at controlled growth of multi-walled carbon nanotubes (MWNTs); however, it is rarely succeeded in the synthesis of single-walled carbon nanotubes (SWNTs), [1] not along controlled growth. Is it unfavorable for the growth of SWNTs? A positive answer is given through our efforts. By employing a point-arc microwave plasma (MP) CVD system, and preparing the substrate with a sandwich-like coating structure (Al<sub>2</sub>O<sub>3</sub>/Fe/Al<sub>2</sub>O<sub>3</sub>), high yield, selective growth of millimeter long, vertically aligned SWNTs have been successfully synthesized.[2-3] In this presentation, the role of the sandwich-like structure for producing extremely dense catalytic nanoparticles, the functions of the point-arc MPCVD concerning the nucleation and growth mechanisms of vertically SWNTs are discussed and summarized in comparison with some other catalyst preparation methods and conventional MPCVD methods.

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## **New technology for directional control of Multi-walled Nanotubes using van der Waals forces to substrate pattern**

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In order to achieve electronics applications of Carbon nanotubes (CNTs), it is very important to develop the directional control technology of CNTs. So far, some technologies using an applied electric field have been reported by several groups<sup>1</sup>. However, there are a lot of cases in which the electric field cannot be applied. We propose a new method of directional control of Multi Walled Carbon Nanotubes (MWNTs) without electric field. The method is based on van der Waals force between CNTs and a patterned substrate, and enables us to change the direction from vertical to horizontal. The substrate consists of a catalytic metal pattern and a dielectric block. We used the hot-filament CVD and Co catalyst. The growth temperature was about 500°C. SiO<sub>2</sub> was used as a material for dielectric block. We successfully grew up a bundle of MWNTs vertically and then horizontally, according to the surface structure of the block. This work was supported by the Advanced Nanocarbon Application Project, which was consigned to Japan Fine Ceramics Center (JFCC) by New Energy and Industrial Technology Development Organization (NEDO) of Japan.

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## Versatility of the Fe/Al<sub>2</sub>O<sub>3</sub> system for high-yield carbon nanotube growth by thermal CVD of C<sub>2</sub>H<sub>4</sub>

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We present a study of carbon nanotube (CNT) growth by atmospheric pressure thermal CVD of H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> mixtures [1,2], and demonstrate that Al<sub>2</sub>O<sub>3</sub>-supported Fe catalysts give excellent yields of MWNTs and SWNTs at growth temperatures from 700-800 °C. The catalysts are prepared by a variety of methods, including e-beam evaporation of Al<sub>2</sub>O<sub>3</sub>/Fe films on bare, oxidized, and microstructured silicon substrates; impregnation of Al<sub>2</sub>O<sub>3</sub> fiber cloth with a solution of Fe(NO<sub>3</sub>)<sub>3</sub> in isopropanol; and Fe film deposition and Fe-IPA solution impregnation with porous Al<sub>2</sub>O<sub>3</sub> membranes (Whatman Anopore) having pore diameters of 20, 100, and 200 nm. The Al<sub>2</sub>O<sub>3</sub>/Fe (1/20 nm) films on Si give vertically-aligned CNT films thicker than 1 mm in fewer than 15 minutes of growth, and lift-off patterning enables growth of self-supporting CNT structures with widths as small as 2 μm and aspect ratios exceeding 100. Fe nanoparticles formed upon heating of the Al<sub>2</sub>O<sub>3</sub> fibers give aligned MWNT growth perpendicular to the cylindrical surfaces and ends of the 20 μm diameter fibers. Comparative experiments with a Mo/Fe/Al<sub>2</sub>O<sub>3</sub> film on Si show that Mo is critical for high-yield SWNT growth from Fe in H<sub>2</sub>/CH<sub>4</sub> yet gives poor-quality multi-walled CNTs (MWNTs) in H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub>, whereas the Fe/Al<sub>2</sub>O<sub>3</sub> film gives negligible CNT growth in H<sub>2</sub>/CH<sub>4</sub> [3]. Our results emphasize the synergy between the catalyst and gas activity in determining the morphology, yield, and quality of CNTs, and reinforce that a specific metal-support system can be successful with variety of catalyst preparation techniques and substrates.

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## Carbon nanotube growth studies using gas activity gradients introduced by novel sample configurations

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We present a study of carbon nanotube (CNT) growth by thermal CVD using novel configurations of silicon substrates coated with thin film catalysts, revealing the dependence of growth on the activity [1] of the gas mixture and the gas flow pattern around the samples. For example, no CNT growth occurs on short (1x1 cm) samples of a Mo/Fe/Al<sub>2</sub>O<sub>3</sub> film in pure CH<sub>4</sub>; however, the flow over a long sample (1x15 cm) decomposes into a higher activity mixture of CH<sub>4</sub>, lower hydrocarbons, and H<sub>2</sub>, causing catalyst clusters to evolve into mats of CNTs with bimodal spatial profiles of yield (G/Si ratio) and quality (G/D ratio) measured by Raman spectroscopy [2]. Furthermore, "capping" the sample by resting a piece of Si<sub>3</sub>N<sub>4</sub>-coated silicon wafer on top of the sample restricts gas diffusion to the catalyst, causing a 200-500% increase in CNT yield along with a moderate decrease in quality. In numerous experiments varying the gap between the cap and sample, we observe an inverse relationship between the yield and quality of CNT films.

Similar experiments are performed with Fe/Al<sub>2</sub>O<sub>3</sub> films in H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub>, where the CNT growth rate is at approximately 100 times greater than in H<sub>2</sub>/CH<sub>4</sub>. The thickness of vertically-aligned CNT films varies considerably depending on the sample position, and changes significantly along long samples, demonstrating the strong effects of gas activity on yield. In mixtures having relatively high Ar or low C<sub>2</sub>H<sub>4</sub> concentrations, circular patches of millimeter-thick vertically-aligned CNTs nucleate near the sample edges where the flow field has high circulation, yet only micron-scale tangled films grow near the center of the sample where the gas supply is restricted by the boundary layer. Capping these samples gives uniform thick film growth around the edges yet restricts gas access to the center. However, "shielding" these samples by spacing the cap 1-2 mm above the catalyst gives a uniform film across the sample due to high convective circulation in the gap.

Compared to a parametric study which uses a large number of small sample experiments, our long sample method uses a much smaller set of experiments at more widely spaced conditions and reveals the relationship between CNT structure on gas activity at very high resolution. Tuning the flow resistance to the catalyst by capping the sample enables uniform high-yield CNT growth over large substrate areas, and retains the cost and scalability advantages of atmospheric-pressure thermal CVD.

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## Online BET Analysis of Single-Wall Carbon Nanotube Growth and its Effect on Catalyst Reactivation

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A system combining pulse CVD reaction and cryogenic gas sorption (BET) measurement capabilities was designed to allow the sequential synthesis and online analysis of SWNTs. Cooling treatment in liquid nitrogen (77K) during BET measurement was found to be efficient for restoring catalysts when deactivation occurs after carbon deposition. By this treatment the methane conversion could be enhanced by up to seven times, such as from 5.8% to 42.6% mol. When the temperature changes from 850°C to 77K, the metal particles on the tip of nanotubes might contract and be separated from the graphite layer of the nanotubes, leading to more active sites on metal particles being exposed. The single point BET analysis of SWNT has been tested as an efficient method for the rapid online analysis of SWNTs produced by chemical vapor deposition (CVD).

## Fundamental understanding the growth of carbon nanotubes by microkinetic modeling

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Growth of carbon nanotubes involves many physical and chemical elementary steps such as adsorption and desorption of hydrocarbons, surface reaction of intermediates on the metal surfaces, segregation of the surface carbon into the bulk phase, diffusion of carbon through the metal particles, as well as precipitation of the carbon to form carbon nanotubes. A microkinetic model including all the steps in the CNT growth has been established, where theoretical methods such as transition state theory and unity bond index-quadratic exponential potential (UBI-QEP) have been used to estimate the kinetic parameters. It was found that microkinetic modelling is a powerful tool for a detailed understanding of the CNT growth. Microkinetic modeling is able to predict the effects of the catalyst composition, the metal crystal size, and the reaction conditions such as the temperature, carbon sources, and pressure on the CNT growth [1,2]. A microkinetic model assisted catalyst design for CNT synthesis will be also discussed.

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## Effect of the molecular structure of carbon source on carbon nanotube growth and quality

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Carbon nanotubes have been synthesised from camphor, camphor analogues (camphorquinone, norcamphor, norbornane, camphene, fenchone), and various other precursors (menthone, 2-decanone, benzene, methane). It has been shown that the mechanism of tube growth is unlikely to depend upon the production of reactive five and six membered rings, as has been previously suggested<sup>1</sup>. The results also suggest that the presence of oxygen in the precursor does not significantly improve the quality of tubes by etching amorphous carbon. It is suggested that the control of the flux of the precursor to the catalyst is more important in the production of high quality tubes. Comparison of radial breathing modes in the Raman spectra of samples grown from camphor to those grown from methane and benzene show similar distributions of diameters, which are different to samples grown from 2-decanone.

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## The role of substrate surface for catalyst formation for CNT growth by CVD

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For the localized integration of the carbon nanotubes into systems one used the precise control of the catalyst, growth temperature and gas pressure. But we have found that substrate surface has also influential role. In this present investigation CVD technique was used to grow carbon nanotubes using methane as feedstock gas at 1000°C. Ni was used as catalysts. Different thicknesses of Ni (0.5 nm, 1 nm, 2 nm, 5 nm, 10 nm and 30 nm) were sputtered on native oxidized Si and thermal oxidized Si substrate (200 nm). Carbon nanotube formation strongly depends upon the initial catalyst particle size, which act as seed. There have been differences of the nanotube formation observed in two different kind of substrates used. Upon heating catalyst particle coalescences and form bigger and bigger particles for those coated on oxidized Si substrate. 0.5 nm thick Ni form around 20 nm in size catalyst particles in compared to around 200 nm cluster using 30 nm Ni. Therefore the nanotube formation also changed with respect to density and size. 0.5 nm thick Ni promotes highly dense and lower in diameter (around 20 nm) nanotube and 30 nm thick Ni catalyst results very low yield and thicker (around 60 nm in diameter) nanotube. Where as, Ni does not form well separated bigger particles (islands) coated over native oxidized Si substrate upon heating. High density carbon nanotubes were grown over this kind of substrate. Therefore we conclude that, modification of substrate surface could also be used to tailor the catalyst formation (size, density) which controls the nanotube growth.

## Parameters optimization of carbon nanotube growth by CVD method in fluidized bed reactor

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Single walled carbon nanotube have been produced from decomposition of hydrocarbon on Co-Mo/MgO in a fluidized bed reactor. Various parameter such as catalyst composition, type of gas, Hydrocarbon /H<sub>2</sub> Ratio, Total flow of gas, residence time and Temperature have been studied by the method of design experiments. The effect of these parameters on the yield, type and quality of carbon nanotube were investigated. TEM, SEM, TGA, X-ray diffraction, Raman spectroscopy and BET characterized the synthesized material. By methane decomposition at the best condition, single- walled carbon nanotube with high quality without any amorphous carbon , high yield (100%) and with 1nm diameter were obtained.

## **Low temperature growth of SWCNT by plasma enhanced chemical vapor deposition**

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We demonstrate that single-walled carbon nanotubes (SWNTs) can be grown at 450 oC by plasma-enhanced chemical vapor deposition, which is the lowest growth temperature reported. SWNTs were grown with methane gas on iron catalyst particles dispersed on SiO<sub>2</sub>/Si substrates by using a mixture of ferrocene and commercial photoresist. In this report, we discuss effects of plasma power and growth temperature on growth of SWNTs.

## **Direct Photolithographic Route to Selective Growth of Single-Walled Carbon Nanotubes Using a Modified Photoresist with Ferrocene**

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We report a direct photolithographic route to selectively grow SWNTs using a simple mixture of ferrocene and conventional photoresist. The catalytic photoresist (Cat-PR) plays roles as both a catalyst and a photoresist for selective growth of SWNTs whose diameters are in the range of 1.0~1.5 nm. It is also demonstrated that suspended CNTs between three-dimensional stands can be easily prepared by using Cat-PR patterns as an etch mask.

## Temperature and reaction time effects on the synthesis of SWNTs by methane CVD in a fluidized bed reactor

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Mass production of single-walled carbon nanotubes (SWNTs) by cost-effective process is still a challenge topic for further research and application of CNTs. Our group focused on catalysis and reaction mechanism and fluidization engineering of methane CVD process to prepare SWNTs[1][2]. Here we report on the effects of temperature and reaction time on the growth of SWNTs from methane in a lab-scale fluidized bed reactor. Fe supported MgO catalyst was used in the process for consideration of further easily purification of as-grown product [1]. Gas chromatography (GC) online analysis was used to get the real-time conversion of methane. The products were characterized by transmission electron microscopy (TEM), thermogravimetric analysis (TGA) and Raman spectroscopy. High quality of SWNTs was found before ten minutes reaction and more amorphous carbon will grow for longer time. Low reaction temperature decreases the activity of the catalyst, while high temperature will quicken up the catalyst deactivation. After a series of experiments, we get the optimal operating conditions of reaction time and temperature in fluidized bed process. Keywords: SWNTs ; Fluidized bed; CVD; reaction time and temperature;

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## Growth of SWNTs and MWNTs from titanium-cobalt bimetallic particles as a catalyst

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Bimetallic particles of Ti and Co have been used to grow single-walled and multi-walled carbon nanotubes (SWNTs and MWNTs). The particles were generated by laser ablation and size-classified with a differential mobility analyzer. Firstly, diameter-controlled MWNTs were grown on Si substrate from 5-nm particles by thermal chemical vapor deposition using a mixture of acetylene and argon (mixing ratio = 1:9) at 510 and 610 C. The flowrate and pressure of the mixture were 200 sccm (standard cubic centimeters per minute) and 1 kPa, respectively. Titanium has been found to enhance the MWNT growth significantly. There is an optimum Ti fraction for the growth, as confirmed by evaluation of the growth probabilities of MWNTs. Secondly, SWNTs were grown from 2.5-nm Ti-Co particles at 590 C. In this case, the acetylene-argon mixture was greatly diluted by hydrogen (e.g., mixture:hydrogen = 1:19). Raman spectra for the radial breathing mode of the SWNTs indicate that the SWNT diameters are somewhat smaller than the particle diameters. A possible growth-enhancement mechanism by Ti is discussed. This work was supported by the Advanced Nanocarbon Application Project, which was consigned to Japan Fine Ceramics Center (JFCC) by New Energy and Industrial Technology Development Organization (NEDO) of Japan.

## **Production of clean single-walled carbon nanotube by floating catalyst system**

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Single-walled carbon nanotube were prepared by floating catalyst system. A Solution with the mixture of toluene, ferrocene (0.01-0.02 g/ml and thiophene (0.4-0.6wt.%) is sprayed in a vertical reactor furnace with hydrogen gas (250ml/min) by a atomizing nozzle. The reaction temperature was 1100°C and it was conducted for 60 min. TEM, SEM, XRD and BET surface area technique were utilized to characterize the purified samples. Results show that single walled carbon nanotube without any amorphous carbon was produced. Because of changing the design parameters of the atomizing nozzle, cause very small clusters of iron is produced and the carbon nanotubes that grown on this clusters, are single -walled with the specific size. We conclude that this method can produce single walled without any amorphous carbon.

## Single-walled carbon nanotubes grown from diameter-controlled iron nanoparticles

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Single-walled carbon nanotubes (SWNTs) were synthesized from diameter-controlled catalytic Fe nanoparticles by hot-filament chemical vapor deposition (CVD). The nanoparticles were produced by laser ablation of an Fe target, classified with a differential mobility analyzer, and then deposited on a substrate. As the carbon source, a mixture of acetylene and argon gases (acetylene:argon = 1:9) was introduced into a CVD chamber, in which the substrate was placed. Hydrogen was also added during the growth. The substrate temperature and total gas pressure were 590 °C and 125 Pa, respectively. The filament temperature measured with a pyrometer was approximately 1000 °C. The resultant carbon nanotubes were evaluated by transmission electron microscopy and Raman spectroscopy. As a result, it has been found that high quality SWNTs with narrow diameter distributions are grown from Fe nanoparticles with diameters of 2.0 nm or smaller. This work was supported by the Advanced Nanocarbon Application Project, which was consigned to Japan Fine Ceramics Center (JFCC) by New Energy and Industrial Technology Development Organization (NEDO) of Japan.

## **Continuous production of bulk carbon nanotubes on floating catalysts on MgO in a fluidized bed reactor**

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Carbon nanotubes are synthesized by continuous feeding of hot MgO fine powders and a floating catalyst (e.g. ferrocene), in feed gas streams, into high-temperature zone of a fluidized-bed reactor. At the hot zone, iron nanoparticles seeds for growth of carbon nanotubes are deposited on the MgO powder from the floating catalyst precursor. MgO powder in a part of feed gas stream is heated to the reaction temperature, while the ferrocene in another part of the feed stream is reached to about 400°C. The simultaneous contact of the high-temperature catalyst and the feed in the hot zone of the fluidized-bed reactor significantly enhances the quality of carbon nanotubes. The carbon nanotubes grown on the Fe/MgO catalyst is continuously removed from the reactor. Therefore, the process is viable for continuous large-scale production of carbon nanotubes. This process is used for synthesis of carbon nanotubes on Fe/MgO, using ferrocene as the source of iron nanoparticles and methane, as the carbon source, at 1000°C. The MgO powder was prepared by citrate method. SEM micrographs show high density bundles of 10-20 nm size nanoparticles are deposited on the Fe/MgO catalyst.

## The role of catalytic particle state in multi-walled carbon nanotube growth

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Multi-walled carbon nanotubes were deposited by microwave chemical vapor deposition on Fe, Co, and Ni catalyst layers. By adjusting the deposition temperature and time predominantly either a tubular structure or a bamboo-like structure was obtained. The corresponding growth rates of these forms were determined. The activation energy of diffusion and the diffusion coefficient of carbon in the catalyst particles was evaluated to be as high as 0.3 – 0.6 eV and  $0.4 - 1 \cdot 10^{-10} \text{ m}^2/\text{s}$  for the tubular structure and 1.4 – 1.6 eV and  $0.6 - 1.8 \cdot 10^{-11} \text{ m}^2/\text{s}$  for the bamboo-like structure. These data prove the occurrence of a liquid catalyst state during tubular growth and of a solid state in the case of bamboo-like growth. It is likely, that surface melting of the catalyst particles can also occur during the growth process. The tube growth is limited by time due to the metastable state of the catalyst particles.

## **Directional growth of carbon nanotubes synthesized by Fe-catalyzed chemical vapor processes on patterned substrates**

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The main efforts for the application of carbon nanotubes for future electronic devices is to grow at a large scale, well oriented and defect-free CNTs. For these reasons, we investigated different methods to control structural properties, location and direction of carbon nanotubes during the growth process. In particular, different types of substrates such as SiO<sub>2</sub> resist-coated, SiO<sub>2</sub>, Si and polysilicon trenches/pillars types have been prepared. These grooved structures were used to pattern a layer of Fe-catalyst. Different catalyst deposition techniques were investigated to identify the most effective way to obtain well-defined islands for the growth of defect-free CNTs: the metal evaporation, the spin-coating and impregnation methods from iron salts solutions. Carbon nanotubes have been synthesized on the Fe-patterned substrates by thermal decomposition of methane CH<sub>4</sub> at 900 °C and 750 torr. Substrates characterization has been carried out pre and post the CNT synthesis. In order to obtain a better understanding of the effect of the surface condition on the growth of the CNTs, such substrates underwent different surface treatments. Moreover, depending on the wetting properties of the catalyst, the nucleation phase of the CNTs can even be hampered, giving this new hint on the control of the CNTs growth.

## Formation of CNT's by Temperature Programmed Decomposition of Methane over Co Catalysts

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The mechanism of CNT formation during catalytic decomposition of hydrocarbons has been extensively studied. However the majority of the studies describe only the final steady state step of filament growth and there are facts, like the type of species involved during the CNT nucleation step, the role of hydrogen in CNT formation or the catalyst deactivation by encapsulating coke formation, that are still matter of discussion. With the aim of having a more deep knowledge of CNT formation mechanism, in the present paper we report the results of temperature programmed decomposition of methane on Co-Mg-Al coprecipitated catalysts. The results obtained indicate that the duration of the induction period, ascribed to CNT nucleation, and the catalyst deactivation can be modulated with the temperature and with the Hydrogen concentration. The rate of CNT growth follows a complex pattern with respect to hydrogen concentration and this must be taken into account in the developing of mecha nistic kinetic models.

## Multi walled carbon nanotubes formation on Cobalt and Iron oxides

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Multi-walled carbon nanotubes are produced by catalytic decomposition reaction using  $C_2H_2$ ,  $C_2H_4$  or aromatics compounds on supported Fe-Co oxide catalysts at temperatures between 600°C-800°C. Its production strongly depends on several parameters such as: i) the nature of the catalyst support, ii) the metal loading, iii) the Co composition in the sample and iv) the activation and reaction conditions. Different cobalt and iron phases were identified by Mössbauer spectroscopy and X-Ray diffraction techniques as a function of the cobalt composition. For instance, between 10 wt% and 50 wt% of Co,  $\alpha$ - $Fe_2O_3$ ,  $Fe_3O_4$  and  $CoFe_2O_4$  phases were identified while at higher Co content,  $Co_3O_4$  phase crystallises and  $\alpha$   $Fe_2O_3$  was only observed. However, the influence of the different Co and Fe oxides on the multi-walled nanotube production have not yet been fully investigated. In this work, multi-walled carbon nanotube deposition reaction applying ethylene fluxed over different Co and Fe oxides at 700°C is studied. For all samples, amorphous carbon species (metal carbides and graphitic-like carbon species) were formed. The maximum multi-walled nanotubes yield was observed by TEM technique for the  $CoFe_2O_4$  mixed phase followed by  $Co_3O_4$ . Carbon nanotubes were not observed for  $\alpha$ - $Fe_2O_3$  and  $Fe_3O_4$  model compounds after catalytic reaction.

## **Catalyst free low temperature direct growth of carbon nanotubes on SiGe islands and Ge quantum dots**

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A metal catalyst free growth method of carbon nanotubes (CNTs) has been developed using chemical vapor deposition (CVD) of CNTs on carbon implanted SiGe islands on Si substrates. From SEM and Raman measurements, the fabricated CNTs are identified as single walled CNTs (SWNTs) with diameter ranging from 1.2 to 1.6 nm. Thick and curly oxide nanofibers were also obtained as a by-product of the growth process but could be dissolved using HF treatment. Essential parts of the substrate preparation after CVD SiGe growth and carbon implant are a chemical oxidization by hydrogen peroxide solution and a heat treatment at 1000degC prior to CNT growth. We believe that these processes enhance surface decomposition and assist the formation of carbon clusters, which play a role in seeding CNT growth. Though further investigation is required to improve the density of the SWNTs, the growth technique would be a practical technique for growing metal-free CNTs for a variety of applications, while at the same time opening up the prospect of merging CNT devices into silicon VLSI technology. We will also present results that demonstrate the application of this CNT growth technique to germanium quantum dot substrates.

## **The growth of carbon nanotubes through catalyst control with support using chemical vapor deposition**

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The control of diameters as the technical growth of carbon nanotubes (CNTs) has been remained important factors that the size of the catalytic particles is known to determine the size of the CNTs. We investigated the synthesis of CNTs through catalyst control with support. The catalytic synthesis was prepared by a sol-gel process. Nanopowders were mixed in solution including catalyst by magnetic stirring. This catalytic solution was completely dried in furnace. After that, CNTs were deposited from acetylene at 950 oC for 30 min by thermal chemical vapor deposition. The atomic force microscopy was used for the analysis of surface morphology of nanopowder. X-ray energy-dispersive spectroscopy (EDS) was employed for the composition analysis of nanopowder synthesized by catalyst. The analysis on characteristics of CNTs was carried out using micro-Raman spectra, scanning electron microscopy and high-resolution transmission electron microscopy.

## **Controlling growth of carbon nanotubes in micro-holes by thermal chemical vapor deposition at low temperature**

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Vertically aligned carbon nanotubes (CNTs) have been synthesized in micro-holes by a method of chemical vapor deposition at low temperatures between 450°C to 550°C for the usage as emitters of displays. It is found that preheating the reaction gas of C<sub>2</sub>H<sub>2</sub> at 700°C enhances the reactivity of C<sub>2</sub>H<sub>2</sub> and contributes to its effective decomposition on the surfaces of the catalyst particles heated even at a low temperature of 450°C. We have also found that the activity of the catalysts is strongly affected by the film thicknesses and their ratios of the layered catalysts of Co and Ti. It is confirmed that the length of CNTs can be controlled by the thicknesses of catalyst films and the growth temperature. The longer CNTs have been obtained at the thinner thicknesses of Co and Ti or at the higher growth temperature. It is evidenced that the turn-on voltage of the field emission from the CNTs prepared at the low temperature has the similar value as that from the CNTs prepared at higher temperatures.

## ***Ab-initio* Molecular Dynamics Study of Reactions Involving Hydrogen or Oxygen in Carbon Nanotube Growth**

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Recently the use of alcohol as a carbon source [1] or the addition of water [2] in CVD growth enabled the production of high quality carbon nanotubes (CNTs). We study two sorts of reactions involving hydrogen or oxygen in CNT growth using *ab-initio* molecular dynamics code [3]. **Dissociation:** When a CH<sub>4</sub> molecule is supplied to a 13-atom Co catalyst nanoparticle, the molecule sticks to the particle and three of H atoms are dissociated from the molecule in 0.87 ps. The dissociation is caused by a peculiar structure where C and H atoms of the molecule bond to one Co atom, and the H atom also bonds to a neighboring Co atom. When a CH<sub>3</sub>OH molecule is supplied, all of H atoms are dissociated in 0.52 ps. **Cleaning:** Two water molecules remove a carbon atom with dangling bonds, which can act as a kernel for amorphous material, from a six-membered ring. An oxygen molecule removes the carbon atom even at lower temperatures. A hydrogen molecule, however, does not remove it. When all of the dangling bonds are terminated by H atoms, no more reactions happen. Generally, hydrogen and oxygen seem to suppress and to accelerate the reactions, respectively.

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## Controlling growth of carbon nanotubes

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Carbon nanotubes (CNTs) are promising materials for many possible applications like field emitters, transistors, reinforcing fibers for composites, resonators, chemical sensors, etc. Carbon nanotubes are produced by arc-discharge, laser ablation and chemical vapor deposition (CVD) methods. CVD is the only suitable method for the large scale production of CNTs. Controlled growth of CNTs on various platforms has to be achieved so as to realize the possible applications. In this study parameters for the carbon nanotubes produced by CVD are explored. Both thermal and plasma enhanced chemical vapor deposition (PECVD) methods are studied. Different parameters, i.e. hydrocarbon source, catalyst, temperature, which are effective on the carbon nanotube growth are investigated. Optimum parameters for the growth of CNTs by thermal and PECVD are presented.

CNTs have also been used as atomic force microscopy (AFM) probes. We also show the use of both arc-discharge and CVD CNTs as AFM tips. Pre-produced arc-discharge CNTs are manually attached onto the AFM tips by use of a nanomanipulator in the scanning electron microscope (SEM). CVD CNTs are directly grown on the apex of the AFM tips. We have compared the performance of different kinds of CNT AFM tips and commercial Si / Si<sub>3</sub>N<sub>4</sub> AFM tips.

## **Innovative synthesis of carbon nanotubes by chemical vapor deposition using Fe/Mo nanoparticle arrays as catalyst for the growth process**

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The unique electronic, mechanical and chemical properties of carbon nanotubes making them most promising candidate for the building blocks of molecular-scale machines, and nanoelectronic devices. Keeping in view the potential applications, in the present work, the synthesis of vertically aligned carbon nanotubes has been investigated thoroughly by simple and cost effective process. Benzene and ethanol have been used as precursors for the growth of carbon nanotubes under different experimental conditions on Si (100) substrates. On the other hand, iron/molybdenum nanoparticles arrays have been used as catalysts for the growth of vertical alignment of carbon nanotubes. Prior to the growth of the carbon nanotubes, iron oxide/molybdenum oxide nanoparticles have been obtained by using poly (styrene-block-acrylic acid) micelles. The tunability of micelles in the range of 20-50 nm is obtained by choice of solvents, polymer solution concentration and spin coating rotation speeds. After obtaining the mixed oxide nanoparticle arrays, they have been reduced to metal nanoparticles under H<sub>2</sub> atmosphere at 400°C for 15 min. The deposited carbon nanotubes have been characterized by X-ray diffraction, Raman spectroscopy, and high resolution scanning electron microscopy and transmission electron microscopy techniques.

## Iron encapsulated carbon nanotube and its properties

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Iron encapsulated carbon nanotube have been prepared using iron compounds and carbon precursor as starting materials by vapor phase reaction. It was obtained by one pot reaction. This process does not need cap elimination procedure or subsequent metal encapsulation step. The obtained iron encapsulated carbon nanotube was named as "Meta-Carbo". The structure of Meta-Carbo was analyzed by transmission electron microscopy (TEM), EDX, and X-ray diffraction (XRD). The field emission property of Meta-Carbo was also examined. It showed relatively low threshold of electric field.

## Surface Modifications During CVD growth of SWNT in an Electric Field

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Surface modifications of SiO<sub>2</sub> created during chemical vapor deposition of single walled carbon nanotubes (SWCNTs) are studied. The CNTs are grown using a multilayered film with Al<sub>2</sub>O<sub>3</sub>, Fe and Mo as catalyst. The CVD process includes a fast heating step in addition to the application of an electric field using Mo electrodes patterned on the substrate. The combination of these two techniques not only directs the growth of CNTs but also induces surface modifications of the SiO<sub>2</sub> embedding the CNTs in the middle of trenches. The trenches, with depths of a few nm and widths of a few hundred nm are characterised using AFM, SEM and EDX. An explanation of the phenomena that is based on field emission from the growing CNTs is also discussed.

## Surface Diffusion: The Low Activation Energy Path for Nanotube Growth

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Surface-bound, catalytic chemical vapour deposition (CVD) allows selective, aligned growth of nanotubes (CNTs) and nanofibers (CNFs). So far, the growth process has been optimised largely empirically, because the catalyst interaction with the carbon precursors is not fully understood. Previous theoretical growth studies mainly focused on nucleation. However, a key factor is the kinetics of carbon supply. We present a systematic study of the thermal and plasma enhanced (PE) CVD growth of CNTs/CNFs with Ni, Co and Fe thin film catalysts. We show that reducing the Fe/Co catalyst thickness below 2 nm causes a transition from larger diameter (>40 nm), bamboo-like CNFs to small diameter (~5 nm) CNTs with 2-5 walls. This is accompanied by a 50 times faster growth rate. We determine the activation energy for each growth mode and catalyst material. For PECVD we get a common low activation energy of 0.23-0.4eV, much lower than for thermal deposition [1]. The carbon diffusion on the catalyst surface and the stability of the precursor molecules, C<sub>2</sub>H<sub>2</sub> or CH<sub>4</sub>, are investigated by ab-initio plane wave density functional calculations [2]. We find a low activation energy of 0.4eV for carbon surface diffusion on Ni and Co (111) planes, much lower than for bulk diffusion. The energy barrier for C<sub>2</sub>H<sub>2</sub> or CH<sub>4</sub> dissociation is at least 1.3eV and 0.9eV, respectively, on Ni(111) planes or step-edges. Hence, the rate-limiting step for plasma-enhanced growth is carbon diffusion on the catalyst surface, while an extra barrier is present for thermal growth due to gas decomposition. Our findings are relevant for the catalyst assisted growth of nanomaterials in general: provided the precursor dissociation barrier is removed, the growth can proceed via diffusion on a solid catalyst particle at low temperature.

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## Kinetics of methane pyrolysis over different catalysts

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The pyrolysis of methane and methane-hydrogen mixtures over Fe, Co, and Ni catalysts with Mo, W and other metals additives on different supports ( $\text{Al}_2\text{O}_3$ , MgO,  $\text{La}_2\text{O}_3$ ) is studied at 600 - 1000 °C using gravimetric technique. The catalysts are synthesized by combustion synthesis. As it is stated, the pyrolysis either includes an induction period or starts with maximal rate and becomes slower with time. In all cases the dependence of the reaction rate on linear gas velocity has an extremal form. The presence and duration of induction period are dependent on the catalyst nature and catalyst particle size. The activity of the catalysts of the same composition varies with the manner of their production and activation. Transmission electron microscopy shows that the synthesized products represent carbon nanofibers, multi-walled carbon nanotubes, or double- and triple-walled carbon nanotubes, depending on the synthesis conditions. The productivity of laboratory-scale continuous reactor is amount to 10 - 15 g/h. The purification and solubilization of carbon nanotubes prepared are studied.

## **Optical emission spectra from plasma during PE-CVD growth of decorated carbon nanotubes**

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It has been shown that decorated multiwall carbon nanotubes, with graphitic thorns protruding near the tips of the tubes, show remarkable electron field emission properties [1].

We show optical emission spectra from the cathode sheath of the glow discharge during various stages of the production of these tubes. The optical emission spectra of the plasma are presented in conjunction with field emission characteristics of the produced CNT films.

Optical emission lines of hydrogen and C<sub>2</sub> are observed and monitored at different substrate temperatures.

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## Utilization of MWCNT for the detection of antigen-antibody reaction in cancer diagnosis

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Semiconducting single-walled carbon nanotubes (SWCNTs) are known to detect biomolecules by forming FET (field effect transistor). In this study, metallic multi-walled carbon nanotubes (MWCNTs) are shown to be used as a sensor for the detection of cancer marker. The detection of cancer marker is important as its expression has recently been reported to promote tumor angiogenesis [1]. Several studies showed that the expression is up-regulated in several tumors. In this study, nanoelectrode plates with a single MWCNT and two metal electrodes are fabricated first and the surface of MWCNT is modified by attaching pyren molecules to avoid non-specific binding of proteins. Model solution containing Ang.2, common in several kinds of cancer, is added on the plate and Ang.2 is immobilized on the MWCNT surface. When another solution with antibody is added on the plate, there will be an antigen-antibody reaction. In each step, conductance was measured between two metal electrodes to investigate the effect of surface modification and biological reactions. Conductance has been increased when Ang.2 is immobilized on the surface of MWCNT by amide bonding with pyren molecules attached previously. Further increase of conductance was observed when binding between Ang.2 and antibodies took place. We demonstrate that the simple measurement of conductance can be used for the detection of cancer markers and it is expected to be utilized in many applications in the diagnosis of cancers.

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## Nano-contact printing of Co colloid catalyst for growth of vertically aligned carbon nanotubes/fibers

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Applications such as field emission or microelectrode sensor arrays call for the ability to pattern or nm-position carbon nanotubes (CNTs) and fibers (CNFs) with a vertical orientation in controlled arrays over sizable areas. Surface-bound plasma-enhanced chemical vapor deposition (PECVD) allows the selective growth of individual, field-aligned CNFs based on a pre-patterning of the catalyst. Electron beam lithography can provide catalyst patterns with a precision of a few nanometers and is ideal for high value products, however, the serial electron beam writing process is time-consuming and costly. We present a study of nano-contact catalyst printing, representing a low cost route to achieve a uniform sub-micron patterning over large areas. As catalyst, we used a highly purified and concentrated Co colloid (Co nanoparticles ranging between ~2-4 nm in diameter)[1]. The colloid was patterned on Si substrates in features down to ~100 nm size, in form of arrays of regularly spaced lines and dots. PECVD transforms the as-printed catalyst into a vertically aligned CNF pattern, whereby we find that C an increasing<sup>o</sup>for an increase in growth temperature from 300 to 650 catalyst sintering leads to longer and larger diameter CNFs[2]. An optimization of the inking and growth process allows us to selectively nucleate a single, aligned nanofiber per printed catalyst dot.

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## Three-dimensional Internal Order in Multiwall Carbon Nanotubes Grown by Chemical Vapour Deposition

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Chirality control is one of the key goals of nanotube synthesis. Unfortunately, although it is possible to select diameter, production of a particular chirality remains challenging. In multiwall nanotubes the problem is compounded because each layer of the concentric structure has, in general, a distinct chirality. In this study, highly aligned arrays of nitrogen-doped multiwall carbon nanotubes (MWNTs) have been grown by CVD, on adding a nitrogen-containing compound at a critical level to a hydrocarbon feedstock. The resultant MWNTs, which contain about 3 wt% of nitrogen, are comparatively thick yet remarkably straight, and show unprecedented degrees of internal order. Not only are each of the tubular layers of the same chirality, but they appear to be in crystallographic register with one another, giving a  $c/2$  spacing more typical of graphite than of the turbostratic layers usually seen in multi wall tubes. In general, either armchair or zig-zag shells are seen throughout any given tube, as determined by selected area electron diffraction. The result is particularly intriguing as nitrogen doping of nanotubes is usually associated with increasing disorder.

## **On the roles of multilayered metal catalysts in the synthesis of high-quality single-walled carbon nanotubes**

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In this paper, the high quality single-walled carbon nanotubes (SWNTs) were synthesized by multilayered metal catalysts on silicon or silicon oxide substrate in thermal chemical vapor deposition of methane. The roles of multilayered metal catalyst were investigated by systematically varying the combination of multilayered structure. The scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), and micro-Raman spectroscopy were used for characterization. It was found that aluminum supporting layer was very crucial in synthesizing high-purity SWNTs. A thin molybdenum layer in collaboration with an ultra-thin iron catalyst was found very effective in extending the operation window of SWNTs synthesis. The investigation of radial breathing mode (RBM) and the G-band/D-band intensities by micro-Raman measurements would further reveal the strong dependence of the diameter distribution of SWNTs on the different combinations of multilayered structure . An optimized combination was found Mo(0.2 nm)/Fe(1 nm)/ Al(10 nm) on silicon substrate, in which the peak of RBM was sharp and IG/ID ratio was at least 20 from micro-Raman analysis. Furthermore, the Auger electron spectrometer (AES) analysis was utilized to examine the evolution of the depth profile of multilayered structure due to the pre-treatment, which would lead to the examination of the role of each layer. The result of these investigations would be presented and discussed.

## **The effect of catalysts(iron, cobalt and nickel) on the mechanism and kinetics of carbon nanotube growth by thermal CVD method.**

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The kinetics of multi-walled carbon nanotubes (MWCNTs) growth reported so far were mostly based on simulation or deriving the activation energy of one kind of catalyst assuming steady growth. Whether the growth mechanism of MWCNT growth on different catalyst metals can fall into the same mechanism, and whether the nucleation and growth kinetics share the same kinetic controlling mechanism need to be clarified. In this study, we synthesized MWCNTs over different catalysts (iron, cobalt and nickel) deposited by e-gun evaporation and measured the length of MWCNTs varying with time. It was found that there consisted three stages of MWCNTs formation: (1) Nucleation stage by observing the shape transformation of catalyst particles in the initial stage and also by extrapolating the change of length with time to derive the nucleation period. (2) Steady growth stage from which the activation energy of the controlling step could be derived by Arrhenius plot. (3) Growth saturation period, which was caused by amorphous carbon formation. After intensive observations of the relation between the sizes and shapes of the catalyst nanoparticles and the growth rates of MWCNTs at different temperatures over different catalyst metals, it was concluded that the catalyst shape transformation at nucleation stage was important for the growth on nickel and cobalt, but not on iron. As to the steady growth rate, it was found that MWCNTs growth followed the same growth mechanism in all temperature range for iron and cobalt, whereas for nickel there observed a transition of growth mechanism at temperature of ~840°C. There were also observed different growth saturation behaviors on different catalyst metals, which will be discussed in this paper as well.

## Kilogram-scale SWNT Production in a Fluidized bed Reactor

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A chemical vapor deposition (CVD) method of CH<sub>4</sub> cracking on Fe/MgO catalyst in a fluidized bed reactor is realized to mass scale production of SWNT. The catalyst is made by spray drying process, a fluidized bed reactor with inner diameter of 500 mm is used to obtain the SWNT at temperature ranging from 800 to 900 °C, the catalyst preparing process and the reduction condition is found to have significantly influence on the purity and yield of SWNTs. The obtained SWNTs can easily be separated by HCl washing, TGA, Raman and BET result shown that after purification, the SWNTs is over 90% in purity, BET is over 600 m<sup>2</sup>/g, the Raman ratio of G and D band intensity is over 15. 1kg/hr of SWNTs with diameter around 1.2 nm were obtained, which open a new method for mass production of SWNTs.

## **Evaluating nanotube/matrix interface by EELS**

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Here, we present the evaluation of the interface structure of nanotube/matrix using EELS. When using nanotubes as a filler in the composite, the interaction, or affinity, between the tubes and the matrix material becomes important to make the most of the nanotubes. Therefore, in the present study, by utilizing the high-resolution TEM and EELS methods, we will try to develop a way to analyze the interaction between the nanotube and the matrix.

## Towards the optimisation of the large-scale production of MWNTs grown by CVD of ethane on Fe / Al<sub>2</sub>O<sub>3</sub> : reaction kinetics study

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The catalytic decomposition of ethane to produce multi-walled carbon nanotubes (MWNTs) and hydrogen has been carried out on alumina supported Fe catalysts at 900 K. Huge yields up to 2000% in weight of MWNTs were produced per gram of iron catalyst. Electronic microscope observations confirmed the extremely high purity of these nanomaterials (higher than 90%). Furthermore, according to the reaction conditions (ethane / hydrogen ratio, temperature, space velocity...), it is possible to tailor the diameter of the MWNTs. A detailed reaction kinetics study was performed to study the influence of hydrogen and ethane on the yield and morphology of the MWNTs produced. While the order of reaction toward ethane appears positive, hydrogen has a negative impact on the yield of MWNTs during the first minutes on stream. However after several hours on stream, hydrogen seems to maintain the activity of the catalyst, probably via hydrogenation of carbon deposits, thus leaving a part of the active sites free. A kinetic model was proposed to explain these observations. Following this kinetic approach [1], it is possible to optimise the high yield production according to our already reported results in several publications [2-4].

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## Suspended Single-Walled Carbon Nanotubes directly grown in ceramics

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Isolated single-walled carbon nanotubes (SWCNTs) should have different physical properties from bundled ones due to charge transfer and interlayer interactions. Actually, many researchers have measured photoluminescence (PL) and resonance Raman spectra (RRS) of individual single-walled carbon nanotubes (SWCNTs) to reveal the intrinsic electronic structure of SWCNTs. Most of them have used HiPco dispersed in water with surfactant [1,2]. However, the micelle-SWCNTs are not ideally isolated but are expected interaction between SWCNTs and surfactant. For that purpose, really isolated SWCNTs are required.

We synthesize isolated SWCNTs suspended between nanoparticles in air by alcohol catalytic chemical vapor deposition (ACCVD) technique [4] using porous magnesium oxide (MgO) block. The sample showed very narrow RBM Raman lines and PL without any treatment. In this presentation, we will introduce a detailed preparation method of this material and future applications.

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## Aligned growth of isolated single-walled carbon nanotubes programmed by atomic-arrangement of crystalline surfaces

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Because of their unique electronic properties as well as high current density and mechanical flexibility, single-wall carbon nanotubes (SWNT) have been attracted as important building blocks for future nanoelectronics applications, such as quantum wires, non-volatile memories, and chemical sensors. It is essential for these applications to organize SWNTs into rational architectures on the substrate surface. The formation of an aligned array of SWNTs is the first step toward the architectures. The SWNT alignment has been achieved by applying the electric field during their growth or by leading their growth through the gas flow. Here, we report on the synthesis of highly aligned SWNTs on the sapphire surfaces, in which the growth direction is programmed by the atomic arrangement of Al atoms [1]. Interestingly, on the basis of the electron back scattering (EBS) analysis, the SWNTs were found to align along the specific crystalline directions,  $[1, -1, 0, -1]$  for the R-face  $(1, -1, 0, 2)$  and  $[2, -2, 0, 1]$  for the A-face  $(1, 1, -2, 0)$ , which correspond to the anisotropic pseudo one-dimensional array of atoms on these surfaces. The random orientation was observed for the SWNTs grown on the C-face  $(0, 0, 0, 1)$  substrate, reflecting the isotropic arrangement of Al atoms. Our new findings present that the interaction between SWNTs and substrate surface can be applied to pattern or integrate SWNTs.

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## Direct synthesis of suspended single-walled carbon nanotubes on tips of post-treated carbon nanofibers

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Suspended single-walled carbon nanotubes (su-SWNTs) have been shown recently to allow the characterization of their intrinsic properties more accessible, and presumably to enhance the performances of associated nano-devices such as field effect transistors and oscillators, owing to less perturbation from surrounding environments. We have developed a novel three-step fabrication process to directly synthesize su-SWNTs across the tips of post-treated carbon nanofibers (PT-CNFs). This process starts with the growth of vertically-aligned CNFs on Si substrates patterned with catalytic Ni film of 10 nm thickness. The CNFs were then post-treated by energetic Ar plasma in the same reactor to yield a structural transformation from rod-like to cone-shaped geometry, as a result of a co-sputtering/deposition mechanism [1]. The catalytic nanoparticles at tips of CNFs were reduced to a smaller size or even totally removed, depending on the treatment conditions. A thin coating of Si-C was formed on CNFs surface during the post-treatment due to re-deposition of the sputtered atoms [1]. The last step of the fabrication process was the growth of SWNTs using PT-CNTs as templates in a thermal furnace with methane and hydrogen as feed gases. With PT-CNTs obtained under optimum post-treatment conditions, high quality SWNTs were synthesized suspending on the tips of PT-CNFs crossing two Ni pads of up to 10  $\mu\text{m}$  spacing, as revealed by resonance Raman spectroscopy and scanning electron microscopy. The Si-C coating on PT-CNFs surface was found to serve as both catalyst support for SWNTs growth and protective layer preventing the CNFs templates from significant damage during high temperature thermal process with hydrogen. This method allows one to fabricate isolated individual su-SWNTs with more flexibility and makes it possible either to characterize a single isolated SWNT free from environmental interference or to build novel SWNTs-based devices of enhanced performances.

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## Alcohol CVD Growth, Raman and Photoluminescence Spectroscopy of Single-Walled Carbon-13 Isotope Nanotubes

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Using Alcohol catalytic CVD (ACCVD) technique [1] optimized for the efficient production of SWNTs from very small amount of ethanol, SWNTs consisting of carbon-13 isotope (SW<sup>13</sup>CNTs) were synthesized. Raman scatterings from SW<sup>13</sup>CNTs show no change from SW<sup>12</sup>CNTs in spectrum shape except for the Raman shift frequency down-shifted as much as square-root of mass ratio 12/13. On the other hand, SWNTs with mixed 12/13 isotopes from <sup>13</sup>CH<sub>3</sub>-CH<sub>2</sub>-OH and CH<sub>3</sub>-<sup>13</sup>CH<sub>2</sub>-OH show different amount of down-shift in Raman spectra, suggesting that smaller amount of site-1 carbon atom (next to OH) is incorporated into SWNTs; suggesting an important decomposition process of ethanol on catalysts. Furthermore, near infrared photo-luminescence of D<sub>2</sub>O-surfactant dispersions of both SW<sup>13</sup>CNTs and SW<sup>12</sup>CNT were mapped. By comparing the excitation spectra, 'pure electronic' and 'exciton-phonon coupling' [2] transition peaks were clearly identified.

### References

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## Synthesis and Morphological studies on aligned and dispersed MWCNTs

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We have synthesized carbon nanotubes (CNTs) using the Chemical Vapor Deposition (CVD) of Iron Phthalocyanine molecules (FePc). Argon gas was employed to carry the molecules from the sublimation stage (650 °C) to the decomposition region. The FePc molecules were decomposed pyrolytically over SiO<sub>2</sub>/Si(111) substrate in the presence of hydrogen gas at temperatures in the range 800-1000 °C. The gas flow used (Ar: 200-1000 ml/min, H<sub>2</sub>: 200 ml/min) was much greater than the employed in similar synthesis before. The carbonaceous films obtained over the support samples were characterized by SEM, TEM, STM, Raman and XPS techniques. The results show well-oriented multiwall CNTs arrays with morphology and nanotube length (3- 20µm) and diameter dependent on time, temperature and argon flow. The growth of nanotubes starts in the surface of the Iron nucleus formed by the decomposition of the precursor molecule. At 800 °C we found a top growth mechanism where as between 900 and 1000 °C the base growth mechanism is predominant. The carbonaceous material was dispersed by ultrasound in 2-propanol solvent and deposited in silicon and carbon films for microscopic studies. Two main nanotube shapes were found: cylindrical and bamboo-like structures, with diameter in the range 10-250 nm.

## **Molecular Dynamics Simulation of Initial Nucleation Process of SWNT from a Metal Particle on a Substrate**

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Nucleation process of single-walled carbon nanotubes (SWNTs) from a transition metal cluster on a substrate is studied using classical molecular dynamics (MD) simulations. For describing the effect of the substrate, averaged one-dimensional Lennard-Jones potential is employed between the metal cluster and the bottom boundary of the simulation cell. Various sizes of the metal cluster are placed on the bottom boundary of the cubic cell. The number of carbon atoms is adjusted to achieve the constant pressure by adding a new carbon atom to the cell when the metal cluster dissolves a carbon atom.

In case of the weak interaction, the metal cluster kept spherical. Some cap structure appeared from the hump of the metal cluster. On the other hand, in case of the strong interaction, metal atoms tend to take (111) crystalline structure parallel to the substrate and graphite network is formed parallel to the direction as if the metal structure works as a template. In this case, graphitic network grows parallel to the substrate and forms the cap structure at this direction. So the direction of the metal (111) structure may be the key of the nucleation of SWNT.

## **Continuous production of highly pure carbon nanotubes and the application in field emission and thermal conducting fluid**

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Highly pure Carbon nanotubes or carbon nanofibers with tailored diameters from 10 to 100nm was continuously produced by the floating catalyst method using benzene as the carbon source and ferrocene as the catalyst precursor. With controlled amount of hydrogen and water content, the carbon nanotubes thus produced formed a macroscopic rope in the reactor and continuously ejected from the reaction zone. The rope was constructed by the carbon nanotubes with almost no carbon balls or amorphous carbon. The diameter of the carbon nanotubes can be tailored by controlling the retention time. Cutting of the carbon nanotubes was performed by mechanical pulverization and acid treatment. The field emitting and thermal conducting properties were performed using the cut CNTs with length less than 5 $\mu$ m. Acknowledgement: the author would like to thank TECO Nanotech Co., Ltd for their help on field emission test

## **Cross-sectional TEM investigation of Ni- catalysed carbon nanotube films by plasma enhanced CVD**

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Ni-catalysed carbon nanotubes (CNT) on silicon substrate synthesised by PECVD with C<sub>2</sub>H<sub>2</sub> and NH<sub>3</sub> at 700°C are characterised by analytical TEM. The aligned multi-wall CNTs have typical bamboo-like structure, and are capped with conical fcc-nickel particles dissolved with Si. Most of the particle caps have orientation with Ni<110> along the CNT axis with Ni {111} planes as exposed faces, and some are found orientated at Ni<100> direction. The interface between CNT and substrate are investigated. The model of CNTs nucleation is proposed on the base of Ni film refinement due to metal carburisation. A layer of Ni<sub>2</sub>Si and/or Ni<sub>3</sub>C dissolved with oxygen is observed in the interface at the top of amorphous silica on the substrate. Silicidation of the catalyst do not poison CNTs growth but changes the wetting properties of the catalyst with other metals. This catalyst-surface interaction and high conductivity of nickel silicide open the new road for growth CNTs on metal underlayers with controllable Si sublayers [1].

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## High selectivity of single-walled carbon nanotubes grown on silicon substrate by thermal chemical vapor deposition

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High selectivity of single-walled carbon nanotubes grown on silicon substrate by thermal chemical vapor deposition D.L. Ma<sup>1</sup>, C.H. Tsai<sup>1</sup> <sup>1</sup> Department of Engineering and System Science, Nation Tsing Hua University, 101 Sec. 2 Kuang Fu Road, Hsinchu 300, Taiwan, ROC Contact e-mail: [g92348@oz.nthu.edu.tw](mailto:g92348@oz.nthu.edu.tw) Single walled carbon nanotube (SWNTs) have been grown on alumina-supported Co-Mo catalyst by CVD technique at 700~900 oC using ethylene and methane gases, respectively. A series of bimetallic Co:Mo catalyst of various ratios were tested by wet-chemical deposition method on silicon substrate for the growth process. SWNTs with other forms of carbon (multi-walled nanotubes, graphite etc.) were formed when ethylene was used as carbon source and Co:Mo (molar ratios - 1:0~3:3) as catalyst. However, we obtained high quality SWNT of high selectivity using methane and Co:Mo (molar ratio of 2:3) catalyst. Raman investigation showed generally wide and narrow radial breathing mode (RBM) characteristics when methane and ethylene was used as carbon source, respectively, indicating that the diameter distributions of the SWNTs were also varied with the Co:Mo ratio and CVD process conditions. It was found that ,especially for wet-chemical deposition , the calcinations temperature /environmen t was also very crucial in achieving high SWNT selectivity , presumably attributed to the formation of oxides during calcinations and the subsequent CVD pretreatment /growth processes. The mechanisms will be discussed based on an intensive examination by a temperature programmed reduction (TPR) method X-ray photoelectron spectroscopy (XPS) characterization.

## **TEM study on catalyst film transformation and growth of Fe-catalysed CNT film by thermal CVD on Si-supported catalyst**

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The interface between the silicon substrate and a carbon nanotube film grown by thermal CVD has been characterized by high resolution and analytical transmission electron microscopy, including electron spectroscopic imaging. Growth of nanotubes was performed from acetylene and hydrogen mixture at 750 or 900 degrees C. Silicon substrates coated with a thin iron film were heat treated before growth at the deposition temperature in a mixture of flowing argon and hydrogen whereby nanosized particles of (Fe,Si)<sub>3</sub>O<sub>4</sub> silicates were formed. The reduction of the iron silicates particles during CVD at 750 degrees C was accompanied by a disintegration leading to the formation of a high density of smaller (predominantly 5-15 nm) iron silicide particles that catalyzed the growth of a dense and aligned CNTs film at 750 degrees. These particles were reduced to other structures of iron silicides with different catalytic activity during CVD at 900 degrees C, and random multi-wall carbon nanotubes grew from supported particles. The tubes did not contain any inclusions, and it was concluded that the nanotubes grew via a "base-growth" mechanism in both cases. The formation of small silicide particles is a prerequisite for the growth of aligned multi-wall carbon nanotube films.

## **Role of charge transport in carbon nanotube growth: Theoretical analysis**

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Attention is drawn to the number of effects which can take place under the typical conditions of the carbon nanotube growth. The electric field applied to the growing tubes and/or generated as a result of electron emission, thermionic or field-assisted, should affect strongly the carbon supply through the catalyst nanoparticle, enhancing the growth rate. Different aspects of the growth process are analyzed: the nanoparticle catalysis nature, carbon dissolution kinetics, electron emission from the nanotube tips, charge transport in the nanotube - catalytic nanoparticle system, carbon drift and diffusion (probably convective) through the catalyst under the action of the electric field. A fundamental tenet for modeling of charge transport dynamics during the nanotube growth process is proposed, combining recent theoretical developments with classical physics in the fields of metallurgy, electrostatics, and field emission.

## Single walled carbon nanotube growth from lithographically defined nanoparticle

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A semiconducting single walled carbon nanotube (SWNT) is an indispensable component of a carbon-nanotube (CNT)-based field-effect transistor (FET). However, for the high-density and high-yield integration of CNTs in devices, many technological issues still remain in obtaining only semiconducting SWNTs and in controlling their individual position, orientation, diameter, length, and chirality etc. One feasible approach is chemical vapor deposition (CVD) from custom-designed catalyst particles because the catalysts are thought to determine the characteristics of CNTs. We demonstrated the top-down control of diameter and position of Fe catalysts by means of "lithographically anchored nanoparticle synthesis (LANS\*)", and the CNT growth from the patterned particles. LANS was able to control the average diameter of Fe particles less than 2nm with the positioning error less than  $\pm 10$ nm. CNTs were grown by the CVD using ethanol and methane. Yield of the CNTs was strongly dependent on the particle size, CVD temperature, preparation procedure of the particle etc. However, we confirmed that SWNTs were grown from the particles with the root-growth mode and that their diameters were directly influenced by the particle size. These results showed the possibility of top-down control of SWNT characteristics.

\*M. Ishida et. al., Jpn. J. Appl. Phys. 43 (2004) L1356.

## Using Washable Catalyst Support for CVD Synthesis of Carbon Nanotubes

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It is common to use catalyst support for providing high surface area for catalytic chemical vapor deposition (CCVD) synthesis of carbon nanotubes. In this case, an additional process is needed to remove such materials from carbon nanotubes via washing in acidic or basic solutions. Thus, it is of interest to use washable catalyst supports, which can be washed away with water [1]. In the present study, we examined different washable materials for synthesis of carbon nanotubes. The influences of such washable catalyst supports on efficiency of the CCVD process and structure of the carbon nanotubes synthesized were investigated. The main problem associated with this approach is to achieve high porosity of catalyst support. Upon this advancement, this is of particular interest, since it is economical, with easier and controllable purification process. In any case, this approach provides a high performance CCVD process for synthesis of carbon nanotubes. A considerable feature about this approach is that melting points of such catalyst supports are significantly lower than conventional metal oxides. Different synthesis process was observed when the temperature is near to the melting point of the catalyst support. Of course, this can be (but not necessarily) in favor of the CCVD synthesis of carbon nanotubes.

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## Effects of pattern down-sizing in CNT localized CCVD growth

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The unique electronic and mechanical properties of CNTs present an enormous potential for numerous applications. The challenge consists in developing processes for making CNT-based devices in a controlled way. A simple method to produce such devices with high-density CNT networks on a large scale could be to integrate CNTs by synthesizing them directly onto substrates. In the present work, we aim at further elucidating the nature of the phenomena which govern the formation of CNTs networks from catalyst patterns by catalytic chemical vapor deposition. Patterns of a cobalt film are made over thermally oxidized silicon substrates, by means of high resolution e-beam lithography. For the CCVD process, we use methane and hydrogen as feedstock gases, and a synthesis temperature range of 700-900°C. The substrates are characterized after CCVD by FEG-SEM, Raman spectroscopy and HRTEM. A systematic study of the influence of the pattern sizes (down to 50 nm) and the gaps between the patterns (from 500 nm to 20 µm) is being carried out. Our first results show that low-diameter CNTs bridges can be formed between catalyst patterns with a fair alignment. We will present the latest results regarding the CNT bridges (alignment, yield) and the nature of these CNTs.

## Isolated single wall carbon nanotubes by PECVD

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We present here isolated Single Wall Nanotubes (SWNTs) grown by Electron Cyclotron Resonance Plasma Enhanced Chemical Vapor Deposition (ECR-PECVD) on flat silicon based wafer. The novelty of our process is the use of a sputtering system allowing in situ catalyst deposition by plasma sputtering. First, the cobalt ultra-thin film (<2nm) is deposited by ECR assisted physical vapor deposition (PVD) of a wire in pure ammonia. After in situ vacuum annealing (700°C), an ECR acetylene plasma diluted in ammonia (1:2) is used as precursor gas for nanotube growth. The substrate temperature is kept constant at 700°C. Electronic Microscopy (SEM and TEM) characterization of the deposited samples reveals well-separated short SWNTs or DWNT on the substrate after only 5 minutes growth following a base-growth mode. Statistical analysis of SWNTs by TEM indicates a narrow dispersion of diameters centered at ~2,5 nm. At the best of our knowledge, we are the first group that have grown SWNTs by PECVD directly on silicon substrate, while a few other groups succeeded SWNTs growth but only on silica substrates.

## The role of metal catalyst particles in carbon nanotube growth

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In recent years, various production methods for carbon nanotubes (CNTs) have been developed, however precise control of nanotube morphology (e.g. length, diameter) has yet to be realised, a fact which has delayed industrial exploitation of CNTs exhibiting defined morphologies. The development of the aerosol pyrolysis enables the production of large quantities of pure and aligned high quality carbon nanotubes.<sup>1,2,3</sup> Furthermore, depending on the precursor, modified carbon nanotubes can also be generated. For example, the spray-pyrolysis of ferrocene/xylene/triethylborane-based mixtures at 900°C results in a novel "sea-cucumber"-like structure containing carbon and boron<sup>4</sup> rather than B-doped CNTs. In contrast, the addition of N-containing hydrocarbons to ferrocene solutions produces N-doped CNTs.<sup>3</sup> In this context, pyrolysis experiments were carried out at various conditions in order to investigate the nature of the catalyst particles and their role during growth.

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## Long Amorphous Carbon Nanotube Ropes Synthesized by An Arc Discharge at Controlled Temperature

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Long amorphous carbon nanotubes ropes were prepared by a modified arc-discharging furnace[1], which can control temperature from room temperature to 900 °C during the electric arcing process. There are six  $\phi 10 \times 100 \text{mm}^2$  graphite rode anode with a  $\phi 6 \times 80 \text{mm}^2$  hole drilled in them which was filled with a mixture powders of Co-Ni alloy. The six anodes are mounted at an equal distance from each other on a wheel, which can be rotated in order to change the active anode. In our experiments: an arc was generated between the anode and the pure graphite cathode at a current of 100A in a 500 torr of hydrogen atmosphere. The distance between the electrodes was maintained at ~2mm by continuously feeding the cathode throughout the arc process. We observed the ropes formed around cathode and films on the inner wall of the chamber. The results indicate that temperature plays an important role in the formation of these ropes and the purity of the long carbon nanotubes ropes. The normal processes of synthesizing amorphous carbon nanotubes(arc discharge and chemical vapor deposition) can obtain the soot, which the typical morphology is powders[2]. We report that long amorphous carbon nanotube ropes, up to twenty-one centimeters in length and two to five micrometers in width and macroscopic films can be synthesized in hydrogen atmosphere at 650°C by an arc discharging furnace at controlled temperature. In summary, long amorphous carbon nanotubes ropes was obtained and the mechanism of long amorphous carbon nanotubes ropes was explained also in this paper.

### References

- [1] Y.N. Liu, X.L. Song. An electric arc furnace for producing carbon nanotube. Patent No.: 01240373.3 2002 (China).
- [2] L.J. Ci, H.W. Zhu, et al., Applied Surface Science 205 (2003) 39.

## Short Isolated Single-Walled Carbon Nanotubes Synthesized by Arc Discharge Process

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Short and isolated single-walled carbon nanotubes (SWNTs) were synthesized by arc discharge method under 150 Torr H<sub>2</sub> and 50 Torr Ar using carbon back as carbon source, nano Fe particles as catalyst, and FeS powder as growth promoter. The products are web-like, which contain SWNTs with well-crystalline structure. Instead of forming into bundles, most of the as prepared SWNTs are isolated with averaged diameter of 2 nm and lengths ranging from 10 to 30 nm. These isolated SWNTs provide convenience for structural characterization and property measurement of SWNTs, and may also be useful for nano device fabrications.

## Control of SWCNT properties via pre-formed catalyst particle diameter

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Single-walled carbon nanotubes (CNTs) were synthesised by a novel aerosol method based on the introduction of pre-formed iron catalyst particles into the conditions of CNT formation. CO was used as a carbon source. The results of statistical measurements of individual CNT dimensions based on high-resolution TEM images are presented. The geometric mean diameter of pre-formed catalyst particles varied from 1.35 to 2.06 nm (geometric standard deviations about 1.3) with a reactor temperature increase from 1000 to 1400 °C. It was found that the CNT diameters are determined by the catalyst sizes: the ratio between catalyst particle and CNT diameters was close to 1.6 and independent of the experimental conditions, thus revealing some astonishing “universality” in the growth process. Similar ratio was found for experiments with ethanol as a carbon source. However, utilisation of ferrocene and iron pentacarbonyl as catalyst precursors found a large ( $\geq 2.4$ ) ratio between diameters of catalyst particles and CNTs indicating subsequent growth of catalyst particles after CNT nucleation. A proposed geometric consideration of heptagon defect formation allowed us to successfully explain such a phenomenon. A mechanism of CNT formation is discussed.

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## **Carbon Nanotubes and Boron Nitride Nanofibres Synthesized by Radio Frequency Magnetron Sputtering**

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Significant quantities of well graphitised, straight and relatively long C nanotubes (5-30 nm in diameter) were synthesized by radio frequency magnetron sputtering of pure graphite in an argon discharge. Thin films were deposited on molybdenum substrates heated at a temperature ranging from 70°C to 600°C, but only substrate temperatures greater than 450°C resulted in nanotubes. Field-emission scanning electron microscopy revealed that the deposited films possess many fibrous regions. X-ray diffraction analysis has confirmed that the films have a nanocrystalline graphite structure. The nanostructures were characterized by high-resolution transmission electron microscopy. Compared to previous magnetron sputtering work, the nanotubes presented here exhibit a higher degree of graphitization. Various well-graphitised polyhedral nanoparticles were also produced, suggesting that experimental parameters need to be further optimised to improve the abundance of nanotubes. This preliminary study, suggests a direct one-step sputtering route for the production of C nanotubes. Sputtering of a pure hexagonal BN target under the same condition as for C did not produce nanotubes, but instead of nanofibres. Similar products, i.e. nanotubes and nanofibres, were also found in the films synthesized by co-sputtering of C and BN targets.

## **Synthesis of single-walled carbon nanotubes at large scale with high quality by electric arc using metal compounds**

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Ni and Y compounds such as their oxides and carbonates were studied as the catalysts for the synthesis of single-walled carbon nanotubes (SWNTs) using electric arc method. The purity and yield are evaluated using Raman, SEM, TEM, TGA and solution near-infrared (NIR) spectroscopy. Scale up to 50g/run was achieved with ~ 45-60% overall purity and 45-50% yield. The results show the SWNTs produced using these new catalysts are the same as that from Ni-Y catalyst.

## Vertically aligned carbon nanotubes by spray pyrolysis of a natural precursor

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There are many reports on the synthesis of vertically aligned carbon nanotubes from chemical vapor deposition (CVD), microwave plasma CVD and plasma enhanced hot filament CVD. The spray pyrolysis method here we used, is also a promising method for synthesis of vertically aligned carbon nanotubes. This method is sister method of CVD, very simple and inexpensive. This paper presents the growth of vertically aligned multi-walled carbon nanotubes on Si substrate. The mixture of natural oil (turpentine oil) as carbon source and ferrocene as a Fe catalyst precursor are used for synthesis of vertically aligned carbon nanotubes. The turpentine oil is derived from the pine trees especially from *Pinus Palustris* of *Pinaceae* family. The SEM study reveals that carbon nanotubes are vertically aligned perpendicular to substrate surface and these are multi-walled carbon nanotubes confirmed by TEM study. The length of the carbon nanotubes are ~300  $\mu\text{m}$  and diameter between 50-100 nm. In this presentation we will discuss on the further results.

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## Effect of carbon electrode on the yield of macroscopic SWNT net

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Recently, we have developed a new method [1] for producing macroscopic net of high crystallinity single-wall carbon nanotubes (SWNTs) with high yield by arc discharge evaporation of carbon electrode containing 1 at% Fe catalyst in H<sub>2</sub> + Ar gas. However, the yield of macroscopic SWNT net was strongly affected by the kind of carbon electrode materials. Here, we report about the dependency of carbon electrode materials for producing macroscopic SWNT net. Present study suggests that only low-graphitization carbon materials are suitable for producing macroscopic SWNT net, and the temperature of heat-treatment also plays an important role. Such a method is capable of generating SWNT net  $\approx 10$  g/day. The as-grown SWNTs net can be easily purified by a simple chemical treatment. For removing the amorphous carbon coated Fe nanoparticles, as-grown SWNTs net was refluxed in H<sub>2</sub>O<sub>2</sub> solution. EDX and TGA analyses indicate that the Fe content in purified SWNTs is less than 0.05 at%. The present production and purification process of SWNTs is on gram level, and can be scaled up to industrial level of throughput.

### References:

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## Study on the synthesis mechanism of carbon nanotubes in a dc arc discharge process

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We grew carbon nanotubes (CNTs) using the dc arc discharge process and investigated the synthesis factor of CNTs. Various cubical-shaped, catalyst metal deposited, carbon cathode electrodes were used for preparing the CNTs. Transition metal films, applied as catalysts, were deposited at thicknesses between 2000 - 10,000 Å on a carbon cathode electrode using an e-beam evaporator and electroplating system. The carbon plasma was generated at various currents from 40 A to 100 A under varying voltage of between 18 - 30 V, and the pressure of the chamber was maintained at approximately 500 torr using a continuous flow of He gas. The flow of He gas around the carbon cathode was controlled by a sheath structure. The cylindrical hard deposits collected from the carbon cathode were treated using acidic and thermal treatments to purify the CNTs. The purified CNTs were characterized by SEM, XRD, Raman spectroscopy, and TEM. The experimental results showed that the yield and the morphologies of the grown CNTs varied, depending on the condition change and type of catalyst metal of the carbon cathode electrode. The outer diameters of the grown CNTs varied from several nanometers to tens of nanometers, but the inner diameter variations were not significant. Using these results, the growth mechanism of the CNTs and the role of the cathode electrode in the arc process will be discussed. In addition, feasible methods of large scale CNT fabrication will be suggested.

## Towards a wet chemical synthesis of carbon nanotubes with uniform but tunable dimensions and properties\*

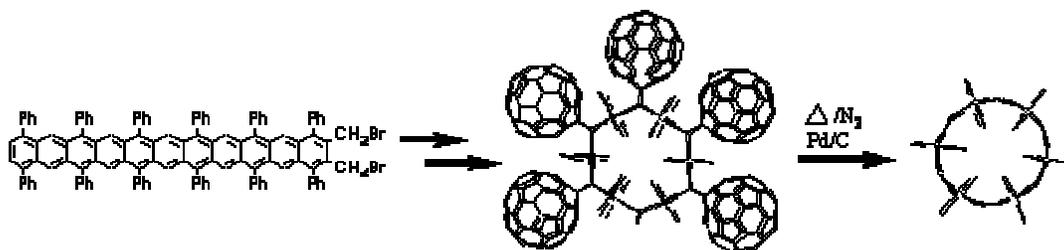
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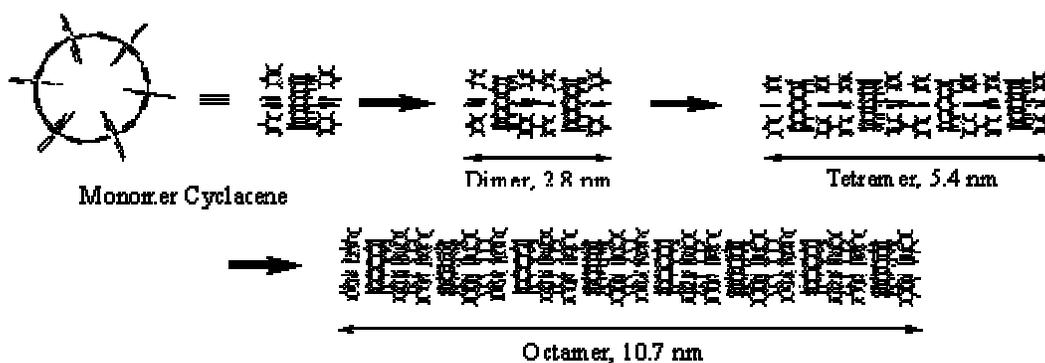
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We propose a new way to synthesize carbon nanotubes by means of wet chemical synthesis. The objective is to develop a high-volume chemical production of single-walled nanotubes with uniform but tunable dimensions and properties. Our approach is a two-stage chemical synthesis. In the first stage, C<sub>60</sub> molecules add in a diastereoselective *syn* fashion across large, phenyl substituted acenes to produce cyclacene (i.e., cyclic acene) molecules with variable diameters, which map directly onto zig-zag carbon nanotubes.



In the second stage, the cyclacenes are iteratively oligomerized to form single-walled nanotubular molecules with variable lengths.



This approach offers a means to prepare uniform batches of single-walled nanotubular molecules that are amenable to chemical functionalization. Likewise, the nanotubes are expected to show excellent solubility in either organic or aqueous solvents, depending upon the nature of the functional groups attached. A range of functional groups can be added, from strongly electron donating to strongly electron withdrawing, and from neutral to ionic. Because functional groups are added

according to a substitution rather than an addition mechanism,  $\pi$ -bonds are not consumed and conjugation is not lost during chemical functionalization.

The experimental synthesis is supported by *ab initio* Density Functional calculations of the equilibrium atomic structure, electronic properties, and quantum transport of these systems. Besides the (12,0) nanotube, which is most closely related to the structure described above, we will also study the stability and electronic properties of narrower nanotubes.

An important objective of the simulations will be to also investigate the effect of chemical functionalization and doping on the nature of frontier orbitals and conductance. Computer simulations will further be used to study the possibility of using short segments of oligomerized cyclacene-based nanostructures as a seed to selectively grow monochiral single-wall nanotubes in a CVD process.

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## **Formation of single-walled carbon nanotubes by laser vaporization:**

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In the reactor previously developed at ONERA to investigate the gas phase during carbon nanotube formation, Laser Induced Fluorescence (LIF) and Laser Induced Incandescence (LII) have been recently undertaken. Continuous vaporization of the target (C:Co:Ni, 96:2:2 %at.) is achieved with a continuous wave CO<sub>2</sub> laser in helium buffer gas [1]. Temperature profiles are known from previous CARS measurements and flow calculation. Soot concentration and sizes are obtained by LII in the hot carbonaceous flow. LIF measurements of the C<sub>2</sub> and C<sub>3</sub> radicals and of Ni and Co atoms are presented. These results are measured as a function of target composition and temperature. The effect of the catalyst nature is observed on the shape of the C<sub>2</sub> spatial profiles. The behavior of the C<sub>3</sub> radical is not so sensitive to catalyst nature. The size evolution of the soot particles definitely changes from linear to non linear when the proper catalyst pair is present into the flow. Soot transformation occurs just before the disappearance of catalyst vapor phases. Comparison of LIF and LII signals allow us to correlate the spatial evolution of gas and soot in the scope of the successive steps of the nanotube growth already proposed in the literature [2].

## **Large scale production and purification of high-quality DWNTs by high-temperature pulsed arc discharge**

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A high-temperature pulsed arc discharge (HTPAD) have been providing us high-quality DWNTs (HQDWNTs) with narrow diameter distributions and good graphitization. The yield of HQDWNTs, however, is about 20 % at the best condition and production rate is 50 mg per day. To improve the yield and production rate and to clarify the production processes of HQDWNTs, we have developed large scale HTPAD apparatus equipped with parallel discharge mechanisms and precise temperature control. With this apparatus, we have succeeded to enhance the production rate up to 1 g per day and to control the diameter and the number of layers.

## **Patterned growth of carbon nanotubes without pre-catalyst deposition**

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Aligned carbon nanotubes (CNTs) can be readily synthesized on quartz or silicon-oxide coated Si substrates using chemical vapor deposition (CVD) methods, but it is difficult to grow them directly on pure Si substrates without pre-deposition of metal catalysts. We will demonstrate that aligned CNTs can be grown on Si substrates by pyrolysis of iron phthalocyanine at 1000C. Scanning electron microscopy and X-ray energy spectroscopy analysis reveal that pre-created patterns on the substrate containing trenches are preferred nucleation sites for nanotube growth due to a high surface energy and possible capillarity effect. A two-step pyrolysis process and a pre-ball milling treatment avoid chemical reactions between Fe catalyst particles and Si substrate which prevent nanotube growth.

## **The study of the influence of sulfur promoter in arc discharge production of SWCNTs using various catalysts**

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The influence of sulfur promoter on the production of SWCNTs catalyzed by various metals in arc-discharge experiments was investigated. The metal composition and concentration of added sulfur strongly affects abundance of web-like material containing SWCNTs. A little or no web-like product was found if no sulfur was used for Fe/Y and Pt/Rh mixtures. The yield increases with increasing concentration of sulfur reaching a maximum and then decreases. There were no webs found for sulfur concentration larger than 2.5 at. % for Fe/Y/S/C mixture. Arc-discharge products prepared at various conditions were characterized by TGA, Raman spectroscopy, X-ray diffraction, optical spectroscopy and TEM. Characterization shows that, at the conditions promoting highest yield of web-like product, this product contains the lowest concentration of metals and the highest concentration of SWCNTs. Addition of proper amount of sulfur to the catalysts increases the relative abundance of SWCNT with larger diameters.

## Chirality control of carbon nanotubes on self-ordered SiC nanofacets

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Chirality control is one of the significant issues for the future application of carbon nanotubes (CNTs). Among many approaches for this purpose a simple CNT formation route via surface decomposition of SiC in vacuum [1] is unique and may give certain idea to solve the problem. We here especially provide vicinal SiC surfaces (eg. 8 degree off), which have super-periodic nanofacet structures by self-ordering [2]. We clearly observed by AFM and in-situ STM significant effects of such ordered surfaces on the CNT formation: the CNTs formed parallel to the vicinal surface after graphitization tend to be aligned perpendicular to the step edges and possibly have single chirality. This may be due to anisotropic strain relaxation at the interface of a graphene sheet and SiC because of unidirectionally ordered nature of the vicinal surface. Locally swelled graphite (~1nm in diameter) by this process initially plays as a nucleus of CNT and is prolonged to the step edge in the next stage. A CNT is finally formed by rolling-up such a string-shaped nucleus. In our model, the chirality of such CNT is simply determined by the vicinal direction of SiC substrate and the CNT growth direction. Therefore it is of very importance to control initial SiC surfaces with highly ordered nanofacets in order to achieve single chiral CNT formation.

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[2] H. Nakagawa, S. Tanaka, and I. Suemune, Phys. Rev. Lett. 91, 226107 (2003).

## Comparison of Efficiencies of Composite Catalysts in Arc-Discharge Synthesis of Single-Walled Carbon Nanotubes Using NIR Spectroscopy

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The quality and yield of single-walled carbon nanotube production depend on multiple factors. The optimization of the SWNT synthesis requires accurate and efficient evaluation of small changes of the quality and yield of bulk quantities of the product as a function of the synthetic parameters. Recently we proposed a quantitative procedure to assess the relative carbonaceous purity of bulk quantities of AP-SWNT soot on the basis of solution-phase NIR spectroscopy.<sup>1</sup> We applied this technique to obtain a detailed map of purity and yield of SWNT soot as a function of Ni/Y catalyst composition in the two-dimensional space of Ni/Y concentrations.<sup>2</sup> We found that a wide range of catalyst concentrations, 3.0-6.0 at. % of Ni and 1.0-2.0 at. % of Y, allows efficient production of high purity SWNT soot. This provides an opportunity to scale up the electric arc discharge synthesis of SWNTs for industrial applications. We will present data on a variety of binary and ternary compositions of different transition and rare earth metals and provide direct comparison of the purity and yield of the SWNT soot between different catalyst feedstock compositions.

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## **Real-Time Study of Nucleation and Growth of Vertically Aligned Single Wall Carbon Nanotube Arrays**

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A molecular beam of carbon containing molecules in combination with time resolved reflectivity was used to create a controlled environment in which the nucleation and growth of vertically aligned single wall carbon nanotube arrays can be studied in real time. The molecular beam environment decouples the source gas and the substrate temperature and eliminates secondary gas phase reactions to allow carbon nanotube growth from heterogeneous reactions only. A beam of acetylene molecules seeded in a mixture of hydrogen and helium impinging on a heated multilayer metal catalyst film consisting of Fe and Al was used to grow up to 400  $\mu\text{m}$  thick arrays. The incidence rate of the carbon containing species is the key variable that determines the onset of vertical alignment, the density in aligned growth, and the type and diameter of nanotubes. The real-time measurements show that the addition of trace amounts of impurities such as water and oxygen affect the nucleation behavior, but not the growth rate in vertically aligned growth. These experimental trends are in contrast with the prevailing models of carbon nanotube growth dominated by carbon diffusion processes and the notion that the particle size is the sole factor that determines the carbon nanotube diameter.

## **n-TEC: a new producer of multi-wall carbon nanotubes and related carbon nanomaterials**

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n-TEC [1] is a Norwegian company specialized in the large scale production of multi-wall carbon nanotubes (MWNTs) by arc-discharge. Our ambition is to offer high quality materials. Because they are grown at high temperature (3000-4000 C), arc-discharge MWNTs have a structure close to ideal. They contain far less defects than nanotubes produced by any other method and are therefore the best choice for every application where high performance is essential. n-TEC is also the only supplier worldwide of a new class of carbon materials: carbon cones. As their name suggests, these carbon materials have a nearly perfect conical geometry. Carbon cones are produced by pyrolysis of hydrocarbons using an exclusive torch plasma process. The properties of this novel material are under investigation. It is very likely that their unique geometry and structure will result in unprecedented electronic, chemical and mechanical properties.

[1] [www.n-tec.no](http://www.n-tec.no)

## Experimental study of mechanism of carbon nanotube formation in the arc discharge

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A model for carbon MWNT formation in the arc discharge has been developed. MWNTs' and metallic nanoparticles' (MeNPs) morphologies have been controlled versus median arc durations for 40 different regimes of arc-discharges provided in gas and liquid phases with use of graphite anodes of different purity grades. Being normalized, all the morphologic distributions resemble each other. Moreover, MWNTs' inner diameter (ID) distributions resemble corresponding MeNPs' size (MS) distributions giving simple equation:  $ID=MS+0.7nm$ , showing that all arc-produced MWNTs are catalytically grown due to adsorption and further graphitization of carbon vapor over MeNPs. Also it has been shown that the anode surface is eroded explosively. This causes a complete atomization of the metallic admixtures and formation of carbon clusters with median sizes of about C15-C20 in conventional Gas-phase Carbon Arc-discharges (with graphite anodes of 99.99% grade) and C50-C100 in Self-regulated Liquid-phase Arc-discharge (with graphite anodes of 99.5-99.8% grade). The atomized metals reach the hot cathode ahead of carbon clusters (>C6) and form metallic nanodroplets with median sizes of Me100-Me500, which start adsorption and graphitization of the arriving carbon clusters (C10-C100) one by one over themselves, forming MWNTs. The nanotube growth is terminated when a larger carbon cluster is adsorbed by the nanodroplet, releasing excess of energy and overheating the nanodroplet, that leaves the nanotube but, being cooled instantly, starts adsorbing the larger clusters forming thicker and shorter MWNTs which growth is quickly terminated because of the overheating. Then such an action is repeated several times causing further nanotubes' shortening, turning them into carbon polyhedral nanoparticles, until the largest carbon clusters arrive to the place of action forming disordered graphite carbons. This model can explain all the main features of carbon nanotube formation in the arc -discharge quantitatively.

## A novel coral-like carbon nanotubes

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A novel coral-like carbon nanotubes was presented in this paper. They were prepared by a modified arc discharging furnace[1] in hydrogen atmosphere with a mixture of Mo-Co<sub>2</sub>O<sub>3</sub>-Mg powders as catalyst at 600°C. This carbon nanotubes presents a microscopic coral-like by a SEM and a TEM observation, and amorphous carbon nanotubes by a HRTEM observation. But the XRD diffraction pattern presents a crystal characteristics compared with normal graphite structure. It is very strange that the results are uniform. We think that these results may be affected by catalyst, atmosphere and temperature. Tried explanations to the formation mechanism of this novel carbon nanotubes have also been proposed.

### References

[1] Y.N. Liu, X.L. Song. An electric arc furnace for producing carbon nanotube. Patent No.: 01240373.3 2002 (China).

## **A Grand Canonical Monte-Carlo Study of the Structural and Adsorption Properties of Zeolite-Templated Carbon Nanostructures**

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We have used the Grand-Canonical Monte-Carlo technique (GCMC) to simulate the vapor deposition of carbon in the porosity of various zeolitic nanopores (silicalite, AIPO4-5, faujasite). The carbon-carbon interactions is described within a Tight-Binding formalism (TB) and the carbon-matrix interactions are assumed to be physisorption. Depending on the pore size and topology, various carbon structures can be obtained. For instance, we show that narrowest single wall nanotube can be synthesized in the cylindrical channel of AIPO4-5 zeolite (pore diameter 7 Å) in agreement with the experimental work of Tang (Nature 2002). We further show that this ultra small nanotube is defective but stable after template removal. We also demonstrate that a zeolite such as silicalite with smaller pores (pore diameter 5 Å) does not allow obtaining nanotubes but a mesh of intercrossing carbon chains. The pore topology of faujasite zeolite (made of tetrahedrally coordinated spherical cavities) allows making a highly porous ordered carbon material that was subsequently tested for H<sub>2</sub> storage along with other perfect nanostructures (graphene layers, nanotube bundles ...) for comparison.

## Fluid Ice in Carbon Nanotubes

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The infiltration of water into carbon nanotubes provides a simple analogue of biologically important trans-membrane channels and so is of large interdisciplinary scientific interest. The structure and dynamics of water/ice confined to the 1-Dimensional nanotube interior are found to be drastically altered with respect to bulk water. Neutron diffraction, inelastic and quasielastic neutron scattering measurements in parallel with MD simulations (performed using the TTM2-F polarizable flexible water model with smeared charges and dipoles) have clearly shown the entry of water into open-ended SWNT and identified an ice-wall plus central water-chain structure. The observed extremely soft dynamics of nanotube-water/ice arises mainly from a qualitatively large reduction in the hydrogen-bond connectivity of the water-chain. An average coordination number of 1.86 was found due to continually breaking/forming of the hydrogen bonds between a water molecule with its two nearest neighbors even at ~50 K. Anomalously enhanced thermal motions in the water-chain, interpreted by a low-barrier, flattened, highly anharmonic potential well, explains the large mean-square displacement of hydrogen and fluid-like behavior of nanotube-water at temperatures far below the nominal freezing point. This behavior agrees qualitatively with the expected water and proton transport via the nominally hydrophobic inner region of transmembrane proteins such as aquaporin, gramicidin, and bacteriorhodopsin.

## **Growing Carbon Nanofibers on Carbon blacks by Non-catalytic Chemical Vapor Deposition**

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We report a simple method to synthesize carbon nanofibers (CNFs) on a reinforced filler-carbon black (CB) by a non-catalytic chemical vapor deposition method. CNFs are fabricated on carbon black at 800 °C by directly decomposing form diluted ethylene (10% C<sub>2</sub>H<sub>4</sub>/Ar). The growth yield and diameters of CNFs on carbon blacks are depending on their specific surface area, reaction temperature and dwell times conducted in-situ by TGA measurements. The new form carbonaceous materials-CNF/CB shows higher specific surface area and better dynamic elastic modulus will be used in potential applications for reinforcement and conductivity.

keywords : A. Carbon nanofibers; B. Carbon Black; C. Chemical Vapor Deposition.

## High yield preparation of metal encapsulated single-wall carbon nanohorns

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We found that single-wall carbon nanohorns (SWNHs) were aggregated around a metal-encapsulated graphitic carbon nanoparticle. SWNHs including a metal-encapsulated graphitic carbon nanoparticle in its center (M-SWNHs) were formed with a high yield (about 70 %) by a laser vaporization method. The mixture of graphite and metal powder in a ratio of 4 : 1 by molecular weight were pressed to form target pellets. We had used Fe, Ni, Co and Ti as metal-catalysts. The target was vaporized by a continuous wave Nd:YAG laser in Ar gas ambient atmosphere (0.10 to 0.30 MPa). The product soot was collected and characterized by transmission electron microscopy (TEM). The TEM images of the product indicate that M-SWNHs consist of a metal nanoparticle core and SWNHs. M-SWNHs had diameters of about 51-190 nm (mean diameter: 130.3 nm). SWNHs are apt to aggregate around smaller metal nanoparticles. The metal nanoparticle core had diameters of about 10-98 nm (mean diameter: 44.9 nm). TEM observation revealed that the metal nanoparticle core was coated by graphite shells of about 0.5-14 nm.

## **The Crystallographic Characteristics of Catalytically Formed Carbon Nanofibers**

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The carbon deposit, formed by CVD - method, using different catalysts: Fe, Co and Ni, was investigated by transmission electron microscopy methods, using JEM-200CX and JEM-2010, equipped by EDS (INCA). It was found that the deposit consisted of nanotubes and nanofibers. Catalyst particles revealed both metal and carbide structure. Experimental conditions for carbide formation have been found. We analysed crystallographic features of different catalyst particles: structure, shape, orientation along the fiber growth direction. Defects in the bulk of some catalyst particles were found and studied. The deformation mechanism, based on the surface tension force, responsible for defects occurrence in catalysts and in fibers, is discussed.

### References:

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## Adsorption States of Organic Materials Inside Single-Wall Carbon Nanohorns

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Single-wall carbon nanohorns (SWNHs), a type of thick nanotube assembling to form spherical aggregates, can store drugs and fuels and release them. In order to understand the adsorption sites inside the hollow spaces of SWNHs so that to control the material release, we studied desorption phenomena of organic materials with conventional thermogravimetric measurements but combining with step-wise removal of defects by combustion. We identified the adsorption sites with three types using xylene [1] and benzene [2]. The deepest sites were on the inside surface of the walls at tips and convex parts, the second deepest sites were on other wall surface regions, and the shallowest sites were in the central region of the hollow space inside the SWNHs. Comparing the desorption of benzene and m-xylene, we found that they were bound to the SWNH walls at the first and second deepest sites, but they condensed through self-interaction at the shallowest site.

References:

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## **Preparation and properties of metal encapsulating carbon nanocapsules (MECNCs)**

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The metal-encapsulating carbon nanocapsules (MECNCs) which are several tens of nanometers in diameter and consist of a graphene sheet structure encapsulating a metallic carbide. MECNCs have a surface covered by a graphene sheet, so they have quite high chemical stability. In the capsule, lanthanide is usually encapsulated as a carbide. Therefore, MECNCs will provide higher imaging and tracing efficiencies as contrast agents or tracers. We prepared the various lanthanide containing MECNCs and their structural change in the purification was studied. MECNCs were oxidized with the heat treatment at 400C or higher, but MECNCs showed no change less than 400C. The cytotoxicity of MECNCs was also studied and no severe cytotoxicity was induced.

## Thermal Conversion of Bundled Carbon Nanotubes into Graphitic Ribbons

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The morphological evolution of purified bundled single-walled carbon nanotubes (SWNTs) heat-treated in a dynamic vacuum from  $T = 200\text{-}2200\text{ }^{\circ}\text{C}$  was investigated by transmission electron microscopy, Raman scattering and optical absorption. Although the thermal evolution of bundled SWNTs was first carried out several years ago, the studies were on material containing the growth catalyst. Here we study the thermal evolution of purified bundled HiPCO and ARC material. Their very different initial diameter distributions lead to very different thermal evolution behavior. As observed before, we also see the transformation to MWNTs, but we also observe for the first time the early development of a new form of filamentary carbon: graphitic nanoribbons (GNR). We propose that GNR's form by the collapse of bundled MWNTs into flattened tubes, or ribbons. All the physical probes we have used give a consistent picture about the thermal transformations in the system. Coalescence is found to occur primarily between 2 tubes and occasionally between 3 tubes. The tighter diameter distribution of the ARC material leads to a more organized approach to more perfectly formed MWNTs (3-11 shells) and to graphitic nanoribbons. We suggest a new theoretical model for the conversion of SWNTs into coalesced tubes and the collapse of MWNTs into GNRs.

## A Novel Structure of Carbon Nanofiber Stacked of Nanocone

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A novel nanoscale carbonfiber stacked by conical graphene layers has been reported. Using anodic aluminum oxide (AAO) as template and petroleum pitch powder as precursor, after thermal treatment a mass and uniform carbon nanofiber was obtained. The diameter and length was measured to be around 300 nm and 60  $\mu\text{m}$ , respectively. The orientation interrelation between the graphene plane and fiber axis was studied by high resolution TEM, the orientation between graphene plane and fiber axis is continuous varied and the range of cone angle is from  $60^\circ$  to nearly  $180^\circ$  along the fiber. This arrangement was similar to the herringbone-type carbon structures, but the angle was not fixed. According to the orientation observation, we proposed that this nanofiber was constructed by stacking conical graphene layers with different cone angles. This architecture is the first time to be synthesized without using catalytic CVD method, thus the growth mechanism should be reexamined. The result is distinct from what have been known for the conventional carbon nanotube obtained from fluid carbon sources and had never been reported in same kind of template procedure as well. Such morphology supports an unprecedented view on its particularity for potential applications.

## **Magnetic properties of metal phosphide nanoparticles periodically inserted in carbon nanotubes**

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Understanding the growth mechanism of carbon nanotubes and controlling their morphology and insertion still remain important challenges. The possibility to fill their inner channel with foreign materials also opens the way to the design of new hybrid materials with novel or enhanced properties, in terms of electron charge/spin transport or magnetic storage. We showed that the use of phosphorus as a co-catalyst enables to modify the kinetic equilibrium between the growth elementary steps of multiwall nanotubes (MWNT) and to induce a mechanism of sequential catalytic growth. Such a mechanism produces nanotube-based filaments periodically inserted with catalyst nanoparticles. The periodically inserted nanoparticles are nickel, cobalt or iron phosphides. We will present our work devoted to the control of the magnetic properties of the inserted metal phosphide nanoparticles and their characterisation by local techniques (MFM and electron holography).

## Atomic Step-Templated Formation of SWNT Patterns

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Single-wall carbon nanotubes catalytically produced on miscut C-plane sapphire wafers grow along the 0.2nm-high atomic steps of the vicinal  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (0001) surfaces, yielding highly aligned, dense arrays of discrete nanotubes on a dielectric material. The nanotubes reproduce the atomic features of the surface, including steps, facets and kinks. The orientation, density and morphology of the atomic steps can be macroscopically controlled by the crystal cutting process. Hence, these findings open up the possibility of assembling nanotube architectures by atomic-scale surface engineering, as a sort of "nanotube epitaxy".

Reference:

A. Ismach, et al., Angew. Chem. Int. Ed. 2004, 43, 6140.

## **A New Structure of One-Dimensional Nanomaterials: Rectangular Multi-Channel Nanotubes**

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For the case of carbon nanotubes, it is common to synthesize single-wall and multi-wall nanotubes. However, for metal oxides, the most common form of nanotubes is one-channel nanotubes. More recently, we proposed a simple solid-state route for preparation of 1D nanostructured manganese oxide [1,2]. Here, a new form of 1D nanomaterials is reported (i.e., even different from multi-wall carbon nanotubes). It was found that a peculiar structure of individual nanotubes is formed in the course of a simple solid-state synthesis of manganese oxide. In this case, nanotubes have rectangular shape instead of conventional cylindrical shape. In fact, each individual nanotube consists of smaller ingredients, which are indeed sheet-like nanoribbons. Of course, these nanoribbons are closely packed and can only be distinguished on broken heads of nanotubes. Both SEM and TEM results confirm this novel structure. High resolution AFM with scanning area of diameter of one individual nanotube was also employed to visualize rectangular structure of these nanotubes with high resolution. In general, rectangular nanotubes can be synthesized by this simple method. Interestingly, these nanotubes have several longitudinal channels across the nanotubes. This provides a great opportunity for diffusion processes. It should be taken into account that better diffusion process requires nano-channels. This is exactly what this novel structure has: low surface area with numerous internal nano-channels.

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## Ordered water inside carbon nanotubes: formation of pentagonal to octagonal ice-nanotubes

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We report on a systematic X-ray diffraction analysis for the ordered water inside single-walled carbon nanotubes (SWNTs) with diameters of 1.09-1.52 nm. Four distinct ordered structures identified in this diameter range were assigned to polygonal ice-nanotubes predicted by molecular dynamics (MD) calculations. The ordering transition temperature rose from 190 K of octagonal ice-nanotubes to 300 K of pentagonal ice-nanotubes without applying high pressure when the SWNT diameter decreased. The results indicate a crossover from bulk to atomic scale phenomena with decreasing SWNT diameter.

## **Resonant Raman Intensity of the Radial Breathing Mode of Single-Walled Carbon Nanotubes**

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The resonant Raman profile of the radial-breathing mode is calculated exactly and within two approximation schemes of different degree of complexity for all 300 single-walled carbon nanotubes in the radius range from 0.2 to 1.2 nm within a symmetry-adapted non-orthogonal tight-binding model. In all the three cases, the matrix elements of the momentum and the deformation potential are calculated explicitly. The two approximation schemes assume a) wavevector-independent matrix elements, and b) tube-independent and wavevector-independent matrix elements. It is shown that scheme (a) reproduces semi-quantitatively the results of the exact calculation. However, the assumption for tube-independent matrix elements in scheme (b) leads to qualitative disagreement with the exact results. Therefore, the application of the latter scheme for prediction of the Raman spectra can lead to incorrect assignment. On the other hand, the tabulated parameters of scheme (a) can be used for predicting the Raman spectra for a given laser excitation energy and diameter distribution of the tubes and to determine the diameter distribution of a given experimental Raman spectrum.

## Raman Spectroscopy of Individual Single-Walled Carbon Nanotubes from Various Sources

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Resonance Raman spectroscopy/microscopy was used to study individualized single-walled carbon nanotubes (SWNTs) both in aqueous suspensions as well after spin-coating onto Si/SiO<sub>2</sub> surfaces. Four different SWNT materials containing nanotubes with diameters ranging from 0.7-1.6 nm were used. Comparison with Raman data obtained for suspensions shows that the surface does not significantly affect the electronic properties of the deposited tubes. Raman features observed for deposited SWNTs are similar to what was measured for nanotubes directly fabricated on surfaces using CVD methods. In particular, individual semiconducting tubes could be distinguished from metallic tubes by their different G mode line shapes. It could also be shown that the high-power, short-time sonication used to generate individualized SWNT suspensions does not induce defects in great quantities. However, (additional) defects can be generated by laser irradiation of deposited SWNTs in air thus giving rise to an increase of the D mode intensity for even quite low power densities (~104 W/cm<sup>2</sup>).

## Correlating electrical and optical properties of individual single-walled carbon nanotubes

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We performed a study on more than 50 individual metallic and semiconducting single-walled carbon nanotubes in order to compare their electrical and optical properties. The tubes were deposited via low-frequency dielectrophoresis, a technique which allows the deposition of both individual metallic and semiconducting tubes from suspension [1]. All tubes were proven to be individual by atomic force microscopy. Half of the samples were additionally analyzed by electron transport measurements and resonant Raman spectroscopy. We present experimental results showing an evident correlation between Raman spectra and electron transport measurements with the nanotube properties.

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## A Raman study of dimetallofullerene peapods

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A peapod is a single-wall nanotube (SWNT), which encapsulates fullerenes. In addition to the simplest peapod, (C<sub>60</sub>)<sub>m</sub>@SWNT [1], metallofullerene peapods have been obtained [2, 3]. We report on the results of a Raman study of peapods filled with La<sub>2</sub>@C<sub>80</sub>s and Ti<sub>2</sub>@C<sub>80</sub>s. We have used a sensitive Raman imaging process in order to locate the peapods in our highly diluted sample. The evolution of the Raman images with respect to the polarisation of the excitation beam demonstrates that the diffusion of peapods is dominated by a strong antenna effect. In conjunction with this effect, we have observed a high diffusion efficiency. It suggests the existence of enhancement effects in peapods strong enough to allow one to detect the signal of a single peapod without the need of additional exaltation effect as resonant Raman or SERS. The Raman spectrum itself differs from that of hollow nanotubes and of metallofullerenes alone. New lines in the low- and intermediate-frequency range appear. These different features will be discussed.

### References

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## The Fine Structure in the Kataura-Plot of DWCNTs

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The radial breathing mode (RBM) Raman response of double-wall carbon nanotubes (DWCNTs) derived from fullerene peapods shows a number of very narrow modes originating from the RBMs of the inner tubes. So far, these modes were chirality assigned on the basis of a systematic study of vibrational frequencies. Since the number of the observed components was considerably larger than the number of geometrically allowed inner shell tube types it was assumed that each inner tube type can grow in up to three outer tube types with different diameters thus giving rise to several slightly offset RBMs.

Measuring the resonance cross section for each of the components allowed to draw an experimental Kataura-plot of transition energies over phonon frequencies. From this, the large number of components turned out to be strongly grouped into species belonging to the same inner tube chirality. The grouping is retained during the growth process, i.e., members of the groups appear and grow collectively. Comparing the RBM frequencies and transition energies with recently published data on dispersed individual HiPco tubes showed that the lowest frequency components in the groups correspond well to the HiPco frequencies. However, the (6,5) and (6,4) tubes now exhibit a fine structure with more than 10 components spread over more than 20  $\text{cm}^{-1}$ . Interestingly, the total width of this splitting increases for decreasing tube diameter. The transition energies for all inner tubes are downshifted by about 50 meV as compared to HiPco. Additionally, the transition energies of the c omponents of one inner tube type decrease slightly with increasing RBM frequency. The origin of this unexpected behavior of the inner tubes RBMs will be discussed based on the assumption that one inner tube type can grow in several outer tube types which imply different hydrostatic pressures on the inner tube depending on the diameter difference.

## Vertically Aligned Ag Coated MWNTs for SERS

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Many SERS-active systems, such as colloid clusters and grating-type substrates with nm dimensions have been studied. In addition, new systems have emerged from carbon nanotubes technology. These SERS samples consist of either single-wall carbon nanotubes adsorbed on silver and gold surfaces [1] or colloidal cluster solutions in which the nanotubes were added in low concentration [2]. Here we consider standing multi-wall nanotubes (MWNTs) as substrates for SERS. The samples were grown by plasma-enhanced chemical vapour deposition [3]. The substrates were then coated with silver and exposed to crystal violet (CV) molecules. The samples coated with colloidal silver clusters generate large enhancement of the Raman signal associated with the MWNTs themselves. Both the radial breathing modes and the tangential modes are enhanced. For the case where CV molecules are adsorbed on the Ag-coated MWNTs the Raman signal strength is comparable to that from a standard colloidal silver system. Work supported by EC STREP program DESYGN-IT, ECFP6-NMP4-CT2004-505626

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## **Infrared-Active Vibrational Modes of Single-Walled Carbon Nanotubes**

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We believe we have observed the IR-active vibrational modes of single-walled carbon nanotubes (SWNTs) for the first time. They were observed by optical transmission through thin films of bundled nanotubes. Because IR-active chemical functional groups, e.g., -COOH, -OH, might also be attached to the tube walls and contribute additional spectral features, we have also studied the effects of chemical purification and long-term high-temperature vacuum annealing on the IR spectrum. Through comparison with theory, we are able to assign much of the sharp structure observed in our IR spectra.

## Electrochemical and chemical redox doping of carbon nanostructures

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Single-wall carbon nanotubes (SWCNT), double-wall carbon nanotubes (DWCNT) and peapods (e.g. C60@SWCNT) are recently studied with respect to redox doping. The change of redox state of these carbon nanostructures could be achieved either by chemical redox or by electrochemical reactions. The n-/p-doping increases the concentration of electrons/holes, respectively, and thus modifies the electronic structure of the different types of nanocarbon. In-situ Raman and Vis-NIR spectroelectrochemistry was used to monitor the charge state of SWCNT, DWCNT and peapods. It is shown that the peapods exhibit characteristic and complex feedback to chemical or electrochemical doping. The study of DWCNT showed distinct response of inner and outer tubes. It is concluded that the in-situ spectroscopy in combination with both the chemical and electrochemical doping are powerful tools for the study of the electronic properties of carbon nanostructures. Furthermore the chemical and electrochemical doping is combined for exploring of the doping behavior of C60@SWCNT in detail, and for clarification of the differences between chemical and electrochemical doping of peapods.

## Raman study under pressure in DWCNT filled with Pbl<sub>2</sub>

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Unpolarized Raman spectra of tangential modes on DWCNT filled with 1D nanocrystalline Pbl<sub>2</sub> semiconductor excited with 647 nm were studied at room temperature and elevated pressure up to 30 GPa. The Raman experiments under pressure were performed in a membrane diamond anvil cell with a 4:1 mixture by volume of methanol-ethanol as the pressure-transmitting medium. The pressure was monitored using the luminescence of a ruby chip inside the cell. The tangential optical phonon modes are sensitive to the in plane stress and splits into a contribution associated with the external and internal tube. Up to 11 GPa we find a pressure coefficient for the internal tube of 3.7 cm<sup>-1</sup>GPa<sup>-1</sup> and for the external tube of 6.3 cm<sup>-1</sup>GPa<sup>-1</sup>. In addition, the tangential band of the external tubes broadens and decreases in amplitude. The corresponding Raman features of the internal tubes appear to be considerably less sensitive to pressure. In the range 11 to 15 GPa we observed a discontinuity in the slope (red shift) of the pressure dependence of the frequency of the tangential modes. This phase transition is associated to a possible structural distortions of the nanotube cross-section. When increasing the pressure furthermore up to 30 GPa the pressure coefficients for the tangential modes associated to the internal and external tubes are the same ( 10.6 cm<sup>-1</sup>GPa<sup>-1</sup>). All findings lead to the conclusion that the outer tubes act as a protection shield fore the inner tubes (at least up to 11 GPa).

## UV-Raman spectroscopy on nanotubes@zeolite

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Nanotubes grown inside the channels of zeolite crystals are constrained by the environment to diameters around 4 Å, and must therefore show a narrow chirality distribution. This, together with the good alignment of the nanotubes, allows the direct comparison of, e.g., optical properties in experiment and theory. We performed UV-Raman measurements and observed a phonon mode at  $\sim 650 \text{ cm}^{-1}$ , resonant at an energy close to 3.4 eV. Since both the optical band gap and the radial breathing mode frequency grow for decreasing nanotube diameter, this implies the presence of even smaller nanotubes as assumed up to now. With an estimated diameter of  $\sim 3 \text{ Å}$ , it is the smallest single-walled nanotubes ever measured. Furthermore, we present the dependence of the Raman spectra on temperature. With help of *ab initio* calculations we discuss the origin of the different Raman peaks. From the temperature dependence we obtain the interaction of the nanotubes with the zeolite environment.

## Temperature dependence of Raman scattering from Single-Walled Carbon Nanotubes

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Raman scatterings from various single-walled carbon nanotube (SWNT) samples were measured over a wide temperatures range (from 4 to 1000 K). The G-band and D-band peaks showed clear temperature dependences; the downshift of Raman shift and the broadening of peak width. The G-band main peak (G+ peak) showed the universal temperature dependence in Raman shift for the various SWNTs samples and for the three excitation laser energies (488.0, 514.5 and 632.8 nm). The downshift of D-band peak was considerably less than that of G-band with increasing temperature. Raman shift, peak width and intensity of most of radial breathing mode (RBM) peaks also have the qualitatively similar temperature dependence as G-band peak. However, some of RBM peaks show the increase in intensity with increase in temperature. Furthermore, these peculiar RBM peaks disappear when SWNTs were isolated, suggesting the unique resonance due to bundling.

## **New Directions of Nanotube Science: Synthesis, Properties, Characterization and Applications of B- and N-doped Carbon Nanotubes**

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We present the latest advances in the production and state-of-the art characterization of B- and N-doped carbon nanotubes. We briefly discuss different approaches to producing these novel doped nano-systems. The use of high-resolution transmission electron microscopy (HRTEM), electron energy loss spectroscopy (EELS), scanning tunnelling spectroscopy (STS), Raman Spectroscopy and allied techniques to characterize these doped systems is reviewed. From the theoretical point of view, it will be demonstrated that low concentrations of dopants (e.g. <0.5 %) could be incorporated within tubes. In this way, the electronic conductance would change dramatically and the mechanical properties would not be altered. In addition, because of the presence of holes (B-doped tubes) or donors (N-doped tubes), their surface would become more reactive. The field emission properties and their use as gas sensors are also discussed. It is clear that these materials possess outstanding properties when compared to pure carbon nanotubes, and it is foreseen that these systems will revolutionize some aspects of nanotube science and technology, thus opening a vast field of experimental and theoretical research.

## **Biased chirality distribution of SWCNTs produced from ethanol via novel floating catalyst method as determined by TEM/ED**

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Recently a novel aerosol method has been developed for synthesis of single-walled carbon nanotubes in our laboratory [1]. In this method, catalyst particles were formed by the physical vapour nucleation method and subsequently introduced into the laminar flow reactor to initiate nanotube growth after mixing with ethanol vapour. The SWCNTs produced by this method are typically with clean surface and of good wall structure. A modified electron micro-diffraction technique in transmission electron microscope was applied to carry out chirality measurements with tens of individual SWCNTs. Both the tube diameter and the helical angle could be accurately measured from electron diffraction patterns with improved S/N ratio. As compared with the natural chirality distribution of SWCNTs, an obvious preference for growth of arm-chair carbon nanotubes was found.

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## Chiralities of double-walled carbon nanotubes synthesized by a novel CVD method

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Individual double-walled carbon nanotubes (DWCNTs) synthesized by using a novel chemical vapour deposition (CVD) process with Fe catalyst particles produced by vaporization with a hot wire generator [1] have been characterized with transmission electron microscopy. Favourable electron diffraction patterns were achieved at optimum conditions for precise measurements of chiralities of the tubes. It is interesting to find that in one of the DWCNTs the inner tube and the outer tube have identical helical angles while many others generally have diverse helical angles.

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## Purity Evaluation of Bulk Single Wall Carbon Nanotube Materials

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We report on our experience using a preliminary protocol for quality control of bulk single wall carbon nanotube materials produced by the electric arc-discharge and laser ablation method. The first step in the characterization of nanotube material is mechanical homogenization. Quantitative evaluation of purity has been performed using a recently reported procedure based on solution phase near-infrared spectroscopy [1]. Our results confirm that this method is reliable in determining the nanotube content in the arc-discharge sample containing carbonaceous impurities (amorphous carbon and graphitic particles). Applying this method for laser ablation samples gives purity values over 100 %. The possible reason for that might be different extinction coefficient meaning different oscillator strength of laser ablation tubes. Thus we propose a new reference sample, which can be used for quantitative evaluation of purity of laser ablation samples. The graphitic part of the carbonaceous impurities has been estimated by X-ray diffraction of 1:1 mixture of nanotube material and C60 as an internal reference. Further we report on attempts to determine the absolute content of SWNTs using X-ray photoelectron spectroscopy (XPS).

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## **Inorganic nanotubes: analysis through modern microscopic techniques and electrical measurements**

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Multi-walled nanotubes made of Carbon, Carbonitride, Boron Nitride, Boron Carbonitride, various Oxide, Phosphate and Sulfide compounds with and without liquid or solid metal fillings are synthesized and thoroughly analyzed using state-of-the-art field-emission analytical 300 kV high-resolution transmission electron microscopes, an atomic force microscope, and two- or multi-terminal electrical measurements on patterned substrates. The results are discussed in the light of inorganic nanotube utilization in various prospective nanoscale devices, including temperature sensors, nanomagnets, nanocomposites, electrical conductors, field-effect transistors, flat panel displays, mass conveyers etc. In addition, fabrication, detailed HRTEM analysis and functional properties of novel unusual inorganic nanostructures, e.g. sulfide and selenide tetrapods, "nanoflowers", biaxial semiconducting nanowires, metal-semiconductor junctions and mezoporous flakes are demonstrated.

## Physisorption studies on carbon nanotubes: experiments and simulations

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We will present some recent experimental results concerning adsorption volumetry studies involving the noble gases and some simple molecules. Through comparison with experimental results on exfoliated graphite, we will discuss the differences between the two substrates as a function of curvature and the role of the underlying layers. Indeed, adsorption on the outer tube surfaces results in successive steps similar to those on exfoliated graphite: however, the number of such steps is reduced, the steps are no longer vertical and the step pressures are greater. Comparative studies using different molecules allow determining the sites of adsorption as well as the associated heats of adsorption on single wall nanotube bundles. A relationship can be determined showing that the pressure at which adsorption on the tube outer wall occurs varies inversely with the tube diameter. Simulation studies shed some light on the quantitative effects of both CNT curvature and the number of CNT walls on the adsorption energies.

## Electronic properties of Cs-intercalated SWNT, derived by NMR spectroscopy.

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We present a NMR study of <sup>13</sup>C-enriched (10 %) SWNT samples intercalated with Cs in different stoichiometries, ranging from CsC8 to non-intercalated SWNT:s. By studying the T1-relaxation rate of the <sup>13</sup>C nuclear spin at temperatures from room temperature down to 10K, we deduce information of the DOS at the Fermi level for the differently doped samples. All samples exhibit a Korringa like behaviour, as expected for metallic system. However deviations are observed at low temperatures for some of the samples which could be interpreted in terms of one dimensional conductors.

## **NMR investigations of C<sub>60</sub> encapsulated inside carbon nanotubes**

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We present a high resolution MAS NMR study of 10% <sup>13</sup>C enriched C<sub>60</sub> encapsulated inside SWNT. From lineshape analysis and relaxation measurements we clearly identified the signature of the C<sub>60</sub> molecules and SWNT. In agreement with previous studies, the isotropic position of the swnt is observed at 114ppm. The isotropic line of <sub>60</sub> molecule is 4ppm paramagnetically shifted and broadened. We will present these results and discuss them in term of C<sub>60</sub> molecule distortions with a modification of its electronic state and suggest some possible hybridized electronic states between C<sub>60</sub> molecules and carbon nanotubes.

## Nitrogen effect on the vertical alignment of N-doped carbon nanotubes

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Although the control of the growth direction of CNTs has known important advances during the last years, very few investigations have been carried out dealing with characterization of the alignment degree. The production of CNTs by catalytic chemical vapour deposition (CCVD) often presents a carpet-like structure composed of vertical aligned multiwalls nanotubes (MWCNT), which can be seen as a crowding end result. Note that only very recently it was reported a quantitative study on the alignment in such carpet of CNTs. N-doped MWCNTs have been grown by PECVD using a low pressure - high density plasma excited via electron cyclotron resonance (ECR) in the microwave range (2.45 GHz, 200W). Briefly, the ECR plasma is made in a mixture of C<sub>2</sub>H<sub>2</sub>:NH<sub>3</sub> (2:1) at 0.2 Pa and the substrate (500nm SiO<sub>2</sub>/Si) is heated up to 700°C and Ni was used as catalyst. Transmission electron microscopy reveals typical defects into the rolled-up graphene sheet walls. From NEXAFS spectra analysis we found that about 70% of carbon nanotubes are vertical oriented. The graphitisation of the sample versus the analysis angle will be discussed in the light of the local measurements made by HR-EELS on a 'bunch' of distorted CNTs and on a single well graphitized CNT. As well, the nitrogen incorporation into the CNTs walls is emphasized and it can partially explain the misalignment by the induced walls curvature.

## Profiling the growth process of vertically aligned SWNTs by in situ optical absorption measurements

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An *in situ* optical absorbance measurement method was developed to study the growth process of vertically aligned single-walled carbon nanotube films produced from alcohol. The thickness of the film during growth was determined using the relationship between the absorbance of the film and its thickness [1]. A model describing the growth is presented, which depends only on the initial growth rate and the catalyst lifetime [2]. The calculated absorbance is compared to absorbance data under various growth conditions. A reduction in film thickness due to burning of the SWNTs is evidenced, but found to be insignificant when the rate at which air leaks into the growth chamber is minimized. The potential to use *in situ* techniques for monitoring growth conditions is also investigated.

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## Photoluminescence of single-walled carbon nanotubes under hydrostatic pressure

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Many potential applications of single-walled carbon nanotubes (SWNTs) are based on their remarkable mechanical properties. However, it is still little known about a response of individual SWNTs to mechanical stress. Here we will present our recent results on the photoluminescence (PL) of nanotubes under hydrostatic pressure in a diamond anvil cell. An application of hydrostatic pressure results in shifts of electronic interband transition energies of SWNTs which are readily detected by the PL even at moderate pressures of a few kbar. The energy shift patterns depend not only on the structure (helicity) of SWNTs, but also on aggregation of nanotubes and their interaction with a surrounding medium. Furthermore, we will describe and discuss the effects of high hydrostatic pressure (up to ~100 kbar) on structural and chemical stability of nanotubes.

## **Resilience of carbon nanotube technology in intense ionizing radiation environments**

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Carbon nanotube (CNT) technologies, which have the potential to significantly advance the state-of-the-art in microelectronics, are attractive for use in NASA missions in extreme radiation environments. We investigated the fundamental limitations of the CNT technology subjected to gamma radiation, by using CNT field-effect transistors (FETs). The studied devices were built with CNTs, grown from metal seeds onto a thin-oxide-coated Si wafer, used as a gate electrode. The gate threshold voltage ( $V_t$ ) of the p-type CNT-FETs was monitored as a function of the cumulative dose. The CNT-FETs maintained functionality to doses exceeding 3 Mrad, and failed at ~10 Mrad. At the present, none of the observed failure mechanisms is considered inherent for the CNT technology. On the contrary, we have a clear evidence of electrical overstress of the gate oxide, typical for the CMOS technology. Thus, we have demonstrated the resilience of CNT technology to intense ionizing radiation environments.

## Distributions of Fullerenes in Carbon Nanotube Production Determined by Ion Mobility Measurements

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Samples from nanotubes produced by various methods have been analyzed by Laser Desorption-Ionization Ion Mobility Time-of-Flight Mass Spectrometry [1]. The measurements find mostly fullerenes in the mass range from 240 to 10000 Daltons. These principle contaminants are produced along with single-wall carbon nanotubes, which are too large to be detected in the mass spectra. Along with the fullerenes many other species are found that appear to be produced in the laser desorption process. The identity and distribution of these additional species depend on the solvent used to disperse the samples, the time the samples sit in air, and the laser power. These contaminants are thus thought to originate from fragments of small carbon clusters reacting with adsorbed air and residual solvents prior to and during laser desorption. Because of their lower mobility, it appears that these contaminants are linear or cyclic organic structures. Some appear to include oxygen due to certain patterns having a difference in mass of 16 Daltons. Large fullerenes in the spectra are identified by their regular pattern of two carbon atom intervals. The distribution of large fullerenes varies among the samples depending on the type of production technique. Large numbers of fullerenes are seen in samples produced by the arc process and by the laser ablation process, whereas, very few fullerenes are seen in samples produced by CVD processes. Comparisons are made of measured drift times and ones calculated based on a simple aerodynamic drag coefficient for free molecular flow, calibrated by fullerene mobilities from the literature [2, 3]. The results show that repeatable patterns emerge in the fullerene distributions that depend on the nanotube production technique, adding to the techniques used to determine the purity and identity of nanotube production.

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## Nitrogen doping of carbon nanotubes

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We investigate nitrogen doping in single and multi-walled carbon nanotubes (SWNT and MWNTs) using a combination of EEL spectroscopy and density functional calculations. Nitrogen doping in SWNTs is limited to concentrations of up to 1%, whereas MWNTs show localised doping of up to 30%. Spatial EELS mapping of individual SWNTs shows nitrogen in the nanotube walls, with two distinct N(1s) peaks at 398.6eV and 402eV [1]. MWNTs show a distinct morphology with 'bamboo-like' interior compartments arranged uniformly along the nanotube length. In addition to the peaks at 398.6 and 402eV, two further N(1s) peaks are discerned, at 400.5 and 406eV. We further investigate variations in the N(1s) and C(1s) edges at different locations within the nanotubes. The high nitrogen concentrations within the tube occur primarily on the inner nanotube surface and within the bamboo wall structures. This region shows a less pronounced  $\pi^*$  C(1s) peak. This nitrogen rich region rapidly becomes amorphous under the irradiating electron beam.

## Small-Angle X-ray Scattering for Surface Analysis of Bundles of 1D Nanomaterials

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An important task of nanotechnology is to bunch one-dimensional nanomaterials to achieve a suitable form for applied purposes. The common approach for this purpose is to use template-based methods. More recently, we reported formation of bundles of 1D nanomaterials via simple synthetic methods (for example see [1]). Unfortunately, it is difficult to investigate such huge bundles by means of TEM as the most common technique for study of 1D nanomaterials. Thus, it is better to employ surface techniques instead of transmission techniques. Since this nanostructured material is not a flat surface, it is not possible to investigate its lateral structure by means of conventional scanning probe microscopic (SPM) techniques. On the other hand, different shapes are formed during bunching process and a single local surface analysis is not representative of the phenomenon. Thus, we use an efficient technique to obtain a statistical data owing to all regions of the surfaces. Small-angle X-ray scattering (SAXS) is one of the most reliable technique for surface analysis in the scale of 0.5 - 200 nm [2]. Here, we discuss possibilities and difficulties of SAXS for study of bundles of 1D nanomaterials. The concept of fractal geometry was used to obtain a statistical measure for comparison of different cases.

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## Confinement of Simple Gases Inside Open Single-Walled Carbon Nanotubes

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Isothermal adsorption of simple gases on external surface of SWNT bundles has been extensively studied both theoretically and experimentally and is well understood now. Endohedral adsorption has been investigated by theoretical and computational methods, however only limited experimental studies have been conducted. In the present project we have investigated endohedral isothermal adsorption of various small gases, such as argon, krypton, nitrogen, and hydrogen at 77 and 87 K. At present, H<sub>2</sub> adsorption is studied at temperatures ranging 15-100 K by volumetric and scattering techniques. High-purity sample (~75%) of SWNT synthesized by two-laser/oven method and opened using an oxidization-based procedure has been used.

At 77 K, formation of two endohedral phases of Ar, the low- and high-density phases, has been observed at 155(5) and 120(5)  $\mu$ torr, respectively. At 87 K, only the low-density phase has been observed at 185(5)  $\mu$ torr. For Kr adsorption at 77 K, the low-density phase has been observed near 177  $\mu$ torr. Existence of the high-density Kr phase near 65  $\mu$ torr has been inferred from the isotherm appearance. Formation of the phases at 77 K appears to be the first order phase transition. However, the nature of the phases remains poorly understood. In addition to the endohedral phases, first-layer and higher-coverage exohedral phases have been identified.

## Characterization of Arc-grown Carbon Nanotubes after different Purification Steps

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We characterized carbon nanotubes by VIS/NIR spectroscopy as introduced by Itkis [1] using the established protocol presented here by U. Dettlaff-Weglikowska [2]. We investigated raw SWCNT material, material after dry oxidation at 370≡ C in laboratory air, and material after additional annealing at 800≡ C under high vacuum. The raw Arc-grown material (produced at Yangtze Nanomaterials Shanghai, at MPI Stuttgart, and at Nanoledge Montpellier) usually contains an effective nanotube fraction of about 15%. By dry oxidation, the content is increased to approx. 30-50%. High temperature annealing removes carboxyl groups and other defects from the nanotubes and leads to the formation of bundles. The effect of annealing on the optical absorption spectra and purity evaluation will be discussed.

[1] M.E. Itkis et al, Nano Lett., 3, 2003, 309-314

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## NEXAFS Studies of Carbon Nanotubes

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We have extended the use of NEXAFS spectroscopy for the study of the electronic structure and chemical composition of pristine, wet-air oxidized, and sidewall-ozonized nanotubes. Near Edge X-Ray Absorption Fine Structure (NEXAFS) spectroscopy is a technique that involves the excitation of electrons from a core level to partially filled and empty states. It is an important element-specific characterization tool capable of obtaining electronic, structural, and bonding information, not only about nanotube carbons but also about those associated with surface functionalities, which are introduced by oxidative processes. In previous work, NEXAFS has been used to measure varying degrees of bond hybridization in mixed sp<sup>2</sup>/sp<sup>3</sup> bonded carbon materials, the presence of defects in nanotubes, amorphous precursors to multiwalled carbon nanotubes, and the nature of oxygen-containing functional groups on carbon nanotubes.

Specifically, we have completed a comparative NEXAFS study of (a) raw and (b) variously oxygenated HiPco single-walled carbon nanotubes, including (i) wet-air oxidized tubes, as well as (ii) ozonized tubes, whose sidewalls have been covalently functionalized with oxygenated functionalities. Solution-phase ozonized tubes are particularly useful for (a) the self-assembly of nanotubes onto metal surfaces and (b) the synthesis of nanotube-quantum dot heterostructures. Overall, our observations are consistent with the loss of the characteristic electronic transitions between the intrinsic van Hove singularities in functionalized, ozonized nanotubes, due to disruption of the p-network upon sidewall functionalization, that correlate with prior data obtained using Raman and near-IR-UV-visible spectroscopies.

In a complementary study, understanding of oxidative processes such as solution-phase ozonolysis in multiwalled carbon nanotubes (MWNTs) has been found to be of fundamental importance in devising applications of these tubes as components in composite materials as well as for development of cutting and filling protocols. We

have demonstrated that NEXAFS is a particularly useful and effective technique for studying the surface chemistry of carbon nanotubes.

Specifically, solution-phase ozonolysis of multiwalled nanotubes leads to the opening of the end caps and functionalization of the dangling bonds with oxygenated functional groups. Ozone likely acts by forming a primary ozonide, which then cleaves in the presence of ambient moisture to yield different functional groups. The presence of carboxylic acids, esters, and epoxides was established by infrared spectroscopy. An important consequence of solution-phase ozonolysis is nanotube purification and removal of amorphous carbon impurities. Our data show that analysis of purified and well-crystallized samples can allow for the correct assignment of NEXAFS resonances, which are seen to be similar to those of graphite. Importantly, we found that NEXAFS is useful for analyzing nanotube surface structure and composition with the potential for surface profiling and thus, is a necessary complementary tool to vibrational spectroscopy in effectively characterizing pristine and functionalized carbon nanotubes.

## Reference standard for carbonaceous impurity measurements in carbon nanotubes

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Near-infrared spectroscopy is a convenient tool for measuring nanotube / non-tubular carbon impurities ratios in carbon nanotube samples<sup>1</sup>. These measurements are based on separation of contributions from nanotubes and impurities to the near-infrared absorption. In the current work we produced a reference standard for NIR measurements using purified laser nanotubes. The sample was oxidized slowly in a thermal gravimetry analyzer (TGA) in 2 % oxygen atmosphere. In these conditions, the sample oxidized in several steps, which were attributed to carbonaceous impurities, nanotubes and graphitic shells based on TEM and Raman observations. Stopping oxidation at 625 °C (this temperature is sample-specific) allowed us to produce a sample with well-defined ratio of nanotubes, graphite and metal catalyst. Since carbonaceous impurities no longer glue nanotubes and particles together, further dispersion and centrifuging allowed us to remove particles (verified by IC P-MS) and produce pure nanotube sample. This sample was used as a reference standard to determine relative contributions of nanotubes and impurities to NIR absorption in  $\pi$ -plasmon background and Van-Hove peak areas. We will also discuss a refinement of this technique for samples with varying diameter distributions, that takes into account energy dependence of absorption.

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## **On-line detection of SWCNT formation in the floating catalyst method**

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Differential electrical mobility analyser (DMA) based method for the on-line detection of SWCNT formation is presented. DMA was used to study three different gas-phase synthesis processes. The SWCNTs were produced via CO disproportionation in the presence of catalyst nanoparticles formed either by metal vapour nucleation or via thermal decomposition of ferrocene or iron pentacarbonyl. Despite the different product morphology and concentration, the on-line measurement was able to distinguish SWCNT formation in each experimental set-up directly from the gas-phase without time-consuming TEM observation. The SWCNT formation was detected as an increase in the geometric mean particle diameter and as a decrease in the total particle concentration of the measured aerosol number size distribution. Furthermore, information regarding the relative SWCNT concentration can also be obtained from the DMA measurement. A theoretical approach to the mobility of nonspherical particles in the electric field is presented in order to convert the electrical mobility size of the high aspect ratio SWCNTs measured with DMA to the physical size of the product. Size-selected SWCNTs were studied with transmission electron microscopy in order to find the correlation between the on-line DMA measurement data and the SWCNT morphology.

## Photoluminescence from SWNTs and DWNTs dispersed in saccharide solution

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Photoluminescence (PL) spectroscopy is a powerful tool to investigate the chirality distribution of CNTs in addition to Raman spectroscopy. Up to date, sodium dodecyl sulfate (SDS) and sodium dodecyl benzene sulfonate (SDBS) are often used for PL as suspender of CNTs in aqueous condition. Since these materials are well known to origin of water pollution, alternative materials are desired for particular applications. In this study, we have investigated PL spectra of SWNTs and DWNTs, which were dispersed in saccharide solutions. In terms of CNTs concentration, carboxyl methyl cellulose (CMC) is reported to be the best chemical [1, 2]. However, the CMC-dispersion tends to quench emission peaks due to too high density of CNTs, especially for HiPco-SWNT. Pectine extracted from apple and citrus also enable us to observe distinct PL peaks of CNTs. These saccharide/CNTs solutions show some red shift in compared to SDS/CNTs and SDBS/CNTs solutions. The environmental effect of PL peak shifts due to surfactants and outer nanotube for DWNTs is systematically studied.

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## Heat treatment purification and opening of SWNT

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We present a detailed and schematic study of the purification and opening of single-walled carbon nanotubes (SWNT). We have studied by Raman spectroscopy and electron microscopy how heat- and oxygen treatment of the SWNT can be optimised to open and prepare the nanotubes for the production of peapods. We also discuss and show how Raman spectroscopy can be used to determine diameter and electronic properties of the SWNT by using both several excitation wavelengths and by analysing both the stoke and anti-stoke side of the Raman spectra.

## Dispersion of long aligned multi-wall carbon nanotubes and elaboration of polymer-based composites

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Aerosol-assisted catalytic chemical vapour deposition enables to produce aligned multi-wall carbon nanotubes (MWNTs) with high catalytic yield and high growth rate. MWNTs contain almost no by-products and their length can reach few mm [1]. Such characteristics are of particular interest for different applications, in particular for conductive or strong polymer-based composites [2]. Our work will be focused on the study of dispersion of such MWNTs in different liquid media and their introduction in a polymer to determine their effects on electrical and mechanical properties. Dispersion has been performed with an ultrasonic (US) probe in organic or aqueous liquid media with or without dispersing agents. Dispersion state and nanotube length were determined by using different techniques such as UV-Vis spectrometry, optical and scanning electron microscopy. Water/sodium dodecyl sulfate (SDS), isopropanol/nafion and toluene/polystyrene were found to be efficient liquid media. MWNTs/polymer composites using ultra-high molecular weight polyethylene (UHMWPE) were elaborated by mixing MWNTs and polymer powder followed by sintering. The effects of different mixing processes (dry mixing or dispersion and mixing of MWNTs in a solvent) on electrical and mechanical properties of composites obtained will be reported. In particular, the percolation threshold is significantly decreased (below 0.1 wt.%) for composites obtained using dispersed nanotubes.

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## Simulations of Bundle Dissociation of Single-walled Carbon Nanotubes: Entropic Effects

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The physical reasons why single wall carbon nanotubes can be isolated only with certain dispersants, and only at very low concentrations is not completely clear, but recent extensive theoretical and simulation studies on solvents such as toluene and polymer mixtures[1,2,3] revealed that critically important re-organization of the solvent occurs upon the addition of the single wall carbon nanotubes and polymer and concomitant change in the entropy, and hence free energy. Modifying this entropic theme a little, we have focused on how configurational order may be controlled through the use of a rather different family of solvents, namely amides. This computational work has been done in tandem with experiment.

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## **Dissipative structures of carbon nanotubes induced by DC electric field**

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Dissipative processes occur in open systems where either matter or energy is exchanged with the outside. The examples include Rayleigh-Benard Convection and BZ reaction. Here, we report that DC electric field in the aqueous dispersion of CNT produce highly organized patterns on the anode surface, which change very slowly with time and disappear when the field is turned off. Freshly prepared CNT dispersion was injected in between two ITO parallel plates. DC electrophoresis drove CNTs toward the anode surface. Once they reached the anode, they remained mobile near the surface. The temporal development involves at least three stages; appearance of periodic patterns and fixation of its period, maturing of patterns (thickening of patterns), and coagulation to node points. There are clear voltage threshold in the development and the dependence on the plate distance.

## Selective Oxidation of Semiconducting Single-Wall Carbon Nanotubes in Hydrogen Peroxide

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Diameter selective oxidation is one of the most important techniques to get narrower diameter distribution of single-wall carbon nanotubes (SWCNTs). Hydrogen peroxide can be used for the oxidation and has an advantage to achieve more homogeneous reaction than a heat treatment in air. Actually, we obtained SWCNTs with narrow diameter distribution from HiPco by simple heating in hydrogen peroxide. The diameter distribution was similar to that of laser ablation SWCNTs. However, we found that the concentration of metallic SWCNTs drastically increased after the oxidation in hydrogen peroxide. Such strange behaviors could not be observed in the oxidation in air. We have roughly estimated the concentration of metallic SWCNTs from optical absorption spectra, and found that 80% of SWCNTs are metallic in the final product. We will show the detailed results and will discuss about future applications.

## **Bundle Dissociation of Single-walled Carbon Nanotube in Amide Solvents**

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Applications of single-wall carbon nanotubes (SWNT) are severely restricted, as they exist in rope-like bundles. Many methods have been suggested to de-bundle the SWNTs, including both covalent and non-covalent functionalisation with surfactants, polymers and macromolecules. These methods have their advantages but the ideal situation must be to dissolve and de-bundle the SWNTs in an appropriate solvent at concentrations that are useful for their implementation in applications. In this work we have analytically characterised the dispersion and de-bundling of SWNTs in different amide solvents. An optical transmission based sedimentation technique was used to ascertain the maximum concentration at which the SWNTs can be dispersed in the different solvents. A viscometry-based technique was used to quantify bundle size as a function of concentration. Near-infrared Absorption and Emission Spectroscopy, Atomic Force Microscopy and Transmission Electron Microscopy were carried out on all solutions confirming excellent dispersion and significant debundling even at high SWNT concentration. Computational studies have been performed in tandem with these experiments in order to better understand the mechanisms involved.

## Nitrogen-doped Nanotubes as Biosensors

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In the search for biosensor materials, carbon nanotubes have proved (due to their size and properties) to be promising candidates. Small gas molecules (O<sub>2</sub>, NO<sub>2</sub> and NH<sub>3</sub>) have been successfully adsorbed onto nanotubes, as have larger protein molecules and DNA. The carbon nanotubes “sense” the presence of biological systems by producing a characteristic change in electrical properties such as current or voltage.

In this work we hope to detect sensing behaviour in nitrogen-doped carbon nanotubes (which have been predicted to be metallic) when they are functionalized with metalloproteins. The proteins *cytochrome c*, *ferredoxin*, *ferritin* and *azurin* have been adsorbed onto nitrogen-doped nanotubes and imaged using Atomic Force Microscopy.

The tubes are integrated into a circuit and I-V curves are measured. UV-visible spectroscopy has also been employed to sense the effect of the protein Fe and Cu metal centres on the nanotubes, and vice versa.

## DNA-Carbon Nanotube Hybrids- Aqueous Solutions and Ultra Thin Films-

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DNA-Carbon Nanotube Hybrids- Aqueous Solutions and Ultra Thin Films- Naotoshi Nakashima<sup>1</sup>, Ayumi Ishibashi<sup>1</sup>, Shingo Okuzono<sup>2</sup>, Hiroto Murakami<sup>2</sup> <sup>1</sup> Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Hakozaki 6-10-1, Fukuoka 812-8581, Japan <sup>2</sup> Department of Materials Science, Graduate School of Science and Technology, Nagasaki University Contact e-mail: [nakashima-tcm@mbox.nc.kyushu-u.ac.jp](mailto:nakashima-tcm@mbox.nc.kyushu-u.ac.jp) The combination of carbon nanotubes and DNA is of interest to many chemical and biochemical areas in both fundamental and application. We have already reported that double-stranded DNA dissolves SWNTs in aqueous solutions[1-2]. Here we report the detail about the preparation and characterization of DNA-solubilized SWNT aqueous solutions as well as the preparation of DNA/SWNTs ultra thin films on solid substrates. DNA/carbon nanotube films were successfully formed by the alternating adsorption of two different DNA/SWNTs solutions onto a quartz substrate. UV-vis-near IR spectra for the obtained DNA-SWNTs films showed absorption bands in the region of 500-600nm and 1000-1400 nm that are assignable to metallic-SWNTs and semiconducting-SWNTs, respectively. The DNA-SWNTs films showed characteristic Raman peaks derived from the SWNTs on the substrate.

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## Reactive Carbon Nanotube Solubilizers

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We have already described that compounds (including polymers) that bear a polycyclic aromatic moiety dissolve CNTs in water or in organic compounds[1-4]. We describe here the design and synthesis of “reactive carbon nanotube solubilizers” that are compounds carrying a reactive moiety for the introduction of desired functional groups. Many different kind of nanotube solubilizers have been thus far reported[4]; however, “reactive carbon nanotube solubilizers” have never been described. We introduced an aromatic moiety to poly(styrene-alt-maleic anhydride) and the synthesized copolymers were found to act as “reactive carbon nanotube solubilizers”.

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## Chemical Functionalization Strategies for Separations of Carbon Nanotubes

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The focus of our group is generating rational chemical functionalization strategies of carbon nanotubes. In particular, complexation with metal-containing molecular complexes (such as Wilkinson's complex) (a) and solution-phase osmylation (in the presence of O<sub>2</sub> and UV irradiation at 254 nm) (b) have been found to be especially sensitive to and selective for nanotube size and for separation of semiconducting vs. metallic tubes, albeit through very different reaction mechanisms. In the first experiment, oxidized carbon nanotubes have been reacted with Wilkinson's complex. It has been found that the Rh metal coordinates to these nanotubes through the increased number of oxygen atoms, forming a hexacoordinate structure around the Rh atom and that this reaction is specific for smaller diameter tubes. In the second experiment, it is believed that OsO<sub>2</sub> (a) initially forms on the nanotubes by the preferential covalent sidewall functionalization of metallic nanotubes and (b) subsequently self-aggregates. The formation of an intermediate charge transfer complex is likely the basis for the observed selectivity and reactivity of metallic tubes.

## First-principles Study of DNA-Carbon Nanotube Hybrids

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Efficient separation of carbon nanotubes (CNTs) according to their structure is of crucial importance for many applications. A number of sorting processes exist which are able to distinguish between metallic and semiconducting CNTs. However, further separating semiconducting CNTs according to their band gap (which is inversely proportional to the tube diameter) represents a more difficult task. Recent investigations of DNA-CNT hybrids [1-3] suggest a powerful new method not only to separate metallic and semiconducting CNTs, but also to sort semiconducting CNTs according to their diameter (band gap). Using density functional theory, we have studied the  $\pi$ - $\pi$  interaction between the nucleic acid bases of single-stranded DNA and the surface of single-walled CNTs. We are reporting results on the binding energy and configuration, as well as on the linear/surface charge density as a function of the DNA wrapping geometry. We furthermore present results from our first-principles studies of the dependence of DNA-CNT binding interaction on the oligonucleotide sequence, and why a particular sequence of repeated deoxy-guanylate-thymidylate units (d(GT)<sub>n</sub>) reportedly [3] seems to yield the best separation results.

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## FUNCTIONALIZATION OF SINGLE WALL CARBON NANOTUBES WITH POLY(ETHYLENE GLYCOL)

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Following a strategy that was originally proposed by Haddon and co-workers, the formation of carboxylic groups, accompanied by cutting and shortening of Single Wall Carbon Nanotubes (SWNT), has been promoted by prolonged sonication of pristine SWNT suspended in an acid-oxidant solution. In particular, modifications induced on HiPco nanotube samples during the cutting and shortening process have been studied by means of Resonant Raman scattering.

Poly(ethylene glycol) (PEG) was subsequently grafted to shortened SWNT (sh-SWNT), yielding a soluble product (sh-SWNT-PEG). We selected PEG for its well-known solubilizing properties and also in view of a possible beneficial effect of PEG chains in minimizing aggregation of SWNT or of bundles of SWNT. In fact stable solutions of sh-SWNT-PEG in common organic solvents can be obtained and studied. Non linear transmission measurements on solutions of sh-SWNT-PEG in CHCl<sub>3</sub> showed a better optical limiting performance relative to that recorded for original SWNT suspended in the same solvent.

Due to its reduced tendency to aggregate, sh-SWNT-PEG can be dispersed over solid substrates to obtain relatively homogeneous films. The study of solid state physico-chemical properties on these materials will possibly disclose opportunities for the realization of innovative devices based on the well known peculiarities of SWNT.

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## Electronic structure calculations of potassium intercalated single-wall carbon nanotubes

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We present results from density functional theory calculations on the geometrical and electronic structure of potassium intercalated (4,4) armchair and (7,0) zigzag single-walled carbon nanotubes. Intercalation of potassium results in notable changes in the geometrical structure, in particular in the zigzag system in which the carbon-carbon bond lengths in the unit cell vary between 1.40 Å and 1.45 Å. The most prominent effect of K intercalation on the electronic band structure is a shift of the Fermi energy which occurs as a result of charge transfer from potassium to the carbon nanotube. In the case of the potassium intercalated (7,0) nanotube the band structure and the position of the Fermi energy indicate a very good metallic conductor. The (4,4) nanotube has the potential to become super-conducting due to the very high density of states at the Fermi energy which is obtained at high intercalation densities.

## Single-Stranded DNA Insertion into Single-Walled Carbon Nanotubes Using Direct Current and Radio Frequency Electric Fields.

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Various chemical and physical techniques on the modification of single-walled carbon nanotubes (SWNTs) have been applied in order to bring out unique properties of SWNTs. Particularly, encapsulation of other functional materials into SWNTs has capabilities for the modification of electronic properties of SWNTs. Here, we report the formation of single-stranded DNA encapsulated SWNTs using two kinds of electric fields. Experiments are performed by applying two kinds of electric fields (direct current (DC) and radio frequency (RF)) to DNA solution. Since DNA exists as negative ions in solution, it is possible to control the dynamics of DNA in solution using the electric fields. The electrodes (anode which is coated with open-ended SWNTs and cathode) are submerged in the solution. In this procedure, DC electric fields are effective in irradiating DNA to the anode because DNA has negative electric charges. On the other hand, RF electric fields are effective in stretching DNA due to the interaction between the external RF electric field and induced dipole moment in DNA. We have succeeded in irradiating DNA to the SWNTs on the anode, and the formation of the DNA encapsulated SWNTs is resultantly confirmed, for the first time, by Raman and transmission electron microscopy analyses.

## **Destructive Adsorption of Oxygen Molecule on Thin Carbon Nanotubes Depending on Chiralities: A DFT Approach**

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Oxygen adsorption changes nanotube electronic structure and sometimes causes destruction of nanotubes. Therefore, understanding and control of oxygen interaction with nanotubes are very important issue for many applications.

In this paper, we investigated the destructive adsorption of singlet oxygen molecule on thin carbon nanotubes depending on the chiral index on nanotubes. We found that (3,3) and (4,2) nanotubes are easily destroyed by oxidation without reaction barrier but (5,0) nanotube has finite barrier for destructive oxidation although their diameters are almost the same. The result is understood by local curvatures at the adsorption site. We will also discuss the destructive oxidation of nanotubes with larger diameters depending on the chiral index.

This work was in part performed under the management of Nano Carbon Technology project supported by NEDO.

## Fluorination of double walled carbon nanotubes

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In the recent years, much attention was paid on the synthesis of double-walled carbon nanotubes (DWNTs) by a catalytic chemical vapor deposition (CVD) method [1-3] because their many physicochemical properties derived from their unique structure such as coaxial structural morphology make them very promising in the fabrication of field emitter and multi-functional filler. The chemical functionalization of DWNTs is a critical factor, especially when considering application fields. In this study, we carried out chemical attachment of fluorine atoms to double walled carbon nanotubes, and evaluate the structural changes of fluorinated DWNTs using various techniques such as high-resolution transmission electron microscope, field-emission scanning electron microscope and Raman apparatus in detail. As a result, we successfully attached fluorine atoms to the sidewall of outer shell in DWNTs through direct reaction with fluorine gas at 200°C for 5 hrs. The stoichiometry of the fluorinated DWNTs is CF<sub>0.30</sub>, based on XPS study, while double-layered structure is sustained after fluorination according to HR-TEM observation.

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## **DFT Study of the Enhancement of Molecular Hydrogen Adsorption on Graphene Layers and Carbon Nanotubes due to Lithium Doping**

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According to the experiments hydrogen adsorption on pure carbon nanotubes (CNTs) and another graphitic materials is very small (2-3 weight % in the most optimistic cases). However, some experiments have reported an adsorption of 14-20 weight % in Li- and K-doped CNTs at ambient pressure and moderate temperatures [1]. We have performed Density Functional Theory (DFT) calculations for the physisorption of molecular hydrogen on pure and Li-doped graphene layers and CNTs. In the doped systems the lithium atom takes its equilibrium position above the center of carbon hexagons. Hydrogen physisorption energies in the Li-doped systems increase by a factor of 2 with respect to the undoped systems. The molecule can be physisorbed on top of a Li atom or next to it in a lateral position, and the binding energy increases in both configurations. Hence, Li-doping increases the physisorption binding energy to graphitic materials, and will then enhance their hydrogen storage capacity, giving qualitative support to the experimental findings.

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## Introduction of Heteroatoms onto Defect Sites and Open Ends in SWNT.

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Chemical functionalisation of SWNT is known to provide species which can be tailored for specific applications and also affects their electronic properties. Thus, recent calculations have predicted interesting chemical properties for heteroatoms (N, O, S), directly attached to SWNT ends, i.e. different bond strength and length, with respect to the tube chirality and electronic properties [1]. We worked out the synthetic procedure, which allows substitution of carboxylic groups on the SWNT open ends and defect sites to amino group without side-wall functionalisation. The next step is the development of this method with respect to introducing other heteroatomic groups. The characterisation of initial materials, intermediate and final products by means of IR and Raman spectroscopy, XPS and microscopy methods is discussed. SWNT species with various heteroatoms on the tube ends have a big application potential.

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## **Band-Gap Sensitive Adsorption of Fluorine Molecule on Sidewall of Carbon Nanotube**

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We report from the first-principles calculations that the band-gap sensitive side-wall functionalization of the carbon nanotube (CNT) is feasible with the fluorine molecule ( $F^2$ ), which can provide a route to the extraction of semiconducting CNTs by etching away metallic ones. The computations are carried out using the generalized gradient approximation (GGA) within the density functional theory. In the small diameter case like (11,0) and (12,0), CNTs are easily functionalized with  $F^2$  regardless of their electronic properties. As the diameter becomes larger, however, the fluorination is favored on metallic CNTs with smaller activation barrier than that of semiconducting ones. Thus low temperature exposure of the  $F^2$  molecule in gas phase can make dominant portion of fluorinated metallic CNTs and unfluorinated semiconducting ones.

## **Continuous removal of amorphous carbon by CO<sub>2</sub> during carbon nanotube synthesis by CCVD**

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Amorphous carbon as an undesirable side product is usually formed in the course of carbon nanotube (CNT) growth. This type of carbon species lowers the quality for almost all of the CNTs applications and thus, somehow should be removed. In this contribution we present the results of experimental study of the effect of CO<sub>2</sub> as a mild oxidizing agent on continuous removal of amorphous products during the growth. Our online FTIR study revealed that small percentage of CO<sub>2</sub> cofed along with the carbon source removed the amorphous products to a large extent and led to a significant improvement in the quality of the product. 2wt% Fe/MgO catalyst was used for the growth of CNTs from methane at 1000oC and the evolution of CO, as product of the reaction between CO<sub>2</sub> and amorphous products, was monitored continuously by FTIR. CO<sub>2</sub> and CH<sub>4</sub> conversions were also calculated from the analyses of the gaseous effluent by gas chromatograph.

## Highly efficient functionalization of carbon nanotubes using microwave heating

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Manipulation and processing of carbon nanotubes (CNTs) has been limited by their insolubility in most common solvents. Considerable effort has been devoted to render CNTs soluble by non-covalent functionalization, covalent functionalization at the graphene sidewall or at the open end, the last being of particular interesting due to inducing permanent solubility without affecting other, wall-structure dependent properties of the CNTs. We will present some of our recently developed microwave-assisted transformations of open-ended insoluble CNTs into soluble CNT derivatives by end-targeting amidation and esterification as well as by use of reactions targeting the sidewalls. The thus obtained soluble CNTs are better suited for fractionation than the non-functionalized material.

## **Structural, electrical properties of in-situ coated carbon nanotubes with NiS nanoparticles by sol-gel process for Solar cell applications**

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Carbon nanotubes have been homogeneously coated with NiS nanoparticles in an in-situ method by introducing thiol groups on to the carbon nanotube wall using a novel process for solar cell applications. In this new process firstly, a cationic polyelectrolyte containing reactive imine groups, polyethyleneimine, has been adsorbed on to the surface of carbon nanotubes. Secondly, 3-mercaptopropionic acid has been anchored by an amidation reaction between its carboxylic group and the imine group of the polyelectrolyte under the treatment of carboimide reagents. These -SH terminated carbon nanotubes are further coated with previously synthesized NiS nanoparticles by an in-situ sol-gel process. The microstructure, phase and composition of the deposited carbon nanotube coated with NiS nanoparticles have been examined by high resolution Scanning electron microscopy and High-resolution Transmission electron microscopy and X-ray diffraction, and X-ray photoelectron spectroscopy techniques, respectively. The optical properties and vibrational modes have been examined by UV-vis spectroscopy and Raman spectroscopies, respectively. The electrical properties have been measured by two-probe sheet resistance technique. The role of the carbodiimide reagents in linking the mercaptopropionic acid with polyethyleneamine covalently and subsequently coating the carbon nanotubes with NiS nanoparticles homogeneously has been explained in detailed.

## Effect of graphite platelet orientation on surface chemistry of oxidized carbon nanofibers

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Carbon nanofibers of different nanostructures are prepared by selecting the actively grown catalysts and the carbon-containing gases. Treating these as-grown carbon nanofibers in the concentrated nitric acid to introduce oxygen-containing groups and anchoring palladium complex onto the oxidized carbon nanofiber are investigated. From the TEM and XRD results, the graphite-like structure remains intact after oxidation. TG-MS and titration is used to determine the number of acidic oxygen-containing groups. The results show that there exists a consistency between these two methods and the number of oxygen-containing groups is strongly dependent on the graphite platelet orientation, viz. the different fraction of graphite platelet edge. TEM, CO pulse chemisorption, and ICP-AES are used to characterize the carbon nanofiber supported palladium catalysts. Similar palladium particle sizes, but significant difference of relative loading of palladium metal have been found. Furthermore, the linear correlation between the ionic oxygen-containing groups and the relative loading indicates that palladium ion is adsorbed at the oxygen-containing groups on the carbon nanofiber

## Atmospheric plasma functionalization of chemically activated MWCNTS

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Currently, functional groups can be introduced onto nanotube surfaces either through conventional solution processing, thermal treatment or vacuum techniques. We have developed an atmospheric plasma dielectric barrier discharge (DBD) process for attaching specified molecular groups to carbon nanotubes without involving the use of wet chemicals, high temperatures and high vacuum. We demonstrate this technique by successfully functionalizing MWCNTs with N, Cl and F groups using ammonia or trichlorotrifluoroethane vapours. Detailed XPS and Raman analysis was used to determine the resultant bonding configurations. The CNTs were initially treated in HCl to remove the metal growth catalyst and subsequently were subjected to a chemical activation route involving reflux in HNO<sub>3</sub>. The chemically activated CNTs after treatment in DBD-NH<sub>3</sub> atmosphere attracted four times (x4) more N atoms compared to their non-activated counterparts. In contrast, the non-chemically activated CNTs after treatment in trichlorotrifluoroethane-DBD atmosphere, attracted eight times (x8) more F and three times more (~3x) Cl atoms, when compared to their chemically activated counterparts. The results are explained in terms of the electron capturing nature of the functional groups.

## **Sensing different gasses at various pressures with carbon nanotubes**

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Carbon nanotube (CNT) field-effect transistors (FETs) were used as pressure sensors for different gasses, such as air, N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, water, etc. Experiments were conducted in an environmental chamber capable of maintaining a constant gas pressure, spanning 8 orders of magnitude. In equilibrium conditions, the gate threshold voltage ( $V_t$ ) shift as a function of the pressure provides a quantitative measure of the molecules interacting with the CNT. For molecules that can be adsorbed on the CNT surface, the desorption was found to depend on both pressure and time; similarly, adsorption was not an immediate process. In one isolated case, a 2 min of CO<sub>2</sub> exposure at 170 mtorr rendered the CNT inoperable; the CNT-FET did not recover at N<sub>2</sub> pressure increased to 1 atmosphere. However, subsequent exposure to atmosphere ambient recovered the initial p-FET characteristics. Ongoing investigations are focused on the better understanding of this effect. We are also experimenting with mild O plasma, which has shown no SEM evidence of destruction of multiwall CNTs and carbon filaments. The use of such O plasma for cleaning CNT surfaces prior to contact deposition has the potential to lower the contact resistance and improve the reproducibility during device fabrication.

## **Chemical Processing of Bundled Carbon Nanotubes into Sub-50 nm Short Segments**

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Short undamage individual carbon nanotubes 20-100 nm in length are required for quantum confinement effects on fundamental properties studies and sensor and nanodevice applications. By conjugating acid-based oxidation reactions in purification and cutting protocols, we have obtained HiPco and arc-discharge SWNT samples with high percent of segments shorter than 50nm. Sidewall damage and surface acid functionalization were removed by high temperature thermal treatment and narrow length distribution samples were separated using semi-preparative HPLC- SEC chromatographic process. The finite size SWNTs have been characterized by TGA, FTIR, AFM and Raman scattering.

## **Point Defects in Single-Walled Carbon Nanotube Circuits: finding, counting, modifying, and characterizing**

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The operational characteristics of nanotube electronic devices such as transistors and chemical sensors are exquisitely sensitive to nanotube bandstructure, nanotube-electrode interfaces, and the presence of point defects. However, since individual defects are difficult to identify and characterize, device engineers continue to idealize nanotubes as pristine, defect-free objects. Scanned probe techniques prove that defects in SWNTs exist and their presence can dominate the measured electronic characteristics. For example, defects in otherwise "metallic" nanotubes can lead to field-effect switching, leading to the misidentification of these tubes as "semiconducting." Complementary electrochemical methods identify defect sites much more efficiently, and allow defect densities to be quantitatively measured and compared among different samples and production routes. A combination of these two techniques is a powerful way to characterize large numbers of electronic devices and then chemically tailor them towards particular applications. We will demonstrate the selective chemical modification of defect sites and the resulting changes to the properties typically measured in three-terminal electronic transport.

## Theory of Nitrogen interaction in carbon nanotubes

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We examine a variety of possible nitrogen defect complexes in carbon nanotubes, in particular the interaction between different defect species. Nitrogen dopants stabilise carbon vacancy formation and can decrease the vacancy formation energy by a factor of nearly three. Nanotube curvature provides a strong driving force for defect coupling along the nanotube axis.

We examine interaction between substitutional nitrogen defects in graphite, and metallic and semiconducting nanotubes, through systematic energetic comparison of substitutional impurities at different spacings. We find no strong interaction between such impurities in the metallic systems, however in semiconducting nanotubes there is a strong binding between substitutional nitrogen at 3<sup>rd</sup> neighbour spacings, primarily along the nanotube axis. We extend this addition study to higher nitrogen concentrations, leading to the suggestion of substitutional nitrogen impurity superlattices and heterogenous island distribution of nitrogen dopants in semiconducting nanotubes.

## Charging and Covalent Sidewall-Functionalization of Single-Walled Carbon Nanotubes by t-Butyllithium

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The reaction of t-Butyllithium with Single-Walled Carbon Nanotubes (SWCNTs) in benzene leads to a covalent sidewall functionalization of the tubes with butyl groups. Moreover, the nucleophilic attack of the lithium organyl is accompanied by a transfer of negative charge to the SWCNTs which is balanced by the positive charge of the Li-ions. In an "in-situ" investigation we were able to verify the negative charge on the SWCNTs by a concomitant shift of the binding energy of the C 1s core levels of the SWCNTs in X-ray induced photoelectron spectroscopy (XPS). The functionalized nanotube samples were further characterized by Raman spectroscopy and scanning tunneling microscopy (STM). STM reveals a decoration of the tubewalls by features which exhibit the expected threefold symmetry of the butyl-groups. The charging of the SWCNTs in solution could also be verified by applying a homogeneous electric field using Au coated glass electrodes. The electrodes were characterized by XPS and atomic force microscopy (AFM). These measurements reveal the appearance of Li on one electrode, and the occurrence of SWCNTs on the counter electrode.

## Fluorination of Carbon Nanotubes.

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Fluorination of carbon nanotubes allows their solubilisation and enables further chemical modification.<sup>1</sup> It can be achieved with elemental fluorine or F<sub>2</sub> gas, with HF as catalyst, enabling coverage up to C<sub>2</sub>F. STM images of fluorinated nanotubes show a dramatic banded structure, attributed to fluorine adding over broad continuous regions with sharp circumferential edges.<sup>2</sup> Change in fluorination behaviour is seen between 200 and 250°C, with an increase in bulk sample resistance and changes in observed FTIR.<sup>3</sup>

Fluorine addition to carbon nanotubes has now been studied using a range of computational techniques. Ionic, semi-ionic and covalent bonding types are identified and characterised. Results are compared with experimental XPS measurements obtained after CF<sub>4</sub> plasma functionalisation,<sup>4</sup> providing fast and non-destructive fluorination, as shown by HR-TEM. Migration barriers and fluorination processes are determined, and the 200-250°C transition in behaviour is associated with specific changes in surface diffusion behaviour.<sup>5</sup> The role of HF in catalysing gas fluorination is explained through the formation of HF<sub>2</sub><sup>-</sup> surface species, and the effect of solvation on fluorination behaviour is discussed. Transition from low to high fluorine coverage is explored, and STM observations<sup>2</sup> for high C<sub>2</sub>F coverage are explained by contiguous axial addition giving a circumferential banded structure.<sup>6</sup>

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## **Preparation of opened single-walled carbon nanotubes and their reversible filling with various materials**

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Single-walled carbon nanotubes have been advocated as perfect candidates for the sustainable minaturisation of electronic and mechanical nanoscale devices. The encapsulation of selected compounds within the inner hollow cavity of SWNTs allows controlled preparation of nano-metre size "nanowires" and "nanocables" with purpose-tailored physical properties. Therefore is crucial to have control of opening and closing their tips. In a previous study we showed that molten CsOH is filled into the carbon nanotubes and can be easily washed out with water leaving opened nanotubes [1]. Following this approach we have explored the use of milder ways to open SWNTs that can be easily scalable for the production of large amount of opened SWNTs [2]. The opened tubes have then successfully been filled in solution with various inorganic and organic materials.

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## Tailoring of Carbon Nanotube Surface Properties by Plasma Treatment and the Preparation of Gold on CNT

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Nanosized gold has recently gained interests as a catalyst material and carbon nanotubes (CNT) are among the possible supports due to their unique properties. Many methods have been reported to attach the gold nanoparticles onto the CNT. The present work demonstrates an electrostatic assembly of the gold nanoparticles on CNT surface. The surface charge of the CNT was tuned by applying two post-treatment methods. Oxidation in HNO<sub>3</sub> introduced acidic surface groups (CNT-HNO<sub>3</sub>), while basic surface groups were introduced by H<sub>2</sub>O-plasma treatment (CNT-Plasma). Zeta-potential measurements showed that the plasma-treated CNFs are positively charged at low pH (below 4.6 ) whereas the acid-treated CNFs and the gold colloid solution applied (5nm, Ted Pella Inc) are negatively charged at every pH. It has been found that 5-7 nm sized gold nanoparticles was uniformly deposited on the plasma-treated CNTs at a pH of 3.5-4.0, while few gold nanoparticles was deposited on the HNO<sub>3</sub>-treated samples. The results have been confirmed by STEM and UV-spectroscopy. This suggests that the electrostatic interaction between the positively charged CNT surfaces and the negatively charged gold colloids plays a key role in the attachment of the gold nanoparticles.

## CHEMICAL MODIFICATION OF CARBON NANOTUBES FOR BONE IMPLANTS APPLICATIONS

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Interest in carbon nanotubes (CNT)(1) has grown at a very rapid rate in the last decade. Their interesting physical and chemical properties open attractive possibilities in many application areas. INASMET is researching in the use of CNTs in the application of bone implants. The carbon nanotubes have an important role in the development of implantable materials that induce the regeneration of damaged tissues. The composite enhances the cell proliferation and differentiation and the CNTs improve the mechanical and electrical properties of the scaffold.

The chemical functionalization of CNTs is a critical factor in the formation of the nanocomposite. In this work the CNTs have been chemically modified to improve their interface with the polymer (polyhydroxyester). Many different types of oxidant agents have been used to functionalise the CNTS with carboxylic acid groups. These groups were converted into acylchloride groups by treatment with thionylchloride to be finally attached with the poly (L-lactic acid), through ester bond(2).

Techniques such as Raman Scattering, Atomic Force Microscopy (AFM) and FTIR have been used for the characterization of the functionalized samples.

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## Effect of chemical treatment on the properties of single wall nanotubes buckypaper

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We studied the effect of chemical treatment on the magnitude and temperature dependence of electrical conductivity, on the optical and infrared absorption, and on the Raman spectra of single wall carbon nanotube (SWNT) bucky-paper, and determine the correlations between the changes in these properties [1]. Ionic acceptor doping of the SWNT bucky-paper (with  $\text{SOCl}_2$ , iodine,  $\text{H}_2\text{SO}_3$ , etc.) causes an increase of electrical conductivity that correlates with an increase of the absorbance in the far infrared region and a blue shift of the frequency of Raman spectral lines. Conversely, treatment with other molecules (e.g aniline,  $\text{PyPhF}_5$  and  $\text{PhCH}_2\text{Br}$  etc.) leads to a decrease in both conductivity and far infrared absorption. The temperature dependence of the conductivity gives a good indication of the presence of metallic charge carriers and is in agreement with the model of interrupted metallic conduction.

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## Theoretical study of point defects and linear dislocations in single walled BN nanotubes

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We examine, combining DFT and DFTB techniques, the formation of point defects as well as linear dislocations in BN nanotubes under electron irradiation. All of the defect species investigated induce a modification on the electronic properties of the tubes, introducing additional electronic states located in the band gap region. Extending the study to divacancy systems demonstrates a strong coupling between vacancy species. This suggests that under electron irradiation, in the presence of a single vacancy, the preferential site for ejecting an additional atom is in the region surrounding the point defect. This mechanism promotes the appearance of extended defects over a random distribution of single point defects. By increasing the length of a linear prismatic dislocation through a stepwise removal of atoms, we show an incremental decrease in the vacancy formation energy as the dislocation line length increases. We find a preference for linear vacancy structures along the nano tube axis, causing contraction in the tube wall and a kink pair in the nanotube related to the presence of five and seven fold rings in the hexagonal lattice.

## Geometric, Electronic and Hydrogen Physisorption Properties of Boron Sheets and Nanotubes

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First principles calculations of the properties of the recently synthesized boron nanotubes (BNTs) [1] and sheets have been carried out. These nanostructures have a buckled surface, with a large buckling height or width of 0.8 Å. This buckling stabilizes these structures, compared to the flat ones, by about 0.20 eV/B atom, and the buckling structure is identical to that of the quasi-planar B96 cluster. BNTs are metallic independently of their helical structure (armchair, zigzag and chiral), in contrast with the behaviour of carbon nanotubes (CNTs). Hydrogen physisorption energies on different sites of the external surface of these nanotubes are about 50-60 meV, smaller than on the external surface of CNTs, which means that BNTs are not appropriate candidates for hydrogen storage. Dissociated chemisorbed states on these nanotubes have lower or similar energies than hydrogen physisorbed states, but the energy barrier from physisorption to dissociative chemisorption is about 1 eV.

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## Selective Synthesis and Morphology Control of II-VI Semiconductor Nanowires

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One-dimensional semiconductor nanostructures are of great interest because of their potential applications in electronics and photonics. In particular, polar II-VI semiconductors are ideal candidates for nano-optics [1], and can nucleate in complex shapes such as nanoribbons or nanosaws. Multi-branched CdSe nanocrystals can enhance the efficiency of hybrid polymer/semiconductor solar cells [2]. Device performance typically depends on the material structure and crystallinity, but assembly is also a critical issue for applications. Direct manipulation of nanostructures into devices is difficult and expensive. Thus, their full potential will only be realized when they can be directly grown into devices and their shape controlled on-demand. We present the selective synthesis and morphology control of a wide range of CdSe, ZnSe and ZnCdSe nanocrystals [3,4]. The samples are grown either by molecular beam epitaxy or by vapour transport. Nanocrystals with tailored morphology, ranging from single wires, ribbons and saws to tetrapods and multipods, can be grown on-demand by choosing the appropriate deposition conditions. The different growth mechanisms and the shape control of these materials are discussed. CdSe and ZnSe nanocrystals show a strong near band edge photoluminescence, while a broadening and downshift of the LO and TO phonons is detected by Raman spectroscopy, compared to the bulk materials.

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## **Catalyst-free Silicon Nanowires and Nanocrystals: Growth and Electron Transport**

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Nanowires (NWs) and nanocrystals (NCs) are amongst the most promising systems for potential applications in quantum electronic and optoelectronic devices and for the investigation of fundamental physics. In principle, they can be used as building blocks to assemble devices in a 'bottom-up' approach. Here we report the bulk production of SiNWs by a vapor transport process without the need of any metal catalyst. SiO<sub>x</sub> powders are thermally evaporated in a high temperature furnace (>1200°C) and nanowires 10-30 nm in diameter nucleate by self-condensation of the vapor in a lower temperature region of the furnace. Chain-like one-dimensional structures are also grown. These are made of small Si beads arranged along a SiO<sub>2</sub> nanowire. Finally, Si nanocrystals 8 ± 1 nm in diameter are prepared by plasma decomposition of SiH<sub>4</sub>. We investigate the electron transport mechanism in these nanowires and nanocrystals using lithographically defined contacts. The electron transport in the nanocrystals is dominated by single-electron charging at low temperatures, and a space charge limited current in the presence of an exponential distribution of trapping states above 200 K. The trap density is within an order of magnitude of the nanocrystal number density, suggesting that most nanocrystals trap single or a few carriers at most.

## Morphology and Structure Transformation of Titanium Oxide

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The phase and morphology transformation of the anatase  $\text{TiO}_2$  were studied under various acidic and basic conditions. Crystallized nanoscale tubular materials have been synthesized by the reaction of anatase  $\text{TiO}_2$  and NaOH aqueous solution. Anatase  $\text{TiO}_2$  nano particles were obtained under further acidic treatment of the tubular materials. The titanate nanotubes constructed with open-ended and multiwall morphologies. The 3~4 layered (the distance between two adjacent layers is about 0.8 nm) nanotubes with inner and outer diameters about 5 and 10 nm respectively, were obtained as the major products. During alkali treatment, crystalline anatase underwent intercalation of the sodium and hydroxide ion to produce layered titanate sheets. On account of the surface charge in the alkali solution, the layered titanium sheet with a rolling-up vector of [001], rolled up to form titanate ribbons and nanotubes in 5 and 10 M alkali solution respectively. When further treated with dilute acid solution, the titanate nanotube transformed to anatase nano particle again. titanium, nanotube, anatase titanium dioxide.

## **Synthesis of Amorphous and Crystalline Bismuth Sulfide Nanotubes**

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Nanotubes of bismuth sulphide were successfully prepared by using anodic aluminium oxide templates, with bismuth nitrate dissolved in ethanol and thiourea dissolved in acetone as precursors. The nanotubes, obtained at 350°C in a reducing atmosphere, had a shell thickness of 13 nm, a diameter of 80 nm, and several microns in length. Their shell had an amorphous atom distribution as measured by X-ray powder diffraction and confirmed with high resolution images of the nanotubes got with a field emission transmission electron microscope; they, however crystallized when the dissolvent was changed to N,N-dimethylformamide, because in this dissolvent the concentration of the precursors could be increased.

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## Solubility and Structure Studies of Mo<sub>6</sub>S<sub>4.5</sub>I<sub>4.5</sub> Nanowire Bundles

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Recently one-dimensional inorganic nanowires have been receiving growing attention as a viable alternative to carbon nanotubes and nanostructured, tube-like materials in general. The most promising of these are the Mo<sub>6</sub>S<sub>9</sub>-xlx family. Easy fabrication, easy dispersability and processability, and uniformity in terms of metallic character as well as diameter, makes Mo<sub>6</sub>S<sub>9</sub>-xlx nanowires one of the most promising one-dimensional materials. Here we present the dispersability study of Mo<sub>6</sub>S<sub>4.5</sub>I<sub>4.5</sub> nanowire soot in a range of common solvents by performing sedimentation studies, Uv-Vis-IR and XPS spectroscopy and electron microscopy characterization. Sedimentation studies, performed combining experiments and theory, show the presence of three phases in the raw material: impurity material, insoluble and soluble nanowire bundles. In addition we describe a successful method to purify the raw material and isolate the nanowire phase. Finally, in order to fully understand the properties of the material it is imperative to confirm the atomic structure of those mono-dimensional objects as well as to understand the packing of the nanowires in bundles. For this purpose here we present a combined High Resolution Transmission Electron Microscopy and aberration corrected Scanning Transmission Electron Microscopy study. This allows us to propose a structure for the isolated Mo<sub>6</sub>S<sub>4.5</sub>I<sub>4.5</sub> nanowires and a superlattice-packing model for the nanowires in bundles. Some applications of this material will be also discussed.

## **BN nanotube formation via an in-situ nitriding reaction**

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High-yield multiwalled boron nitride (BN) nanotubes have been produced using a ball milling - annealing method. Amorphous boron powder was first ball milled in ammonia gas for 150 hours in a steel high-energy ball mill and then annealed in ammonia gas at 1200C for several hours. The BN nanotubes with a diameter less than 10 nm were formed via an in-situ nitriding reaction. The systematic investigation of the formation process at different annealing temperatures and for different times suggests that the formation of the unique multiwalled structure is attributed by a two-dimensional growth of the BN (002) phase and a non-metal catalytic growth.

## **Structural and Mechanical Properties of $\text{MoS}_2\text{-I}_x$ nanotubes and $\text{Mo}_6\text{S}_3\text{I}_6$ Nanowires**

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Using scanning probe microscope we investigate the structure, electronic and mechanical properties of  $\text{Mo}_3\text{S}_6\text{I}_3$  nanowires and  $\text{MoS}_2\text{-I}_x$  nanotubes. The electronic properties are interestingly very sensitive to the stoichiometry of the nanowires, which can be controlled by adjusting the synthesis conditions. In addition to that, we find also remarkable mechanical properties where molecules can be cut and recombined or deformed without any loss of structural integrity. We demonstrate this by deforming the nanowires to highly strained configurations without causing irreversible changes to their structures. The rupturing and/or welding process of these nanowires, using AFM manipulation, shows that the molecules stretch to more than 30% of its relaxed configuration before plastic deformation occurs.

## Single wall boron nitride nanotubes: experimental approaches of their optical properties

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In 2001, we have developed the first route to the synthesis of BN-SWNTs, which consists in the vaporization of a BN target by a continuous CO<sub>2</sub> laser under a N<sub>2</sub> atmosphere<sup>1</sup>. In contrast to C-SWNTs, BN-SWNTs are predicted to behave as insulators with an electronic gap exceeding 5 eV. Measuring such a value on nanotubes is very challenging and we will explain first why methods which have shown to be successful for C-SWNTs fail for BN-SWNTs. In this framework, two experimental approaches have been developed for addressing this issue and will be presented and discussed in this talk. First, the dielectric response of low loss electron energy loss spectroscopy has been recorded in a STEM (Scanning transmission electron microscopy) on individual tubes and provides the first identification of plasmons and of interband transitions in these tubes and the first measure of their gap found to be close to 5.8eV<sup>2</sup>. Second, optical absorption spectra have been measured on macroscopic samples strongly suggest the existence of a Frenkel exciton with a binding energy in the 1eV range<sup>3</sup>.

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## Direct Growth of Boron Nitride Nanotubes on Substrates

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Ten years after the first evidence of boron nitride nanotubes (BNNTs), we report here the first success of growing BNNTs on substrates. BNNTs have stable electronic property, which is independent of their structures. Their band gap (~5 eV) is tunable by substitutions of carbon or a transverse electric field. Previously, BNNTs powders have been synthesized at temperatures >1100 °C. Here, we describe direct growth of pure BNNTs on substrates at 600 °C by a plasma-enhanced pulsed-laser deposition technique. These BNNTs are vertically-aligned on substrates and can be grown at desired patterns and locations [1]. Regular arrays of BNNTs were demonstrated in our experiments. At optimum condition, a well-defined growth region of BNNTs has been identified and explained. According to transmission electron microscopy, these BNNTs have diameters of ~ 10-20 nm and high-order tubular structures with internal tubular channels as small as ~1 nm. Multiple BNNTs can be assembled into vertical bundles with controllable densities. Y.K.Y. acknowledges supports from the Michigan Tech Research Excellence Fund, Army Research Office, CNMS at ORNL, and NSF CAREER Award.

[1] Yap et al., Bulletin of the American Physical Society Vol 50, No. 1, Part 2 (March 2005) page 1346-1347 paper W25 3.

## On the Catalytic Growth of Aligned ZnO Nanowires

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ZnO is a versatile II-VI semiconductor that exhibits piezoelectric and pyroelectric properties. Due to its wide direct band gap of 3.37 eV and large exciton binding energy (60 meV) ZnO is a promising material for optical and electronic devices. Using a simple vapor-liquid-solid process and controlling the growth kinetics a wide range of 1D nanostructures such as nanocombs, nanorings, nanobelts and nanowires have been synthesized. Moreover, aligned ZnO nanowires can be achieved by choosing lattice-matched substrates. Possible applications such as in sensing, optoelectronic and field emission are eminent for these types of nanomaterials. Here it is reported a selective catalytic growth of aligned ZnO structures. The experiments were performed using sapphire, GaN and Si substrates in N<sub>2</sub>/O<sub>2</sub> atmosphere. For the catalytic growth Au structures consisting of thin films and nanoparticles (5, 10 and 20 nm) were used. In addition, ion beam track patterning resulted in the growth of individual aligned ZnO nanowires. This controlled growth will facilitate the successful fabrication of self-aligned gates. The morphology, crystallinity and the photoluminescence behavior of the structures were analyzed. A discussion concerned the mechanism growth and its relation to the catalytic particle size is also shown.

## **Carbon nanotube -- calcium carbonate crystalline composites**

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Composite materials comprising single-walled carbon nanotubes (SWNTs) and calcium carbonate (CaCO<sub>3</sub>) were prepared by precipitation from aqueous solutions. The SWNTs used in the process were functionalized with primary amide groups by treating the acid-purified material with molten urea. The composite materials generally comprised microcrystalline particles with rhombohedral habit characteristic of calcite. Scanning electron microscopy (SEM) investigations revealed that the nanotubes were incorporated into the inorganic matrix and not simply adsorbed to its exterior.

## **Preparation of CNT/conducting polymer nanocables by gamma radiation induced polymerization in the presence surfactant**

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The preparation of a carbon nanotube (CNT)/polymer composite by Ajayan et al.[1] opened up the possibilities of creation of newer functional materials with superior properties by combining CNT with polymers to produce functional composite materials with superior properties.[2]. Several methods have been used to produce CNT/polymer including dissolving polymers in a suspension of CNTs in organic solvents, melt mixing, in situ polymerization, wrapping nanotubes with polymer chains, grafting macromolecules onto CNT[3]. Herein, we report the gamma radiation induced preparation of CNT/ conducting polymer nanocable by oxidative polymerization of the respective monomer in the presence of surfactant. HRTEM reveals the nanocable formation.

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## **Investigation on the mechanical properties of the hybrid nanocomposites reinforced by carbon nanotubes and short carbon fibers**

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Mechanical properties of the carbon nanotubes reinforced composites were studied in our previous study. It is found that the tensile strength and Young's modulus increase 106.6 % and 57.7%, respectively, when 4.0 wt% carbon nanotubes were introduced into the phenolic matrix. Further study has been performed on the mechanical properties of the hybrid nanocomposites when carbon nanotubes and short fibers with equal quantity are added into the phenolic matrix. It is detected that the hybrid nanocomposites has the lowest mechanical property as compare with the mechanical properties of the composites reinforced solely with carbon nanotubes or short carbon fibers. In this study, Raman spectrometer was used to examine the as-synthesis carbon nanotubes, Field Emission Scanning electron microscope (FESEM) was adopted to study the morphologies of the fracture surface. Mechanical properties were tested and its reinforcing mechanism was investigated.

## **Large-scale Oriented PEO Nanofibers Embedded with Super-Long MWCNTs by Eletrospinning**

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Abstract: Well-aligned MWCNT bundles with the length up to several millimeters have been successfully prepared by floating CVD method. By acid treatment and sonication, these super-long MWCNTs can be well dispersed. After preparation of the poly(ethylene oxide) (PEO) solution with addition of well dispersed super-long MWCNTs, the electrospinning process was used to prepare nanofibers of PEO with the diameter of less than one hundred nanometers, in which the super-long MWCNTs are embedded. Transmission electron microscopy (TEM) images indicated that the super-long MWCNTs with the length of several microns can be incorporated in the PEO nanofibers, and present very regular morphology, mostly align along the fiber axis. In this work, we have successfully achieved large-scale fabrication of aligned PEO nanofibers array embedded with super-long MWCNTs by a novel approach, in which the electrode for collecting has been elaborately constructed and a hot air flow is used to help the PEO nanofibers to align during the electrospinning process. Then the super-long MWCNTs can be manipulated to align on a silicon wafer in the same direction or in two different directions on a macro scale of more than 25 centimeters square after removal of the PEO by chemical vapor etching . The large-scale oriented super-long MWCNTs have many prospective applications in electronic devices, such as sensors and circuit elements.

## **CdS-filled carbon nanotubes: structural characterization and electrical behaviour.**

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The huge importance of Carbon Nanotubes (CNTs) in many scientific and technological fields is well known, since their discovery[1]. Some unique properties of CNTs, such as the possibility of tailoring the electrical conductivity, the mechanical resistance together with the small dimensions and high aspect ratio, enable the development of nanotechnology in various fields. The encapsulation of materials inside the CNTs cavity has attracted great interest for a fine tailoring of the physical properties at the nanometric scale. We have developed a new wet chemical method[2] that allowed the filling of CNTs with nanoclusters of various materials, without causing any external material growth. Here we report on the encapsulation of CdS clusters in CNTs, focussing on their morphological and structural characterizations. High resolution transmission electron microscopy analysis permitted to establish the crystalline properties of the CdS nanoclusters and to observe their regularly spacing along the CNTs interiors. AFM and STM-UHV measurements give further informations on the morphology and could indicate changes in the electrical local properties on passing from the CdS-filled areas to the empty areas of the nanotube itself.

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## Singlewall Carbon Nanotubes Enveloped by Dew-shaped Polystyrene

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In this work, we tried to make carbon nanotubes dispersible in both water and organic solvents without oxidation and cutting of nanotube threads. Three kinds of polystyrene-single-walled carbon nanotube (PS-SWNT) composites were prepared with different methods: miniemulsion polymerization, conventional emulsion polymerization, and mixing SWNT with PS latex. The PS-SWNT composite prepared via a conventional emulsion polymerization showed SWNT bundles entirely covered with PS. Whereas the PS-SWNT composite prepared via a miniemulsion polymerization showed SWNT partially covered with dew-shaped PS. The dew-shaped PS-SWNT composite had high electrical conductivity, mechanical strength, and dispersion stability in both water and organic solvents. These indicate that the shape of PS, dew-shape, and the surface coverage are important factors for the mechanical and electrochemical properties, including dispersion states of SWNT in various solvents. The dispersion state also depends on the amount of divinylbenzene in styrene. The dew-shaped PS-SWNT composite synthesized with high divinylbenzene concentration in monomer showed higher dispersion stability and mechanical strength than the composite prepared with only styrene. Because the divinylbenzene makes the crosslinking structure in dew-shape PS, the PS has strong bondings around SWNT without chemical or mechanical damages.

## Mechanical behaviour of polymer/polystyrene-grafted CNx nanotube composites

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Achieving uniform carbon nanotube dispersions in polymeric matrices is a well known problem [1]. Numerous works have reported that nanotube surface functionalization using acid treatments is one possibility to obtain well dispersed nanotubes. However, a novel alternative that avoids acid treatments, consists of using doped carbon nanotubes with nitrogen atoms. These tubes possess reactive pyridine-like and N substitutional sites that are embedded in the hexagonal carbon network. In this paper, we report on the grafting of polystyrene on the surface of multiwalled carbon nanotubes doped with N that exhibit a Bamboo type structure [2], using in situ Atomic Transfer Radical Polymerization (ATRP). The bamboo structure offers advantages versus concentric-cylinder nanotubes in terms of their mechanical performance, because the compartments within N-doped tubes avoid slipping of the concentric tubular shells [3]. Therefore, it is believed that these structural differences will result in changes of the mechanical properties of the polymer nanotube composites. The grafting of polystyrene on nitrogen-doped MWCNTs was investigated by high resolution Transmission Electron Microscopy and allied analytical techniques such as electron energy loss spectroscopy (EELS) and energy dispersive X-ray spectroscopy (EDX) [C.f NT'04]. The PS-grafted CNx nanotubes were subsequently dispersed in a block-copolymer matrix, namely poly (butadiene-co-styrene). DSC measurements were carried out on the nanocomposites in order to determine the role played by the PS-grafted CNx on the matrix. In addition, the mechanical properties of the nanocomposites were studied by Dynamic Mechanical Analysis and by tensile tests. The results are compared with those nanocomposites fabricated with the same matrix and using non-grafted CNx nanotubes.

## **Carboxymethylcellulose as an Excellent Dispersant for Single-wall Carbon Nanotubes Enabling the Formation of Dense and High Quality Thin Films**

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By extending a previous work by Takahashi et al. [1], we have found that carboxymethylcellulose (CMC), an etherified derivative of cellulose, is an excellent dispersant for single-wall carbon nanotubes (SWNTs), realizing very concentrated and stable aqueous dispersion SWNTs [2]. By comparing the absorption spectra, we demonstrate that the concentration of SWNTs reaches more than twenty times as high as that of SDS-aided dispersion. Moreover, this dispersion is found to be very stable showing little change in the absorption spectrum over a month. Also, the dispersions give well-resolved near-infrared photoluminescence peaks, a sign of good isolation of SWNTs. The dispersion can be used to prepare dense SWNT thin films possessing high optical quality and uniformity, again giving photoluminescence whose spectrum shows little alteration from that of the aqueous dispersion, confirming the preservation of the good isolation of SWNTs. Mechanical stretching of the thin films results in strong tube alignment, as demonstrated by considerable dichroism in their absorption spectra. These results have important implications for various industrial applications of SWNTs, because cellulose derivatives are cheap, mass-produced, safe, water-processable and environment-friendly.

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## Transparent Conductive Film based on Carbon Nanotubes and PEDOT Composites

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The improvement of conductivity of transparent conducting film using conducting filler has received considerable attention because of potential applications in display technologies, solar cells, flexible electronic devices and optical devices [1]. But, transparent conductive films such as indium tin oxide (ITO), which is the current industry standard have several problems, such as flexibility and cost. CNTs have been recognized as one of the most promising candidates for conductive materials due to its remarkable conductivities [2-3]. We investigated that The transparent conductive film was prepared with various concentrations of dispersed CNTs in the conducting polymer, poly(3, 4-ethylenedioxythiophene) (PEDOT) solutions on the glass and polyethylene terephthalate (PET) film using bar coating methods. A sheet resistance of 247 ohm/sq and a transmission of 84.7 % were obtained at a concentration of the acid treated CNTs of 0.01 wt%.

## **Supported Coordinative Polymerization : an unique way to potent polyolefin carbon nanotubes composites**

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Since their first observation in 1991 by Iijima, carbon nanotubes have been attracting both academics and industries, owing to their exceptional properties. This new allotropic variety of carbon has been tested as an advanced multifunctional filler in polymer-based nanocomposites. However, the homogeneous dispersion of native carbon nanotubes is relatively difficult to achieve, especially in apolar polymer matrices such as polyolefins. Indeed, carbon nanotubes tend to form long bundles that are thermodynamically stabilized by numerous  $\pi$ - $\pi$  interactions between the tubes. Most of the techniques that have been used to disperse these bundles, e.g., ultrasonication, chemical oxidation or reduction followed by chemical modification of the nanotube surface and subsequent polymer grafting, are susceptible to break down or at least to perturb the extended delocalized  $\pi$  system responsible for the unique properties displayed by carbon nanotubes. An original and much softer method is described here. This technique which relies upon the in situ polymerization of olefin catalyzed by a highly active metallocene complex physicochemically anchored onto the nanotube surface. As a result, carbon nanotubes are homogeneously coated by the in situ grown polyolefin chains, finally leading to the break-up of the nanotube bundles and upon further melt blending with HDPE, to high-performance polyolefinic nanocomposites.

## **Thermal and electrical properties of carbon nanotube/polyurethane foam**

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Carbon nanotubes provide a means to enhance polymers structures where conventional fibre fillers cannot be accommodated; the current example is that of nanotube filled foams. Such systems are particularly interesting because existing catalytically-grown materials, available on a large scale, can readily provide immediate benefits. Electrically conductive foams were produced by dispersing acid treated catalytically-grown carbon nanotubes in a flexible polyurethane matrix. The resulting thermal and electrical properties were examined as a function of loading history. The acid treatment, and associated surface charge, ensured a fine dispersion of the filler throughout the polymer matrix, as confirmed by electron microscopy. Loading fractions as low as 0.5 wt % cause the polyurethane foams to become electrically conductive, without the damaging effects associated with traditional conductive fillers. Thermal properties are also affected, as will be discussed. Electrically conductive polyurethane foams are relevant to anti-static packaging for electronics, and a variety of more functional applications.

## **Polymer Composites with Protein Functionalized Carbon Nanotubes**

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With superior structural and transport properties (high strength and flexibility, high thermal and electrical conductivity, low density) carbon nanotubes are attracting great deal of interest as reinforcing materials in polymer composites [1-3]. We have developed fully integrated nanotube composite materials through the functionalization of carbon nanotubes by attaching protein molecules onto the surface of carbon nanotubes. We have used ferritin and collagen for functionalization of multi wall carbon nanotubes (MWCNT) and single wall carbon nanotubes (SWNT) respectively and poly (vinyl) alcohol (PVA) as the polymer matrix. The investigation of the thermo-mechanical behavior was performed by dynamic mechanical thermal analysis (DMTA). Results demonstrated dramatic enhancement in the mechanical properties of PVA, for example a 100-110% increase in the modulus with the addition of 1.5 wt% of ferritin functionalized MWCNTs. Samples containing functionalized nanotubes showed a stronger influence on glass transition temperature in comparison to composites containing the same amount of non-functionalized nanotubes. In case of collagen modified SWNTs we observed that the SWNTs within the collagen are stretched and straightened and also nicely dispersed. It shows a great deal of enhancement in mechanical properties of composite film with PVA polymer.

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## **MECHANICAL PROPERTIES OF MWNT/CELLULOSE/MELAMINE-FORMALDEHYDE COMPOSITES**

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In applications like coatings and laminates where high mechanical performance including marring resistance are required, melamine-formaldehyde (MF) is of great interest. This amino resin presents high surface performance, good appearance and thermal properties adequate for such function. In our previous works it was found that mechanical performance of MF can be further improved with the addition of various micro carbonaceous fillers (i.e. carbon fibres, carbon black). In turn, reinforcement with carbon nanotubes (CNTs) is attractive to study. Multi-wall nanotubes (MWNT) were purified by an oxidative method. The purity was analysed by X-ray photoelectron spectroscopy (XPS). Treated MWNTs were dispersed in a surfactant, sodium dodecyl sulphate (SDS) water solution (0.5 wt%) by sonication in order to aid dispersion. Next, the dispersion was added in different concentrations to a MF solution (50% solid contents). Alpha cellulose papers were impregnated with the MWNT/MF aqueous solution mentioned above. Composites were prepared by hot pressing. Degree of dispersion and morphology were characterised by light microscopy (LM) and scanning electron microscopy (SEM). Mechanical properties were assessed by means of dynamic mechanical thermal analysis (DMTA), stress-strain and nanoindentation testing. Results showed increment in stiffness and strength and increased strain to failure with only 0.1 wt% MWNT.

## **Structural relaxation, expansivity and glass transition in spin-cast, glassy nanocomposite thin films containing carbon nanotubes.**

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The effect of double-wall carbon nanotubes (CNTs) on the isothermal, structural relaxation of glassy, spin-cast polymer thin films, ranging from 45nm to 145nm, was investigated. Stable, dilute solutions of catalytic-CVD nanotubes and poly(methylmethacrylate) in bromobenzene were obtained after sonication to produce films containing 1 wt.% CNT. SEM and AFM images of films spin-cast on both carbon and silicon substrates showed homogeneous distribution of CNT clusters. Topographical analysis found that most CNTs were below the film surface. The thickness,  $h$ , of freshly-cast nanocomposite films was measured over time using spectroscopic ellipsometry. The films exhibit a gradual decrease in thickness, attributed to structural relaxation of the polymer glass combined with simultaneous solvent loss. In all cases,  $h$  was found to be greater than the equilibrium thickness obtained by cooling slowly from the melt. The initial departure from equilibrium was slightly higher in the nanocomposite films compared to the pure polymer, which might be attributed to a more rigid structure in the nanocomposite. However, the glass transition temperature and rate of structural relaxation in the films were not affected by the addition of CNTs. The ratio of thermal expansivity of the glass to the melt increases with decreasing film thickness in all cases.

## **Structural, compositional, mechanical properties of carbon nanotube reinforced zirconia matrix nanocomposite films by sol-gel process**

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Carbon nanotube reinforced zirconium oxide matrix nanocomposite has been synthesized by simple and cost effective sol-gel process on 440C steel and polished quartz substrates. Homogeneous distribution of carbon nanotubes within the zirconia matrix have been obtained by mixing carbon nanotubes with zirconia sol and followed by condensation into gel formation. The mixed gel, consisting of zirconia and carbon nanotubes has been dried and subjected to conventional calcinations process at different temperatures ranging from 200°C to 1000°C for 1h in argon atmosphere. The deposited and calcined nanocomposites have been characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM), energy dispersive X-ray analyzer, X-ray photoelectron spectroscopy techniques for their structural, morphological and elemental composition of the nanocomposites. Nanoindentation tests of the nanocomposites have shown higher hardness compared to the pristine carbon nanotubes and zirconia films due to an enhanced load sharing of the homogeneously distributed carbon nanotubes in the matrix. At the same time, the fracture toughness of carbon reinforced zirconia matrix nanocomposite has also enhanced due to bridging effect of carbon nanotubes during crack propagation.

## **Molecular dynamics simulations of mechanical properties of BN nanotube/Si-B-N ceramics composites**

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We examine the elastic properties of boron-nitride nanotubes, which are embedded in amorphous silicon-boron-nitride ceramics. We employ molecular dynamics simulations using the Parrinello-Rahman approach. To this end, all systems are modeled with a reactive many-body bond order potential due to Tersoff, which is able to describe covalent bonding accurately. We apply external stress and derive stress-strain curves for various tensile and compressive load cases at given temperature and pressure. In particular we study the mechanical properties of a ceramics composite material made from Si<sub>3</sub>B<sub>3</sub>N<sub>7</sub> matrix and BN nanotubes. Here, we compute the Young modulus for the composite to predict the rate of reinforcement due to the BN nanotubes. Also the influence of the nanotube/matrix-ratio on the elastic modulus of the composite is examined. Finally, we compare the Young moduli derived from the numerical simulations to predictions given by a simple macroscopic rule-of-mixtures, which depends on the volume fraction only, and an extended rule-of-mixtures, which also takes the geometric distribution of the BN nanotubes into account. Our numerical results suggest that the extended rule-of-mixtures predicts the rate of reinforcement of the composite with a relative error of less than 5%.

## **Energetics of helical wrapping of one-dimensional strands around carbon nanotubes**

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Various physical properties of nanotube/polymer composites, including their electronic and mechanical properties, can be affected when the polymers form a crystalline phase about the nanotubes. Morphologically, this layer consists of polymer strands coiling around the nanotubes at well-defined helical angles. Similar helical wrapping is also observed in certain DNA/nanotube hybrids. Common to both systems is the fact that the wrapping agent has a strong one-dimensional character, suggesting that this geometric arrangement is a general feature displayed by linear charge distributions in the presence of a cylindrical structure. Motivated by this suggestion, we theoretically study the interaction of carbon nanotubes with one-dimensional-like strands. With simple models for the electronic structure of the composite, we are able to identify the angular dependence on the total interaction energy whose minimization leads to preferential wrapping angles.

## **Physical mechanism for the mechanical reinforcement in nanotube-polymer composite materials**

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The significant increase in the Young's modulus of nanotube-polymer composites is often correlated with the formation of a crystalline layer of polymers surrounding the nanotubes. Although the improved stress transfer between the stiffer nanotube and the softer polymer matrix has been attributed to the presence of this ordered polymeric layer, the actual mechanism for this stress transfer is unclear. To clarify this matter, we model the polymer-nanotube composite by harmonic chains interacting with a rigid periodic potential, an extension of the so-called Frenkel-Kontorova model. We identify the origin of the reinforcement with the occurrence of a templating transition, in which polymers are constrained by the periodic potential of the underlying nanotube. The model points to the existence of a suitable combination of polymers and nanotube diameters to maximally enhance the mechanical properties of composite structures. The model is tested against experimental data.

## **Electrical and thermal conductivity of single- or multiwalled carbon nanotube - polymer composites**

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The electrical and thermal properties of epoxy composites containing low filler loadings (0.005-0.5 wt%) of single- (SWCNT) or multiwalled (MWCNT) carbon nanotubes were studied. Dispersion of the MWCNTs in epoxy was achieved by mechanical mixing, whereas a pre-treatment of the SWCNT was required to separate the as made SWCNT aggregates. Two treatments were investigated, ball milling and a chemical treatment developed recently by the authors. The electrical conductivity measurements were carried out in order to detect the formation of a percolating CNT network in the composite samples. For the MWCNT-composites the critical filler concentration was found to be below 0.005 wt%, whereas in the SWCNT-composites the formation of percolating network required higher filler concentrations. Having established the presence of such a network, the thermal conductivities of the CNT-polymer composites were measured with a transient method. Based on the experimental results, the phonon transmission in CNT-polymer composites is discussed.

## Carbon nanofibre reinforced PEEK foams

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Carbon nanotubes and nanofibres have intrinsic potential to reinforce fine structures where other reinforcements cannot be accommodated. Previously we have shown that nanofibre-reinforced PEEK fibres have improved mechanical properties, attributable both to the filler and to changes in polymer morphology. In this study, a carbon nanofibre (CNF) filled polymer foam has been produced for the first time. The matrix chosen, poly(ether ether ketone) (PEEK), is a high performance polymer that cannot normally be foamed, due to melt instability. However, CNFs provide a unique contribution to both processability and properties. Here, we demonstrate significant differences between shear and extensional rheological behaviour of these nanocomposite blends; at high shear rates, the viscosity increase due to the nanofibres is modest, comparable that of graphite; in contrast, melt elongation measurements indicate that CNFs, unlike graphite, significantly increase the melt strength of PEEK. This new approach to balancing the rheological properties of the melt allows straightforward fabrication of high quality PEEK foams, with nanofibres uniformly distributed throughout the cell walls and struts. Furthermore, the presence of the nanofiller provides property enhancements, for example, raising the specific strength and stiffness of foam injection moulded samples in bending.

## **Process for Spin Coating Transparent and Electrically Conductive Polymer-Nanotube Composite Films**

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The presentation considers the feasibility of using multi-wall carbon nanotubes (MWNT) as a filler in polymer-based films that are prepared by spin coating a suspension onto glass substrates. The high aspect ratio of MWNT and their good electrical conductivity enable electrical percolation at very low concentrations, so that films can be prepared that conduct electricity while retaining good optical transparency. The coating mixture consists of a solvent with low volatility, a dissolved thermoplastic polymer, and MWNT. Although the MWNT's are driven to aggregate by Van der Waals interactions, the high viscosity of the polymer/solvent solution enables the preparation of metastable, homogeneous dispersions. The films were characterized using optical microscopy, DC resistance and AC impedance measurements, and current sensing AFM (cAFM). Images acquired with cAFM show strong contrast between conductive and insulating domains, with the latter regions dominating the morphology and implying high contact resistances. To optimize the electrical and optical properties of the films, we systematically investigated the effects of the coating viscosity, spin time, and spin rate on the shear-induced aggregation of the MWNT.

## Electrical conductivity of VACNFs-PS membranes

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Polymer membranes have been widely used in various applications, such as fuel cells, gas separation, biology, electronics etc. The conducting polymer membranes are promising materials for construction of e.g. electrochemical sensors. The anisotropy of electrical conductivity in such membranes may be interesting and can be achieved by filling polymer with structured carbonaceous compounds. In this study we investigated the formation of thin polystyrene (PS) membranes, in which regularly patterned vertically aligned carbon nanofibers (VACNF) were incorporated across the PS film. First, the catalyst pattern (Ni-dots, placed at 1  $\mu\text{m}$  distance) was fabricated onto a SiO<sub>2</sub> (400 nm oxide layer) substrate coated with 50 nm molybdenum film. VACNF were grown by dc-PECVD method in C<sub>2</sub>H<sub>2</sub>/NH<sub>3</sub> atmosphere. Then, polystyrene has been spin-coated on the as-prepared VACNF/substrate to form membranes with a thickness of  $\sim 1 \mu\text{m}$ . The VACNF-PS membranes were removed from the substrate using basic wet etching. The electrical conductivity of the composite membrane along and across the membrane was investigated.

## **Carbon Nanotube-Based Composite as Cathode of Lithium Batteries**

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Carbon nanotube has been used for preparation of anode of lithium batteries, but less attention has been paid to it for preparation of cathodes of lithium batteries. Available composite-based cathodes are constructed from appropriate cathode material and carbon active (acetylene black). Carbon nanotubes are promising candidate to be applied for this purpose, since it has been described that generating nano-channels through cathode leads to better battery performance [1,2]. Existence of appropriate nano-channels within the cathode structure provides suitable pathways for Li diffusion which control the battery performance. Carbon nanotubes inserted within the cathode material can provide such pathways. Due to large specific area of carbon nanotubes, it is possible to increase the amount of cathode material in a commercial cathode, which is favor of energy density. On the other hand, an important problem of current cathode materials is their low electrical conductivity. This failure can be improved by Au codeposition [3-5], however, this increases the cathode weight. In this study, different cathode materials were employed for preparation of carbon nanotubes-based cathodes. Influences of different properties of cathode materials on fabrication of carbon nanotubes-based cathodes were compared. Some classifications for choosing appropriate cathode material and carbon nanotubes were suggested.

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## Raman scattering study of the interaction between liquid crystal

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Carbon nanotubes can be ordered by dispersing them in an anisotropic self-organizing matrix such as liquid crystals (LCs) [1]. The efficiency of the ordering is strongly dependent on the interactions between the nanotubes and LC molecules. As the Raman scattering response of carbon nanotubes is sensitive on their surface modification [2], the study of the nanotube Raman modes can be used to probe the interactions with the LC matrix. To elucidate the role of aromatic rings in the LC molecule structure for the interactions with the nanotubes, we compared the response of HiPCO single-wall nanotubes on their own with their response when dispersed in three different liquid crystalline hosts. The hosts have identical end chains but cores varying from a fully aromatic biphenyl to a fully cycloaliphatic bicyclohexane. Whereas a modification was clearly detected through a shift of the RBM Raman modes by two wave numbers towards higher values in case of the biphenyl host, one wave number shift was detected with respect to pure nanotubes for the host with one aromatic ring and no shift when using the non-aromatic host.

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## **Carbon nanotubes dispersed and ordered in self-organizing lyotropic liquid crystalline templates**

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A major challenge in the application of carbon nanotubes is the post-growth treatment, the aims being to overcome flocculation into bundles and imposing high orientational order such that their exceptional anisotropic properties can be exploited in devices. The most successful approach for obtaining single-tube dispersion is to keep the nanotubes in low-concentration surfactant+water solutions, the surfactant often being SDS [1]. At concentrations much higher than what is generally used for this purpose, such solutions form lyotropic liquid crystal phases. Liquid crystals (LCs) have turned out to be excellent hosts for aligning carbon nanotubes [2] but so far only thermotropic LCs have been investigated. In this contribution we present our studies of lyotropic hosts for simultaneous dispersion and alignment of carbon nanotubes. Preliminary investigations have demonstrated good dispersion in SDS+decanol+water mixtures forming the nematic LC phase, i.e. exhibiting orientational but no translational order. Results of optical microscopy and resonant Raman investigations of CNT-LC composites with respect to dispersion and alignment efficiency of different lyotropic hosts on single- and multiwall carbon nanotubes will be presented.

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## **Fully Integrated Carbon Nanotube Composites and Hybrid Materials**

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Carbon Nanotubes, both single wall, double wall and multi-wall, have exceptional stiffness, strength, thermal and electrical conductivity. This paper discusses their full integration in polymeric and ceramic matrices for applications as multifunctional components with optimal structural, thermal and electrical properties. The goals are to mimic in a larger scale the properties of these carbon nanotubes so that they can be used more aggressively on the micro, meso and macro scales. This is achieved through full integration by tip attachment and/or side wall functionalization, coincident polymerization, milling, dispersion and shear alignment. The full integration of these carbon nanotubes into these matrices is accomplished through the architecture of special bonds, designed to foster enhanced mechanical, thermal and electrical properties.

## SWNT-OLEUM: PARTLY ORDERED SOLVENT SHELLS, TEMPLATED CRYSTALLIZATION AND FIBER SPINNING

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X-ray scattering from aligned SWNT fibers swollen in anhydrous sulfuric acid provides unambiguous structural evidence for the long-conjectured partly-ordered solvent shells surrounding an ionic solute [1]. Preferred orientation of SWNT in the fibers is replicated by the diffuse scattering from partly ordered cylindrical "shells" a few molecules thick, wrapped around the SWNT. Acid supercooling and melting of random SWNT-acid suspensions (DSC) vary in temperature and enthalpy with SWNT concentration, confirming that the partly ordered molecules are a new phase. Furthermore, X-ray scattering vs. temperature shows that crystallization of bulklike acid surrounding the structured shells is templated by the aligned SWNTs, while the structured shells remain partly ordered [2]. The (2 0 0) or (2h 0 2) planes of the templated H<sub>2</sub>SO<sub>4</sub> crystallites are parallel to the nanotube axes, from which it can be deduced that the acid molecules are preferentially oriented with a proton in contact with the SWNT surface. This provides solid evidence for the direct protonation of SWNT.

The first-ever well-aligned continuous macroscopic neat single-walled carbon nanotube (SWNT) fibers were produced using conventional spinning techniques. Neat SWNT fibers, containing no surfactant or polymer, were made by spinning dispersions of SWNTs in 102% sulfuric acid into different coagulants. The critical role of sulfuric acid in dispersing and aligning SWNTs during fiber formation has been explored. Characterization shows alignment greater than any other macroscopic neat SWNT material reported to-date while providing insight into the fundamental hierarchy and nature of SWNT fiber formation [3]. Electrical, thermal, and mechanical measurements indicate that neat SWNT fibers hold tremendous potential for future applications.

We propose that charge transfer electrons and highly oxidizing superacid is responsible for the unique partly ordered structure.

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## Superhydrophobic surfaces using carbon nanotubes forests

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In this work the effect of pressure on the contact angle of a water drop on superhydrophobic Carbon Nanotube (CNT) forests is considered. Superhydrophobic CNT forests are obtained from a new and simple functionalization strategy, based on the gold-thiol affinity. Using a specifically devised experimental setup, we then show that these surfaces are able to withstand high excess pressures (larger than 10kPa) without transiting toward a roughness-invaded state, therefore preserving their low adhesion properties. Together with the relatively low technical cost of the process, this robustness versus pressure makes such surfaces very appealing for practical integration into microfluidic systems.

## **Influence of Length on Cytotoxicity of Multi-Walled Carbon Nanotubes against Human Acute Monocytic Leukemia Cell Line THP-1 *in Vitro* and Subcutaneous Tissue of Rats *in Vivo***

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Carbon nanotubes (CNTs) are single- or multi-cylindrical graphene structures that possess diameters of a few nanometers, while the length can be up to a few micrometers. These could have unusual toxicological properties, in that they share intermediate morphological characteristics of both fibers and nanoparticles. Here, we investigated the activation of the human acute monocytic leukemia cell line THP-1 *in vitro* and the response in subcutaneous tissue *in vivo* to CNTs of different lengths. We used 220 nm and 825 nm long CNT samples for testing, referred to as "220-CNTs" and "825-CNTs", respectively. 220-CNTs and 825-CNTs induced human monocytes *in vitro*, although the activity was significantly lower than that of microbial lipopeptide and lipopolysaccharide, and no activity appeared following variation in the length of CNTs. On the other hand, the degree of inflammatory response in subcutaneous tissue in rats around the 220-CNTs was slight in comparison with that around the 825-CNTs. These results indicated that the degree of inflammation around 825-CNTs was stronger than that around 220-CNTs since macrophages could envelop 220-CNTs more readily than 825-CNTs. However, no severe inflammatory response such as necrosis, degeneration or neutrophil infiltration *in vivo* was observed around both CNTs examined throughout the experimental period.

## **Electrospinning of covalent functionalized CNT reinforced nanofibers**

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Functionalization of CNTs is advantageous because functional groups can prevent the aggregation of nanotubes and in addition favor their solubilization in organic solvents [1,2]. The attached functional groups can be used as precursors for the subsequent attachment of a wide variety of other functional groups. We report here the side chain covalent functionalization of SWNTs and MWNTs by various groups to induce solubility of CNTs in organic solvents. Electrospinning[3] was used to incorporate the functionalized CNTs to align in polymeric matrices (Poly(vinylidene fluoride, etc) and form composite nanofibers. The electrospun nanofibers are expected to have the combined benefits of nanofibers with the merits of CNTs.

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## **Characterization and application of multi-walled carbon nanotubes synthesized by a combination of floating reactant method and post high temperature treatment**

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Multi-walled carbon nanotubes are very attractive material as a filler to add an electrical conductivity for polymer materials. In such an application, huge mass of multi-walled carbon nanotubes are required for commercial use, therefore we adopted a floating reactant method for the production of multi-walled carbon nanotubes. The structural characterization of the as-grown and thermally treated nanotubes was performed with SEM, TEM, XRD, Raman spectroscopy and so on. Also the powder properties of these nanotubes were measured. After mixing the nanotubes with epoxy resin, the electrical conductivity of the resin and the dispersion of nanotubes in the resin was evaluated. Main characteristics of these nanotubes after high temperature treatment are relatively wide distribution of diameters ranging from 20 to 70 nm and linear, long macro-morphology (aspect ratio > 100), highly straight and crystalline layers, very low interlayer spacing (0.3385 nm) and low R value ( $ID/IG = 0.0717$ ), high G' intensity over intensity of G band ( $G'/G = 0.85$ ). The unusual microstructure with a partially cross-sectional shape was observed in the multi-walled carbon nanotubes. The nanotubes are easily dispersed in epoxy resin and exhibits good electrical conductivity compared to carbon black/epoxy composite.

## Manipulate Visible Ultralong SWNTs Under Optical System

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In this study, we report the development of manipulating visible ultralong single-wall carbon nanotubes (SWNTs), 6 mm long at least, synthesized by Fe-catalysed decomposition of ethanol, bubbled by Ar and H<sub>2</sub> [1], in chemical vapor deposition (CVD) system under optical system. We found that a considerable amount of amorphous carbon was produced in the reaction process of growing SWNTs and covered the SWNTs to indicate where they lay. The SEM images in the cross-section of the visible ultralong SWNTs broken via exerting external tension force show the evidence of SWNTs uniformly covered with a great deal of amorphous carbon. The electrical properties of visible ultralong SWNTs manipulated from raw sample to another wafer deposited electrode pairs have been characterized. Despite covered amorphous carbon, they still show the semiconductor behavior by applying the bias between source and drain. We believe that using proper purification process will remove the amorphous carbon surrounding SWNTs and recover the electrical properties of the SWNT field-effect transistors. This method reveals the feasibility of manipulating SWNTs into any shapes or putting them on any devices under ordinary optical system. It would be a convenient way to provide a broad range of applications in nanoscience and nanotechnology.

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## **Raman- and Absorption Spectroscopic Studies on Chirality Dependent Growth of Single-Walled Carbon Nanotubes Mediated by Boron and Nitrogen Doping**

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We report a spectroscopic study of the effects of nitrogen (N) and boron and nitrogen (BN) doping of carbon nanotubes using HRTEM, Raman and absorption spectroscopy. The diameter distribution, relative populations and electronic bandgaps of semiconducting SWNTs produced by the modified arc-discharge process were studied and show that boron preferentially mediates the growth of low chiral angle species leading to the observation of dominant Raman modes from zig-zag or near zig-zag nanotubes. Raman spectra, in the region of the radial breathing mode (RBM), confirm the presence of nanotubes with diameters between 1.15-1.58nm. While RBM spectra of the nitrogen doped samples show very little change in the diameter distribution, boron-nitrogen doping produces a rapid change in Raman intensity towards peaks corresponding to nanotubes with smaller diameters. Absorbance spectra show that as the BN doping in the anode is increased the average ES11 mode energy increases, which we also attribute to changes in the populations, in favour of smaller diameter nanotubes. The n,m indices of the dominant frequencies observed in the most heavily BN doped material are identified as (16,0) and (14,1) nanotubes using an updated Kataura model. This confirms predictions that during synthesis boron acts as a surfactant to reduce the number of dangling bonds at the growth edge for low chiral angle nanotubes. As a result growth is enhanced for zig-zag species, thus offering a natural count erpart to recently methods which preferentially produce armchair rich materials.

## **Preparation of thin film by using chemically functionalized multi-walled carbon nanotubes**

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Multi-walled carbon nanotubes (MWCNTs) are composed of strong graphene  $sp^2$  bonds that hinder their functionalization. Consequently, the preparations of MWCNTs solid bodies have been found to be difficult. However, we believe that the preparation of MWCNTs solid bodies could be realized by making the surfaces of MWCNTs active by forming defects that facilitate the functionalization as well as binding between tubes. Here, we report the synthesis of films using chemically functionalized MWCNTs, and their physical properties. First, the as-grown MWCNTs were air oxidized and treated with HCl to remove amorphous carbon and catalytic metal particles respectively. The resultant samples were treated with 6M-HNO<sub>3</sub> at 373K for a specified period of time to induce defects on the surface of the tubes. As a consequence, the surface becomes functionalized with carboxylic acid. Then, these functionalized tubes were polymerized to prepare MWCNTs film using the following steps. Firstly, the functionalized MWCNTs were ultrasonicated for 1h in N, N-Dimethylformamid. Then, the polymerizing agent N, N-Dicyclohexylcarbodiimide was added to the dispersion and stirred at room temperature for 24 hours. Finally, MWCNTs films with different thicknesses were prepared by filtering MWCNTs dispersion with varying concentrations. The physical properties of these films will be reported in detail.

## Self assembled carbon nanotubes and their applications

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Since their discovery as a by product of the arc discharge process, carbon nanotubes have received an increasing academic and industrial interest due to their exceptional mechanical and electronical properties [1-4]. Recently we discovered reversible adsorption properties of organic species present in an aqueous medium by CNT's and seems to be an exceptional candidate for the depollution of water. However, carbon nanotubes are fluffy powder which make them uncomfortable for manipulation and it is of interest to prepare these carbon materials with a macroscopic shape in order to facilitate their handling and recovery. We reported here a new synthesis (CVD) based on a confinement growth of the carbon nanotubes. After reaction, all nanotubes are tangled up and kepted the macroscopic shape of the so called confinement reactor (cylinder, cube, sphere...) and exhibit a high mechanical resistance. This new material can be easily used to separate organic species (traces or more) from an aqueous medium by selective adsorption, the pollutants are reversibly desorbed in an organic solution which allowed the starting material to be reused. Self assembled nanotubes can also be used in catalytic process (i.e selective oxydation of H<sub>2</sub>S...) or as reinforcement materials. References:

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## **Integration of naturally short Multi Wall Carbon Nanotubes into the anode materials of Li-ion-batteries**

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Naturally short MWNTs (sh-MWNTs) produced with use of Self-regulated Liquid-phase Arc-discharge, SLA, were functionalized and integrated into the anode materials of Li-ion-batteries (LIBs). Median lengths and outer diameter of the sh-MWNTs are controlled within the ranges of 150-350 nm and 7-10 nm, correspondingly. Also SLA enables selective production of metallic and semiconducting MWNTs. These features provide better infiltration rates and higher capacities of the sh-MWNTs' anodes. The substitution of the commercial graphite with reasonable amounts of specially treated sh-MWNTs results in electrodes having capacities doubled over the best commercial LIBs (so far, up to 600mAh/g) and demonstrating an excellent cycle life performance.

## Carbon Nanotubes as Gas Sensors: Tailoring Sensing Properties by Surface Functionalisation.

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Carbon nanotube-based gas sensors can be key devices in the call for the development of low-cost sensing elements and low-power consumption gas sensors. We have now developed chemical gas sensors with an active layer of functionalised multi-walled carbon nanotubes.<sup>1</sup> Functionalisation was performed using RF-Plasma under different reaction conditions and plasma composition (oxygen, ferrocene, acrylic acid), and films were prepared by drop coating functionalised nanotubes dispersed in glycerol.<sup>2</sup> XPS analysis demonstrates that the chemical composition depends on the plasma conditions, and SEM micrographs shows that the morphology of the films depend on the type of functional groups.

Detection of hazardous gases was investigated for controlled concentrations of different gases (NO<sub>2</sub>, CO, NH<sub>3</sub>, ...). Room temperature experiments indicated that the best response was obtained for sensors with oxygen functionalised nanotubes. These results were compared with theoretical *ab initio* calculations, showing the different adsorption properties for the gases under consideration.<sup>2</sup> Interaction of gas molecules with different functional groups on pristine and on defectuous carbon nanotubes was analysed. In particular, distinct interaction for gas molecules with oxygen functionalised defect sites was demonstrated. These results enabled a better understanding of the functional groups present after plasma functionalisation and their interaction with the gas molecules.

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## Catalyzing Carbon Nanotube Coalescence.

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In order to fabricate carbon nanotube junctions and networks with novel electronic properties, it is necessary to understand the nanotube coalescence mechanism from an atomistic point of view. Nanotube-nanotube materials could be achieved by controlling the growth of carbon nanotubes using chemical vapour deposition methods in conjunction with organometallic compounds containing Fe and S. Alternatively; it may be possible to achieve coalescence or connect carbon nanotubes by controlling the surface chemical activity between nanotubes. In this context, carbon nanotubes could be joined at defect sites, but a better control of surface defects and the introduction of novel types of imperfections are still needed to catalyze the formation of covalent nanotube interconnections.

Here, we report novel possibilities capable of achieving carbon nanotube coalescence and nanotube junctions, using high-resolution transmission electron microscopy (HRTEM) and resonance Raman studies. In particular, the role played by different types of hetero-atoms in substitution within the lattice or as interstitials between nanotubes is analysed. In order to gain insight in the mechanisms involved, a theoretical analysis was performed using AM1 Molecular Dynamics (MD) simulations at different temperatures, as well as *ab initio* calculations. The electronic properties of the new systems have also been studied.

## **Vertical alignment of single walled carbon nanotubes with colloidal self-assembly**

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Aligned carbon nanotubes have attracted great attraction for many potential applications such as field emitters, biological sensors, and electronic devices. It is essential for the highly effective use of these applications to immobilize SWNTs vertically on the substrate surface at room temperature. We selected mono-disperse silica colloidal particles with self-assembled monolayer to fabricate vertical alignment of single walled carbon nanotubes (SWNTs), and have planted SWNTs into a substrate coated self-assembled monolayer of silica using electric field. Single walled carbon nanotubes individually suspended in dimethylformamide have been placed between two electrodes in a dc field. Under the influence of a dc electric field, SWNTs assemble as individual tubes vertically on the positive electrode with self-assembled monolayer of silica. FE-SEM was used for the characterization of vertical alignment of SWNTs.

## **Optical Ignition of Nanotubes-Doped Energetic Materials**

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Ignition of energetic Materials via optical triggering has several important practical benefits: (1) the optical signal is immune to electromagnetic interference, ambient conditions of pressure and temperature, and (2) pulse-delivery is not dependent on materials that might degrade over time. Single-walled carbon nanotubes that ignite when exposed to a conventional photographic flash are the ideal candidates for providing the ignition sites, the so-called hot spots, for energetic materials initiation. Our recent experiments on a variety of nanotubes-doped energetic materials demonstrate that the absorbing particles prone to opto-thermal behavior create hot sites of reactions that proceed to ignite the energetic materials and leads to a transition from deflagration to actual detonation of the materials.

## **Carbon nanotubes: A modified model for numerical simulations of elasticity moduli**

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Exceptional mechanical, electrical, transport, optical, electronics etc., properties of carbon nanotubes (CNTs) and their nanoscale sizes, reflect attention of many researchers from the world. It is interesting to be mentioned, tha

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Exceptional mechanical, electrical, transport, optical, electronics, properties of carbon nanotubes (CNTs) and their nanoscale sizes, reflect attention of many researchers from the world. It is interesting to be mentioned, that these nanomaterials have extraordinary mechanical properties (high stiffness and axial strength, high Young's modulus), [1,2], "as a result of their samples cylindrical graphitic structure, [3]". The aim of the work presented can be formulated as follows: to give a modified model for numerical simulations of elasticity moduli of different carbon nanotubes samples. On the basis of observations by transmission electron microscopy (TEM) at room temperature and assuming that nanotube is equivalent to a clamped homogeneous cylindrical cantilever beam, paper [3], a modified model has been developed. Numerical algorithm and numerical FORTRAN programs, designed by authors, have been used for conducting of numerical simulations. Formulas for elasticity moduli, as functions of geometry of tube (length, outer and inner diameters), temperature, vibration energy for different individual nanotubes has been obtained. Graphics of temperature, versus mean-square vibration amplitude have been given as well. As conclusion could be mentioned, that the programs work very easy and quickly because of their universal character. The comparison between numerical results obtained, and the results in [3], shows a very good coincidence.

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## **Molecular Dynamics Simulations of the mechanical and electronic properties of nanotubes**

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Density Functional based (DFTB) Molecular Dynamics (MD) simulations were carried out to examine the mechanical and electronic properties of nanotubes under axial elongation. The mechanism of breaking tubes at finite temperatures were studied. Likewise, the electronic properties, including electronic transport, during the stretching process were investigated. As examples, armchair and zigzag Carbon and molybdenum disulfide nanotubes were chosen. The results are compared with corresponding experimental data.

## Direct Tensile Tests and Buckling of WS<sub>2</sub> Nanotubes

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The mechanical properties of macroscopic materials and particularly the strength are greatly affected by the presence of defects; therefore the theoretical strength (ca. 10% of the Young's modulus) is not achievable for them. On the contrary, nanotubes which are almost defect free should achieve the theoretical strength which would be reflected in superior mechanical properties. In this study, both tensile tests and buckling experiments of individual WS<sub>2</sub> nanotubes were carried out in a high resolution scanning electron microscope. Tensile tests of MoS<sub>2</sub> nanotubes were simulated by means of a density-functional tight-binding (DFTB) based molecular dynamics (MD) scheme as well. The combination of studies shows that the WS<sub>2</sub> nanotubes are both ultra-strong (tensile strength of ca. 16GPa) and flexible distinguishing them from other known materials. Fracture analysis using recently proposed models indicated that the strength of such nanotubes is governed by a small number of defects. A fraction of the nanotubes attain the theoretical strength indicating absence of defects.

## Physical Properties of Continuously-Spun Fibres of Carbon Nanotubes

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We report on the mechanical properties of fibres consisting of pure carbon nanotube fibres directly spun from an aerogel of carbon nanotubes formed during synthesis by chemical vapour deposition. The continuous withdraw of product from the gas-phase imparts a high commercial potential to the process, either for the production of particularly strong fibres or for the economic production of bulk quantities of carbon nanotubes. Tensile tests were performed on these fibres produced from the dissociation of three different hydrocarbons, namely: ethanol, ethylene-glycol and hexane, with a range of iron (catalyst) concentrations. The conditions were chosen to lie within the range known to enable satisfactory continuous spinning, the iron concentration being varied within this range. Increasing proportions of single wall nanotubes were found as the iron concentration was decreased, conditions which also produced fibres of best strength and stiffness. The maximum tensile strength obtained was 1.46 GPa (equivalent to 0.70 N/tex assuming a density of 2.1 g/cm<sup>3</sup>). The experiments indicate that significant improvements in the mechanical properties can be accomplished by optimising the process conditions.

## Repair of Defective Nanotubes

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The development of nanotechnology is very important for constructing future nanosized devices. Carbon nanotubes are expected as one of the key materials in this field, because of their unique structure and properties. However, for this purpose high quality or defect-free nanotubes are crucial. Recently, we have achieved to repair the defects of nanotubes such as pentagon-heptagon pairs and vacancies in hexagon networks by inducing current. Two kinds of double-walled carbon nanotubes (DWNTs) were examined. One is DWNTs with a permanent bend of plastic deformation which was artificially induced into straight DWNTs and has defects of pentagon-heptagon pairs. The other one is waved DWNTs and curled DWNTs which were prepared by catalytic chemical vapor deposition and have native defects of pentagon-heptagon pairs and vacancies. Using a nanomanipulator system installed in a transmission electron microscope, we manipulated an individual DWNT and introduced the current into it. All of defective DWNTs become straight when the circumference density of current rises up to 2 ~ 7 mA/nm, indicating that the defects disappear by the Joule heating. The onset current density is very close to that of the sublimation for each DWNT. Our findings will allow developing the nanotube devices with high performances.

## Current-Induced Permanent Bend in Carbon Nanotubes

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Carbon nanotubes are nanometer wide cylinders with extraordinary mechanical properties and unique electronic properties, and thus promising building blocks for nanosized electronic and electromechanical devices. For realization of these nanotube devices, a well-controlled process of plastic deformation of individual nanotubes is crucial. Substitution of hexagons by pentagons and heptagons is known to cause a permanent bend in the tube. We have explored a process for inducing the permanent bend in a straight nanotube by adopting a current flow as the energetic perturbation. Nanotubes examined were double-walled ones. An individual nanotube was manipulated using a nanomanipulator system installed in a transmission electron microscope. By introducing current to a nanotube elastically bent under mechanical duress we achieved to induce a permanent bend of plastic deformation in the originally straight nanotube. The most bending angles are between 20° and 30°, which are formed by the insertion of pentagon-heptagon pairs in a nanotube. The onset of the plastic deformation, which is measured by the circumference-density of current, is more than twenty times smaller than that of the sublimation. The onset decreases with increasing the diameter of nanotubes and the energy of the electron beam used in the transmission electron microscope.

## **Spatially selective removal of carbon nanotubes**

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For fabricating a nanotube-based integrated circuit, it is necessary to place nanotubes only at specified positions. However, high-density nanotube growth almost always results in the growth of unnecessary nanotubes at unspecified positions, which would cause short circuits, because controlling the growth direction of individual nanotubes independently is still impossible. Thus, selective removal of unnecessary carbon nanotubes from a high-density nanotube network is a crucial issue. In this report, we propose a simple method for removing unnecessary nanotubes. This method consists of a local irradiation of low-acceleration-voltage electron beam in a scanning electron microscope (SEM) and annealing in air [1]. Spatially selective removal of single-walled carbon nanotubes (SWNTs) from a random SWNT network grown by chemical vapor deposition (CVD) is demonstrated [2]. Using conventional electron beam lithography for the local electron irradiation, it would be possible to fabricate various kinds of nanotube networks.

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## **Zeptogram detection using carbon nanotube oscillators**

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We demonstrate an application of a nanotube cantilever for zeptogram-level mass detection. This paper presents a quantitative method to measure the oscillation amplitude of a nanotube cantilever using a focused electron beam of a scanning electron microscope. The quality factor of  $\sim 1000$  for the nanotube cantilever is revealed and the resolution of the resonant frequency is achieved to be  $\sim 10$  Hz, which corresponds to a mass range of less than 100 zg at room temperature.

**Anisotropic heat transfer of carbon nanotubes: Non-Fourier heat conduction and thermal boundary resistance with surrounding materials**

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Characterization of thermal properties of carbon nanotubes is one of the primary issues towards their device applications. The current work aims to provide various anisotropic thermal properties of single walled carbon nanotubes (SWNTs) by means of non-equilibrium molecular dynamics. Firstly, Non-Fourier heat conduction is investigated by applying local heat pulse with duration of sub-picoseconds to SWNTs. Prominent heat waves originated from the radial breathing mode are identified with certain relaxation time. Secondly, thermal boundary resistance between an SWNT and surrounding Lennard-Jones (LJ) materials is considered. The entire SWNT was subjected to a heat pulse to observe the interfacial heat transfer. The resulting trend of thermal resistance suggests that the key physics for heat transfer depends on the phase of the LJ material. For the gas phase, heat transfer is diffusive where random molecular collisions are in charge. On the other hand, in the solid phase, the dominant part of heat transfer can be attributed to certain modal interactions which can be modeled by the convolution of lattice vibrations of the nanotube and the LJ matrix. Finally, anisotropy of SWNT heat transfer is characterized by comparing the thermal boundary resistance (conductance) with axial conductivity under influence of surrounding matrix and bundles.

## Visualization and Mechanical Manipulation of Hexagonal Phase Boron Nitride Nanowires Using Nanomanipulator

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Hexagonal phase boron nitride nanowires (BNNWs) [1] with diameter of 8~32 nm were synthesized at room temperature by electron-cyclotron-resonance chemical vapor deposition technique through the upstream Ar plasma cracking of nitrogen, hydrogen and diborane mixed gases. The nanomanipulator system adds a virtual-reality interface to an atomic-force microscope (AFM), thus providing a tool that can be used to image and manipulate nanometer-sized sample in a controlled manner. Computer graphics are used to reconstruct the surface for the user, with color or contours overlaid to indicate additional data sets. Moreover, a force feedback stylus, which is connected to the tip via software, allows the user to directly interact with the macromolecules [2]. The resulting energy loss and mechanical wear depend largely on which mode of motion occurs. At the macroscopic scale, rolling is preferred over sliding, and it is expected to have an equally important role in the microscopic domain [3]. We report on experiments in which BNNWs are manipulated with AFM on silicon substrate. As the AFM tip scans BNNWs, the interaction forces of pushing and cutting BNNWs are monitored, which in turn can collect information about the frictional, mechanical, and topological properties of BNNWs. When AFM tip push and cut BNNWs, the interaction forces of the probe, BNNWs and substrate are collected from nanomanipulator system. In accordance with information collected from nanomanipulator system, the rupture force, push force and mechanical properties of individual BNNWs on the nanometer scale will be measured and presented.

## Chiral Dependence of Large Deformation in Carbon Nanotubes

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Mechanical properties of carbon nanotubes (CNTs) to deformation and strains have attracted much attention because they are nanometer wide seamless cylinders consisting of  $sp^2$  bonding network. It is well known that mechanical properties of carbon nanotubes are dependent on their structural details. The mechanical properties of single-walled carbon nanotubes with chiral vector type of (5,5), (6,3), and (8,0) under uniaxial tensile deformation have been analyzed using a tight binding (TB) method. The results showed that the Young's moduli are about 1TPa for all types and the tensile stress does not depend on the chirality. The deformation due to bond angle change dominates the tensile stress in large loading region. In order to confirm these results we have performed the calculations using a first principles density functional theory based on the local density approximation (DFT), and discussed the limit of TB simulation. It is found that TB results are in good agreement with the DFT results.

## Mechanical and Electromechanical Properties of Suspended Polypyrrole Nanotube

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Mechanical and electromechanical properties of suspended poly-pyrrole (PPy) nanotubes were measured. PPy nanotubes were positioned and suspended using the ac electrophoresis method and conventional electron beam lithography processes. From the force-distance measurements, the elastic modulus of suspended PPy nanotubes was estimated to be 3-4.5 GPa based on both a string and clamped beam model. The resistance of the PPy tube was decreased in electromechanical measurements with increasing pressure using a metal coated AFM tip as an electrode and pressure source. 1.36 GPa of maximum contact pressure on the tip-tube contact was estimated to reduce the contact resistance for making to 6.8 Wcm in a lateral configuration.

## **Bending experiments on multiwalled carbon nanotubes**

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We have studied experimentally via AFM imaging the bending of multiwalled carbon nanotubes (MWNT) over surface obstacles such as thin metal lines. The MWNTs have diameters in the range of 2-8 nm and are of a very good quality. The bending profile is determined from the interplay of the elastic energy of the MWNT and the van der Waals attraction energy between the substrate and the tube.

## Coiled Carbon Nanotubes as Self-Sensing Mechanical Resonators

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The application of suspended or cantilevered carbon nanotubes (CNTs) as mechanical resonant sensors involves complicated sample preparation and measurement techniques. The use of intrinsically coiled multiwalled nanotubes, which demonstrate remarkable mechanical properties [1, 2], enables to avoid these complications. After adsorption on a silicon substrate, coiled CNTs retain a three-dimensional structure with sections of free-standing windings that reveal characteristic mechanical resonances. We propose the application of the coiled CNTs, which are attached to electrical gold contacts and reveal a piezoresistive-like response, as convenient mechanical resonant sensors that do not require a complicated detection of the nanotube resonant oscillations [3]. When exciting the nanotube windings either electrically or acoustically, the fundamental resonances (ranging from 100 to 400 MHz) can be detected. The resonators are sensitive to mass changes as small as a few attograms.

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## **Detecting mechanical motion of suspended SWNT quantum dots through transport measurements**

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We have constructed doubly-clamped single-walled carbon nanotube (SWNT) devices with suspension lengths varying from 100 nm to a micron. We want to detect the mechanical motion of the SWNT-devices through transport measurements at low temperatures, where they behave like quantum dots. We show measurements (at  $T \sim 300$  mK) where we find evidence for phonon assisted tunnelling (PAT). The harmonic PAT-spectra found in several suspended devices, have an energy spacing (hundreds of meV's) that coincide with the energy of the longitudinal vibration-mode (stretching) of SWNT's. We are also looking for signs of flexural displacement (bending-mode) of the suspended nanotubes in the Coulomb-blockade regime, by driving them electrostatically with an RF-voltage on a back-gate electrode (up to 200 MHz).

## **Mechanical Properties of Multi-walled Carbon Nanotubes (MWNTs) and Helically Coiled Carbon Nanowires (HCNWs)**

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We have developed a method which detects the resonance frequencies for an "electrostatically driven" cantilever. Using a single MWNT as the cantilever, we have measured its resonance frequencies from which we determine the bending modulus as a function of defect density in the MWNT. The MWNTs were produced from a catalytic decomposition of three different precursors: (i) xylene/ferrocene, (ii) xylene/ferrocene/melamine, and (iii) trimethylamine (TMA)/ferrocene. The first two precursors are used to compare the mechanical properties of typical CVD-grown to bamboo-type MWNTs. Nanotubes prepared using the third precursor shows relatively fewer walls (~ 4-20 compared to ~15-40) and defects compared to those prepared from the xylene/ferrocene mixture. The HCNWs were also prepared using a catalytic CVD process in which xylene and acetylene were used as the primary carbon source. A multi-metal catalyst formed from a mixture of ferrocene and indium isopropoxide served as the seed to initiate the growth of these helical coiled nanostructures. The shear modulus and spring constant for the HCNWs will be presented.

## Thermal effects on optical transition energies in single wall carbon nanotubes

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Temperature dependent optical transition energies in single wall carbon nanotubes (SWNTs) have been studied over a wide range of temperatures using tunable resonant Raman scattering. Individual SWNTs are grown across trenches etched in quartz substrates to eliminate effects of interaction with the substrate, surfactant molecules or other nanotubes. As the temperature is increased from -160 C to 300C, E22 is observed to shift down in energy for all measured tubes, by as much as 50 meV. This is in contrast to previous measurements performed on nanotubes coated in surfactant and nanotubes in bundles, which show chirality dependent up-or down-shifts in E22. We find that the change in E22 comes from temperature dependent electron-phonon coupling and that the thermal expansion can be ignored for nanotubes in air. However, the chirality dependent thermal energy shifts for nanotubes in surfactants and bundles cannot be explained by electron-phonon interactions. It is likely that these experiments are dominated by different thermal expansion coefficients of the nanotubes and its environment causing thermally induced axial stress on the nanotubes.

**Packing and chirality of double-walled carbon nanotubes :  
a transmission electron microscopy and electron  
diffraction study**

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The atomic structure of bundles of double-walled carbon nanotubes synthesized by catalytic chemical vapour deposition is investigated using transmission electron microscopy and electron diffraction. Small and well-crystallized bundles reveal unambiguously the presence of double-walled nanotubes with identical chiralities and diameters in single bundle (each bundle presenting different chiralities and diameters) [1]. We have also investigated rings of double-walled carbon nanotubes and we observed the twist of the bundle along the ring circumference [2].

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## Room Temperature Peierls Distortion in Small Diameter Nanotubes

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First-principles calculations are performed to investigate the electronic, structural, and vibrational properties of single-wall carbon nanotubes with very small diameters. In particular, we focus on the (3,3), (4,2), and (5,0) tubes which are potential candidates for the 4 Å-diameter tubes synthesized inside zeolite channels. With such a narrow diameter, the electronic properties of these nanotubes near the Fermi level cannot be understood starting from the graphene sheet model, although this zone folding model is quite successful in the case of large diameter tubes. Our results indicate that perfectly-cylindrical (3,3) and (5,0) tubes are metallic, while the (4,2) tube is semiconducting with a small indirect band gap. The calculated radial breathing modes agree with experimentally measured Raman spectrum, giving strong support that these small radius tubes are indeed present inside zeolite crystals. However, the dynamical properties of the both the (5,0) and (3,3) nanotubes suggest the structures to be metastable in its cylindrical form. Above room temperature, both the C(5,0) and C(3,3) tubes are found to undergo a Peierls transition which is mediated by an acoustical long-wavelength and an optical  $q=2k_F$  phonons respectively. In the armchair geometry, the electron-phonon coupling parameter  $\lambda$  originates mainly from phonons at  $q=2k_F$  and is strongly enhanced when the diameter decreases. These results question the origin of superconductivity in small diameter nanotubes.

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## Interlayer Spacings of Generalized Carbon Nanotubes

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We study the dependence of structural stability of nanotubes/nanofibers on their diameter and heat treatment temperature using *ab initio* density density functional formalism. We construct a model to describe generalized carbon nanotubes, which shows that polygonal face structures can be possible under high heat treatment. This theoretical prediction has been confirmed experimentally. Furthermore, the possible mechanism on increase or decrease of interlayer spacing in carbon nanofibers will be compared with experimental data.

## **Model-based computation of pair correlation functions for carbon nanotubes**

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The powder diffraction patterns for carbon nanotubes of given chirality and diameter have been computed using the Debye equation. The geometrical models were constructed by generating the Cartesian coordinates of atoms and then relaxed using the Brenner-Tersoff potential. Such obtained diffraction data were converted to real space pair correlation functions by the Fourier transformation. The obtained results show spread of the interatomic distances depending on chirality and on curvature of the carbon nanotubes which are paracrystalline in nature. Similar behaviour was observed in our previous simulations in which the paracrystalline form of disorder was introduced by appropriate form of the Debye-Waller factor with the standard deviations of the interatomic distances proportional to square root of the interatomic distances [1, 2].

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## **Identification of Haeckelite nanotubes by analysis of pair correlation function**

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A family of Haeckelite nanotubes has been generated by rolling-up flat, periodic arrangements of pentagons, hexagons and heptagons. The resulting structures have been relaxed using the Brenner-Tersoff potential. Powder diffraction patterns have been computed for three main types of the Haeckelite structures: rectangular, hexagonal and oblique starting from the Cartesian coordinates of atoms and then converted to real space pair correlation functions via the Fourier transformation. The resulting data are compared with calculations for perfect carbon nanotubes. The predicted pair correlation functions for the Haeckelite nanotubes provide an unambiguous and direct tool for identification of their structures. The presented procedures can be used for further studies of other Haeckelite structures as well as for various carbon systems containing non-six membered rings as defects.

## **Mobility of native and electron-irradiation-induced point defects in carbon nanotubes**

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Understanding the mechanism of point defect production and migration in carbon nanotubes is important for the complete comprehension of the nanotube growth and electron irradiation-stimulated transformations in nanotubes, e.g., welding and coalescence. We study the behavior of carbon nanotubes under high-energy (300 keV) electron irradiation both experimentally and theoretically. We show that multi-walled nanotubes shrink by a loss of atoms from the inner shells of the tube and by diffusion of interstitials in the axial direction through the inner hollow of the tube. Thus, experimental evidence is given that nanotubes can act as nanoscale pipes for the transport of atoms. We further study the details of defect production under electron irradiation and the annealing of single vacancies and interstitials via migration and mutual annihilation. We demonstrate that the electron threshold energy for displacing carbon atoms and the defect production rate strongly depend on the diameter of the nanotubes. We also address the effect of nanotube atomic network curvature on the defect migration.

## Ab initio modeling of fullerene peapods

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Molecular arrays of fullerenes encapsulated inside carbon nanotubes (fullerene peapods) are promising new materials for a wide range of applications. The fullerene peapods have been recently investigated using tight binding model and density functional theory (DFT) [1,2]. Physically correct description of molecular interactions in fullerene peapods requires inclusion of the correlation effects (dispersion interactions). Both previously employed approaches, however, are incapable to describe van der Waals bonding properly. Here we present results of highly correlated ab initio calculations at the MP2 level of theory and compare them with less accurate DFT and semi-empirical tight binding methods.

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## Quantum-chemical calculations of Peierls distortions in (5,5) carbon nanotube

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Low temperature dynamics of small radius metallic carbon nanotubes (CNT) is determined by Peierls mechanism. However quantitative estimations of Peierls distortions in CNTs are contradictory [1]. We have employed cluster method [2] for infinite periodic one-dimensional structures implemented within MOPAC package with PM3 Hamiltonian [3] to study ground state and low energy valence isomers of armchair (5,5) CNT as characteristic representative of metallic CNTs.

According to our calculations the ground state of (5,5) CNT is Kekule structure with 0.003 nm difference between long and short bonds leading to mean-field Peierls gap of the order of 0.1 eV at zero temperature. The transition state between three equivalent ground state minima is also dimerized with approximately the same long-short bonds difference. In this state all perpendicular to the tube axis bonds are short while others are long. The latter type of dimerization does not lead to band gap opening. Energy difference between ground and transition states is about 0.5 eV per unit cell of sixty atoms.

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## **Electronic structure and surface chemistry of nitrogenated MWCNTs probed by NEXAFS spectroscopy**

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Multi-walled carbon nanotubes (MWCNTs) have been exposed to NH<sub>3</sub> atmospheric plasmas in a dielectric barrier discharge (DBD) system. Near edge X-ray absorption fine structure (NEXAFS) have been employed to obtain information on the electronic structures of nitrogenated MWCNTs. Regardless of N concentration, the C K edge NEXAFS spectra contained a relatively large  $\pi^*$  peak, indicative of the graphite like bonding of the tubes. The  $\pi^*$  feature at the N K edge clearly revealed three different nitrogen configurations in the energy region 398-403 eV, which were attributed to pyridine-like, molecular N<sub>2</sub> and graphite-like structures respectively. The O K edge spectra showed evidence for the presence of oxygen on the surface of MWCNTs. In situ rapid thermal annealing to temperatures up to 900 C provided information on the thermal stability of the nitrogen and oxygen moieties. C K edge spectra did not show any significant change with temperature, suggesting the overall bonding configurations with the C atoms remained unaltered. Loosely bonded molecular N<sub>2</sub> and O<sub>2</sub> were totally released at 900 C. In contrast the nitrogen graphite-like structure showed improved thermal stability. Angular dependent analysis of the N K edge  $\pi^*$  resonances did not show a pronounced polarization dependent effect. Real time X-ray photoelectron spectroscopic measurements show evidence of a weak interaction of O<sub>2</sub> with the surface of nitrogenated MWCNTs compared to the pristine ones.

## Kohn Anomalies and Diameter Dependent Peierls Distortions in Nanotubes

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Kohn anomalies are distinct features of the phonon dispersion in metallic systems, associated to the presence of a Fermi surface [1]. Graphite is a semimetal. Nanotubes can be metals or semiconductors. Graphite has two remarkable Kohn anomalies at the G-E<sub>2g</sub> and K-A<sub>1g</sub> modes [2]. The anomalies are revealed by two sharp kinks in the phonon dispersions. By an exact analytic derivation, we show that the slope of these kinks is proportional to the square of the electron-phonon coupling [2]. These anomalies are enhanced in metallic nanotubes due to the reduced dimensionality of the Brillouin zone, but are absent in semiconducting. Direct ab-initio calculations are necessary to properly describe the nanotube phonon dispersions. However, these are practically unfeasible with the required accuracy for diameters > 0.7 nm, given the increasingly big unit cells. We overcome this problem by developing a new adaptive refolding method [3], which allows us to efficiently and precisely calculate the complete temperature-dependent phonon-dispersions and the shape of the Kohn anomalies for any nanotube of any diameter and any chirality. At 0 K all metallic nanotubes are not stable and undergo a Peierls distortion [3,4]. For diameters <0.4 nm, the anomaly is so strong to induce a Peierls distortion at room temperature [5]. We show that the Peierls distortion temperature decreases exponentially with the tube diameter. Thus, for the nanotubes generally used in experiments, with diameters >0.8 nm, we find that this temperature is smaller than 10<sup>-8</sup>. This implies that no Peierls distortion can be observed at room temperature. However phonon softening, signature of Kohn anomalies, will be present even for large diameters.

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## **Room temperature electronic transport in as-produced and annealed CVD-produced multi-wall carbon nanotubes**

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The electronic properties of multi-wall carbon nanotubes (MWNTs) have attracted much attention because they could lead to nano-sized electronic devices. Using chemical vapor deposition (CVD), MWNTs are produced in large quantities at a low cost. CVD-produced MWNTs, however, generally contain a considerable amount of structural defects due to their low temperature synthesis. Since these defects act as scattering centers in electron transport and thus limit the electronic mean free path (EMFP), high-temperature annealing should lengthen the EMFP. This expectation is based on the previous experiments in which annealing eliminated structural defects in various carbon materials including nanotubes. In this study, we investigate how high-temperature annealing affects the transport properties, especially EMFP, of CVD-grown MWNTs. To measure the EMFP of a nanotube, we submerged samples into liquid mercury and measured the variation in conductance. We found that the EMFP is much longer in nanotubes annealed at 2700°C compared with that of as-produced ones. The annealed nanotubes show quasi-ballistic electronic transport with the EMFP reaching a few microns, even at room temperature.

## Ab initio study of the $\pi$ -stacking interaction between organic molecules and carbon nanotubes

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The  $\pi$ -stacking interaction between various planar organic molecules (such as benzene, azulene, pyrene and DDQ), and carbon nanotubes is investigated within the framework of ab initio calculations [1]. The adsorption of these molecules on the sidewall of the cylindrical carbon structure induces a small binding energy compared to conventional covalent functionalization. Such a weak interaction is found to be only physisorption and leads to minor and predictable modifications of the electronic structure. These changes in the electronic behavior of the host carbon nanotube are ruled by the relative positions of the molecular levels of the isolated molecule and both the valence and conduction bands of the perfect tube.

The adsorption of the benzene molecule on carbon nanotubes with various diameters and chiral angles is investigated more specifically [2]. Our ab initio calculations suggest that for small diameter tubes, the most favorable adsorption site is one type of C-C bond. The disparities between the inequivalent bonds of a CNT are discussed in terms of the  $\pi$ -orbital axis vector misalignment. Moreover, the curvature and the chirality effect on benzene adsorption are analyzed, showing that large diameter nanotubes are the most reactive ones.

Although the  $\pi$ -stacking interaction is weak, molecular physisorption could have an impact on the electronic transport properties of the carbon nanotubes. A tight-binding scheme, parametrized with first-principles calculations, is able to tackle with the complex electronic transport properties of chemically grafted conducting nanotubes with a random coverage of physisorbed molecules. Our calculations suggest that the effect will be strongly dependent on the nature of the attached molecules [3]. Such result could have important consequences on the understanding of the (bio)sensing capability of molecular objects such as nanotubes.

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## **Ballistic Thermal and Electrical Conductance Measurements on Individual Multi-wall Carbon Nanotubes**

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Electrical and mechanical properties of single carbon nanotubes (CNTs) have been studied in depth. However, very few thermal measurements on individual nanotubes have been reported to date although CNTs have been predicted to show extremely high thermal conductivity and are expected to display a 1-dimensional (1D) phonon density of states. We already proposed that CNTs should be ideal test beds for studying ballistic phonon transport and thermal conductance quantisation and recently this has been theoretically confirmed. The measurements reported here aim to measure the thermal properties of individual CNTs and to study phonon transport and thermal conductance quantisation in CNTs. We report thermal measurements on individual carbon nanotubes using a temperature sensing scanned microscope probe. An arc-grown bundle of multiwalled nanotubes (MWNTs) is mechanically attached to a thermal probe. The heat flow down individual MWNTs is recorded as a function of the temperature difference across them. Simultaneous measurements of thermal and electrical conductance are recorded. The size of the conductance steps observed at room temperature and the correlation between electrical and thermal conductance steps are discussed and we present evidence for ballistic transport of both phonons and electrons in these tubes.

## **AC electrical characterization of SW-nanotube/metal contacts**

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In this paper, we will present the influence of the metal/nanotube contact using frequency analysis. The studied device is a single-wall carbon nanotube deposited on an isolating substrate. Three electrodes (10 nm of Au on 5 nm of Ti) have been processed on top of the nanotube to form side-contacts. Two types of measurements were performed: impedance variation with the applied signal frequency (RLC measurements) and low frequency noise measurements. From RLC measurements, the extracted AC parameters lead to an equivalent RC electrical model associated to each electrode. This model is in accordance with Landauer formalism and includes metal/nanotube interface phenomena i.e. tunneling through metal nanotube interfaces and electrostatic coupling due to the barrier potential. This transport model describes our AC and DC current/voltage measurements. From our model we can distinguish different contact effects e.g. series resistance including the intrinsic nanotube resistance. Low frequency noise measurements have shown that the noise is dominated by the tunneling process. Using the suggested equivalent RC model, the calculated output noise is found to be in very good agreement with the measured output noise, hence validating the model.

## High- $T_c$ Superconductivity in entirely end-bonded multi-walled carbon nanotubes

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One-dimensional (1D) systems face some obstructions that prevent the emergence of superconductivity, such as a Tomonaga-Luttinger liquid (TLL), spin fluctuation, small density of state due to van-Hove singularity, Peierls transition, and charge-density waves. A carbon nanotube (CN), an ideal 1D molecular conductor, is one of the best candidates for investigating this possibility. Although a variety of intriguing quantum phenomena has been reported in CNs, only two groups have reported intrinsic superconductivity with a transition temperature ( $T_c$ ) as low as  $T_c = \sim 0.2\text{K}$  [1] and that identified only from the Meissner effect [2] in single walled CNs (SWNTs). No other studies reproducing these results have so far been reported. In addition, those correlations with 1D phenomena, particularly with TLL, which is a non Fermi-liquid state arising from an electron-electron interaction in 1D systems, have never been clarified. Here, we will present superconductivity with the onset temperature ( $T_c$ ) as high as 12 K in multi-walled CNs (MWNTs), which were synthesized in nanopores of alumina templates [3]. This  $T_c$  is approximately 30-times larger than that in SWNT ropes [1]. We find that end-bonding of MWNTs by an electrode is crucial for realizing high- $T_c$  superconductivity, because it makes contact to all of the shells possible and intershell effects lead to elimination of a TLL and growth of superconductivity.

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## Gate-controlled Tomonaga-Luttinger liquid and atomic-like behaviors in peapod quantum dots

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Nano-peapods, which are single-walled carbon nanotubes (SWNTs) encapsulating a series of fullerenes, such as C<sub>60</sub> and C<sub>82</sub> that encapsulate Gd(Gd@C<sub>82</sub>), in their inner space, have recently attracted considerable attention; this is because their remarkable nanostructures yield exotic electronic states [1] and charge transport [2]. On the other hand, SWNTs are within a 1D ballistic charge transport regime and have exhibited a variety of quantum effects, such as quantized energy levels, Tomonaga-Luttinger liquid (TLL), and atomic-like behaviors as quantum dots. How such phenomena are affected by encapsulating a series of fullerenes, however, has not yet been investigated in peapods. Here, we will present the 1D quantum phenomenon in peapod quantum dots, encapsulating a chain of C<sub>60</sub> molecules. Anomalously high values of power  $a$  ( $1.6 < a < 12$ ) observable in power laws in conductance versus energy relationships are found. This power is very sensitive to the applied back gate voltage. Atomic-like behaviors with doubly degenerate ground states, which are confirmed by single electron spectroscopy at low back gate voltages, reveal that a portion of the power ( $1.6 < a < 3$ ) originates from the TLL via the occupied electronic levels, which originate from the subbands unique to the peapods [1]. We also clarify that the encapsulated C<sub>60</sub> molecules contribute only to the construction of the electronic states and do not directly contribute to the power laws and atomic-like behaviors in the peapods quantum dots.

## **Electromechanical instability in suspended carbon nanotubes**

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We have theoretically investigated electromechanical properties of freely suspended carbon nanotubes when a current is injected into the tubes using a scanning tunneling microscope. We show that a shuttle-like electromechanical instability can occur if the bias voltage exceeds a dissipation-dependent threshold value. An instability results in large amplitude vibrations of the carbon nanotube bending mode, which modify the current-voltage characteristics of the system.

## Evidence for Luttinger-Liquid Behavior in Crossed Metallic Single-Wall Nanotubes

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Transport measurements through crossed metallic single-wall nanotubes are presented. We observe a zero-bias anomaly in one tube which is suppressed by a current flowing through the other nanotube. These results are compared with a Luttinger-liquid model which takes into account electrostatic tube-tube coupling together with crossing-induced backscattering processes. Explicit solution of a simplified model is able to describe qualitatively the observed experimental data with only one adjustable parameter.

## Tuning the conductance of single walled carbon nanotubes by ion irradiation in the Anderson localization regime

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Defects are known to modify the electrical resistance of carbon nanotubes [1,2]. They can be present in as-grown carbon nanotubes, but controlling externally their density opens a path towards the tuning of the nanotube electronic characteristics. In this work consecutive Ar<sup>+</sup> irradiation doses are applied to single-walled nanotubes (SWNTs) producing a uniform density of defects. After each dose, the room temperature resistance versus SWNT-length dependence ( $R(L)$ ) along the nanotube is measured by using atomic force microscopy. Our data show an exponential dependence of  $R(L)$  indicating that the system is in strong Anderson localization regime. Simulations demonstrate that mainly di-vacancies contribute to the resistance increase induced by irradiation. By comparing experiments and theory, we conclude that 1 out of 4 Ar<sup>+</sup> ions creates one di-vacancy and that a 0.03% of di-vacancies produces an increase of three orders of magnitude in the resistance of a 400 nm SWNT length. The theoretical calculations also predict a linear dependence of the localization length with the distance between di-vacancies, in good agreement again with the experiments.

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[2] Sylvain Latil et al. Phys. Rev. Lett. 92, 256805, (2004)

## Shot noise and electron-phonon coupling in carbon nanotubes

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We have investigated shot noise in individual SWNTs and MWNTs at 4.2 K over the frequency range 650 - 850 MHz. At small currents, our SWNT samples display a Fano-factor of  $F \sim 1$ , reminiscent of a single tunnel junction behavior. At large bias, we observe a strong reduction in the Fano factor both in SWNTs and MWNTs. Using the theory by Nagaev, we may interpret this noise suppression as originating from inelastic processes caused by electron-phonon scattering, both due to acoustic and optical phonons. We find that the electron-phonon scattering length in a SWNT decreases rapidly above 0.1 V and it is about 5 nm at a bias of 0.5 V. In disordered MWNTs, we observe a Fano-factor of  $\sim 0.1$ , clearly less than expected for diffusive conductors.

## Nature of the metallic ground state in functionalized C<sub>60</sub>-peapods

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We report on results of the doping-induced changes in the electronic properties of C<sub>60</sub>-peapods investigated by high resolution angle-integrated photoemission spectroscopy. It was recently demonstrated that bundles of SWCNT do not display Fermi liquid behavior but rather Tomonaga-Luttinger-liquid behavior which manifests itself as a power law renormalization of the density of states in the vicinity of the Fermi level [1]. Upon doping-induced charge transfer from the potassium intercalant to the tubes, a crossover to a Fermi liquid behaviour was observed at the point where all tubes in a bundle have become metallic [2]. The results on the K-intercalation of C<sub>60</sub>-peapods show similar behaviour and give further insight on hybridization strength and charge transfer between the C<sub>60</sub> guests and the SWCNT hosts.

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[2] H. Rauf et al., Phys. Rev. Lett. 93, 096805 (2004) Work is supported by DFG PI440/1

## Current instability and diamagnetism in small-diameter carbon nanotubes

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We investigate the phase diagram of carbon nanotubes taking into account the competition between the Coulomb and the phonon-exchange e-e effective interaction [1]. This allows for instance to understand the transition from the Luttinger liquid behavior for strong repulsive interaction (pertinent to individual nanotubes) to superconducting behavior for sufficiently screened Coulomb interaction [2] (as in the case of massive ropes [3]). Moreover, we point out the existence of more exotic phases for strong electron-phonon coupling, characterized by the singular behavior of the charge velocity in the electron liquid. This analysis is of particular interest for carbon nanotubes of very short radius, and it leads to the conclusion that the Luttinger liquid behavior breaks down in the (3,3) nanotubes due to the development of a divergent susceptibility for current excitations [4]. We show that the phenomenology derived from this regime is consistent with the appearance of a gap in the single-particle spectrum as well as with a divergent diamagnetic signal, as observed in the experiments carried out in carbon nanotubes of small diameter [5].

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## Localization of electronic states by charged metallofullerenes in nanotube peapods

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We investigate the effects of the electrostatic interaction produced by charged metallofullerenes in nanotube peapods, with the aim of accounting for the narrowing of the gap that has been measured experimentally in semiconducting nanotubes at the location of the metallofullerenes [1]. We show that, when the charge of the metallofullerene gives rise to an attractive potential for the electrons in the nanotube, localized electron states arise in the nanotube around the position of the fullerenes. The number of bound states formed within the nanotube gap depends on the strength of the electrostatic interaction, while their extension is in general of the order of a few nanometers [2]. Our analysis is consistent with the fact that the narrowing of the gap has been measured only in peapods with endohedral metallofullerenes, and it points at the possibility of having control of the gap reduction by means of suitable variations of the metallofullerene charge and the number of bound states formed within the gap.

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## **Separate Evaluation of Resistivity and Contact Resistance of Single-Wall Carbon Nanotubes with Multiple Electrodes**

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We investigated electronic transport in single-wall carbon nanotubes attached to multiple electrodes. Resistance measurements using a pair of electrodes with different gaps enabled nanotube resistivity to be separately evaluated as well as contact resistance. We found that the resistivity depends on nanotube diameter. Electrodes with gold or palladium exhibit contact resistance of the order of 10 kilo Ohm. Contact resistance is insensitive to back gate voltage, contrary to the Schottky-barrier transistor model.

## Tunnelling Conduction in Carbon Nanotubes and Networks

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We have analyzed conduction data on single-wall carbon nanotube (SWNT) networks and on individual SWNTs. In individual SWNTs, there is some evidence for power laws in the current-voltage (I-V) characteristics, and in the low-field conductance as a function of temperature [1]; the coefficients are related approximately as expected for tunnelling into Luttinger liquids, but the nonohmic power law in the I-V characteristics is seen only over a limited range of voltage and only at low temperature. In these individual SWNTs and also in SWNT networks, the overall conduction behaviour appears consistent with fluctuation-assisted tunnelling between metallic regions, reflecting the fact that in one-dimensional conductors the resistance is dominated by the defects and junctions that interrupt charge transport. This behaviour is retained in SWNT networks after chemical treatments that change the density of charge carriers, and can also be found in vanadium pentoxide and conducting polymer nanofibres [2].

## A Three Terminal Carbon Nanotube Relay

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A carbon nanotube nanorelay has been fabricated. A freely hanging MWNT is attached to a source electrode. By applying a voltage to a gate electrode situated below the nanotube, the nanotube is induced to bend until it makes contact with a drain electrode [1]. The operating characteristics will be described and compared with theoretical predictions. Two operating modes have been studied. The first, "contact mode", requires physical contact between the nanotube and the drain electrode and shows hysteretic behaviour. The second "non-contact" mode uses field emission to make electrical contact between the nanotube and the drain. In this case we observe a self-annealing behaviour at the source electrode on operation and the hysteresis is suppressed.

## Transport study of nanotube with adsorption of pi-conjugated molecules

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We present a mesoscopic study of electronic transport in carbon nanotubes with physisorption of pi-conjugated molecules. Our approach addresses large structures in order to treat realistic randomly located adsorption. The results indicate that the conduction regime (and its characteristic lengths, e.G. elastic mean-free-path) are sensitive of the HOMO-LUMO gap of the conjugated molecule. Hence adsorption of benzene (gap=5eV) does not affect conduction properties of carbon nanotubes, whereas azulene (gap=2eV) is responsible for a finite electronic mean-free-path at Fermi level.

## Towards Supersensitive Bolometers and Electron Coolers Based on Carbon Nanotubes

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Carbon Nano Tubes (CNT) are being intensively developed for novel electronics. Electron cooling by superconductor-insulator-nanotube (SIN) tunnel junctions could be extremely effective due to the small volume of the CNT. Cold-Electron Bolometer with a CNT as absorber should demonstrate record sensitivity due to the very low temperature that is predicted to be reached in the CNT (less than the phonon temperature). Objectives of this work are to demonstrate effective electron cooling in superconducting nanostructures comprising a CNT; and to develop a supersensitive Cold-Electron Bolometer (CEB) based on a cooled carbon nanotube as absorber. We have made a first attempt to develop a carbon nanotube cold electron bolometer CNTCEB. A prototype of a generic layout was designed and masks were fabricated. First samples with SWCNT show that with this technique we can connect a CNT to electrodes by SIN tunnel junctions. When measuring in a 3-probe mode we observed two barriers, one at about 2eV corresponds to Al and another at about 0.5eV corresponds to the CNT. Single wall nanotubes grown using chemical vapour deposition presumably contain many defects and as a result they have a high resistance and a single electron tunneling mechanism with a typical Coulomb blockade features measured at temperature about 300 mK. The measured resistance of the semiconducting single-wall CNT is too high for practical applications but further progress is expected with metallic multiwall CNT and ropes of such tubes.

## Random telegraph noise in carbon nanotubes

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The switching of resistance between two discrete values, known as random telegraph noise (RTN), was observed in individual single-walled carbon nanotubes (SWNTs). The mean lifetimes in high-current and low-current states have been studied as a function of gate voltage and temperature as well as bias voltage. By analyzing the statistics and features of the RTN, the noise mechanism for SWNTs has been investigated. The RTN observed in semiconducting SWNTs is sensitive to the gate-voltage, detectable only in a very limited range of the gate-voltage. The noise is related to the charge traps surrounding the tubes. As for the metallic SWNTs, the exponential dependence of mean lifetimes with respect to the inverse bias voltage was observed without gate-voltage dependence. Reversible motion of a defect, activated by inelastic scattering with conduction electrons, is suggested to be responsible for the observed RTN. Regarding the  $1/f$  noise as a superposition of many two-level current switchings, our results imply an important role of defect motions as a source of the  $1/f$  noise for the nanotube devices.

## **SINGLE WALLED CARBON NANOTUBE LOOPS INVESTIGATED BY ELECTROSTATIC FORCE MICROSCOPY AND ELECTRICAL TRANSPORT MEASUREMENTS**

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We have investigated the properties of coils and loops of CVD grown single walled carbon nanotubes (SWNT). The electrostatics of the samples are examined by electrostatic force microscopy (EFM) and the transport properties are investigated by making SWNT-loop devices. The nanotubes are grown on doped Si substrates capped with 400 nm oxide and under certain growth conditions SWNT's with lengths up to 150 micro meters are grown. Along these long tubes loops are found and the ends are often terminated with a coil. The diameters of the loops are from one to ten micro meter. For certain loops we find an EFM phase shift in the loop interior proportional to the EFM-voltage. A quantitative analysis of the data shows that the observation may originate from a static charge density of about  $2E-8$  C/cm<sup>2</sup> being confined in the loop interior. Thus our observation may indicate that nanotubes can serve as barriers for surface charges such that the interior of a loop form an isolated island on which static charges reside. The effect is stable for extended periods of time but can be removed by touching the interior of the loop with the conducting AFM tip. The loops are also interesting as model systems for quantum rings and preliminary results of transport measurements will be presented.

## **GaAs based semiconducting heterostructures with carbon nanotube**

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We have studied carbon nanotubes combined with Molecular Beam Epitaxy growth of III-V semiconducting heterostructures. The nanotubes are introduced in the crystal during a growth interrupt. By standard lithographic processes and wet chemical etching structures can then be defined, resulting in GaAs devices bridged by carbon nanotubes. This new method of combining carbon nanotubes with GaAs heterostructure devices opens up a whole new range of possible hybrid electronic systems.

## Theoretical study of the electronic transport along ion-irradiated carbon nanotubes

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In the work presented by C. Gómez-Navarro et al. ("Tuning the conductance of single walled carbon nanotubes by ion irradiation in the Anderson localization regime", P114) consecutive Ar<sup>+</sup> irradiation doses are applied to single-walled nanotubes (SWNTs) producing a uniform density of defects. After each dose, the room temperature resistance versus SWNT-length [R(L)] along the nanotube is measured. The experimental data show an exponential dependence of R(L) indicating that the system is within the strong Anderson localization regime. Our theoretical simulations, performed with a combination of a first-principles Local Orbital Density Functional method and standard Green-function techniques, confirm this view and also demonstrate that mainly di-vacancies contribute to the resistance increase induced by irradiation and that just a 0.03% of di-vacancies produces an increase of three orders of magnitude in the resistance of a 400 nm SWNT length. In this work we present a detailed discussion of the theoretical results and the effect of the temperature on the conductance fluctuations.

## Self-assembled switches based on electroactuated nanotubes

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Nanotubes are very promising as core elements of nano-electro-mechanical systems (NEMS). Understanding the interplay between the physical, geometrical and electrical parameters of the system is crucial to accurately design nanotube NEMS [1,2]. We present a combined theoretical and experimental (AFM based) study [3] which allows the quantitative determination of the electrostatic deflection efficiency of suspended MWNTs as well as their Young's modulus. A generic method for properly designing and scaling actual devices is deduced from these results. As an example, we present two-terminal nanotube electromechanical switches based on singly clamped, self-assembled and suspended MWNTs. The self-assembly technique relies on the chemical modification of a patterned substrate. This local functionalization guides the selective deposition of MWNTs from an organic solvent [4]. The switches show extremely sharp transitions (pull-in) between an Off-state (no physical contact between the tube and the actuating electrode) and an On-state (tube in physical contact) with the current changing by several orders of magnitude within a 100mV change of the actuating electrode bias.

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## Single-walled carbon nanotube contacted to superconducting leads

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Single-walled carbon nanotubes (SWCNT) coupled to superconducting leads are excellent systems to study low-dimensional electronic transport in superconductor-1D metal-superconductor (SNS) junction. We have grown SWCNT by chemical vapour deposition and contacted them to superconducting Al/Ti leads. In an intermediate coupling regime the S-SWCNT-S junction shows Kondo resonances and the interplay with the proximity effect from the superconducting leads is examined in the line of [1] on multi-walled carbon nanotubes. For a Kondo temperature greater than the superconducting gap an increase of the Kondo peak is observed when the leads become superconducting. Furthermore a sub-gap structure develops due to multiple Andreev reflections through the SWCNT.

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## Tunneling spectroscopy of disordered multiwalled carbon nanotubes

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The tunneling density of states has been studied on disordered multiwalled carbon nanotubes. The tunneling conductance shows a large zero-bias anomaly, whose temperature and voltage dependence is successfully compared with the non-perturbative theory of electron tunneling into a disordered 1D electrode. The environmental Coulomb blockade is expected to set in at lower energies, where junctions can be considered to be zero-dimensional. In one of the samples, Coulomb blockade behavior is revealed over a wide range of temperatures. In this sample the tunneling is also studied using a superconducting counterelectrode, and the observed reduction of the conductivity is found to be in quantitative agreement with the Coulomb blockade theory.

## Quantum dots of carbon tubes: physical properties.

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Quantum dots made of individual metallic carbon nanotubes are theoretically studied under the influence of a magnetic field applied in the axial direction. After assessing the mechanical stability of the heterostructure by Monte Carlo simulations, the dependence of the electronic properties on the size of the nanotube quantum dot and applied magnetic field have been investigated within the Peierls approximation in a tight-binding model. The transport gaps induced by the magnetic field are found to be different to those of the perfect constituent tubes, and a lack of periodicity of physical properties on the magnetic flux due to the presence of topological defects. The spin coupling to the magnetic field is also incorporated via a Zeeman term in the hamiltonian; we have found huge differences between in the up and down local density of states which may be explored for future applications of carbon nanotube quantum dots as spintronic devices. The the temperature dependence of the magnetic properties has also been explored and we have found a diamagnetic response very similar to that of perfect tubes. Finally, transport properties of the dots are investigated by the determination of characteristic curves of current versus voltage curves and as a function of the dot sizes.

## Electron Transport and Hot Phonons in Carbon Nanotubes

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Single wall carbon nanotubes have unique properties that make them strong candidates for future electronic devices. They can act as ballistic one-dimensional quantum wires. However, high field measurements show that the electron scattering by optical phonons breaks the ballistic behaviour [1]. Here, we demonstrate the key role of phonon occupation in limiting the high-field ballistic transport in metallic carbon nanotubes [2]. The electron phonon couplings, required for the evaluation of the transport scattering lengths, are directly measured from the experimental phonon dispersions and Raman spectra [3,4] as well as computed using density functional theory [2]. From these EPCs we obtain a simple formula for the electron mean free path for optical phonon scattering in high-field quasi-ballistic transport:  $L=65d/(2n+1)$ , where  $L$  is the scattering length,  $d$  the nanotube diameter and  $n$  the phonon occupation [2]. From the comparison of our results with the scattering lengths fitted from experimental I-V curves, we show that the optical phonon occupation is greatly increased during high-bias electron transport. The effective temperature of this occupation is several thousands K. This sets the ultimate limit of ballistic transport in nanotubes. The phonon generation induced by electron scattering is analogous to the photon generation by stimulated emission in semiconducting lasers. This suggests that nanotubes, under high bias, can act as a possible source of coherent phonons.

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[2] M. Lazzeri et al. cond-mat/0503278

[3] S. Piscanec et al. Phys. Rev. Lett. 93, 185503(2004)

[4] M. Lazzeri et al., to be published

## Photon assisted tunneling in a carbon nanotube quantum dot

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The unique properties of SWCNTs, i.e. small spin orbit coupling, small phonon density of states, and small abundance of nuclear spins, are expected lead to long coherence times of electron spins in the dots. This opens up the opportunity for a scalable electron spin quantum computing concept, if microwaves can be coupled to the system providing local control over the spin state. However, photon assisted tunneling (PAT) can cover single qubit operations done with local ESR as known from experiments with GaAs quantum dots. Therefore, we studied the effect of PAT in carbon nanotubes. Our experiments show enhanced transport through excited states due to PAT as well for states above the ground state as for states below.

## Quantum transport in individual carbon nanotubes under high magnetic field

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We investigate the quantum transport in different individual carbon nanotubes in light of magneto-transport experiments in intense (60T pulsed) magnetic field. Large magnetic fields are required to probe field dependent gap modulation and quantum interference effects along the circumference of the tube. Such experiments along with a control of the electrostatic doping of the tube with a back-gate voltage constitute a unique tool to explore the exceptional electronic properties of this material. We bring evidence that the field dependence of the conductivity is a fingerprint of the modes of electronic conduction and their interplay with the band structure (helicity), the static disorder and the location of the chemical potential of the tube [1]. We infer the characteristic lengths of the electronic transport (the electronic mean free path and the phase coherence length) which are differently modified by the Fermi level location, depending on the disorder.

[1] Gate-dependent magneto-resistance phenomena in carbon nanotubes, G. Fedorov, B. Lassagne, M. Sagnes, B. Raquet, JM Broto, F. Triozon, S. Roche, E. Flahaut, Phys. Rev. Lett 94, 66801 (2005)

## Breakdown of ballistic transport in zigzag and chiral metallic nanotubes

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Metallic single-walled carbon nanotubes were suggested to be ballistic conductors. Their quantum conductance is believed to be unaffected by the presence of short range defects. The argument has been developed in a rigorous way for (n,n) armchair tubes [1] and widely tested on them [2]. Here we show using the TranSiesta code [3] that a Stone-Wales defect reduces the conductance in non-armchair tubes near the Fermi level. In a zigzag tube the conductance is reduced by one unit of the quantum conductance; in a chiral tube the conductance drops by an amount between zero and one unit, depending on the relative orientation of the defect with respect to the tube axis. Localized defects thus lead to a breakdown of ballistic transport in quasi-metallic tubes. For armchair tubes a Stone-Wales defect modifies the conductance only away from the Fermi level in excellent agreement with previous studies [2,3]. We also present transport calculations under finite bias for perfect and defected nanotubes.

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[2] H.J.Choi et al., Phys. Rev. Lett. 84, 2917 (2000) [3] M. Brandbyge et al., Phys. Rev. B 65, 165401 (2002)

## **Electrical Properties of a Multi-Wall Carbon Nanotube measured along the lateral direction**

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Until now, most of the electrical measurements of 1-dimensional nanowires including carbon nanotubes have been done along the longitudinal direction except the scanning tunneling microscope measurements. Here, we present a scheme to measure the electrical properties of 1-dimensional wires along the lateral direction. To verify the validity of this scheme, we show the I-V characteristics obtained from the electrical measurements of a multi-wall nanotube along the lateral direction. And, the potential application of this method would also be discussed.

## Using carbon nanotubes as nanopipettes for transport of solid material

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We have studied electron transport and electromigration in multiwalled carbon nanotubes filled with iron. By studying individual tubes, using an instrument joining scanning probe microscopy and transmission electron microscopy (SPM-TEM [1]), we show that these nanotubes act as diffusive conductors with a resistivity similar to that of natural, defect rich, graphite. At high current densities we observe electromigration of iron, driven by the electron "wind-force". During the electromigration the iron resides mainly in the hollow core of the nanotubes and this enables reversible transport of iron inside the tubes. Such a process, driven by electromigration, has previously been discarded by theoretical modelling [2]. We demonstrate how the tubes can be used as nanopipettes for transports of solid material to, and from, electrically conducting substrates [3].

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[2] P. Král and D. Tománek, Phys. Rev. Lett. 82, 5373 (1999)

[3] K. Svensson, H. Olin and E. Olsson, Phys. Rev. Lett. 93, 145901 (2004)

## **Consequences on the electrical transport of metallic single-walled carbon nanotubes due to doping with nitrogen and phosphorous**

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The temperature-dependence of the charge transport metallic single-walled carbon nanotubes doped by nitrogen and phosphorous was investigated. At room temperature, although nitrogen and phosphorous are expected to drive the nanotubes to be n-type conductors, for the case of nitrogen, both, p- and n-type conduction and for the case of phosphorous, only p-type conduction was observed. In the low-energy limit towards lower temperatures both types of doped nanotubes do not behave as Luttinger-liquids, but show significant deviations. The results are addressed to the differences in the doping-levels and the bond-types of nitrogen and phosphorous atoms within the carbon lattice host.

## Carbon Nanotube Devices for High Frequency Electronic Applications

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Carbon nanotubes (CNT) possess a unique combination of electrical, mechanical, and thermal properties that offer advantages for high frequency electronic applications. This work describes progress on three CNT devices aimed at high frequency electronics: a) CNT field emitters for high current density electron field emitters for a THz frequency electromagnetic source, the "Nanoklystron"; b) CNT Schottky diodes for THz detection; and c) CNT mechanical relays for high performance RF switches. The nanotube field emitter sources are based on uniform periodic arrays of CNT bundles that have been optimized to give high current density emission, typically 1.5-1.8 A/cm<sup>2</sup> at fields of 4 V/micron. Integrated electrode structures for extraction and focusing are also under investigation. The CNT Schottky diodes are produced using dissimilar metal contacts over the ends of a semiconducting SWNT. The diodes exhibit rectifying behavior with ideality factors of 1.5-1.9, reverse breakdown voltages greater than -15V, and nA leakage currents. Finally, the CNT mechanical switches are made using lateral suspended SWNTs grown over recessed electrodes. Preliminary switching and RF modeling results on these devices will be reported.

## **Electrical probing and mechanical manipulation of long, suspended single-walled nanotubes**

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We have fabricated devices consisting of individual suspended carbon nanotubes (CNTs) spanning trenches up to 120 microns long and up to 500 microns deep. The carbon nanotubes are grown via chemical vapor deposition over bare SiO<sub>2</sub>, or pre-patterned gold, platinum or palladium electrodes, forming complete electronically addressable devices without exposure of the CNTs to resists or etchants. These CNT devices allow study of the intrinsic transport properties of the nanotubes without disorder induced by the substrate or chemical residues from conventional lithography. Transport characterization has been performed using either fixed electrodes or a nanoprobe configuration in a scanning electron microscope (SEM) that provides direct electrical contact to, and enables mechanical manipulation of, the CNT. An additional mobile probe may act as a gate electrode, allowing identification of metallic and semiconducting nanotubes. The ability of in-situ manipulation of the CNTs using the probes allows characterization of both unstressed (straight) and stressed (bent) CNTs. Details of the growth and fabrication procedures and characterization of transport on these long, suspended CNTs will be presented. This work was supported by the PEER program of the Army Research Laboratory.

## Simulation of a Toroidal Carbon Nanotube as a Step Motor

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In the modern world, some kind of activities need a high precision and this may be a differential. There is a class of motors named 'step motors' that start and stop his movements, with a highly precision. Step motors are simple to drive and control. For a example, the opto-mechanical set on a DVD reader, needs a known limit to the dynamic position error. In this work, we propose the molecular dynamic simulation for a toroidal carbon nanotube system that works as a stepper motor. The simulation was made by classic molecular dynamics with standard parametrization. Simulations are based on intervals of 2 ps with step size of 0.001 ps without bath relaxation. Several simulation temperature was done and the system worked properly. The obtained results are so satisfied in a limited time response of the set. In our calculations this system has approximately of 3000 carbon atoms. We also propose that the probe when moving (by conservation of lineal moment) impels the nano carbon ring in felt opposite to the probe movement, in similar way to the hamster running in a rotative cage. These fact can be useful for the constructions of new molecular machines.

## Electronic transport of two gate-defined coupled quantum dots in carbon nanotubes

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Numerical results are presented for the transport properties of a strongly correlated model which simulates two or more gate-defined quantum dots (QDs) in carbon nanotubes (CNTs). Recent experimental results (cond-mat/0502634) have characterized the transport properties of up to two gate-defined coupled QDs in CNTs above the Kondo Temperature. The flexibility afforded by the top gates in defining the size of the QDs implies that it is possible to create QDs with correlation energies considerably higher than the ones observed in a CNT spanning the gap between contacts. It is the purpose of this work to analyze the properties of the correlated Hamiltonian appropriate for CNTs in a broad region of the parameter space, with an emphasis in the effects caused in the transport properties by stronger correlations and new phenomena created by the coupling of two or more QDs in the same CNT.

## Contact dependence of carrier injection in carbon nanotubes: an *ab initio* study

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We combine *ab initio* density functional theory with transport calculations to provide a microscopic basis for distinguishing between 'good' and 'poor' metal contacts to nanotubes. Comparing Ti and Pd as examples of different contact metals, we trace back the observed superiority of Pd to the nature of the metal-nanotube hybridization. For Pd interacting with nanotubes or graphite, this hybrid state is associated with an inter-layer state, and allows carrier injection with the Fermi momentum of the nanotube. Based on our Landauer-Büttiker transport results, we furthermore suggest that the 'optimum' metal-nanotube contact combines a weak hybridization with a large contact length between the metal and the nanotube.

## Field emission from individual MWNT

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Electron field emission from multi-walled carbon nanotubes has been a hot topic for the last 10 years. Prototype products such as low energy consumption lamps and flat panel displays have already been realized [1, 2], but some issues concerning the emission from individual tubes are still unsolved. Here we investigate the electron field emission from individual MWNT and how the current is influenced by a change in the emitter temperature. The temperature can increase to above 2000 K which is caused by strong ohmic heating under high electron emission [3]. The simulations carried out indicate a non-linear Fowler-Nordheim plot for emission currents above 10  $\mu\text{A}$  which can be explained with the enhanced emission current as a result of an increased emitter temperature. In the model we have also looked at the temperature dependent resistance of the MWNT which has a strong influence on the outcome. The presented model is also compared with experimental results measuring electron field emission using a combined STM-TEM setup.

## Requirements to realize uniform emission all over the panel of CNT-FED

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The field emission display (FED) using carbon nanotube (CNT) array as emitters is expected as high quality display with low energy consumption. The difference of luminance between the neighboring pixels should be less than 5% to realize uniform emission all over the panel. In this paper, we clarified the required number of emission site for each pixel by using the statistical method. The distribution profile of emission current density from each multi-wall carbon nanotube is evaluated by emission profiler scanning Faraday cup with a 10  $\mu\text{m}$  hole. The distribution is assumed to be Gaussian and the estimated average value divided by the estimated standard deviation is approximately 0.5. The required emission site number for each pixel is calculated to be approximately 3000. To reduce the required number of emission site, the standard deviation should be reduced by utilizing carbon nanotubes with more uniform diameter and length. This work was partially funded by the New Energy and Industrial Technology Development Organization.

## **Field emission effect depends on the tip structure of CNTs synthesized on the aluminum oxide template**

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Field emission properties of carbon nanotubes on AAO template with modified tip shapes were studied experimentally. Fe catalyst assisted CNTs were synthesized by chemical vapor deposition with the methods of pore widening and catalytic reduction. At the low pressure of C<sub>2</sub>H<sub>2</sub> + H<sub>2</sub> + Ar precursor, dense and good crystalline carbon nanotubes were grown uniformly on AAO template. Also, we successfully diminished the AAO crack and warp due to the difference of the thermal expansion coefficients of AAO and aluminum by careful temperature controlling of the substrate at 6250C synthesized temperature. Grown CNT's morphology, shape, crystal structure and density were characterized by field emission scanning electron microscope (FESEM), micro Raman spectroscopy and high resolution transmission electron microscopy (HRTEM). Measured threshold electron emission field and current of grown CNTs with 400 μm gap were 1.65 V/μm and 10 mA at 3 V/μm, respectively, without modification of the tip shape. Electron emitting characteristics and stabilities of CNTs were improved by modifying the tip shape. We will discuss the effect of tip shapes of CNTs to the field emission of CNTs with experimental results.

## STATISTICAL PROPERTIES AND SCREENING EFFECTS IN CNT-BASED ELECTRON FIELD EMISSION CATHODES

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There have been calculated emission properties of (CNT)-based cathodes with taking account statistical spread in parameters of individual emitters and screening effects, decreasing the electrical field amplification factor. A numerical method for solution of the Laplace equation for surfaces of complicated geometry has been developed. This permits evaluation of the electrical field amplification factor for both single CNT's and massifs containing up to 225 emitters, as a function of the distance between nanotubes. It is shown that the statistical spread in parameters of individual nanotubes promotes a deviation of the current-voltage emission characteristics of CNT-based cathode from the classical Fowler-Nordheim dependence inherent to an individual nanotubes. This deviation, most notable at low voltages, was observed in a number of experiments. The calculations performed imply the optimal distance between nanotubes in a massif, providing the maximum magnitude of the emission current density at prescribed value of applied voltage. The role of edge effects in the screening phenomenon is established.

## Directed growth of carbon nanotubes with improved field emission properties

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During the last few years, carbon nanotube (CNT) research has significantly developed, and production of good quality single-wall nanotubes and multiwall nanotubes (MWNTs) has been made possible. Nevertheless, directed growth of nanotubes for specific applications is still a difficult task. Using an unconventional carbon precursor, camphor, vertically aligned MWNTs have been grown by a simple and economic chemical vapor deposition (CVD) method [1]. In the present study we have achieved directed growth of MWNTs in three dimensions on bare silicon substrate as well as nickel- and cobalt-coated silicon substrates, with the controlled use of ferrocene catalyst. MWNTs grown from camphor with 1 wt% ferrocene catalyst have shown appreciable field emission (FE) properties [2]. For the sake of further improvement of FE characteristics of camphor-grown CNTs, in the present study we changed the catalyst concentration in the CVD reactor, and investigated its effect on the FE characteristics of the CNTs grown. We find that a controlled increase of metal content at the CNT growth stage reduces the turn-on field significantly and also increases the maximum emission current density considerably. Best results are obtained with 1.5 wt% ferrocene in camphor, which gives  $\sim 10 \mu\text{A}/\text{cm}^2$  current density at a low turn-on field of  $0.8 \text{ V}/\mu\text{m}$ , and the maximum current is in the range of  $20\text{-}30 \text{ mA}/\text{cm}^2$  at low applied field of  $5.6 \text{ V}/\mu\text{m}$ . Additional encouraging feature of camphor-grown CNTs is that no ultra-high-vacuum is necessary for such a good FE performance. All our experiments are carried out in an ordinary pressure range of  $10^5\text{-}10^6$  torr. With these features, our CNTs are all set to qualify for flat panel display devices.

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[2] M. Kumar, K. Kakamu, T. Okazaki, Y. Ando, Chem. Phys. Lett. 385 (2004) 161-165.

## Photoelectron emission Microscopy of the screen-printed Carbon Nanotubes film

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Carbon Nanotubes (CNTs) have attracted attention as a field emission electron source for application of vacuum nanoelectronics, such as a CNT Field Emission Display (CNT-FED). The uniformity of the emission current is very important for the applications. One of the non-uniformity causes is in the difference of the work function of the CNTs. We investigated the distribution of work function of the CNTs film by using photoelectron emission microscope (PEEM). The microscope image shows some bright points. It suggests that the points originate in difference of the work function from other CNTs and would be vulnerable to field emission. To confirm the above suggestion, we made the triode structure by using the screen-printed CNT, the PPSQ insulator [1] as insulating layer, and the Al gate electrode, and applied the voltage to the gate electrode. We confirmed the point where the brightest on the PEEM image is emitted electrons at the lowest voltage.

[1] N.Yasuda, et al., Bull. Chem. Soc. Jpn. 74, 991 (2001)

## MOCVD synthesis of carbon nanotubes on porous alumina for field emission applications\*

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Carbon nanotubes (CNT) are most promising for vacuum electronics because of unique field emission (FE) properties. Low operation fields, high current densities and chemical inertness provide attractive cold cathode applications in X-ray tubes, FE-displays etc. Prototype devices, however, suffer from inhomogeneity and instability of emitters. Therefore, we have investigated the chemical vapor deposition (CVD) of CNT from propylene and metallocene precursors on mesoporous alumina substrates at temperatures around 800°C. Molecular beam mass spectrometry up to 300amu has been adapted and used for in-situ analysis of the gaseous boundary layer above the porous substrate during CNT growth by means of differential pumping of the reaction chamber. Various hydrocarbon and ferrocene fragments were identified. The mass flow conditions of precursor and carrier gases and temperature distribution in the CVD reactor was simulated by the commercial code FLUENT. Uniform temperature distributions were obtained at the substrates, but stagnation flow was not achievable. SEM and TEM images revealed samples with CNTs of about 20nm in diameter and some  $\mu\text{m}$  length, which were well anchored to the alumina substrates. Integral measurements with luminescent screen revealed uniformly distributed emitters with strong processing effects and stable peak current densities of 1A/cm<sup>2</sup> in pulsed operation. High resolution scans with a FE scanning microscope showed up to 105emitters/cm<sup>2</sup> at 20V/ $\mu\text{m}$ , and single emitters showed current drifts and bistable fluctuations at  $\mu\text{A}$ -levels. The impact of these results for applications will be discussed. \* Project funded by VolkswagenStiftung, Germany.

## **Electron focusing effect of the field emission from the single-wall carbon nanotube**

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We observe that the electron emitted from an open-capped single-wall carbon nanotube are focused in the first principles simulations. We investigate the direct evolution of the wavefunction which contribute the field emission current by integrating the time-dependent Schrödinger equation and analyze the symmetry of the wavefunction. In addition, we study the change of the focusing size with respect to the diameter of the tube.

## **In situ characterization of field emission from individual carbon nanotubes in the scanning electron microscopy**

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The field emission properties of individual carbon nanotubes (CNTs) have been investigated in the field emission-scanning electron microscopy. The measured field emission of bended nanotubes (BNTs) showed both Fowler-Nordheim (FN) and non-Fowler-Nordheim behaviors. Under an applied electric field, BNTs are straightened to align themselves along the electric field line. As the electric field increases, the electron emission was started after fully straightening toward the anode electrode and BNTs showed the FN behavior. However, some BNTs showed that the field emission was occurred during their geometrical straightening to parallel the electric field line, showing the Non-FN behavior. In addition, the field emission of as-straightened CNTs (including MWNT, DWNT, and SWNT) successfully followed conventional FN theory with a single linear slope in the F-N plots below their limitation current levels corresponding to the saturation region of emission current. The results indicate that an increase in field enhancement factor of BNTs by their field-induced straightening during field emission is a plausible mechanism for the non-FN behavior in the field emission of CNTs.

## **Comparison of electric field concentration on carbon nanotubes and carbon nanocoils**

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Carbon nanomaterials, such as carbon nanotubes, helical carbon nanocoils, show excellent field emission properties, which are expected for the uses of electron emitters for the field emission display. The calculations for the concentration of the electric field on the tip of a straight carbon nanotube, the side wall of a bended carbon nanotube and the surface of a carbon nanocoil have been performed using a finite element method. The experimental results show that the turn-on voltages of field emission from the side wall and the tip of a single carbon nanotube are about 570 V and 150 V, respectively. The voltage ratio is about 3.8. The calculations have confirmed that the electric field intensity of the tip is about 2.8 times stronger than that of the side wall, which is considered to be a dominant factor in changing of the turn-on voltage. It is also obtained from the calculations that the strength of electric field around the top ring of a coil is increased with the decrease of the tubular diameter of the coil and has a similar value for that at the tip of a straight carbon nanotube, suggesting that the efficiency of the field emission from nanocoils would be higher than that from nanotubes.

## **Coaxial quantum cathode based on alkali metal intercalated carbon nanotube**

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A new scheme of carbon nanotube-based field emission cathode is proposed. The cathode is a metallic CNT filled with alkali metal atoms separated from the nanotube by an insulating layer (coaxial quantum wire with M-I-CNT structure). The spectrum of size quantization energy levels is calculated in free electron approximation for this wire taking into account the inner electric potential generated in the cathode between the alkali metal and nanotube. The current density of field emission from the quantum wire surface is calculated in quasi-classical approximation. The anode is supposed to be tubular and the cathode is placed on its axis. The current density of field emission from size quantization energy levels in radial direction grows exponentially as a function of inner potential. It is shown that generating the inner electric potential up to several tenth of a volt can lead to increasing in the current density by one order of magnitude.

## **Fabrication and Performances of Nano Emissive Displays for Large Area HDTV Applications.**

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The Nano Emissive Display (NED) is a novel low-drive voltage Field Emission Display fabricated at Motorola which uses selective growth of CNT's for effective electron emission in a self-focusing and self-regulating planar structure. The starting point in the NED fabrication resides in compatibility of the CNTs technology with conventional low cost manufacturing processes. This paper describes the development of the NED technology for large HDTV application. It reviews the development and optimization of a nano-supported catalyst and large area hot filament CVD technique permitting selective, direct CNT growth into low cost planar triode devices at temperatures compatible with glass substrates. Since high quality displays must keep short-range non-uniformity below the eye's threshold for detecting variation. We solved this issue by controlling the current emitted per subpixel, using a narrow statistical distribution of the CNT/pads emitters and a ballast layer. Thus, the maximum current obtained from large FE sub-pixel depends on the statistical dispersion of the CNT/pad geometry, and the sub-pixel design. We demonstrate how the CNTs and the device structure allows us too meet targets of luminance, color purity and uniformity Finally, we present the characteristics of packaged 5 inch prototypes with the pixel size of a 42" HDTV(0.726 mm) and demonstrate color video operation.

## **Field emission characteristics of dot-patterned multi-walled carbon nanotubes grown by thermal chemical vapor deposition**

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Multi-walled carbon nanotubes (MWCNTs) are usually grown to be vertically aligned with a high population density by thermal chemical vapor deposition. Such densely populated CNTs shows, in most cases, poor field emission characteristics due to the electrical screening effect. This study reduced the number density of CNTs using an adhesive tape treatment, which has been applied to screen-printed CNT emitters. The CNTs were grown on catalyst dots which had the same geometry as those used for the triode-type field emitter arrays. For such dot-patterned CNTs, the tape treatment decreased the CNT density by three orders of magnitude, drastically improved the turn-on electric field from 4.8 to 1.8 V/ $\mu\text{m}$ , and changed the emission image from spotty to uniform luminescence. We also report the long-term emission stability of dot-patterned CNTs by measuring the emission currents with time at different duty ratios.

## **TDDFT-MD simulation of ultrafast carrier decay in nanotubes: Dependence on the lattice temperature**

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Realization of electronic and opto-electronic nanoscale devices is one of the most challenging subjects in nanotube applications. Carrier lifetime is crucial for optimizing the clock frequencies of the devices. Experimental observations using femtosecond laser spectroscopy [1,2] suggested a rapid carrier decay in nanotubes, which was attributed to electron-electron coupling in the early stage and electron-phonon coupling at a later stage. Recent theoretical treatment of electron-phonon coupling [3] necessitates the inclusion of electron-electron coupling.

We present a microscopic study of hot carrier dynamics in vibrating carbon nanotubes. Using the computer code FPSEID [4], which couples time-dependent density functional simulations with classical molecular dynamics, we are able to monitor both types of coupling simultaneously in real time. We investigate the electron-electron coupling in early stage by monitoring the time dependence of the potential energy of the lattice. In order to clarify the electron-phonon coupling contribution, we further investigate the dependence of the lattice dynamics on the initial lattice temperature.

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## Diameter-Selective Encapsulation of Metallocenes in Single-Walled Carbon Nanotubes

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Encapsulation of organic or inorganic molecules into single-walled carbon nanotubes (SWCNTs) has opened a new route for fabricating new hybrid-nanostructures. The electronic structures of SWCNTs can also be modified through molecule encapsulation. Here we report that diameter selective encapsulation of two metallocene compounds bis(cyclopentadienyl) cobalt (CoCp<sub>2</sub>) and bis(ethylcyclopentadienyl) cobalt (Co(EtCp)<sub>2</sub>) has been observed in SWCNTs. In particular CoCp<sub>2</sub> is observed to only fill nanotubes of one specific diameter in HiPCO nanotubes. By contrast, Co(EtCp)<sub>2</sub> is preferentially encapsulated into SWCNT with diameters above a threshold value. Electron transfer from the cobalt ions to the nanotubes has been directly observed through a change in the charge state of the encapsulated molecules. The filling of the tubes is found to induce a red-shift of the photoluminescence emission which is attributed to the formation of localized impurity states below the conduction band of the nanotubes.

## **Cylindrical Waves for Pure, Intercalated, and Embedded Nanotubes**

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The linear augmented cylindrical wave methods is elaborated and implemented as software for calculation of the nanotubes electronic structure. Consideration was carried out in the muffin-tin and local density functional approximations for the electron potential. We consider that the electron potential is spherically symmetric in the vicinity of atoms and constant in the interatomic space up to two potential barriers. The electronic structure of individual and embedded in a crystal matrix SWCNTs is calculated. A delocalization of the nanotube electrons into the matrix region results in a strong band-structure perturbation. In the case of armchair nanotubes, the delocalization is responsible for a high-energy shift of the sigma states and growth of the electron density of states at the Fermi level. For the semiconducting nanotubes, it causes a decay of the minimum energy gap and the formation of a metallic state. The effect of embedded nanotube metallization correlates with the transport properties of devices with nanotubes encapsulated in a semiconductor crystal.

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## **Exciton dynamics in semiconducting single-walled carbon nanotubes**

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Overview of the spectroscopic properties and theoretic methods used for description of the electronic spectra of single-walled carbon nanotubes (SWNT) is presented. To define the origin of the electronic excited states of SWNT, femtosecond fluorescence up-conversion and frequency-resolved femtosecond transient absorption measurements were used for selective excitation/probing of particular nanotubes in a micelle-dispersed preparation enriched with individual nanotubes. Analysis of the temporal and intensity profiles of the signals enable us to unambiguously identify the exciton nature of elementary excitations in semiconducting nanotubes, and the predominant dynamical process as a remarkable manifestation of exciton-exciton annihilation. Relevant theoretical model describing very fast exciton relaxation processes is developed. Our studies convincingly support the conclusion that the longest wavelength electronic excitations are of excitonic origin.

## **Stress-induced shifts of photoluminescence of single-walled carbon nanotubes**

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We will present results of the near-infrared photoluminescence mapping of individual semiconducting single-walled carbon nanotubes after freezing and cooling the water-surfactant dispersions of nanotubes down to 16K [1]. The nanotubes undergo large axial strain deformations because of the difference of the thermal expansion coefficients of the ice-matrix and nanotubes. This results in large shifts of interband transition energies of nanotubes observed in the photoluminescence spectra. The signs and relative magnitudes of the shifts depend on the structure and chirality of nanotubes and agree well with tight-binding model calculations. This effect was found to be helpful for assignment of higher interband transition energies to specific nanotube structures.

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## **Third-Order Nonlinearity In Carbon Nanotubes: Modeling And Comparison With Experiments**

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A theoretical analysis of the third-order nonlinear optical processes in a rectilinear single-wall carbon nanotube (CNT) illuminated by the external electromagnetic field is presented. The analysis is based on the full quantum mechanical approach to the electron motion in CNT. For this purpose, the quantum kinetic equations for the electron density matrix in a CNT has been obtained and solved analytically by the perturbation method. Two components of the third-order polarizability tensor related to the third-order harmonic generation and to the self-action of waves in a CNT has been calculated both for zigzag and for armchair CNTs in the wide frequency range. We show that the CNT's qualitative spectral characteristics (the location of spectral maxima, their density and intensity) are essentially influenced by the CNT type. Spectral characteristics in the vicinity of the plasmon resonance have also been analyzed. Theoretical results are compared with that of experimental measurements by different techniques including the pump-probe measurements. The comparison demonstrates good correlation between the theory and the experiments. Thus, one can conclude that the model developed can serve as an adequate tool for the modeling of nonlinear optical processes in CNTs. Authors acknowledge a support from the INTAS Ref. Nr. 03-50-4409.

## Fast photoresponse of CVD nano-graphite films

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We demonstrate that the temporal profile of the electric pulse generated in the CVD nano-graphite (NG) reproduces the shape of the incident nanosecond light pulse in the spectral range 266 - 5000 nm.

NG film with thickness of few micrometers was grown using chemical vapor deposition (CVD) technique on Si substrates. The film consisted of graphite crystallites with thickness of 2-20 nm and length of 1 - 3  $\mu\text{m}$  [1]. We measured dc electric signal induced in the film due to optical rectification effect. The measured light power/voltage conversion was as high as 1 V/MW at  $\lambda = 500$  nm, while the shape of the dc signal reproduces the shape of the laser pulse [2]. The observed strong and fast second-order optical nonlinearity of the NG film in the spectral range that spans from UV to IR suggests that NG is a promising material for manufacturing wideband detectors of laser radiation.

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## **Photovoltaic and photoconductor devices using SWNT in polymer films.**

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The persistent demand for new types of material for photovoltaic (PV) and photoconductor (PC) devices in the near-infrared (NIR), triggered our curiosity to explore the potential application of single-wall carbon nanotubes (SWNTs) finely dispersed in conjugated conducting polymer films. We have successfully fabricated PV and PC devices in the following configuration Al/SWNTs-polymer/ITO/quartz. The latter unveils very promising optoelectronic properties over a broad spectral range from 300 to 1600 nm. These prototypical devices especially exploit the intrinsic NIR light harvesting properties of semiconducting SWNTs, the electronic transport properties of both semiconducting and metallic SWNTs, and the electronic interactions between SWNTs and polymer. Several techniques were utilized to support our conclusions such as spectrally resolved photocurrent, photoluminescence and optical absorption spectroscopy as well as IV electrical measurements under illumination with solar simulators. Choosing SWNTs and polymers with different electronic structures, we shall demonstrate that the optoelectronic properties of nanotubes-polymer thin film devices are readily tunable, so far have never been reported.

## **Electrically Conductive Amorphous Carbon Nanotube Thin Films from a Renewable Source of Turpentine Oil**

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The electrically conductive amorphous carbon nanotubes (a-CNT) films were deposited on single crystal silicon (Si) (100) and glass substrates by pulsed laser deposition (PLD) at room temperature in high vacuum of  $10^{-5}$  -  $10^{-6}$  Torr, using CNT solid target (CNT-target). The CNT were prepared by newly developed spray pyrolysis chemical vapor deposition. The renewable source of turpentine oil was used as a carbon precursor material. After purification process, the CNT were pressed into pellets with a hydraulic presser in order to use as a CNT-targets for PLD. The CNT-targets were ablated for 1500 laser shots at 10 Hz repetition rate with various laser energy (LE) from 140 to 260 mJ/pulse. The substrate was mounted at a distance of 45 mm. Raman spectra of a-CNT films deposited at 140 mJ showed broad peak indicates the amorphous structure of the films. The Raman intensity is found to increase, while the G peaks line width is found to decrease with higher LE indicates the crystallization upon increase of LE. The optical band gap (OBG) of a-CNT films is higher compared with graphitic carbon (deposited using graphitic target, GC) and camphoric carbon (deposited using camphoric carbon target, CC) films deposited at the same parameters. Though, we found that the electrical resistivity (RES) of a-CNT films is lower compared with GC and CC films deposited at the same parameters. The OBG and RES of a-CNT films are found to decrease with higher LE. Details will be discussed during the conference presentation.

## **Transient photorefractive effect in single walled carbon nanotubes**

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We present continuous wave photomodulation spectroscopy of single-walled carbon nanotubes dispersed in a polymer matrix. The spectrum is dominated by a modulation of the ground state absorption lineshape, such as observed in electromodulation experiments. Our interpretation is that upon photoexcitation charge states are formed, diffuse and get trapped in the sample, generating strong local electric fields, which modulate the absorption of neutral species. This phenomenon is thus similar in nature to the photo-refractive effect. The intensity dependence of the signal is consistent with a quadratic field dependence. We find a lifetime of the photogenerated charges in the range of 40 ms. The lack of selectivity in the excitation points to an efficient migration of the photoexcited states, either the singlet excitons or the charges resulting from their dissociation.

## **Polarization dependence of the optical absorption properties of single-walled carbon nanotubes**

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Polarization dependent optical absorption properties of single-walled carbon nanotubes (SWNTs) have been elucidated from measurements of our vertically aligned SWNT film grown on quartz substrates. We discovered the remarkable and different polarization dependencies of UV absorption peaks observed at 4.5 eV and 5.25 eV, which are observed regardless of the diameter or preparation method of SWNTs [1]. Origins of these absorption peaks and their important relevance to the optical properties of graphite are revealed. A new method of determining a nematic order parameter of the vertically aligned SWNT films by separating out the absorption peak at 4.5 eV has been developed. Accordingly, the bare optical absorption cross-sections of the SWNTs for 0.5 - 6 eV were determined for both parallel and cross-polarized lights. The tail of the non-collinear absorption peak at 5.25 eV contributes appreciably to the absorption of cross-polarized light in the inter-subband region below 3 eV. This analysis enables quantitative evaluation of the UV absorption baselines formed in vis-NIR region from the optical absorption spectra. The author (YM) was supported through the 21st Century COE Program, "Mechanical Systems Innovation", by MEXT.

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## Relaxation processes in Raman and photoluminescence of single-wall carbon nanotube

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Relaxation processes in Raman and photoluminescence (PL) spectroscopies have provided an important role for obtaining (1) Raman and PL intensities, (2) relaxation time, (3) temperature dependence and so on (M. S. Dresselhaus et al, Physics. Report, 2005). Because of anisotropy of the electron-photon and electron-phonon matrix elements in the k space (J. Jiang et al, PRB in press), many optical properties has a strong chirality dependence which will be useful for obtaining diameter and chirality distribution of CVD nanotube sample by comparing theoretical results with experiments (Y. Oyama et al unpublished). The theoretical results are compared with recent PL experiment and fast optics of (6,5) single chirality sample (S. G. Chou, PRL in press).

## OPTICAL AND ACOUSTIC SENSORS BASED ON CARBON NANOTUBES THIN FILMS: A MULTI-TRANSDUCER APPROACH FOR VOCs DETECTION

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Single-Walled Carbon Nanotubes (SWCNTs) are advanced nanostructured materials with promising sensing properties in terms of sensitivity, low sub-ppm limit of detection, on-line and real-time vapors detection, at room temperature [1,2]. Here, Standard silica optical fibers (SOFs) sensors based on light reflectometry at a wavelength of 1310 nm and acoustic sensors based on quartz crystal microbalance (QCM) 10 MHz AT-cut quartz resonators, incorporating Langmuir-Blodgett (LB) films consisting of tangled bundles of single-walled carbon nanotubes (SWCNTs), have been designed, fabricated and tested for Volatile Organic Compounds (VOCs) detection, at room temperature. The transducing principles are based respectively on complex dielectric function and mass change induced by target analyte molecules adsorption within the sensitive overlayers. The results obtained indicate high sensitivity, very low limits of VOCs detection, fast responses and a clear dependency of the optical and acoustic sensors sensitivities on the nanomaterial thickness. Furthermore, the simultaneous use of chemical sensors with complementary transducing principles, coated by the same sensitive nanomaterial, can increase the amount of extracted informations by pattern recognition techniques [3] such as principal component analysis (PCA) and artificial neural networks (ANNs) for sensed VOCs discrimination.

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## Exciton Relaxation in Single Wall Carbon Nanotube by sub-20 fs Time Resolved Optical Spectroscopy

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Ultrafast pump-probe measurements were performed on a film of SWNTs grown using a modified gas phase process (HiPco) and embedded in PMMA. Pump-probe experiments were conducted using ultrabroadband light pulses spanning the visible and the near IR wavelength range, generated by non-collinear optical parametric amplifiers<sup>1</sup>. Visible pulses had a temporal duration of 7 fs and spectral extension from 500 nm to 700 nm, resonant with the second excitonic level (Ex2); the near IR pulses had 30 fs duration and were centered at 1300 nm, resonant with the first exciton (Ex1). All traces showed that the internal conversion between Ex2 and Ex1 has a time constant of  $40 \pm 5$  fs, confirming for the first time some previous estimations. It was also possible to measure the lifetime of the Ex1 state, which has a time constant ranging from 400 fs to 800 fs.

Some pump-probe traces show strong modulations due to the main vibrational modes of NTs: the C=C stretching at 1591 cm<sup>-1</sup> and some Radial Breathing Modes (RBM), ranging from 239 to 254 cm<sup>-1</sup> and dephasing with a 1.2-ps time constant. The C=C stretching appears to be frequency-modulated by RBM, revealing unharmonic coupling between these two modes.

## Photoluminescence from SWNTs Suspended on Pillars in Free Space

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Photoluminescence (PL) is now widely obtained from SWNTs using the micelle encapsulation method. We have been using a different approach, in which SWNTs are suspended in free space from features on patterned substrates. This approach is advantageous in that no post-synthesis processing is necessary, and thus the nanotubes remain unaltered and essentially pristine. Nanotubes prepared in this way are also excellent PL emitters. This method has enabled the measurement of PL from single, isolated SWNTs as well as from large ensembles of SWNTs. Here, I will describe recent results of particular interest including temperature-induced spectral changes and ambient-induced effects.

## Exciton binding energy in carbon nanotubes

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The optical properties of carbon nanotubes are assumed to be dominated by excitonic effects. Exciton binding energies between 100 meV and 1 eV have been predicted, depending on diameter, chiral angle, and surrounding medium. Experimental proof for these large binding energies, however, has been missing so far. Here we present direct experimental evidence for the excitonic character of absorption and emission in carbon nanotubes and determine the exciton binding energies of several nanotube chiralities [1]. We measured the energies of the p-like exciton states by two-photon absorption. By comparing one-photon and two-photon luminescence excitation spectra, we find binding energies between 300 and 500 meV, assuming an hydrogen model for the excitonic states. Our results are strongly supported by *ab initio* calculations of two-photon absorption spectra.

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## High optical-quality nanotube polymer composites for photonic devices applications

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Single wall carbon nanotubes (SWNTs) are a promising material for ultrafast applications in telecommunications [1]. It is thus of critical importance to have nanotube films with high optical quality. The nanotube distribution in a film or polymer-based composite must be homogeneous on a scale smaller than 1550 nm, the wavelength most commonly used in telecommunication devices [2,3]. Here, we report the fabrication and characterisation of SWNTs-based transparent films, produced from aqueous and organic solutions. We characterized spray-coated pure nanotube films and nanotube-polymer composites using UV-VIS-IR absorption and micro-Raman spectroscopy at different excitation wavelengths. Optical microscopy reveals areas with a homogeneous distribution of nanotubes (over visible light wavelengths), which generate a strong SWNT Raman signal even though the individual nanotubes cannot be resolved. Saturable absorption was investigated using the Z-scan technique. The high optical quality of our films makes them promising candidates for applications as nonlinear-optical elements in telecommunication devices.

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## **Micro-photoluminescence spectroscopy of individual single-walled carbon nanotubes**

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We have studied microscopic photoluminescence (PL) and photoluminescence excitation (PLE) spectroscopies of individual single-walled carbon nanotubes (SWNTs) suspended on grooves with width of ~2 μm. Strong luminescence was obtained at the position only where the SWNT was suspended from the SiO<sub>2</sub>. PL spectral widths were as narrow as 8~20 meV at room temperature, and PLE spectral widths were ~50 meV. The chiralities (n,m) were assigned by the peak energies of PL and PLE spectra which correspond to E11 and E22, respectively. Although such chirality assign was possible for most individual SWNTs observed in the present measurement, the data scatter by a few ten meV even for the same chirality. We have also studied effect of external electric field on the PL spectrum using FET structure. PL intensity was modulated by the gate and drain bias voltages.

## **Carbon Nanotube- Polyvinylalcohol Nanocomposite Film Devices: Application for Femtosecond Fiber Laser Mode-Locker**

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We fabricated a single wall carbon nanotube (SWNT)/polyvinylalcohol (PVA) nanocomposite self-standing film for a saturable absorption device usable in mode-locked Erbium fiber short pulse laser. We integrated a 30- $\mu$ m-thick SWNT/PVA film into a conventional FC/PC fiber connection adaptor with the film sandwiched by a pair of fiber ferrules. A ring fiber laser inserted with the SWNT/PVA saturable absorber operated very easily in mode-locked short pulse mode with the shortest pulse width of 180 fs. This result demonstrates that the SWNT/PVA film is very promising as a passive mode-locker for femtosecond Er-doped fiber lasers. The easy controllability of film thickness and SWNT concentration enables fine material tuning, being profitable in the future laser improvement. The easy device fabrication using conventional fiber connection techniques with reproducible device performance will make the laser construction easy and reliable.

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**Optical transitions and phonon-related processes in different samples of carbon nanotubes using resonance Raman and photoluminescence excitation spectroscopies.**

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We will present resonance Raman and photoluminescence excitation (PLE) spectroscopy results on different single-wall carbon nanotube (SWNT) samples. The Raman measurements were performed with a quasi-continuous set of excitation laser lines between 1.6 and 2.7 eV. HiPco and CoMoCAT SWNT samples are measured, both as grown and dispersed in aqueous solutions with different wrapping agents (SDS or DNA). We will discuss the (n,m) dependence for the resonance Raman intensities and widths, as well as the specific (n,m) populations in the samples, based on theoretical results for the resonance Raman cross-section. We will also report PLE measurements in different samples of carbon nanotubes, where both direct and phonon-assisted optical transitions are observed. These results will be discussed in terms of excitons and phonons in carbon nanotubes.

## **Photoluminescence and resonant inelastic light scattering from double wall carbon nanotubes**

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We observe photoluminescence in stable aqueous suspensions containing predominantly double wall carbon nanotubes. Infrared photoluminescence excitation mapping shows bands which are in general, narrower than from single wall carbon nanotubes. Detailed comparison shows branching and spectral red-shifts in the 14meV range. We use resonance inelastic light scattering to compare the resonant profiles with the recorded PLE maps and to detect the presence of metallic tubes. The influence of the second wall and the surrounding surfactant on the luminescence spectra will be discussed in detail. We compare our findings to electron transition energies recently measured for neat SWNT samples. Our findings demonstrate also that in a significant fraction of tubes there is no quenching of luminescence due to the second wall indicating possible correlations in the helicity of the two tubes.

## **Polarized-Photoluminescence Excitation Spectroscopy of Aligned Single-Walled Carbon Nanotubes**

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Optical transitions of (6,5) and (7,5) single-walled carbon nanotubes (SWNTs) were investigated by polarized photoluminescence excitation (PLE) spectroscopy of 2-dimensionally aligned individual nanotubes in gelatin-based thin film. Optical transitions for perpendicularly polarized light to the nanotube axis were directly observed in addition to well assigned transitions for parallel polarization. While all PL peaks in PLE spectra were classified into either 'pure electronic' or 'electron-phonon coupling' peaks by measuring PLE spectra of isotopically modified SWNTs consisting of carbon-13 isotope, all the observed 'pure electronic' peaks were consistently assigned to electronic transitions corresponding to incident light polarized parallel or perpendicular to the nanotube axis. These results are consistent with the considerably asymmetric structure of electronic energy dispersion relation predicted by GW-level DFT results. This large asymmetry resulted in very close energetic values between transitions for parallel and perpendicularly polarized light, suggesting the apparently wide resonance window if depolarization effect is imperfect, for example, SWNTs are bundled or surrounded by some dielectric materials such as gelatin or surfactant.

## **Anisotropic Saturable Absorption of Single Wall Carbon Nanotubes Aligned in Polyvinyl Alcohol**

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We report anisotropic optical absorption and saturable absorption (SA) properties of aligned single wall carbon nanotubes (SWNT) embedded in the mechanically stretched polyvinyl alcohol (PVA) film. Polarized absorption spectra of the film showed a strong anisotropy for the near-infrared band gap transition of semiconductor SWNT with a dichroic ratio of 7.4, indicating the good alignment of the embedded SWNT. The SA property of the band gap transition measured using a polarized femtosecond fiber laser showed a strong polarization angle dependence for the stretched film. When the polarization of light is parallel to the stretching direction, the absorption saturation of the stretched film became more efficient than that of the unstretched film because of the apparently stronger transition moment.

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## Optical spectrum of carbon nanotubes under electric fields

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The theoretical understanding of the optical properties of single-wall carbon nanotubes is an important problem to address since low energy lasers beam are being used to identify the chirality and diameter of the tubes and their electronic character [1-3]. When a carbon nanotube is under the influence of a laser beam, optical transitions are allowed between the Van Hove singularities and they can be observed experimentally in the absorption spectra. External magnetic and electric fields modify the energy spectrum of CNT's inducing changes on the optical phenomena at low frequencies. In recent works [4-5], we have studied the effects of a transverse electric field on the energy spectrum of CNT's and we found that energy gap modulations can be induced by changing the strength and the in-plane direction of the applied electric field. This particular angular dependence leads to remarkable changes in the energy spectrum of CNT's for certain electric field values. In this work we present theoretical calculations for the optical absorption coefficient of carbon nanotubes under an additional external electric field applied. We study the dependence of the dipole selection rules for the optical transitions on the external electrostatic potential for different light polarizations. We analyze the angular effect on the electro-optical spectrum of carbon nanotubes of different diameters.

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## Chiral Selectivity in the Charge Transfer Bleaching of Single Walled Carbon Nanotube Spectra

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Near-infrared fluorescence and absorbance spectroscopy was used to study the reactivity of single-walled carbon nanotubes with organic acceptor molecules including azobenzenes and cyanoquinones. We observed spectral bleaching of the nanotube first van Hove transitions consistent with an electron transfer reaction occurring from the nanotubes to the organic acceptors. Subsequent addition of electron donors resulted in complete recovery of the unreacted nanotube spectra. The reaction kinetics were found to have a strong chiral dependence, with rates being slowest for large bandgap species and increasing for smaller bandgap nanotubes. The chiral-dependent kinetics could be tuned to effectively freeze the reacted spectra at a fixed chiral distribution. Such tunable redox chemistry may be important for future applications in noncovalent modification of nanotube electronic properties and in chiral selective separations approaches.

## Environmental effects on carrier dynamics in singlewalled carbon nanotubes

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Singlewalled carbon nanotubes (SWCNTs) do have many intriguing physical properties, and optical ones are currently under intense investigation. In such quasi one dimensional systems, the electronic density of states presents squarerootlike singularities. SWCNT are therefore expected to have a highly structured emission and absorption spectra, with resonances at the optical transitions corresponding to pairs of these vanHove singularities. This promised fruitful applications to SWCNTs of the whole bunch of optical techniques, such as photoluminescence and excitation spectroscopy for sample characterization, or timeresolved measurements to study the carrier dynamics.

Nevertheless, grown samples of nanotubes, which aggregate into bundles of a few tens owing to vander Waals interaction [1], did not show any photoluminescence. Previous ultrafast spectroscopy experiments have brought evidence of a tunnel coupling between semiconducting and metallic SWCNT within a bundle, which accounts for the absence of photoluminescence and of any temperature dependence of the relaxation dynamics [2].

More recently, direct observation of the intrinsic photoluminescence at the band gap of semiconducting nanotubes has been reported in suspensions of SWCNTs in water [3]. The addition of a surfactant combined with ultrasonic agitation allows to separate bundles and leads to individual nanotubes embedded in micelles of surfactant. Ultrafast spectroscopy measurements on such lightemitting suspensions have been carried out on nanotubes grown by the HiPCO method [4]. They show a multi component decay dynamics of the photocreated carriers with a slow component of about 10 ps. It is attributed to interband carrier recombination in resonantly excited HiPCO SWCNTs.

We present here a study of ultrafast carrier dynamics in both suspensions of individual SWCNTs (iNTs) and bundles of SWCNTs (bNTs) by means of two color pumpprobe experiments in the visible and nearer domains (0.75 to 1.53 eV). This allows a direct comparison between light emitting and nonemitting samples. Note that iNTs and bNTs samples have been made from an unique source of SWCNTs

obtained by laser ablation and purified by ultrasonic and chemical treatment. We observed for both iNTs and bNTs samples transient photobleaching of the first interband transition. Relaxation times are about one order of magnitude much slower in nanotubes suspensions than in nanotubes bundles, showing the removal of the tunnel coupling between metallic and semiconducting tubes inside a bundle. The nonexponential shape of the signal is attributed to the inhomogeneous nature of the nanotubes distribution.

The overall dynamics appears at least one order of magnitude slower in laser nanotubes than in HiPCO nanotubes. A slow component of 250 ps decay time has been measured on isolated nanotubes, giving a lower bound to the SWCNT's radiative lifetime. Moreover, we defined a relaxation rate reflecting the losses during relaxation processes. It shows that 87% of the carriers relax down to the lowest excited level in iNTs, and only 50% in bNTs. This is interpreted as a signature of the removal of the tunnel coupling and a passivation of defects created by the purification treatment.

These observations underline the important role of the environment in carrier dynamics and more generally in electronic properties of SWCNTs.

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## **THEORETICAL AND EXPERIMENTAL STUDIES OF CARBON NANOTUBES: A REVIEW**

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Carbon nanotubes (CNTs), discovered by Iijima, in 1991 a new era in nanoscience. These nanomaterials play important and actual role in different applications - technique, desing of devices in electronics, nanocomputers, aircraft, transistors etc. Many researchers from all the world devoted their studies on these nanomaterials , not only because their extraordinary physical, mechanical, chemical, electrical etc. properies, but also of their atomistic scale (nano) sizes. It is intersting as well, to point out the fact that the chirality nanostructure of (CNTs), contribute too of their so good applications. The aim of the paper, presented could be formulated as follows: to generalize, to analyze and to discuss recent publications on theoretical approaches and experiments of carbon nanotubes. Classical structural mechanics theories, and novel approaches as classical molecular dynamics, extended bond potentials have been presented as well. Experimental studies by tunneling electron microscopy (TEM), and scanning tunneling microscopy (STS) have been discussed. Some concluding remarks with main results for example: the paper could be used as background for development of novel modified models, based on the classical mechanics for describing of mechanical behavior of (CNTs), comparison between theory and experiments have been given too.

## **Carbon Nanotubes Embedded within Polymer Macro-Tubes**

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In a recent paper [1], we developed an electrochemical method for preparation of macro-tubes of conductive polymers. By this method, it is possible to fabricate large macro-tubes with diameter of ca. 100  $\mu\text{m}$  and a few millimeters long. Since it is known that composites of conductive polymers and carbon nanotubes are of practical interest due to similarities of these materials. In the present research, we would like to propose a new structure of carbon nanotube/polymer composite. According to large scale of aforementioned polymer macro-tubes, it is easy to handle them. Thus, it is possible to incorporate a bundle of carbon nanotubes into the polymer macro-tube. In this case, the polymer macro-tube can be completely filled with the carbon nanotubes. Moreover, the internal walls of these macro-tubes are sufficiently rough to provide strong connections with the carbon nanotubes. Therefore, the bundles of carbon nanotubes have sufficient stability for practical applications and can be easily handled. Carbon nanotubes embedded within polymer macro-tubes exhibit superior properties. Possibility for controlling interconversion of semiconducting and metallic forms of conductive polymers provides a new opportunity for controlling electrical properties of this carbon nanotubes-based composite. This is also accompanied by enhanced transport properties due to longitudinal structure of macro-tubes.

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## **Fano-like line shapes in STM Response of a Luttinger Liquid with a Kondo Impurity**

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We study the STM (Scanning Tunneling Microscopy) response of a Luttinger liquid with a Kondo impurity. The system can be realized by adding a magnetic impurity to a quantum wire or carbon nanotube. At low temperatures we map the system to a boundary problem, and use Bosonization and Boundary Conformal Field theory techniques to calculate the finite-temperature Green's functions. The local density of states is calculated for different temperatures and distances from the impurity. We discuss properties of the uniform and Friedel terms in the STM current, and show that the local differential tunneling conductance has an asymmetric line shape.

## Diffusion through Flower-Like Bundle of Manganese Oxide Nanofibers

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More recently, we proposed a simple method for preparation of manganese oxide nanofibers with diameters ranging from 10 to 50 nm [1]. Interestingly, in this synthesis procedure, individual nanofibers entangle together to form large micro-particles. They have peculiar shapes similar to flowers and blooms. This peculiar shape is of practical interest for systems involving diffusion processes. In the present work, we discuss superior diffusion of ions through labyrinth of bunched nanofibers. Diffusion of an electroactive ion within these flower-like particles was investigated from statistical point of view [2,3]. Similar to the previous report devoted to diffusion through nanostructured materials [4], it was found that such complicated structure provides appropriate nano-channels for ion diffusion. Thus, this complicated entanglement of nanofibers is accompanied by superiority of chemical diffusion. In this direction, we attempt to propose a model for diffusion of electroactive films through these complicated nanostructures. Since these microparticle have flower-like shape, the diffusion coefficient is stronger when the preliminary diffusion of electroactive ions begins from the flower head. This can be attributed to the peculiar shape of the particles generated in the course of solid-state synthesis.

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## Family pattern in electron-phonon matrix elements and relaxation time in carbon nanotubes

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The electron-phonon matrix elements in single-wall carbon nanotubes are derived in the frame of density functional tight binding [1]. The diagonal and off-diagonal deformation potential, the overlap integral change with respect to the phonon mode, and the curvature effect are explicated included. The matrix elements thus obtained are in quantitative agreement with ab initio calculations for electron-phonon coupling. We then apply our matrix elements to study the relaxation time in metallic and semiconducting tubes, focusing on transport and optical properties, respectively. For metallic tubes, the electron mean free path near the Fermi level is estimated for each phonon mode and the results are consistent with the experimental measurements in low and high bias voltage ranges. For semi conducting tubes, we find a family pattern for the life time [2] at the second van Hove singularities, which can compare with the measured life time by Raman spectroscopy [3] and fast optical experiment [4]. Finally, we apply our matrix elements to radial breathing mode (RBM) Raman intensity [5] and find that a family pattern also exist in RBM matrix elements. The family behaviors in Raman and photoluminescence can help experimentalists to characterize nanotube chirality.

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## Experimental Electron Phonon Coupling in Graphite and Nanotubes

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Electron-phonon coupling (EPC) is a key physical parameter in nanotubes. Ballistic transport, superconductivity, excited state dynamics, Raman intensity and phonon dispersions fundamentally depend on the electron phonon coupling. However, so far, no direct measurement of the optical phonons EPCs has been shown. Here, we present the direct experimental measurement of the optical phonons EPCs in graphite and nanotubes. These measurements are based on the phonon dispersions and the phonon line-widths in graphite and nanotubes [1]. We prove that the EPC is the major source of broadening of the G and G<sup>-</sup> Raman peaks in graphite and metallic nanotubes [2]. In particular, we show that the EPC interaction explains the differences in the shape of the Raman spectra of metallic and semiconducting nanotubes and their trends as a function of tube diameter. We dismiss the common assignment of the broad G<sup>-</sup> peak in metallic nanotubes to a plasmon Fano resonance. Thus, we measure the graphite EPCs in three independent ways: from the optical phonon dispersions around G [1], from the Raman D peak dispersion [1] and from the width of the Raman G peak. We then directly measure the EPCs for nanotubes in two independent ways: By fitting the width and the position of the G<sup>-</sup> peak as a function of diameter for nanotubes in the 0.8-2 nm diameter range. The experimental EPCs compare extremely well with the theoretical ones, which we compute with density functional theory [1,3]. Both the experimental and theoretical EPCs show that the curvature has a negligible role on the EPC matrix elements for the commonly used nanotubes, with diameters larger than 0.8 nm. Thus the EPCs of nanotubes of arbitrary chirality and diameter can be obtained from graphite. Finally, our results show that previous calculations, based on tight-binding models, significantly underestimate the experimental EPCs.

[1] S. Piscanec et al., Phys. Rev. Lett. 93, 185503 (2004)

[2] M. Lazzeri et al., to be published [3] M. Lazzeri et al., Cond-mat/0503278

## **Carbon Nano-tubes for the fabrication of high on-off ratio field-emission transistors**

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We report a novel high on-off ratio field emission transistor fabricated based on plasma enhanced CVD grown CNT's on silicon substrates. The growth starts with a deposition of 5nm Nickel layer on silicon substrate by e-beam evaporation. The growth of tubes is achieved in a DC-PECVD reactor at a temperature of 550°C and in the presence of hydrogen and acetylene in DC plasma. Prior to introduction of acetylene into the reactor, the catalyst layer is activated using H<sub>2</sub> blow for nano-island formation. The grown tubes are coated with titanium-oxide using a CVD reactor followed by depositing a metal layer. The samples are then mechanically polished to expose the tube tips and they are ashed in an RF-plasma system. In this structure the nano-tube acts as the cathode whereas the metallic layer behaves as the surrounding gate of the transistor. A second substrate is needed to act as the anode electrode and it is placed opposite to the main substrate. The emission current versus anode-cathode voltage has been examined, showing an on-off ratio of 10<sup>4</sup> with a gate voltage of 12 V applied between gate and cathode side. The physical characteristics of the tubes have been studied using SEM and TEM.

## **Metal-semiconductor transition in single-wall carbon nanotubes induced by low energy electron irradiation**

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Electronic devices were constructed from metallic singlewalled carbon nanotubes with Ti/Au contacts and Si/SiO<sub>2</sub> back-gates. The conductance showed negligible variation with gate voltage at room temperature, and metallic single-electron transistor (SET) characteristics at low temperatures (T~30K), where transport is dominated by Coulomb blockade. Conductance peaks were observed over the entire range of gate voltages, as expected from a metallic quantum dot. When such a device was exposed to a low dose (10<sup>15</sup>cm<sup>-1</sup>) of low energy (1KeV) electron irradiation, a suppression of conductance was observed at small gate voltages. The transfer characteristics resembled that of an ambipolar field effect transistor at room temperature and an ambipolar SET at low temperatures. Conductance peaks occurred at negative and positive gate voltages, separated by a conductance gap (G=0). The ON-state conductance decreased dramatically (two orders of magnitude) and the width of the conductance gap increased, as the irradiation dose was increased. This metal-semiconductor transition and band-gap modulation can be attributed to inhomogeneous electric fields generated as a result of surface charging during electron irradiation, consistent with recent theoretical predictions. Our results demonstrate the possibility of generating 1-dimensional metallic field effect transistors (1D METFETs), with the use of local modulating gates.

## Air-stable n-type single-walled carbon nanotubes with alkali-metal encapsulation performed by plasma ion irradiation

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Single-walled carbon nanotubes (SWNTs) have attracted much attention due to their outstanding electronic properties. Recent experiments have shown that alkali-metal doping converts *p*- to *n*-type conduction of semiconducting SWNTs. However, this method has the inherent problem of air-stability. For this reason, we have carried out an interdisciplinary experimental approach using plasma ion irradiation to create cesium-encapsulated SWNTs (Cs@SWNTs)[1]. Pristine and Cs-encapsulated SWNTs are sonicated for several hours in *N,N*-dimethylformamide solution and spincoated on a Si substrate with Ti or Au electrodes. Then, their electronic transport properties are pursued. Source-drain current ( $I_{DS}$ ) is measured as a function of gate bias voltage ( $V_G$ ) or source-drain bias voltage ( $V_{DS}$ ). Judging from  $I_{DS}$ - $V_G$  characteristics of Cs@SWNTs at room temperature in vacuum, it is found that Cs@SWNTs show *n*-type transport behavior, while pristine SWNTs show only *p*-type transport conductivity. This conversation of conduction type can be explained by charge transfer from Cs atoms to SWNTs. After measurements in vacuum, air-stability of Cs@SWNTs is investigated, and Cs@SWNTs-FET behaves as *n*-type semiconductor even in air though the amount of current a little bit decrease. These results signify that the encapsulation inside SWNTs by plasma ion irradiation has a potential for controlling the electronic structure of SWNTs.

[1] G.-H. Jeong et al., *Chem. Commun.* (2003) 152; *Phys. Rev. B* **68** (2003) 075410.

## **Ultrasensitive Real-time DNA Sensors Based on Carbon Nanotube Field-Effect Transistors Modified by Peptide Nucleic Acid**

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Recently, high-sensitive detections of DNA hybridization have attracted great attention to a lot of fields such as genomics, clinical diagnosis, practical pharmacy, and so forth. In this abstract, we have sensitively detected DNA hybridization using carbon nanotube field-effect transistors (CNTFETs) in real time. Amino modified peptide nucleic acid (PNA) oligonucleotides at 5' end were covalently immobilized onto the Au surface of the back gate. After target full-complementary DNA introduction with 1, 10, or 20 fmol/L at the PNA probe-modified Au back-gate surfaces, the drain current-drain current gradually increased while monitoring in real time. The increase in conductance for the p-type CNTFET device was consistent with an increase in negative surface charge density associated with binding of negatively charged oligonucleotides at the surfaces. Amount of net source-drain current between before DNA introduction and after DNA hybridization linearly increases as a function of DNA concentration. Therefore, for 11-mer PNA oligonucleotide probe, full-complementary DNA with concentration as low as 1 fmol/L solution could be effectively detected. Our CNTFET-based biochip is a promising candidate for the development of an integrated, high-throughput, multiplexed DNA biosensor for medical, forensic and environmental diagnostics.

## **Carbon Nanotube and Silicon Nanowire Biochemical Sensors\***

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Nanowire-based chemical sensors utilize a simple and effective sensing mechanism based on the change in conductance of a semiconducting nanowire (NW) as a molecule attaches to the wire or a receptor bound to the NW. Here we report on our work on nanowire chemical sensors utilizing carbon nanotubes (CNT) and silicon nanowires in field effect transistor configurations. The nanotubes are grown using Fe catalyst particles and methane CVD, resulting in SWNT spanning Mo or Ti/Au electrode gaps ranging from 100 nm to 2 microns. The Si NWs are grown by silane CVD from nanoscale Au catalysts, followed by patterning of Ti/Au electrodes. We have demonstrated both gas and liquid phase chemical sensing using unfunctionalized CNT devices. The liquid phase testing has been aimed at measurements of amino acids in water. Conductance measurements for arginine, aspartic acid, and tryptophan showed significant differences in the magnitude and sign of the conductance change for each amino acid as the concentrations were varied. We will also report on our ongoing efforts to functionalize Si/SiO<sub>2</sub> and CNT surfaces to enable chemically specific detection of biomolecules of interest, via protein receptor (enzyme/antibody) binding to the respective ligand. \*Work supported by NASA ESMD BioNano program

## Conductivity control of single-walled carbon nanotubes by electron beam exposure

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We have recently found that low-energy electron-beam exposure extinguishes the optical characteristics of single-walled carbon nanotubes (SWNTs) [1]. This suggests the possibility that electron-beam exposure can modify their electronic properties. In this work, we investigated the effect of the low-energy electron-beam exposure on the electronic characteristics of SWNTs, aiming to control their conductivity. We fabricated metal-on-tube-type SWNT-FETs using CVD-grown SWNTs. The current-voltage characteristics measured at low temperature (< 40 K) changed markedly when the SWNT channel was exposed to an electron beam even at a low exposure dose (the order of  $10^{-5}$  C/cm<sup>2</sup>). That is, the metallic SWNT-FET was changed to a semiconductive one. Furthermore, increasing the exposure dose resulted in enhanced semiconductive characteristics (increased band gap). These results indicate that the SWNT conductivity can be controlled by adjusting the exposure dose of the electron beam.

[1] S. Suzuki, K. Kanzaki, Y. Homma and S. Fukuba, Jpn. J. Appl. Phys. 43, L1118 (2004).

## **Fabricatin of Crossed Semiconducting and Metallic Nanotubes: CNT-gated CNT-FET**

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We have developed a method to fabricate crossed junctions between semiconducting and metallic carbon nanotubes combining electric field directed chemical vapour deposition growth and dielectrophoretic alignment. By using a thin insulating layer to separate the nanotubes we were able to fabricate an ultra-small field effect transistor where the current through the semiconducting nanotube was controlled by a gate voltage applied to the metallic nanotube. We also demonstrate the use of metallic nanotubes as electrical leads for nanotube devices.

## 1D-Carbon nanotubes on 2D-semiconductor

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We demonstrate an approach to growth carbon nanotubes on a semiconductor substrate based on CVD process. The semiconductor underlayer acts as a catalyst to the growth of carbon nanotubes in C<sub>2</sub>H<sub>2</sub> at 800oC as well as a basement for the hetero-junction after the growth of the carbon nanotubes. Magnetization measurement showed that the heterojunction, i. e. carbon nanotube - semiconductor, shows magnetism of semiconductor substrate in the hysteresis loop, suggesting a possibility for promising building block for spintronics. Furthermore, emission current measurement suggests a possibility for an efficient nano scale electron emitter. The results can be a first step in realizing a multi-dimensional system 1D(carbon nanotube) coupled to 2D (semiconductor, insulator, or ferroelectrics etc.) substrate, where the substrate layer will be designed to act as a catalyst.

## Chemical and optical control of self-assembled nanotube transistor performances

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Nanotube transistors operation depends critically on the nanotube-substrate and nanotube-electrodes interfaces. Consequently, surface chemistry appears as the best way to act on these nano-devices. We show how a self-assembled molecular layer can be used to direct the selective placement of individual nanotubes and modify the electrical transport properties of the devices. The first point is based on the functionalisation of the gate oxide by an aminosilane layer which allows the selective bounding of nanotubes. Most interestingly, the amine termination of this layer can be protonated or deprotonated to improve the device characteristics [1]. Moreover, the nanotube-electrodes interface brings a second target for chemical optimization of the transistors [2]. This optimization relies on the control of the Schottky barrier height at the contacts which drastically affects the efficiency of carrier injection. Combining modifications of both interfaces leads to the spectacular improvement of all the device parameters. Finally, chemistry can also be used to produce new functions. Functionalization of nanotube transistors with chromophore molecules produces phototransistors. Their characteristics are controlled by photons of adjustable wavelength (UV-visible range) set by the choice of the molecule.

[1] Auvray et al, Nanoletters 5, 451 (2005).

[2] Auvray, Borghetti et al, APL 84, 5106 (2004).

## Surface passivation of carbon nanotube field-effect transistors

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Suppression of the large hysteresis is one of the most important issues to be addressed for carbon nanotube field-effect transistors (FETs). Although some groups have reported that passivation using PMMA is effective to suppress the hysteresis [1], the long term stability and reproducibility were quite poor in our experiments. In this work, we have investigated reliable surface passivation technology. The passivation using a SiO<sub>2</sub>/PMMA double layer was effective for the long term stability. The hysteresis has not appeared for more than a month. By introducing pretreatment using H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub>, reproducible suppression of hysteresis is possible. This suggests that amorphous carbon and/or photoresist adsorbing on nanotube surface is one of the origins of hysteresis in nanotube FETs.

[1] W. Kim et al., Nano Lett. 3, 193 (2003).

## Nanomagnetism in Fe filled carbon nanotubes

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Carbon nanotubes filled with ferromagnetic materials like Fe have potential application in different fields. They can be used in magnetic recording media, in the biomedicine, or as individual filled carbon nanotube as sensors for the magnetic force microscopy, respectively. In this work we report on the correlations between structural characteristic and magnetic properties of these filled carbon nanotubes both in the as grown state and after an annealing process. By optimisation of the used thermal decomposition process of ferrocene marked hysteresis loops can be measured by using the alternating gradient method. Unusually high coercivities (up to 130mT) and strong anisotropies (in terms of the alignment of tubes on Si- substrates) with an easy axis perpendicular to the substrate plane are observed. By an annealing process at 645°C for 20h the paramagnetic Gamma-Fe and the cementite phases inside the nanotubes can be completely transformed in the ferromagnetic Alpha-Fe phase, whereas an enhanced magnetic saturation moment (up to factor 2) and a decrease in anisotropy are realised. At an annealing temperature of 675°C the nanotubes are already destroyed and the magnetic characteristics are changed dramatically (disappearance and decreasing of coercivity)

## Magnetoresistance of Disordered Carbon Nanotubes

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Localization effects, resulting from an interplay between disorder and magnetic fields in charge transport, are typically studied for systems with simple bandstructure like quantum wires or free electrons in confining potentials. CNTs, though, are known for their peculiar bandstructure, which has shown to cause some intriguing effects in combination with weak-localization in recent experiments. [1] We study the interplay of the nontrivial bandstructure with disorder and magnetic fields in single wall CNTs at realistic lengths of several 100 nm, within the Anderson model for tight binding hamiltonians. We quantify the elastic mean-free-path as well as the localization length in the full energy spectrum. Furthermore, we match the complicated magnetoconductance behavior with the bandstructure distortions caused by magnetic fields and identify the correction caused by weak localization.

[1] Bernhard Stojetz et. al., cond-mat/0410764

## **Synthesis and characterization of magnetic-metals encapsulated single-walled carbon nanotubes**

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Single-walled carbon nanotubes (SWNTs) filled with magnetic metal atoms such as Fe, Ni and Co are expected to be a fascinating new kind of materials which have great potential application in data storage, magnetic ink and nano-sensor for the magnetic force microscopy. In this work the performance of filling Fe and Ni atoms in SWNTs are first investigated through the combination of chemical method and plasma irradiation technology. Metal organic materials such as ferrocene and nickelocene are selected as the precursor for Fe and Ni atoms sources during the filling process and then the metal organic filled SWNTs are further exposed to plasma irradiation atmosphere in order to decompose metal organic materials and release Fe or Ni atoms inside SWNTs. The structure and morphology of SWNTs filled with magnetic metal atoms is confirmed using various technologies which include HRTEM, EDX, XPS, and Raman Spectrum analyses. The magnetic properties of SWNTs filled with Fe and Ni are examined by means of superconducting quantum interference device (SQUID) measurements.

## Band structure and quantum interference in multiwall carbon nanotubes

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We report on low temperature conductance measurements on multiwall carbon nanotubes in perpendicular and parallel magnetic field. An efficient gating technique allows for a considerable tuning of the nanotube doping level. This enables us to study extensively the action of nanotube bandstructure on electron quantum interference effects like weak localization, universal conductance fluctuations and the Aharonov-Bohm effect. We show that the magnetoresistance is strongly suppressed at peaks at certain gate voltages which can be linked with the bottoms of one-dimensional electronic subbands. This assignment allows a detailed comparison of theoretical calculations with the experimental data. In agreement with the theory, a pronounced energy dependence of the elastic mean free with a strong enhancement close to the charge neutrality point is observed. In large parallel magnetic field, we observe a superposition of  $h/2e$ -periodic Altshuler-Aronov-Spivak oscillations and an additional  $h/e$ -periodic contribution. The latter contribution shows a diamond-like pattern in the  $B/V_{\text{gate}}$ -plane, which reflects the magnetic field dependence of the density of states of the outermost shell of the nanotube.

**Magnetic properties of an assembly of magnetic nanoparticles encapsulated in carbon nanotubes : experimental results and Monte-Carlo calculations**

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*B.*

The next generation of materials for magnetic recording media will require the design of high density regular arrays of ferromagnetic nanoparticles. However, due to the high density, the volume of the nanoparticles and then the anisotropy barrier are extremely small. The particles are then superparamagnetic down to very low temperatures. To avoid this, the solution consists in synthesizing vertical nanoparticles [1]. A way of creating an assembly of vertical ferromagnetic nanoparticles is provided by the growth of carbon nanotubes with a plasma-enhanced catalytic CVD process. Indeed this process requires the presence of catalytic transition metal nanoparticles (Fe, Co, Ni) which are ferromagnetic. These nanoparticles stand at the top of the nanotube at the end of the synthesis, thus creating an array of nanoparticles.

We have studied the magnetic properties of Co nanoparticles vertically aligned on top of carbon nanotubes. The influence of the shape of the particles has been investigated by means of Monte-Carlo simulations [2,3]. We were able to quantify the influence of the aspect ratio in the magnetic properties of an assembly of vertically oriented nanoparticles encapsulated into carbon nanotubes. Our results show that an aspect ratio superior to 4 does not affect quantitatively the magnetic properties of the assembly of nanoparticles

## **THEORETICAL AND EXPERIMENTAL STUDIES OF CARBON NANOTUBES: A REVIEW**

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Carbon nanotubes (CNTs), discovered by Iijima, in 1991 a new era in nanoscience. These nanomaterials play important and actual role in different applications - technique, desing of devices in electronics, nanocomputers, aircraft, transistors etc. Many researchers from all the world devoted their studies on these nanomaterials , not only because their extraordinary physical, mechanical, chemical, electrical etc. properies, but also of their atomistic scale (nano) sizes. It is intersting as well, to point out the fact that the chirality nanostructure of (CNTs), contribute too of their so good applications. The aim of the paper, presented could be formulated as follows: to generalize, to analyze and to discuss recent publications on theoretical approaches and experiments of carbon nanotubes. Classical structural mechanics theories, and novel approaches as classical molecular dynamics, extended bond potentials have been presented as well. Experimental studies by tunneling electron microscopy (TEM), and scanning tunneling microscopy (STS) have been discussed. Some concluding remarks with main results for example: the paper could be used as background for development of novel modified models, based on the classical mechanics for describing of mechanical behavior of (CNTs), comparison between theory and experiments have been given too.

## Sorting carbon nanotubes via dielectrophoresis

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Whenever the electronic properties of carbon nanotubes matter, it is beneficial to use single-walled carbon nanotubes, which have been sorted by their metallicity. Dielectrophoresis at high electrical-field frequency allows to sort out the metallic tubes from a mixed suspension [1]. The theoretical modelling of the process predicts the yield of separation to be intrinsically at 100% [2,3]. Experimentally this yield is affected by the residual bundle content of the nanotube suspension, the electrical-field frequency and the surfactant content.

We will present the optimum conditions for separation. Due to our recent progress in upscaling the method, we are now able to base our analysis on optical absorption spectroscopy in addition to resonant Raman spectroscopy.

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## Atomic scale modelization of the nucleation of C-SWNT towards atomic scale modelization

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The formation of single-wall carbon nanotubes requires the presence of a metal catalyst whatever the technique used. To understand their growth mechanism, we have initiated a theoretical study in order to simulate the segregation and the self-organisation of the carbon atoms at the surface of metallic nanoparticles. We have developed a semi-empirical model based on the tight-binding method to describe binary systems. A minimal basis is used to obtain a transferable tight-binding parametrization of the C-C, Ni-Ni and Ni-C interactions applicable to binary systems. Using this model, we have investigated the first stage stages of the nucleation process using Monte Carlo simulations in the grand canonical ensemble and demonstrated the role played by the metal in the dissolution-segregation process of carbon atoms. We have also studied the effect of carbon atoms on the structural and catalytic properties of (100) and (111) metallic surfaces. These studies show different behaviours of the surface as a function of the carbon coverage.

## An alternate mathematical model for single-wall carbon nanotubes

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The usual description of atomic positions of the atoms forming a carbon nanotube is based on the high symmetry of these tubes. Each chiral nanotube is a single orbit of its symmetry group  $G = \{ (C_q^r / na/q)^t C_n^s U^u \mid t=0,1,-1,2,-2,\dots, s=0,1,\dots,n-1, u=0,1 \}$  with trivial stabilizer. There is a one-to-one correspondence between the set of all the atoms of the nanotube and the set  $S = \mathbf{Z} \times \{0,1,\dots,n-1\} \times \{0,1\}$ , where  $\mathbf{Z} = \{\dots,-2,-1,0,1,2,\dots\}$  is the set of all integers. The use of  $S$  as a mathematical model offers some advantages, but the description of nearest neighbours of an atom is rather complicated and the scalar product has an unusual expression.

Our aim is to present an alternate rather different description which can be more advantageous in certain cases. Let  $\mathbf{e}_0 = (1,0)$ ,  $\mathbf{e}_1 = (\cos 2\pi/3, \sin 2\pi/3)$ ,  $\mathbf{e}_2 = (\cos 4\pi/3, \sin 4\pi/3)$ . The points  $x_0\mathbf{e}_0 + x_1\mathbf{e}_1 + x_2\mathbf{e}_2$  corresponding to all the elements of the subset  $L = \{ (x_0, x_1, x_2) \mid x_0 + x_1 + x_2 = 0, 1 \}$  of  $\mathbf{Z}^3$  are distinct and form a honeycomb lattice. This allows us to use the set  $L$  as a mathematical model for honeycomb lattice. In this description the nearest neighbours of  $x = (x_0, x_1, x_2)$  are  $(x_0 + s(x), x_1, x_2)$ ,  $(x_0, x_1 + s(x), x_2)$  and  $(x_0, x_1, x_2 + s(x))$ , where  $s(x) = (-1)^{x_0 + x_1 + x_2}$ . The symmetry transformations and the geometric invariants have a very simple form. The subset  $T = \{ (x_0, x_1, x_2) \mid x_0 + x_1 + x_2 = 0 \}$  of  $L$  corresponds to the translation subgroup of  $G$ .

By starting from a fixed element  $c$  of  $T$  we define in  $L$  the following equivalence relation:  $x \sim y$  if  $x - y$  is an integer multiple of  $c$ . The coset  $[x] = \{ y \mid y \sim x \}$  corresponding to  $x$  is  $[x] = x + \mathbf{Z}c$ . We use the factor space  $L = L / \sim$  formed by all the cosets  $[x]$  as a mathematical model for the carbon nanotube with the chiral vector  $c$ . There is a one-to-one correspondence between the set of all the atoms of the nanotube and the set  $L$ . Each rational number is a class of equivalent fractions, called its representatives. In computation, the rational numbers are replaced by representatives but the result does not depend on the representatives we choose. In a very similar way, in our approach [ <http://xxx.lanl.gov>; , math-ph/0403011 ] each atom of the nanotube corresponds to a coset  $[x]$  and in computation we use representatives of these cosets. A mathematical object defined on  $L$  can have geometric or physical meaning only if it is independent on the representatives we choose. In our approach the scalar product has the usual form, and generally, *the equations and dispersion relations occurring in the usual theories become simpler and more symmetric*

[ <http://fpcm5.fizica.unibuc.ro/~ncotfas>; ].

## **Direct structuring of single-walled carbon nanotube (SWNT) free standing thin films using e-beam and focused ion-beam (FIB).**

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The desire for the creation of novel nanoscale materials and devices has led to the developing field of nanolithography and the need to fabricate nanoscale materials and devices for nanoscale applications requires nanolithographic methods. However, manipulating matter at the nanometre scale requires reproducible dimensional control at the nanometre scale. Single walled carbon nanotubes (SWNTs) can be reliably fabricated into free-standing films less than 200nm thick [1]. Recently these thin film have been used to fabricate electronic devices [2]. The interest to fabricate nanoscale devices for nanotechnological applications has led to a variety of nanolithographic techniques. However, most of these rely on an intermediate step. Here we report on two direct structuring of SWNT thin films which have reproducible dimensional control at the nanometre scale. Free standing SWNT thin films were structured by means of e-beam from a scanning electron microscope and by means of a FIB. The results were examined by SEM and TEM.

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## **A theoretical study of curvature effects in defective nanotubes**

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Defects have a profound impact on the properties of materials. It was recently shown that nanoporous carbon materials might be active as catalysts for oxidative dehydrogenation reactions although perfect graphite is more or less inert. We have therefore studied how defects change the properties of a graphene sheet and furthermore how these effects are influenced by the curvature in nanotubes (CNT). Our Density Functional Theory calculations show that defects lead to motifs, which are combinations of non-hexagonal rings. These motifs occur due to rebonding of undercoordinated atoms at the defects. The curvature in the CNTs facilitates the rebonding and relaxation such that the formation energy for defects is lower in CNTs compared to graphene. The curvature also introduces a preferred orientation, which aligns the defects with respect to the tube axis. The presence of the defects perturbs the  $\pi$ -band such that a defect state appears close to the Fermi level. The chirality influences the character of the state and its energy depends on the curvature. This defect state leads to an increased density of states at the Fermi level and we therefore connect these defect motifs with the chemical activity of nanoporous carbon materials.

## **STRUCTURAL INVESTIGATION OF NANOTUBE CARPETS AND FIBERS AT THE MICROMETER SCALE USING SYNCHROTRON MICROFOCUS X-RAY DIFFRACTION**

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X-ray scattering experiments performed on iron containing nanotube carpets [1] and nanotube fibers [2] gave access to structural parameters such as the nanotube alignment in both materials, or the nature and orientation of iron-based nanoparticles and nanowires in carpets. These parameters are averaged over the X-ray beam size, the diameter of which usually ranges between 0.1 and 1mm. For X-ray microdiffraction, beam diameter is about 1  $\mu\text{m}$ . It allowed us to perform local analysis of carpets from their basis to their top, and of fibers from their skin to their core. For nanotube carpets, new results concerning the nature of catalytic particles at the nanotube root will be presented. The dependence of nanotube alignment with synthesis procedure will also be shown. For nanotube fibers, the average nanotube alignment was found to be a relevant parameter for improving their mechanical and electrical properties [3,4]. Local alignment, across the fiber diameter, will be discussed on the basis of our X-ray microdiffraction experiments.

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## Influence of monoatomic steps of nickel during the nucleation of C-SWNTs

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The growth of single-wall carbon nanotubes differs from that of multishell tubes insofar as catalysts (Fe, Co, Ni,.) are necessary for their formation. Recent in situ studies have been developed to analyse the formation of carbon nanofibres from methane decomposition over supported nickel nanocrystals [1]. The high-resolution TEM images reveal that monoatomic steps are present at the Ni surface and that a graphene sheet terminates at each of these steps. To understand the origin of this process, we have performed calculations at atomic level. We have developed a semi-empirical model based on tight binding method to describe binary systems such as nickel-carbon systems. Using this model, we have investigated the key role played by the monoatomic steps during the nucleation process using Monte Carlo simulations in the grand canonical ensemble and demonstrated that metallic step edges act as growth centres for graphene growth. We have also analysed the carbon binding energy to the nickel step with energy total calculations.

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## Ion irradiation induced B/N implantation onto carbon nanotubes

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Boron and nitrogen doping of carbon nanotubes can be used to achieve more control over the electronic properties of nanotubes, and, due to impurity-stimulated cross-linking of nanotubes, even over the mechanical properties. As an alternate to the conventional chemical methods of doping, we study ion irradiation induced boron and nitrogen implantation onto carbon nanotubes. We use atomistic computer simulations with an analytical potential and density functional theory force models to simulate impacts of the ions and to calculate the characteristics of the most abundant defects which appear under irradiation.

We show that up to 40% of the impinging impurity ions can directly occupy the  $sp^2$  positions in the nanotube atomic network. We also determine the optimum irradiation energy for the efficient  $sp^2$  substitution. As annealing could further increase the number of  $sp^2$  impurities due to dopant atom migration and annihilation of vacancies, we also study the migration of impurity atoms over the tube surface.

Our results indicate that ion irradiation is a promising way to introduce B/N impurities in carbon nanotubes and thus control the properties of carbon nanotubes in a controllable manner and at low temperatures.

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## The Adsorption of Hazardous Organic Compounds onto Carbon Nanotubes Synthesized by Thermal Pyrolysis

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Carbon nanotubes (CNTs) have structures that surface area is large like porous nanomaterials. For this reason, CNTs have attracted a great interest in materials of pollutants adsorption and energy storage. Recently, it was reported that dioxin, which is an environmental pollutant, is well adsorbed onto CNTs compared with activated carbon [1]. In this work, volatile organic compounds adsorption, exemplified by benzenes and methylethylketon, onto CNTs is demonstrated. For the analysis of adsorption characteristics, CNTs were prepared by the thermal pyrolysis method, using a solution of catalytic metal particles and ethanol or organic solvent such as xylene. XRD (X-Ray Diffraction), HRTEM (High Resolution Transmission Electron Microscope), FE-SEM (Field Emission Scanning Electron Microscope) and Raman spectroscopy were used for the characterization of synthesized CNTs. HRTEM images and Raman scattering indicated that the CNTs were clearly multi wall structures. Adsorption and desorption characteristics onto the CNTs were measured by BET (Brunauer-Emmett-Teller), TGA (Thermal Gravimetric Analysis) and TPD (Temperature Programmed Desorption). Also, two different activated carbons, which are common adsorbent for the treatment of hazardous pollutants, and commercial CNTs were used for the comparison with the result obtained from the prepared CNTs.

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## Location Control of the Growth of Carbon Nanotubes using Focused Ion Beam Selective Milling

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One of the most interesting properties of carbon nanotubes grown by the floating-catalyst method of ferrocene is their selective growth on oxide substrates, which was for example successfully used to locate the growth of carbon nanotubes by patterning SiO<sub>2</sub> domains on Si substrates [1]. Here we report on the growth location control of carbon nanotubes by focused ion beam (FIB) selective milling of SiO<sub>2</sub> on silicon substrates. By this technique a variety of carbon nanotubes structures, including on 3D surfaces, are constructed, without the need for a template or chemical etching of SiO<sub>2</sub> as in standard photolithography techniques.

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## **Novel actuator with single-wall carbon nanotubes as actuating material**

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Single-wall carbon nanotubes (SWCNTs) possess electromechanical properties that have been simulated and demonstrated. These properties can be utilised for the development of novel actuators with high efficiency. If electrical charges are injected into a SWCNT located in an electrolyte the length of the covalent bonds of a mechanically unstressed tube changes. The resulting strain can amount to over 1 %. Considering a tube with a typical length of about 10  $\mu\text{m}$  this effect would result in a change of length of approximately 100 nm or a force of about 5 nN. For technical applications however this is by far not sufficient.

Therefore a concept of a novel actuator will be presented. A version of this actuator (length 4 mm, width 5 mm, thickness 1 mm) will perform changes of length of more than 10 micrometers or forces of several 10 N. The core of this concept is a microsystem with about  $10^{13}$  aligned SWCNTs that are electrically and mechanically connected. An electromechanical model for SWCNTs describing these properties will also be presented. For the realisation of this new type of actuator a novel fabrication process with industrial potential is under development.

## **Production and investigation of composition, structure and properties of fullerene-like structures' metal derivatives**

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Synthesis of new metalloderivative fullerene-like structures such as metal-filled nanotubes, exo- and endometal C<sub>60</sub> derivatives is a purpose of the work. Our purpose is also to investigate their composition, structure and properties. Physical installations (lithium implanter for Li@C<sub>60</sub> synthesis, installation for catalytic nanotubes synthesis) and techniques of chemical synthesis are developed for synthesis of metal-filled fullerenes and nanotubes. Optimal parameters of compounds synthesis are determined. Germanium- and iron-containing nanotubes exo- and endo-metallocplexes of fullerene C<sub>60</sub> with alkaline and transitional metals are synthesized. Composition, structure and properties of synthesized combines were investigated by the methods of mass spectrometry, electronic paramagnetic resonance, nuclear magnetic resonance, X-ray fluorescence and X-ray structure analyses, spectroscopy of Raman scattering, electron spectroscopy, raster Auger microscopy and Mossbauer spectroscopy and thermoanalysis. Assumptions were made of ways of received compounds formation. Possible fields of the results application were determined. They are: micro- and nanoelectronics, magnetic materials, materials for hydrogen storage, components for creation of new polymer composites, materials for lithium ionic accumulators. This work was supported by the ISTC project No.2511 and Programs of RAS.

## Molecular Dynamic Simulations of Single-Wall Carbon Nanotube CVD Growth

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A modified Brenner type, Morse potential is implemented [1] for the GROMOS biomolecular simulation package [2]. Using the modified simulation package, growth of single-wall carbon nanotubes, as a function of the local catalyst environment in a methane chemical vapour deposition process, is investigated. Modeling of unrestricted and channel restricted growth of nanotubes using catalysts of various sizes and compositions at different temperatures is presented.

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## **In situ characterization of field emission from individual carbon nanotubes in the scanning electron microscopy**

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The field emission properties of individual carbon nanotubes (CNTs) have been investigated in the field emission-scanning electron microscopy. The measured field emission of bended nanotubes (BNTs) showed both Fowler-Nordheim (FN) and non-Fowler-Nordheim behaviors. Under an applied electric field, BNTs are straightened to align themselves along the electric field line. As the electric field increases, the electron emission was started after fully straightening toward the anode electrode and BNTs showed the FN behavior. However, some BNTs showed that the field emission was occurred during their geometrical straightening to parallel the electric field line, showing the Non-FN behavior. In addition, the field emission of as-straightened CNTs (including MWNT, DWNT, and SWNT) successfully followed conventional FN theory with a single linear slope in the F-N plots below their limitation current levels corresponding to the saturation region of emission current. The results indicate that an increase in field enhancement factor of BNTs by their field-induced straightening during field emission is a plausible mechanism for the non-FN behavior in the field emission of CNTs.

## Gas Phase Electrophoresis of Carbon Nanotubes grown in Low Pressure CVD process.

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Present work is devoted to experimental study of carbon nanotubes motion under external electric field applied directly inside low pressure CVD reactor. Gas phase catalytic decomposition of carbon-containing molecules is most promising method for large-scale carbon nanotubes production. Products of this CVD contain a mixture of SWNTs, MWNTs, encapsulated particles and amorphous carbon. Separation of species is important problem. One of the possible solutions is in situ separation using different electron affinity, ionization potential and mobility of species. Main part of presented setup is stainless steel tubes heated to 1100 K, which is connected to gas supply upstream and filter downstream. Electric field may be applied between the grounded tube and additional axial electrode. Three regimes were explored - "thermal CVD" without field, "PECVD" with field higher than breakdown value, and "electro trapped CVD" with intermediate field. Experiments were made in flow of C<sub>2</sub>H<sub>2</sub>/Ar /H<sub>2</sub> mixture with a small impurity of Fe(CO)<sub>5</sub> injected for catalytic iron clusters creation. We have analyzed nanostructured carbon deposit on both electrodes and outlet filter with TEM and SEM microscopy. Most significant result concerns the trapping of CNTs by relatively small electric field in intermediate case. Estimations of CNTs mobility and specific charge are performed.

## **Synthesis of silicon carbide nanomaterials using multi-walled carbon nanotubes as templates**

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In this work, we have studied the growth of silicon carbide nanomaterials SiC nanowires (SiCNWs) and SiC nanotubes (SiCNTs) via reaction of highly dispersed silicon powder with multi-walled carbon nanotubes (MWCNTs) as templates. MWCNTs were obtained by thermal CVD-method from mixture of ferrocene and toluene under Ar flow at atmosphere pressure. The MWCNTs growth temperature was 1123K. The pyrolysis of the ferrocene/toluene mixture at 1123K results in large-scale well-aligned structure of MWCNTs in the diameter ranges 15-120 nm and length is about 1.5-2.0 mm. The thermally expended (exfoliated) graphite was used as a heater because this material feebly interacts with silicon under this condition. The heater had a form of boat. Typically, the experiments were carried out in a boat containing MWCNTs covered with Si powder at temperature region at 2000-2200K under argon flow at atmosphere pressure. The reaction mechanism, structure and morphology of these SiC nanomaterials are discussed. Characterization of the MWCNTs, SiCNWs and SiCNTs was performed by X-ray powder diffraction (PXRD) analysis, high-resolution transmission electron microscopy (HRTEM) and scanning electron microscopy (SEM). This work supported by the Programs of RAS and ISTC (project No. 2511).

## NMR INVESTIGATIONS ON ALKALI INTERCALATED CARBON NANOTUBES

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Single-wall carbon nanotubes (SWNT) exhibit outstanding electronic properties that promise to open up wide opportunities for nanoscale applications. Intercalation of SWNT bundles with various alkali metals is expected to modify the electronic band structure and to shift up the Fermi level. Therefore it is possible to tune and control the electronic properties of these novel carbon materials via alkali metal intercalation. We report results from  $^{13}\text{C}$ - and alkali-NMR measurements on alkali intercalated SWNT. Li and Cs were reversibly intercalated in SWNT. By performing temperature dependent  $^{13}\text{C}$ -NMR measurements, the density of states at the Fermi level  $N(E_F)$  is determined. We demonstrate that upon intercalation a pure metallic nanotube system can be obtained. In a second step temperature dependent alkali-NMR was performed. Inequivalent alkali sites are evidenced, leading to preferential sites of intercalation and alkali-carbon hybridization.

## Electrostatics of individual SWNTs investigated by EFM

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Due to their unique geometry, carbon nanotubes are often looked as molecular wires and some of their remarkable transport and field emission properties are indeed related to their shape. Although the previous properties have been extensively studied, comprehensive study of the electrostatic (i.e. static charge distribution) in individual carbon nanotube has been seldom reported [1]. We report experimental study of static charge distribution in individual Single-Walled Carbon Nanotubes (SWNTs) grown on Si + 115 nm SiO<sub>2</sub> substrate [2]. We describe local electrostatic experiments on individual SWNTs by Electrostatic Force Microscopy (EFM) in dry nitrogen atmosphere. We demonstrate that EFM can accurately measure the amount of charges per unit length. We show that excess charges are fully delocalized along all the studied nanotubes and that classical electrostatics approach describes accurately all the observed effects. Upon imaging and locally charging SWNTs by EFM, we address issues like system capacity, charge per unit length, and diameter dependence of charge.

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## **Complement activation and protein adsorption by carbon nanotubes**

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As a first step to validate the use of carbon nanotubes as novel vaccine or drug delivery devices, their interaction with a part of the human immune system, complement, has been explored. Haemolytic assays were conducted to investigate the activation of the human serum complement system via the classical and alternative pathways. Western Blot and SDS-PAGE (Sodium dodecyl sulphate-polyacrylamide gel electrophoresis) techniques were used to elucidate the mechanism of activation of complement via the classical pathway, and to analyse the interaction of complement and other plasma proteins with carbon nanotubes. We report for the first time that carbon nanotubes activate human complement via both classical and alternative pathways. We conclude that complement activation by nanotubes is consistent with reported adjuvant effects, and might also in various circumstances promote damaging effects of excessive complement activation, such as inflammation and granuloma formation. C1q binds directly to carbon nanotubes. Protein binding to carbon nanotubes is highly selective, since out of the many different proteins in plasma, very few bind to the carbon nanotubes. Fibrinogen and apolipoproteins (AI, AIV, CIII) were the proteins that bound to carbon nanotubes in greatest quantity.

## SWNT Fluorescence Spectrum Changes Induced by Light-Assisted Oxidation

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We have previously shown that the oxidation of single-wall carbon nanotubes (SWNTs) can be significantly accelerated by light irradiation [1]. However, evidence regarding the selective oxidation of SWNTs remained obscure because SWNTs aggregate and form bundles (the bundle-effect). Here, we report on changes in the fluorescence spectrum of individual single-wall carbon nanotubes (SWNTs) caused by light-assisted treatment. Well dispersed HiPco SWNTs in a surfactant solution of NaDDBS were mixed with  $H_2O_2$  (we refer to this as the SWNTs- $H_2O_2$  solution) and treated with/without light irradiation. The fluorescence spectra of the SWNTs- $H_2O_2$  solution after treatment with light (whose wavelength was 600-700 nm or 400-500 nm) showed that the intensities of some emission peaks were greatly reduced and some others decreased slightly; in contrast, the spectra of SWNTs- $H_2O_2$  without light irradiation remained almost unchanged. Moreover, we found that the PH level of the SWNTs- $H_2O_2$  solution decreased as the treatment time increased. However, the spectra peaks that decreased after light-assisted treatment could not be recovered when the PH level was restored to the same level as before light treatment. The observed effect was therefore different from the PH effect on the spectra of SWNTs, indicating that the SWNTs were destroyed or removed by the light-assisted oxidation treatment. These results provide evidence that light irradiation accelerates the structural changes of SWNTs in water-NaDDBS- $H_2O_2$  with SWNT-structure selectivity.

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## LCVD of Carbon Nanotubes, Catalytically Grown on Iron-Based Nanostructures Prepared by Laser Pyrolysis

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Iron based nanostructures, such as core-shell iron-carbon and iron-iron oxide nanoparticles were synthesized by the laser pyrolysis technique [1]. The Fe-based nanocomposite structures were obtained in a flow reactor. They could present interesting features for the catalysis of carbon nanotubes (CNTs) like low particle sizes (2-7 nm), sharp diameter distributions, homogeneous dispersion and chemical stability. Particularly the exterior carbon coating, besides the role of protection and confinement could potentially create carbon nuclei for the initiation of carbon nanotubes growth [2]. We report on the formation and growth of CNTs by laser-induced CVD (LCVD) [3] using low concentration of Fe-C nanocomposites dispersions as supported catalysts on cleaned silicon substrates.. The morphologies of the obtained deposits were examined by SEM, TEM, HRTEM and AFM analytical techniques.

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## Low energy instabilities of small-radius zig-zag nanotubes

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We study the electronic properties of the small-radius zig-zag nanotubes by looking for instabilities in the Luttinger liquid description of the correlated electron system. Ab initio calculations [1][2] show that (5,0) and (6,0) zig-zag nanotubes are metallic due to the large curvature, with three sub-bands crossing the Fermi level. On the top of this scheme, we incorporate the effects of electronic correlations by analyzing the low-energy scaling behaviour of the interactions in the different channels [3]. The phase diagram is investigated by taking into account the competition between the Coulomb repulsion and the phonon-mediated e-e interaction. A charge-density-wave instability is found over a large region of the phase diagram at different doping levels, consistently with the Peierls instability obtained by some authors [2][4]. It is for exceptionally large screening effects from the environment that the superconducting correlations are enhanced in the electron system, though a superconducting instability could be only triggered for very large values of the electron-phonon couplings, which seem to be beyond reasonable expectations in the small-radius zig-zag nanotubes.

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## Photoemission of insulator-coated carbon nanotubes

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Photoelectron emission is investigated for insulator-coated carbon nanotubes. Two layers are coated on the carbon nanotubes. High photoemissive materials, such as TiO<sub>2</sub> or alkali-halide, are used for the outer layer, while high electron amplification materials, such as MgO, through electron avalanche by the high local electric field around nanotubes are used for the inner layer. A semiempirical theoretical model is suggested based on the relation between photon's penetration depth and electron's escape length. By carefully adjusting the thickness of the two coating layers, the structure for high photoemission is suggested. And finally, the recent experimental data is analyzed by this model.

## Local Modification and Characterization of the Electronic Structure of Carbon Nanotubes

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The work of my Ph.D. aims at the investigation of the structural and electronic modification of carbon nanotubes (CNT) by atomic defects. The main tool for this investigation is the low-temperature scanning tunneling microscope (LT-STM 4K). Whereas the 1D electronic properties of perfect SWCNT are dependent on chirality and diameter only, defects can considerably alter locally these properties on the nanometer scale. For example, defects acting as tunneling barriers on the SWCNT could offer the possibility to create "quantum dots with leads" when only a small section of a metallic SWCNT is decoupled from the rest of the tube by two such defects. The role of hydrogen-ion induced modifications will be investigated with particular care as the local change from the usual  $sp^2$ -bonding configuration to the  $sp^3$ -configuration upon hydrogen chemisorption at a carbon atom will drastically change the electronic configuration due to conversion of p-states to  $\sigma$ -states. A further part of the project consists in understanding the physical nature of the observed electronic modifications using theoretical models and calculations. At this point we are able to place CNT on Au(111) surfaces with controlled CNT density and also to assign the measured individual SWCNT with STM/STS methods using electronic structure data obtained by optical spectroscopy from the literature. We are currently investigating the creation of hydrogen-ion induced defects on HOPG (control of density) and its electronic effects (spectroscopy), this work will be extended to SWCNT soon.

## Determination of Nanotube Density by Gradient Sedimentation

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Density gradient centrifugation is a high resolution technique for the separation and characterization of large molecules and stable complexes. Densities can be resolved to better than 0.001 g/cm<sup>3</sup>. We have analyzed various nanotube structures and complexes of these with biomolecules by preparative centrifugation in sodium metatungstate-water solutions. Bundled single-wall nanotubes, multi-wall nanotubes and acid solubilized single-wall nanotubes formed sharp bands at well defined densities. Our preliminary data suggests a density of ~1.8 and 2.1 g/cm<sup>3</sup> for bundled SWNTs and MWNTs, respectively. The structure of the material in each band was confirmed by transmission electron microscopy. The densities obtained have been compared with calculated densities for these structures. For complexes of single-wall nanotubes with various biomolecules (amino acid mixtures, proteins and RNA) the densities were found to spread over a broad range, probably because there are different degrees of association resulting in different amounts of biomolecule bound per unit length of nanotube.

## Electrical Resistance and Contact Properties of Carbon Nanotube Coated Surfaces

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Although ballistic conductance has been demonstrated along individual CNTs, quantum limits dictate that the contact resistance between a single nanotube and a metal contact can be no lower than a few kOhms [1,2]. Ideally, this resistance can be lowered at a macroscopic level by using millions of nanotubes in a parallel contact. We are aiming to understand the contact properties of nanotube-nanotube interfaces as well as nanotube-metal interfaces for industrial applications such as microrelays. We have designed samples and experiments to measure the sheet resistance of SWNT and MWNT films, the contact resistance between two CNT-coated surfaces, and the contact resistance of CNT/metal interfaces. CNTs are grown on silicon wafer substrates from an Al<sub>2</sub>O<sub>3</sub>/Fe/Mo thin-film catalyst deposited by electron beam evaporation [3]. Samples with different patterns of the CNT film and Au are tested in 4-point and Kelvin configurations. After annealing the samples in high-purity Ar, the contact resistance between two CNT films decreases for annealing temperatures at and below 300 °C, but increases drastically at temperatures above 300 °C. This increase is likely caused by oxidation of the CNT surfaces. The sheet resistance is not affected by annealing at these temperatures. We also observe that the contact resistance between two CNT films decreases significantly as the samples are pressed together. Upon oscillation of the load from a light to a firm preload, the resistance oscillates and reaches a "steady-state" resistance after a few cycles.

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## Cross sectional studies of iron filled carbon nanotubes

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Recent transmission electron microscope (TEM)- scanning tunneling microscope (STM) studies have shown that the iron in iron filled carbon nanotubes can be transported by electromigration [1]. The velocity and direction of the motion can be controlled by the magnitude and direction of the electron flow. A threshold current density,  $7 \times 10^6$  A/cm<sup>2</sup>, for electromigration was observed. The corresponding force was estimated to be of the order of 1 pN per iron atom. The necessary force can be expected to depend on the structure of the interface between the nanotube and the iron filling. In the TEM-STM holder the long axes of the nanotubes are perpendicular to the electron beam and the electrons are traveling through both the tube and the iron filling. In order to further study the details of the interface between the tube and the filling it is necessary to prepare cross sections of the carbon nanotube. A method to prepare thin cross section TEM specimens has been developed. Results on the structure of the carbon layers in the tubes, the iron filling and the interfaces will be discussed.

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## Fractal Analysis of Carbon Nanotubes by Means of Electrochemical Methods

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Fractal geometry is a powerful tool for study of complicated structures. This is of particular interest for nanostructures, as appropriate geometrical models are useful to understand complicated structures. A simple and powerful technique for fractal analysis of surfaces is to use electrochemical methods. This just needs simple electrochemical measurements without deep electrochemical analysis. Recent generalizations [1-4] indicate the domain of validity of these methods for fractal analysis. By simple attachment of carbon nanotubes to an electrode surface, it is possible to inspect its fractal structure. Such fractal analysis corresponds to surface structure of the carbon nanotubes film, not its bulk structure. This analysis is of particular interest, as it is sometimes needed to inspect surface structure of carbon nanotubes attached to a surface. The results were compared with those obtained from non-electrochemical techniques. In general, electrochemical techniques are reliable and simple methods for fast fractal analysis of carbon nanotubes, and can be easily performed by non-specialists. Fractal dimension as a quantitative measure is a useful tool for comparative study of different cases.

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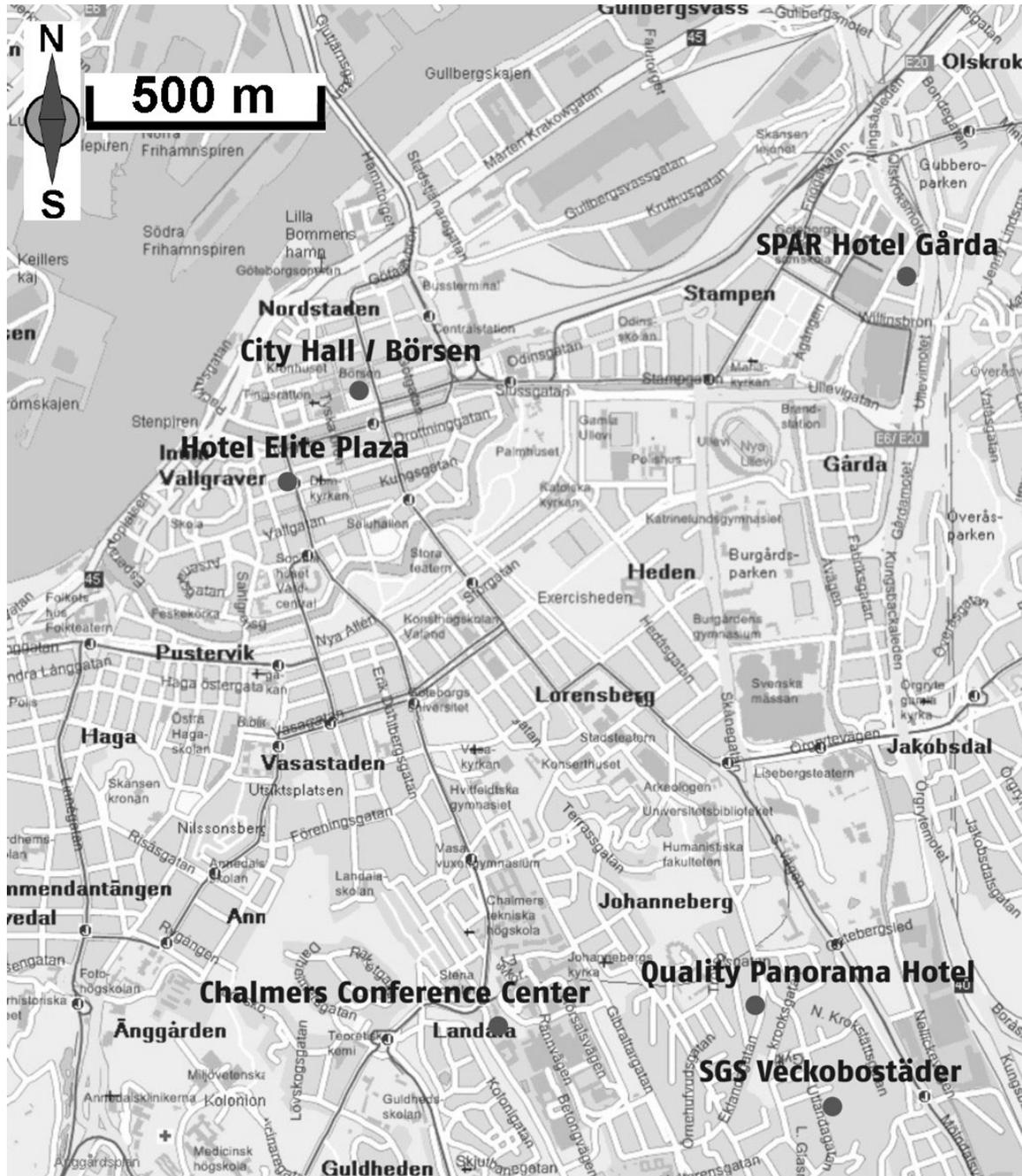
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## Map of Göteborg showing sites of NT'05 activities



## Important telephone numbers

Emergencies: 112

Landvetter airport: 941100

Conference center: 772 3950

**Hotels** (changes in bookings should be done via Inspiro)

Elite Plaza Hotel: 720 40 00

Quality Panorama Hotel: 767 70 55

Spar Hotel Gårda: 752 03 00

### **Student rooms**

SGS Veckobostäder: 7081330

### **Youth Hostels**

Göteborgs Mini-Hotel: 241023

Göteborgs Vandrarhem: 401050

Slottskogens Vandrarhem: 426520

Stigbergslidens Vandrarhem: 241620

Masthuggsterrassens Vandrarhem: 424820

Barken Viking: 63 58 00