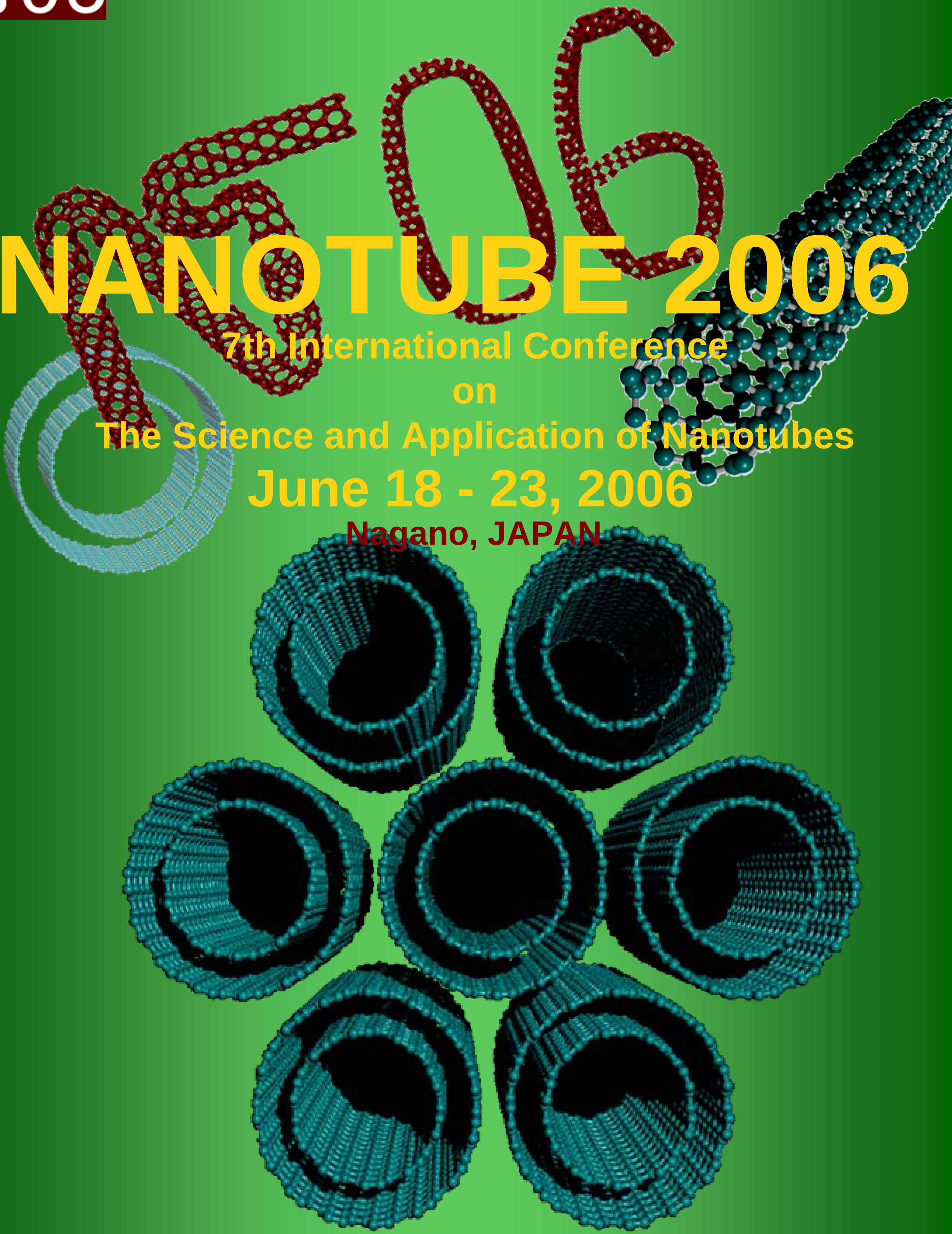
NANOTUBE 2006

7th International Conference
on
The Science and Application of Nanotubes

June 18 - 23, 2006

Nagano, JAPAN



History of the Nanotube Conference Series

Since their conception in 1999, the Nanotube 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 increased gradually, reaching 430 at NT'05 on Göteborg.

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. The NT'05 conference has been brought back to Europe, and NT'06 will take place in Japan.

Common to all conferences is a venue located close to a strong center of Nanotube research activity, and a local organization team active in Nanotube research. Contributions, presented in oral "Poster+" and Poster sessions, 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. Many of these desirable commonalities have been captured in the "Charta of the Nanotube Conference Series (see http://nanotube.msu.edu/nt06/nt-charta.html)".

Previous NT Conferences

NT99	NT01	NT02
East Lansing, USA	Potsdam, Germany	Boston College, USA
NT'03	NT04	NT05
Seoul National University, Korea	San Luis Potosi, Mexico	Göteborg, Sweden

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Charta of the Nanotube (NT) Conference Series

1. **Purpose.**

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

2. **Target attendance.**

2.1 NT conferences are open to all interested and active in nanotube research.

2.2 The number of attendees may be limited to maintain the informal spirit of communication. Young researchers are treated with higher priority.

3. **Format.**

3.1 The organizers will assist in maximizing opportunities for sharing knowledge in an informal atmosphere.

3.2 NT conferences are held in one single plenary session. Parallel sessions are to be avoided.

3.3 Presentations of problems and needs is encouraged as much as presentation of solutions.

3.4 Contributions play a key role at NT conferences. At least half the conference time shall be devoted to contributed presentations.

4. **Contributed presentations.**

4.1 To provide maximum exposure to contributed results, contributors are invited to summarize their findings in a Poster format. The main purpose of Poster presentations is to facilitate asynchronous scientific discussions related to each specific contribution.

4.2 The organizers secure adequate time and space for poster sessions. Creative ways to enhance communications, including refreshments, are encouraged.

4.3 Poster+ sessions, consisting of brief 2 minute/2 viewgraph summaries of contributions, may precede Poster sessions, to enhance the exchange of information in a balanced manner. All contributors are encouraged to expose their findings to everyone in this way if Poster+ sessions are offered.

4.4 At large conferences, Poster+ presentations may be substituted by a brief overview of the topic of a focussed poster session, presented by an expert in the field at the beginning of the session. Referring to specific contributions in the session, the Poster Chair should summarize the major progress, the major obstacles, and desirable future directions in the field. Ideally, this should occur in a democratic manner, representing all/most contributions. All contributors are encouraged to communicate their findings to their assigned Poster Chair for presentation well ahead of the conference.

5. **Invited presentations.**

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

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

6. **Venue.**

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

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

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

7. **Financial matters.**

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

8. **Miscellaneous.**

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

NT'06 Conference Schedule (18-23 June 2006)

Date / Time	June 18 (Sun.)		June 19 (Mon.)	June 20 (Tue.)	June 21 (Wed.)	June 22 (Thu.)	June 23 (Fri.)
08:30-09:00			Opening Ceremony Announcements	8:45 Announcements	8:45 Announcements	8:45 Announcements	8:45 Announcements
09:00-09:45			Keynote lecture 1: H. Shinohara	Keynote lecture 2: K. Suenaga	Keynote lecture 3: P.C. Eklund	Keynote lecture 4: P. Kim	Keynote lecture 5: P. Avouris
09:45-10:15	Nanotube Tutorial I (10:00-12:30)		Invited talk 1: K. Hata	Invited talk 4: A. Hartschuh	Invited talk 7: M. Strano	Invited talk 10: C. Schönenberger	Invited talk 13: T. Ando
10:15-10:40			Introduction to posters A: A. Windle	Introduction to posters C: S. Arepalli	Coffee break (30 min.)	Introduction to posters E: J. Fischer	Introduction to posters G: M.S. Dresselhaus
10:40-12:30			Poster session A (with coffee)	Poster session C (with coffee)	Intro to Bio-Impact: M. Takemura Invited talk 8: V. Castranova Invited talk 9: A. Bianco	Poster session E (with coffee)	Poster session G (with coffee)
12:30-14:00	Lunch (90 min.)	CCTN'06 Satellite Symposium (12:50-18:00)	Lunch (90 min.)	Lunch (90 min.)	Excursion (12:35-18:00)	Lunch (90 min.)	Lunch (90 min.)
14:00-14:30	Nanotube Tutorial II (14:00-17:00)		Invited talk 2: E. Joselevich	Invited talk 5: R. Capaz	Lunch (60 min.)	Invited talk 11: E. Campbell	Contributed talk 7
14:30-15:00			Invited talk 3: Y. Nakayama	Invited talk 6: A. Jorio	Excursion (12:35-18:00)	Invited talk 12: K. Atkinson	Contributed talk 8
15:00-15:30			Contributed talk 1	Contributed talk 3		Contributed talk 5	Invited talk 14: L. Dai
15:30-16:00			Contributed talk 2	Contributed talk 4		Contributed talk 6	Invited talk 15: J. Haruyama
16:00-16:30			Coffee break (30 min.)	Coffee break (30 min.)		Coffee break (30 min.)	Coffee break (30 min.)
16:30-16:55			Introduction to posters B: T. Hayashi	Introduction to posters D: T. Heinz		Introduction to posters F: S. Roche	[1] Concluding Remarks [2] Announcement of NT07 conference [3] Closing Ceremony
16:55-18:00	Registration (17:00-20:30)		Poster session B (with snacks)	Poster session D (with snacks)		Poster session F (with snacks)	
18:00-20:30		Welcoming Reception (18:00-20:30)			Conference Banquet (18:30-21:00)		

NT’06 Sponsors

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Keynote lectures

Nanotube Peapods: A New Class of Carbon Nanotube Hybrids

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During the past decade, carbon nanotubes encapsulating fullerenes, metallofullerenes (the so-called peapods) and other functional molecules have been synthesized and characterized by HRTEM, STM/STS, Raman, X-ray, FET and other measurements. In many cases, these nano-peapods have found to exhibit structural and electronic properties which are not normally observed in conventional carbon nanotubes. The novelty in electronic structure for the peapods comes mainly from hole or electron doping to the nanotubes from the encaged molecules. Here, we will report synthesis, structures and electronic properties of nano-peapods encaging a series of metallofullerenes and other functionalized molecules.

One of the fascinating features of metallofullerene-peapods such as Gd@C82, Ce@C82 and Ti@C82 peapods is that one can perform a local band gap engineering at the site where metallofullerenes are endothermally inserted. TEM and STM images together with electron energy loss spectra have suggested that the metallofullerenes can be spaced regularly as close as 1.1 nm in a high-density peapod structure, while 1.1 - 3 nm spacing has often been observed in a low-density peapod. About 10% of over 200 SWNT images showed locally modified semiconducting band gaps. We found that the synthetic yield of metallofullerene peapods varies considerably from one fullerene to another.

Furthermore, metallofullerene-peapods have exhibited ambipolar FET behavior with both n- and p-channels easily accessible by simple electrostatic gates. Similar results were obtained from more than 10 independent devices composed of a small bundle of metallofullerene peapods. Because the encaged metallofullerenes provide 2-6 electrons to the carbon nanotubes (electron-doping), the electronic transport properties of these peapods can drastically be altered with respect to the intact nanotubes.

HR-TEM imaging of molecules and ions trapped inside carbon nano-spaces

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Carbon materials have long been known to possess “nano-spaces,“ where a variety of materials can be accommodated. The mechanism of storing objects inside the carbon nano-spaces, however, has not yet been fully understood. In order to reveal the storing mechanisms of carbon nano-structures we have tried by using the high-resolution transmission electron microscopy (HR-TEM) to visualize various molecules and ions trapped inside porous nano-carbon materials. Attempts to encapsulate various fullerene molecules and ions inside the carbon nanotubes and nanohorns were made. Results will provide direct identification of the preferable adsorption sites for examined molecules and atoms.

(1) K. Ajima et al., Adv. Mat., 16 (2004) 397
(2) K. Urita et al., Nano Lett., 4 (2004) 2451
(3) L. Guan et al., Phys. Rev. Lett., 94 (2005) 045502
(4) Z. Liu et al., Phys. Rev. Lett., 96 (2006) 088304
(5) Supported by NEDO and JST. In collaboration with Nagoya University, Meijo University, Beijing University, and Chiba University.

Carbon Nanotube and Graphene Chemical Sensors

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Semiconducting nanowires (SNW) and single-walled carbon nanotubes (SWNT) are currently being investigated for a variety of applications as electronic chem/bio sensors. Most of these sensors rely on a perturbation of the nanofilament resistance and/or transconductance induced by the chemical attachment of molecules to be detected. The mechanism by which nanotubes “sense” this attachment, be it via physisorption or chemisorption, or by specific chemical binding, remain somewhat obscure in many cases. We begin this presentation with an overview of these sensor devices and what they can do, and indicate how close some of these devices may be to the market place. Next we turn to research performed in my group that has attempted to document the sensitivity of SWNTs to environmental interaction,i.e., to chemisorption and physisorption of vapors, etc., including recently published results that indicate that even gas collisions with the tube wall can be easily detected via the SWNT resistance and thermoelectric power. We close by presenting progress in moving toward a graphene-based chemical sensor. We will present results of fundamental studies made to synthesize atomically thin sp2 carbon films. We are able to produce n-Graphene Layer (nGL) systems on various substrates, where n=1,...,20 layers. This is achieved either by direct mechanical transfer of HOPG to the substrate, or by generating nGL “rafts” in solution and depositing them from this suspension. Results of Raman scattering studies on nGLs will be presented that probe the interaction between the graphene layers and their coupling to the substrate.

Electrical Transport in Molecules, Nanotubes and Graphene

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In this presentation, I will start with reporting our recent progress of synthesizing extremely long length scale individual single walled nanotubes (SWNTs) and multiwalled nanotubes (MWNTs). Employing microscopic mechanical manipulations, we demonstrated fabricating complex structure device fabrications [1]. In addition, electrical transport measurements in long SWNTs allow us to probe the 1-dimensional resistivity and mean-free path of these materials at wide temperature ranges.

In the second part, we will discuss the transport in nanotubes-single molecule hybrid system. We have developed a method to construct such a system, in which cut single walled carbon nanotubes are covalently attached to molecular wires through an amide linkage. Using this versatile method we have tested a number of different types of molecules, including species with chemical functionality that allows the molecular conductance to be switched [2].

Finally, I will discuss the unusual transport phenomena discovered in single atomic sheet of graphene [3]. Recent advances in micromechanical extraction and fabrication techniques for graphite structures now permit graphene to be probed experimentally. In this part, I will report an experimental investigation of magneto transport in a high mobility single layer of graphene. Adjusting the chemical potential using the electric field effect, we observe an unusual half integer quantum Hall effect for both electron and hole carriers in graphene.

[1] B. H. Hong et al., Proc. Nat. Acad. Soc. 102, 14155-14158 (2005).
[2] X. Guo, et al., Science 311, 356- 359 (2006).
[3] Y. Zhang, Y. Tan, H. L. Stormer, and P. Kim, Nature 438, 201-204 (2005).

Keynote lecture - 005 - Friday, June 23

Carbon Nanotube Electronic and Optoelectronic Devices and Circuits

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Although a number of different electronic devices based on SW-CNTs have been demonstrated, most of the emphasis has been placed on CNT field-effect transistors (CNTFETs). Such devices have superior characteristics, but also pose a set of new challenges. These include understanding the quasi-1D transport physics, deciphering the different device scaling laws, understanding the barriers at metal-nanotube interfaces, doping them, etc. In my talk I will discuss these issues and demonstrate solutions that allow the fabrication of not only individual devices with excellent characteristics, but also more complex integrated circuits, such as ring oscillators, based on a single CNT molecule. Self-assembly procedures of such devices on high-k dielectrics based on reversible functionalization of the CNTs will also be presented.

Unlike silicon, semiconducting CNTs allow the direct absorption and emission of light. I will discuss the nature of the excited states of CNTs and their production by photon and electron excitation. Radiative recombination of independently injected electrons and holes in an ambipolar CNTFET leads to single nanotube molecule light sources. I will also show that the CNT 1D-character, strong e-h interactions and weak e-phonon interaction allows for efficient intramolecular impact excitation by hot carriers in CNTs under unipolar conditions. Our theoretical analysis shows that impact excitation rates are many orders of magnitude higher in CNTs compared to 3D solids. Impact neutral exciton production rates are typically twice those of impact ionization and the initial distribution of excitations produced is very different from that produced by photon excitation. Examples of naturally occurring and fabricated structures that emit unipolar electroluminescence will be discussed.

Invited talks

From Super Growth to DWNT forests, CNT solids, Flexible Transparent CNT films and Super-Capacitors and Much More

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This presentation will provide an overview of our recent development of the Super Growth CVD. First, the synthesis of highly efficient impurity free SNWT forest will be described. Second, the growth dynamics will be explored with our recent advance in CNT synthesis. Characterizing of the physical and chemical properties of SWNT forests will be given. Various applications of the super-growth CVD, spanning from material and energy storage to flexible transparent CNT films and super-capacitors would be presented. Third, various new forms of carbon nanotube material, such as DWNT forests and CNT solids, made by utilizing the super-growth technique will be demonstrated. Lastly, challenges and future projects that are planed will be summarized.

Invited talk - 002 - Monday, June 19

Epitaxial Approaches to Carbon Nanotube Organization

Ernesto Joselevich

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The organization of carbon nanotube arrays on surfaces is a critical prerequisite for their large-scale integration into nanocircuits. In this presentation we will provide an overview of the recent advances toward the controlled formation of organized nanotube structures guided by different crystal surfaces, their morphologies and the possible mechanisms of their formation. We found that single-wall carbon nanotubes (SWNTs) catalytically produced on miscut c-plane sapphire wafers grow along the 0.2 nm-high atomic steps of the vicinal alpha-Al_2O_3 (0001) surfaces, yielding highly aligned, dense arrays of discrete nanotubes [1]. The nanotubes reproduce the atomic features of the surface, including steps and kinks. We also demonstrate the aligned growth of SWNTs by periodically nanofaceted surfaces, leading to the formation of either unprecedentedly straight and parallel nanotubes, or to wavy nanotubes loosely conformal to sawtooth-shaped faceted nanosteps [2]. It is also possible to create carbon nanotube crossbar arrays in one growth step by simultaneous nanofacet-directed and field-directed growth in perpendicular directions. Lattice-oriented, atomic step-templated and nanofacet-directed nanotube growth may be rationalized as nanotube-extended versions of incommensurate lattice-directed epitaxy, ledge-directed epitaxy, and graphoepitaxy, respectively. These different modes of nanotube epitaxy open up new possibilities for assembling nanotube architectures from the bottom up by surface engineering. We will as well show some unprecedented - and at times funny - nanotube structures, which form by other modes of nanotube epitaxy, not yet fully understood. We will stress that in the same way as epitaxy has advanced materials science and technology, nanotube epitaxy could advance nanotube science and technology.

[1] Ismach, A; Segev, L.; Wachtel, E.; Joselevich, E. *Angew. Chem. Int. Ed.* **2004** , *43* , 6140.

[2] Ismach, A; Kantorovich, D.; Joselevich, E. *J. Am. Chem. Soc.* **2005** , *127* , 11554.

Invited talk - 003 - Monday, June 19

Current Induced Reversible Deformation of Carbon Nanotubes

Yoshikazu Nakayama

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We induced a permanent plastic deformation in an originally straight double-walled carbon nanotube by applying current to an individual nanotube that had been bent elastically under mechanical duress. The onset of plastic deformation, as measured using the current circumference-density, is less than 1/20 that causing sublimation. Applying a large current to the permanent bend in the nanotube recovered the original straight shape. Its onset circumference-density is close to that of sublimation. The plastic bending deformation and its recovery can be performed cyclically, indicating that the deformed structure is metastable.

The minimum energy path calculation with a bond-order potential well explained the experimental results and suggests the following model. The moderate energetic perturbation under the strain induces bond switching to form Stone-Wales defects, and the pentagons and heptagons in the defects move to minimize the total energy. Thereby, the plastic deformation of the permanent bend is completed, because the adequate substitution of pentagons and heptagons for hexagons permanently bends the tubes. When the high energy is given to raise the temperature up to that of sublimation, the bond switching occurs to recover the bend.

Our findings will allow developing the nanotube static devices and actuator devices with high performances.

Near-field optical imaging of single-walled carbon nanotubes

Achim Hartschuh [1], Huihong Qian [2], Tobias Gokus [2], Alfred J Meixner [2],
Neil Anderson [3], Lukas Novotny [3]

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Photoluminescence and Raman spectroscopy are powerful tools for studying the electronic and vibronic properties of single-walled carbon nanotubes (SWNTs). Experiments on individual SWNTs, in particular, remove ensemble averaging involving different nanotube chiralities and can help to refine our understanding of nanotube physics. The spatial resolution achieved in conventional microscopy, on the other hand, is limited by diffraction to about half the wavelength of the excitation light. Thus, the spectroscopic data obtained results from spatial averaging over ~300 nm along the investigated nanotube.

Near-field optical techniques surpass the diffraction limit and can provide new insights into material properties on the nanometer scale. The technique we use is based on the local field enhancement at a laser-illuminated metal tip that acts as a highly confined excitation source. We present simultaneous photoluminescence and Raman spectroscopy of SWNTs with a resolution of about 10 nm [1,2]. We visualize the spatial extent of electronic states and probe emission energies along individual nanotubes [3]. For different sample materials, we observe a varying degree of localization of photoluminescence indicating the presence of bound excited states. Our results will help to clarify the influence of the local dielectric environment and of structural defects on the emission properties of SWNTs.

[1] A. Hartschuh et al., Phys. Rev. Lett. 90, 095503 (2003).
[2] N. Anderson et al., J. Am. Chem. Soc. 127, 2533 (2005).
[3] A. Hartschuh et al., Nano Lett. 5, 2310 (2005).

Invited talk - 005 - Tuesday, June 20

Excitons in Carbon Nanotubes

Rodrigo B. Capaz [1], Catalin D. Spataru [2], Sohrab Ismail-Beigi [3],
Steven G. Louie [4]

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[2] Columbia University

[3] Yale University

[4] U. C. Berkeley and Lawrence Berkeley National Laboratory

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We calculate several properties of excitons in single-wall carbon nanotubes (SWNTs) (binding energies, sizes, optical activities and radiative lifetimes) using a combination of *ab initio* and empirical methods. First, we present a theoretical analysis and first-principles calculation of the radiative lifetime of excitons in semiconducting SWNTs. Assuming a thermal occupation of bright and dark exciton bands, we find an effective lifetime of the order of 10 ns at room temperature, in good accord with recent experiments [1]. Second, employing insights and results from the first-principles calculations, we develop an empirical method consisting of a symmetry-based, effective-mass, variational approach with tight-binding wavefuntions. This approach provides exciton binding energies in good agreement with available first-principles results and its simplicity allows calculations for a variety of diameters (d) and chiralities. The exciton binding energies present an overall decrease with $1/d$, with strong chirality dependence and family behavior. The exciton sizes scale with d, also showing family behavior. We also address the important issue of bright-dark exciton splittings, which are found to decrease as $1/d^2$. Dependence of these properties on the dielectric screening will also be addressed, in the light of recent experimental measurements.

[1] C. D. Spataru, S. Ismail-Beigi, R. B. Capaz, and S. G. Louie, Phys. Rev. Lett. 95, 247402 (2005).

Nature of Optical Transitions in Carbon Nanotubes and Population Analysis

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The nature of the optical transitions in carbon nanotubes will be discussed, addressing the excitonic versus band-to-band photophysics, and the phonon related states. The most intense (so called E_{ii}) transitions are measured up to the fourth optical level in semiconducting tubes (E^S_{44}). Surprisingly we find that, while the first and second optical levels are excitonic, the third and fourth levels are band-to-band transitions. The exciton binding energies and their dependence on tube diameter are directly extracted from the E_{ii} data. Other weak absorption/emission peaks will be addressed too, focusing on the exciton-phonon side bands. The E_{ii} and ω_{RBM} are now established for all single-wall carbon nanotubes in the diameter range between 0.6 and 2.3nm, and energy range between 0.7 and 3.0eV. The intensities of the E_{ii} transitions are studied for (n,m) population characterization using optics. Characterization of HiPco, CoMocat and Alcohol samples are discussed, and they suggest the preferential production of large chiral angle tubes when going to diameters below 0.9nm.

The Chemistry of Single Walled Carbon Nanotubes: Applications to biomolecule detection, nanotube separation, and electronic networks

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Recent advances in the spectroscopy of single walled carbon nanotubes have significantly enhanced our ability to understand and control their surface chemistry, both covalently and non-covalently. Three distinct systems under investigation in our laboratory highlight these advances.

Molecular detection using near-infrared light between 0.9 and 1.3 eV has important biomedical applications because of greater tissue penetration and reduced auto-fluorescent background in thick tissue or whole-blood media. We have pioneered the use of carbon nanotubes as tunable near-infrared fluorescent sensors that are highly photo-stable In one system[1], the transition of DNA secondary structure from an analogous B to Z conformation modulates the dielectric environment of the single-walled carbon nanotube (SWNT) around which it is adsorbed. The SWNT band-gap fluorescence undergoes a red shift when an encapsulating 30-nucleotide oligomer is exposed to counter ions that screen the charged backbone. We demonstrate the detection of the mercuric ions in whole blood, tissue, and from within living mammalian cells using this technology. Similar results are obtained for DNA hybridization and the detection of single nucleotide polymorphism. We also report the synthesis and successful testing of near-infrared β-D-glucose sensors[2] that utilize a different mechanism: a photoluminescence modulation via charge transfer. The results demonstrate new opportunities for nanoparticle optical sensors that operate in strongly absorbing media of relevance to medicine or biology.

Covalent and non-covalent chemistries that are selective to single-walled carbon nanotubes of a particular electronic type have become increasingly important for electronic structure separation and on-chip modification of nano-electronic devices[3]. We have performed mechanistic studies to answer longstanding questions regarding their nature. Transient Raman and photoluminescence data collected in-situ reveal a series of two first-order reactions involving an adsorbed intermediate, and covalently bound product. The latter step can be deactivated by changing the structure of an absorbed surfactant phase, further supporting the mechanism. We discuss progress utilizing this chemistry to separate and sort single walled carbon nanotubes by their electronic structure using a 4-hydroxybenzene diazonium reagent.

Lastly, arrays and networks of metallic and semi-conducing carbon nanotubes are finding application in flexible electronics, as chemical and biological sensors, and as electronic interconnects. However, these systems demonstrate an environmental sensitivity and chemical reactivity that complicates processing, and facile incorporation into devices. We have studied the irreversible binding of adsorbates to such networks using electrical transport and Raman spectroscopy. The results are described theoretically using a continuum site balance model and mass action network involving the adsorbate-substrate interaction[4]. All such devices in the literature and in our laboratory are shown to possess both reversible and irreversible binding sites that can be modeled independently. A simple analytical test is presented to distinguish between these two mechanisms from the transient conduction response of these arrays.

(1) DA Heller, et al. Science 311 (2006) 508-511.

(2) PW Barone, et. al. Nature Materials 4 (2005) 86-92.

(3) MS Strano: Journal of the American Chemical Society 125 (2003) 16148-53.

(4) CY Lee and MS Strano. Langmuir 21 (2005) 5192-96.

Invited talk - 008 - Wednesday, June 21

Pulmonary Response to Aspiration of Single Walled Carbon Nanotubes

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Single walled carbon nanotubes are being investigated for applications in microelectronics, structural materials, and bone grafting. It is anticipated that commercial production of single walled carbon nanotubes will grow rapidly. In light of high anticipated production, worker exposure and possible adverse health effects are concerns. Therefore, the potential effects of pulmonary exposure to these nanoparticles was investigated. Mice were exposed by pharyngeal aspiration to purified single walled carbon nanotubes at 10, 20 or 40 μg/mouse. Pulmonary damage, inflammation, and fibrosis were monitored 1 60 days post-exposure. Aspiration generated two size fractions of nanotules (aggregates and more diffuse nanoropes). Pulmonary exposure to nanotubes resulted in an acute damage and inflammatory response, which returned toward the control state after 7 days post-exposure. Deposits of aggregated nanotube material were found in the terminal bronchiolar and proximal alveolar regions. Response at deposition sites of aggregates was the formation of granulomas, characterized by encapsulation of aggregates by epithelioid cells and rapid and progressive fibrosis. In addition diffuse intersitial fibrosis was observed in distal alveolar regions in the absence of visible nanotube aggregates. This interstitial fibrosis was apparent 7 days post-exposure and progressed through 60 days post-exposure. Labeling the nanotube material with gold prior to aspiration allowed deposits of nanoropes to be visualized in these distal alveolar speta. It is concluded that, although exposure to single walled carbon nanotubes did not cause prolonged inflammation, a progressive fibrotic response was observed. In light of such a pulmonary response, it appears prudent to avoid excessive inhalation of this material in the workplace.

Nanobiotechnological Applications of Functionalised Carbon Nanotubes

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Carbon nanotubes (CNT) are attracting the attention of several scientists, due to their unique structural, mechanical, electronic, chemical and biological properties [1]. These nanoobjects hold a lot of promises on biomedical applications for different reasons: high stability, water solubility, lack of intrinsic immunogenicity, efficient payload capacity, and cellular uptake [2]. The organic functionalisation has facilitated the manipulation of this nanomaterial and it has also opened the way to the potential use of CNT as novel vectors for cell internalisation of therapeutic molecules. Therefore, functionalised CNT can be considered as a promising alternative to the common drug delivery systems.

In this context, we have recently developed a novel non-viral delivery system based on cationic CNT for transfer of nucleic acids [3]. In addition, we have explored the possibility of targeted delivery of small organic molecules (antibiotics) and peptide-based synthetic vaccines [4, 5]. In this presentation we will describe the functionalisation and biological properties of nanotubes loaded with different active cargos. These conjugates are able to penetrate into the cells with reduced toxicity [6]. Their potential use for the delivery of plasmid DNA, drugs or peptides will be summarised. We will also address the critical issue of toxic effects [7].

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Gated Magnetoresistance in Carbon Nanotubes

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One of the basic building blocks of spintronic devices is the spin-valve, which is formed if two ferromagnetic electrodes are separated by a thin tunneling barrier. In such devices, the electrical resistance R depends on the orientation of the magnetization of the electrodes. It is usually larger in the antiparallel than in the parallel configuration. The relative difference of R, the so-called magneto-resistance (MR), is then defined to be positive. The MR may become anomalous (negative), if the transmission probability of electrons through the device is spin or energy dependent. This offers a route to the realization of gate-tunable MR devices, because transmission probabilities can readily be tuned in many devices with an electrical gate signal. Using carbon nanotubes with ferromagnetic contacts in a field-effect geometry, we demonstrate a spin field-effect transistor (Spin-FET), in which the amplitude and the sign of the MR are tunable with the gate voltage in a predictable manner.

We have studied both the MR in multi and single-wall carbon nanotubes using PdNi alloy to form ferromagnetic source and drain contacts. The two contacts have different shape rendering different magnetic switching fields. Two-terminal resistances are in the range of 5-100, k. The typical MR signal amounts to a 2-3 % in magnitude, in agreement with simple expectations from Julliere's model for tunneling MR, but the MR can also be enhanced to values up to 10 %. The most striking observations are sign changes in the MR. The MR oscillates in a regular fashion with gate voltage Vg

This oscillation is shown to be due to resonant tunneling.

We acknowledge fruitful discussions with R. Egger, C. Bruder and W. Belzig. We thank M. Calame, M. Gräber, S. Ifadir, and D. Keller for the preparation of SWNT devices, C. Sürgers (Karlsruhe) for magnetic measurements, and L. Forro

(EPFL) for providing the MWNTs. This work has been supported by the EU RTN network DIENOW, the Swiss National Center (NCCR) on Nano-Scale Science, and the Swiss National Science Foundation.

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Aligned Carbon Nanofibre - Polymer Composite Membranes

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Polymer membranes have been widely used in various applications, such as fuel cells, gas separation, biology, electrochemical sensors, electronics etc. Conducting polymer membranes are promising materials for construction in many areas. The anisotropy of electrical conductivity in such membranes may be interesting and can be achieved by filling polymers with structured carbonaceous compounds.

In this study we investigated composites made of thin transparent polymer membranes, in which regularly patterned vertically aligned carbon nanofibers (VACNF) or arrays of carbon nanotubes were incorporated across the film. Using electron beam lithography or nanoimprinting, patterned catalyst nanoparticles are prepared for the growth of the carbon nanostructures. The polymer matrix is added by a spin-coating method that the nanostructures can withstand. The membranes can be removed from the substrate with wet etching. The electrical properties of the composite membranes along and across the membrane were investigated.

Invited talk - 012 - Thursday, June 22

Multifunctional Carbon Nanotube Yarns and Transparent Sheets: Fabrication, Properties, and Applications

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Individual carbon nanotubes (CNTs) have spectacular measured properties that are of great commercial interest. These include over ten-fold higher strength than other comparable materials, a higher thermal conductivity than diamond, a thousand-fold higher current carrying capability than copper, and other fascinating and useful properties. The problem has been the difficulty of assembling many trillions of nanotubes into yarns and sheets that retain the spectacular properties of the individual nanotubes. An approach commonly used involves an initial step of dispersing the carbon nanotubes in either a melt or liquid, which suffers from number problems such as high viscosity at high concentrations, breakage of the nanotubes and the degradation of length-based properties, particularly thermal and electrical transport.

These problems have been circumvented by the development of a new process for the formation of continuous carbon nanotube yarns and transparent sheets. The CNTs are first grown in forests on silicon wafer with a special topology that provides for continuous recruiting of CNTs. Once a continuous assembly of CNTs is formed, it can be twisted to form a yarn, as in spinning of textile fibres like wool or cotton, or it can be used directly as a ribbon or sheet, which has the structure of a fine non-woven textile web.

This solid-state method of assembling CNTs provides a number of important advantages, such as, elimination of breakage of CNTs during dispersion and preservation of length, elimination of residual traces of solvent that decrease electron and phonon transport, and, most significantly, formation of materials consisting almost entirely of CNTs.

The presentation will detail aspects of the solid-state method of production of the electrically conducting yarns and transparent sheets, their properties, and some of the exciting applications that have been identified so far. These will include demonstration that the CNT yarns can be used for cold electron emission displays and intense light sources operating at low potentials, artificial muscles, supercapacitors, and impact-resistant incandescent light sources. The demonstrated uses for CNT sheets include planar sources of polarized broad-band incandescent radiation, microwave welding of plastics to make defrostable windows, sensors having low 1/f noise and low temperature dependence, and fabrication of highly elastomeric electrodes.

Invited talk - 013 - Friday, June 23

Metallic Nanotubes and as a Perfect Conductor

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Interesting transport properties of carbon nanotubes are reviewed briefly from a theoretical point of view. In metallic nanotubes, in particular, there is no backscattering even in the presence of scatterers unless their potential range is smaller than the lattice constant of a two-dimensional graphite. When there are several bands at the Fermi level, a perfectly conducting channel transmitting through the system without being scattered back exists. There can be various perturbations breaking this symmetry. The perfect channel can easily be destroyed by a small perturbation, while the absence of backscattering is very robust. The inter-wall conductance in double-wall nanotubes is calculated for various incommensurate structures. It is negligibly small due to cancellation among different sites and appears only because of incomplete cancellation in the presence of sharp tube boundaries.

Aligned Carbon Nanotube Nanocomposites and Nanodevices

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We have previously developed a simple pyrolytic method for large-scale production of aligned carbon nanotube arrays perpendicular to the substrate. These aligned carbon nanotube arrays can be transferred onto various substrates of particular interest in either a patterned or non-patterned fashion. The well-aligned structure provides additional advantages for not only an efficient device construction but also surface functionalization (both the inner and outer wall). The surface functionalization of aligned carbon nanotubes is particularly attractive, as it allows surface characteristics of the aligned carbon nanotubes to be tuned to meet specific requirements for particular applications while their alignment structure can be largely retained. These aligned carbon nanotubes with tunable surface characteristics are of great significance to various practical applications, including nanotube sensors and optoelectronics. For instance, we have previously immobilized glucose oxidase (GOX) onto the aligned multi-wall carbon nanotube arrays by electropolymerization of pyrrole in the presence of GOX. The resultant GOX-containing polypyrrole-carbon nanotube coaxial nanowires were shown to be promising new sensing active materials for making advanced glucose sensors with a high sensitivity. Also, single-strand DNA chains have recently been chemically grafted onto aligned carbon nanotube electrodes, leading to novel aligned carbon nanotube-DNA sensors of a high sensitivity and selectivity for probing complementary DNA and target DNA chains of specific sequences. More recently, we have also developed a rational approach to partially coat perpendicularly-aligned carbon nanotube arrays with an appropriate polymer thin film along their tube length to create synergetic effects, which provide the basis for developing novel sensors for the detection of chemical vapors, thermal and mechanical stimuli with a high sensitivity, good selectivity, excellent environmental stability, and low power consumption. In this talk, we will summarize our work on the preparation of polymer and aligned carbon nanotube nanocomposites and nanodevices. Potential applications of aligned carbon nanotube nanocomposites with other materials (e.g. metal nanoparticles) will also be discussed.

High-Tc Superconductivity in Entirely End-bonded Multi-walled nanotubes

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One-dimensional (1D) systems face some obstructions that prevent the emergence of superconductivity, such as Tomonaga-Luttinger liquid states and Peierls transition. Carbon nanotubes (CNs) are one of the best candidates for investigating the possibility of 1D superconductivity and its interplay with such obstructions. Only two groups to our knowledge, however, have experimentally reported superconductivity in CNs [1],[2]. In contrast, interestingly B-doped diamond and CaC_6 could exhibit superconductivity with T_c of about 11K [3].

Here, we report that entirely end-bonded multi-walled CNs (MWNTs) can exhibit superconductivity with a T_c as high as 12 K [4], which is approximately 30 times greater than T_c reported in [1]. We also find that the emergence of this superconductivity is very sensitive to the junction structures of the Au electrode/MWNTs. This reveals that only MWNTs with optimal numbers of electrically activated shells can allow superconductivity due to intershell effects. Recent measurement results in magnetization will be also shown.

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Introduction to societal impacts of nanotubes

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The societal impacts of nanotubes and other nanomaterials including their potential risks have been proactively discussed by people concerned in Japan as well as the USA and Europe. In this presentation, several projects to address these issues in Japan are introduced. For example, important issues for the establishment of organized evaluation of the health impacts of nanomaterials such as the provision of standardized testing materials and their nanoscale dispersion in the air and water have been discussed in the projects.

Contributed abstracts

June 19 (Monday)

Selective growth and characterization of aligned metal-filled carbon nanotubes

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Multi-walled carbon nanotubes can be filled with various elements and compounds. Among these materials magnetic fillings have significant potential for new applications in electronic or biomedicine.

Here we show CVD-routes for the growth of metal-filled carbon nanotubes (Fe, Co, Ni, alloys) on pre-structured silicon substrates and on electrochemically produced alumina substrates. The nanotube dimensions (diameter, length, filling) can be influenced by the nature of the catalyst on the substrate as well as by the reaction conditions. The filled nanotubes were obtained due to continuous decomposition of metal-containing precursors (e.g. metallocenes, metal-carbonyls) in an Ar atmosphere at about 700°C. Beside the synthesis the filled multi-walled carbon nanotubes were investigated with x-ray diffraction (XRD), Mössbauer spectroscopy and high resolution characterization techniques (TEM, SEM, FIB) to obtain further information about the tube-dimension, the composition, the crystal size and the crystal orientation of the metal-nanorods. In addition the magnetic properties of nanotube ensembles were studied (AGM, SQUID) and compared with theoretical data.

Effect of the reaction conditions in the production of multi-wall carbon nanotubes employing Fe-Mo /MgO catalyst

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Multi-wall carbon nanotubes can be produced by catalytic chemical decomposition reaction (CCVD) using methane on supported iron and molybdenum oxides supported on MgO catalysts. The carbon nanotube yield and its physic-chemical properties depend on the catalyst composition and its preparation method, the type of reactor and the experimental conditions. This work is part of a research program aimed at a systematic investigation of the parameters controlling the reaction operating conditions for the multi-walled carbon nanotube production over a FeMo/MgO catalyst.

We investigated the influence of the temperature, the methane /hydrogen ratio in the mixture and reaction time on the carbon nanotube yield, outer diameter and thermal stability properties. These materials were synthesized in the catalytic decomposition of methane in the 800°C- 975 °C, at different methane space time (0.022-0.087 g.h/mol) and reaction time (10-30 min) in a horizontal quartz reactor. The nature of carbon deposit on the catalyst surface was characterised by transmission electron microscopy (TEM) and thermo-gravimetric (TG) techniques.

Our results showed that the highest carbon nanotube yield (about 0.24 mol of C/ g catalyst) correspond to a temperature of about 950 °C, methane space time of about 0.030 g.h./mol and reaction time of 30 min. This sample also showed the highest thermal stability. Differences in carbon nanotube diameters were evidenced as a function of the reaction conditions.

Growth of CNTs by thermal CVD on Sintered Alumina plates at atmospheric pressure using Fe catalyst

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Abstract: carbon nanotubes are grown from a methane feedstock by thermal chemical vapor deposition on sintered alumina plates as catalyst support. The alumina plates were sintered at 1700°C. Alumina powder that it used for fabrication of plates is industrial grade and not pure and has 0.66% (mass percent) Fe element. Fe particles are catalyst for CNTs growth. So, CNTs are successfully grown on these specially treated substrates at 950°C degree and 1 atmosphere pressure using methane as the precursor gas. Some growth of CNTs are bamboo-like and Y-shaped in this experiments. For increasing the quantity of CNTs growth, we used an easy technique to increase the surface density of Fe particles on alumina plate. With scratching a piece of iron on sintered alumina plates, many Fe particles remain on the surface of alumina plates. Remained Fe particles on alumina have various sizes and So, various kinds of CNTs, have been grown.

Key words: Sintered Alumina, Fe catalyst, thermal CVD, Y-shaped Carbon nanotubes.

Effect of $CoO\text{-}MoO/Al_2O_3$ catalyst calcination temperature on the uniformity of the synthesized carbon nanotubes diameters

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This paper is a study on the effect of catalyst calcination temperature on the uniformity of the synthesized carbon nanotubes diameters. The synthesis of carbon nanotubes was performed in catalytic chemical vapor decomposition (CCVD) of methane over $CoO\text{-}MoO/Al_2O_3$ catalyst. The catalyst used in this study was prepared via conventional impregnation method and calcined at temperatures ranging from 300^oC to 750^oC. For synthesizing nanotubes materials, an amount of 200 mg catalyst was used and the reaction was conducted at a temperature of 700^oC for 90 min. The deposited carbons on the catalyst surfaces were characterized using transmission electron microscope (TEM). The experimental results clearly show that the catalyst calcination temperature does affect greatly the uniformity of the carbon nanotubes diameters. The carbon nanotubes obtained from the $CoO\text{-}MoO/Al_2O_3$ catalyst, calcined at 300^oC, 450^oC, 600^oC, and 700^oC had the diameters of 13.4 ± 8.4, 12.6 ± 5.1, 11.1 ± 4.2, and 9.0 ± 1.4 nm, respectively. This shows that an increase in the catalyst calcination temperature produces carbon nanotubes with narrower diameter distributions. The catalyst that calcined at a temperature of 750^oC and above was inactive in CCVD of methane. This finding discloses that nearly uniform carbon nanotubes have been tailored by $CoO\text{-}MoO/Al_2O_3$ catalyst prepared using a simple preparation method at the calcination temperature of 700^oC.

Effect of the process factors on the vertical growth of Carbon Nanotubes

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It is well known that Carbon Nanotubes(CNTs) are the best candidate for field emitter source. There has been a great deal of interest in improving emission properties of CNTs. It has been reported the vertical growth of CNTs enhances field emission properties.

Our experiments are implemented by using Direct Current PECVD at low temperature of 480 centigrade. 100nm-thick Ni catalyst layer was deposited on the glass substrate by RF sputtering. The Ni catalyst layer, which are actually islands or particles separated each other, was prepared by etching with the DC plasma of NH_3 gas. And then CNTs were grown using a gas mixture of C_2H_2 and NH_3. In order to examine the effect of the process factors on the vertical growth of CNTs, gas pressure, gas mixture ratio(C_2H_2/ NH_3), and applied volts were investigated respectively.

It was found that the vertical growth of CNTs depended on the gas mixture ratio and the applied voltage. As gas mixture ratio or gas pressure increases, CNTs growth rate increases. It turns out that the optimal gas pressure, gas mixture ratio(C_2H_2/ NH_3) and applied voltage are 0.5, 8torr and 450volts, respectively.

Fe nanoparticles produced by scratching technique as catalyst for CNTs Growth

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Abstract: The Fe catalyst nanoparticles were produced on Sintered alumina plates by scratching a peace of iron on sintered alumina plates. The CNTs(Carbon Nanotubes) were synthesized on these alumina plates using thermal chemical vapor deposition. The alumina plates were used as catalyst support for growth of CNTs. With scratching a piece of iron on sintered alumina plates, many Fe micro and nano particles remain on the surface of alumina plates. The remained Fe particles on alumina plates were preheat treated in quartz tube furnace at 950 °C and 1 atmosphere pressure using 200 sccm flow rate (95%Ar + 5%H_2) gas. So, the Fe nanoparticles got round and the greater Fe particles was made porous. The CNTs were grown on these specially treated substrates at 950°C degree and 1 atmosphere pressure using methane as the precursor gas. CNTs were grown in the holes of porous Fe particles. Characterization of Fe nanoparticles before and after preheat treatment was carried out using SEM and XRD.

Key words: Carbon nanotubes, Fe catalyst, Sintered Alumina, scratching technique, thermal CVD.

Catalyst-Thickness Dependence on the Synthesis of Brush like Long Nanotubes by Thermal Chemical Vapor Deposition

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The millimeter-long brush like aligned carbon nanotubes have been synthesized by using a conventional thermal chemical vapor deposition technique. Ethylene was used as a source gas of carbon and helium was used as a carrier gas. A little amount of water vapor was also introduced with the carrier gas during the deposition process. Thin layers of Fe with different thicknesses were used as the catalyst and Al_2O_3 buffer layer was used between the SiO_2 substrate and the Fe catalyst. The synthesized nanotubes were characterized by Raman spectroscopy and transmission electron microscope (TEM), which confirmed that the nanotubes synthesized with 1 nm-thick catalyst were single-walled one. The clear radial breathing mode peak was observed in the Raman spectra, which confirmed the existence of SWNTs. The diameters of the SWNTs estimated from the Raman peaks were varied in the range of 1.5 to 2.5 nm and also agreed well with the TEM. The number of walls of the nanotubes was found to increase with increasing the thickness of Fe catalyst. The observation of TEM was performed to confirm the number of walls of nanotubes.

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Controlling the position of carbon nanotube by dip-pen nanolithography

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Since single-walled carbon nanotube (SWNT) was discovered, it has been one of the most promising material in the field of nanotechnology because of its interesting electronic,mechanical properties and extremely small features. Such extremely small features of SWNT have both advantages and disadvantages for use in nano-scale devices. One of the disadvantages is the difficulty of controlling the location of the SWNT which was either grown or distributed on the substrate.

In general, It takes a lot of complicated process to incorporated grown SWNT into an active element of a nano device. In order to solve this problem, we contrived a new kind of technology that could control the position of the SWNT by utilizing dip-pen nanolithography. We have made the patterned-ferritin with a nanometer scale islands using dip-pen nanotechnology and have grown SWNTs by chemical vapor deposition on the patterned substrates.

The synthesized SWNTs have diameters of 1~4 nanometer and lengths of 5~10 micrometer. The field effect transistor devices which used the as-grown SWNT as a conducting channel were fabricated. Electrical transport properties of the fabricated devices were measured.

Synthesis of carbon nanotubes by chemical vapor deposition and laser ablation methods and their spectroscopic characterization

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Nanotubes are synthesized from wet chemistry and thin film multilayer catalysts by chemical vapor deposition of alcohol,cyclohexane, heptan and acetonitrile. Vertically aligned nanotubes with lengths of several hundred microns are grown from nanometer thin metal films. Nanotubes are produced by laser ablation from a variety of metal and metal oxide catalysts. Carbon 13 enriched laser ablation targets are used to produce isotope engineered nanotubes. The synthesized nanotubes are investigated by resonance Raman and optical absorption spectroscopy with regard to the carbon 13 content, diameters, defect concentration and nanotube yield. Transmission and scanning electron microscope images are shown to give evidence of sample cleanliness and nanotube alignment.

Understanding the Catalytic Activity of Metals in the Nucleation and Growth of Carbon Nanotubes

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A variety of metal catalysts can be used for Carbon Nanotubes (CNT) nucleation and growth. Catalytic activity can be predicted by analysing the corresponding metal-carbon phase diagram. However, depending on the carbon source, the catalytic activity, in particular the type of carbon nanostructure grown, can be significantly modified. While it is obvious that the thermodynamic properties of the carbon source in combination with the selected metal control the reaction, the exact details of the interplay between these two parameters remains largely unknown. In this communication, we report the catalytic activity evaluation of typical (Ni, Co and Fe) and atypical (such as Al, Na, Pt, Pd, Cs, and Ti) catalysts, combined with two very different carbon sources, methane and ethylene, under a wide range of synthesis parameters including temperature, pressure, and gas flow. We have found that diverse metals are capable of catalysing CNT nucleation and growth. Analysis of the intermediate metal carbide formation reveals the differences in catalytic activity for a selected metal with different carbon sources and in particular, why transition metals are the best catalysts. In addition, depending on the metal catalyst used, the CNT grown under comparable synthesis conditions show various morphologies. The implied variation in CNT properties promises a wide range of applications extending across many technologies.

Building the Catalyst for the Growth of Single-Walled Carbon Nanotubes

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The elucidation of catalyst particle specific features favorable for carbon single-walled nanotubes (SWNTs) growth is crucial in order to take control over the characteristics of grown nanotubes. A mass spectrometer attached to the CVD growth technique offers opportunity for parametrical studies of catalyst features during SWNTs growth, by in-situ evolution of catalyst activity. The result, combined with calorimetry and Raman studies, exposes the catalyst features and corresponding synthesis conditions favorable for nanotube growth. We found that for successful nanotube growth the V-shape liquidus line of the catalyst-carbon binary phase diagram is a crucial feature. Moreover, the sequential introductions of hydrocarbons with ^{12}C and ^{13}C isotopes, during nanotube growth by using monometallic Fe and bimetallic Fe/Mo catalysts, revealed that the lifetime of the catalyst and the growth termination process strictly depend on catalyst composition. Ab initio calculations elucidated that the interfacial interaction between Fe nanoparticles and alumina support material affects on nanoparticles properties. Molecular dynamics simulations corroborated the V shape liquidus line for supported Fe-carbon binary phase diagram. The relationship between catalyst features and synthesis conditions favorable for nanotube growth is discussed.

Growth kinetics of multi-walled carbon nanotubes studied by Tapered Element Oscillating Microbalance (TEOM)

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One of the most promising methods to the multi-walled carbon nanotubes (MWNTs) production at an industrial scale is the catalytic chemical vapor deposition (CCVD). However in spite of the importance to control the process for further optimization of the MWCNTs properties there are surprisingly few works that investigate the kinetics of MWCNTs in a systematic way. Main reason is in the inherent difficulties of accurate nanoscaled instrumentations. In this contribution monitoring the growth of MWNTs produced by CCVD process of decomposition C_2H_6:H_2 gas is reported using a Tapered Element Oscillating Microbalance (TEOM) probe. Growths in the TEOM microreactor is investigated with catalytic particles (Fe, Ni) dispersed on different supports. The samples involve catalytic particles deposited on high surface area powders like alumina or zeolites as well as flat or patterned Si (100) substrates. These quite different samples are used in order to accurately investigate limitations due to gas diffusion in highly porous media such as the catalytic powders with high surface area. Furthermore, the kinetic dependence with partial pressure of the incoming C_2H_6:H_2 gas mixture is then in detail explored on the Fe/Al_2O_3 catalyst. Subsequently, the kinetic orders relative to the constituents of the gas are determined. These results thus bring insight to improve and control the CCVD growth of MWCNTs.

Molecular dynamics studies of phase diagrams for Fe-C nanoparticles adsorbed on oxide substrates

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Interaction of iron catalyst nanoparticles with a substrate may influence nucleation and growth mechanism of carbon nantobutes (CNT) by shifting the melting temperature of the supported iron particles. To account for this effect we have used *ab initio* calculations to develop empirical potentials between iron nanoparticles and oxide substrates. Simulations have been performed on Fe/Al_2O_3 system with Al_2O_3 substrate fully relaxed. We have demonstrated that the surface rearrangement effects are significant but can be naturally incorporated into a simple Morse potential, which describes the total nanoparticle-substrate binding. The influence of different substrate surface terminations and positions of Fe layers on the strength of binding are discussed. To better understand the melting and phase transition properties of suspended nanoparticles, molecular dynamics (MD) simulations are performed to determine the melting point of Fe-C nanoparticles ($\sim$ 1-4 nm size) as a function of size and carbon concentration. The temperature dependence of the total energy and the Lindemann index characterize the melting of nanoparticles. For free (unsupported) Fe-C clusters, it is observed that the eutectic point (in the phase diagram) shifts with nanoparticle size. Results for different substrates are discussed. Research sponsored by Honda Research Institute, USA.

Modeling the Melting of Metal and Metal-Carbide Clusters

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The growth rate and mechanism of carbon nanotubes is expected to be significantly affected by the phase of the catalytic metal-carbide particles. For example, carbon atoms that are released from the catalytic decomposition of feedstock may dissolve more readily into liquid phase particles, whereas surface diffusion of carbon atoms to the ends of growing carbon nanotubes may dominate when the catalytic particles are solid. It is therefore important to understand the melting properties and dynamics of these particles, as well as the dependence in the melting points on cluster size, substrate adhesion and carbon content.

In this presentation we will discuss molecular dynamics and DFT studies of the melting properties of catalytic metal and metal-carbide clusters, including the effect of varying the cluster size, cluster-substrate adhesion strength and carbon content. We will show, for example, that the melting dynamics of supported metal clusters is very similar to that of free clusters, and that the melting points of these clusters can be predicted by the same model if one accounts for the substrate-induced increase in cluster curvature of the supported clusters.

Growth of vertically aligned and diameter controlled carbon nanotubes from monodispersed Fe-(V,Ti)-O nanoparticles

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Monodispersed Fe-V-O and Fe-Ti-O nanoparticles which have high diameter controllability and high catalytic activity to grow carbon nanotube (CNTs) were prepared by liquid-phase synthesis. Vertically aligned dense CNTs with diameters of 3.7 ± 0.6 nm and 4.3 ± 0.7 nm were grown from the Fe-V-O and Fe-Ti-O nanoparticles with diameters of 3.1 ± 0.5 nm and 3.8 ± 0.6 nm, respectively. It was found that the CNTs from Fe-V-O nanoparticles consist of 14 % single-, 74 % double- and 12 % triple-walled CNTs. The catalytic activity of the nanoparticles peaked at 20-25 at% Ti for Fe-Ti-O nanoparticles, and 10 at% V for Fe-V-O nanoparticles. Energy dispersive X-ray spectroscopy of nanoparticles before and after the CNT growth revealed the depletion of V and Ti in the nanoparticles during CNT growth, which indicates a segregation in the nanoparticles.

Simplified synthesis of carbon nanotubes using hot-filament CVD in one atmospheric nitrogen

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A simplified deposition method for carbon nanotubes (CNTs) using a hot-filament enhanced chemical vapors deposition (HF-CVD) has been reported. A tungsten coil was used as a hot-filament to decompose ethanol vapor over a Fe-Co-zeolite powder and to heat the substrate. The experiments were performed in a nitrogen atmosphere at 1 atm. The influence of process parameters such as thickness of catalyst, substrate temperature, flow rate of nitrogen and deposition time, on the formation of CNTs was investigated using scanning electron microscopy, transmission electron microscopy and Raman spectroscopy. It was found that the tube diameter was affected by the thickness of catalyst, while the uniformity of the tube diameter was strongly affected by the flow rate of nitrogen and the distance between filament and substrate (dsf). By optimizing the growth conditions, multi-walled CNTs with a diameter of $<$ 20 nm and a length of $>$5 μm were successfully obtained. Moreover, it was observed that the morphology and purity (intensity ratio of G-band to D-band) of the CNTs obtained under nitrogen atmosphere were comparable with those obtained under argon atmosphere. However, they showed less quality than CNTs deposited under vacuum condition, regardless of growth conditions. The model of forming CNTs in this experiment will be discussed.

Towards the optimisation of the large-scale production of MWNTs grown by CVD of ethane on Fe / Al_2O_3 : 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].

Synthesis of Carbon Nanotubes on the Graphite Fiber Paper Supported Catalyst

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Many researches have been developed to improve the methods for CNTs growth. Of these methods, chemical vapor deposition (CVD) has the advantage to synthesize CNTs with a few impurities at lower temperature compared with other methods, such as laser ablation and arc discharge. Also, CNTs can be successfully synthesized on thin substrate supported nanosized particles or most patterned plate by CVD method, as long as the temperature of the substrate is sustained in growth [1]. In this work, synthesis of CNTs on the graphite fiber paper is reported. A liquid hydrocarbon is used as carbon source. An ultrasonic atomizer is prepared for evaporating the liquid carbon source at room temperature, instead of a heating method. It helps the vaporized solution to be continuously introduced into the CVD furnace. The CVD furnace is controlled at 650°C. The morphology of samples was characterized by energy dispersive X-ray spectrometer (EDX-HORIBA), Raman scattering (LabRam HR), FE-SEM (S-4700, HITACHI), high resolution transmission electron microscope (HRTEM-JEOL JEM 2010).

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Centrifugal Classification of Nanoparticle Catalysts for Diameter Controlled Carbon Nanotube Growth

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Monodispersed catalytic nanoparticles by a liquid phase synthesis [1] were highly size classified via a centrifugal classification technique to improve diameter controllability of carbon nanotubes (CNTs). The centrifugal classification of nanoparticles is facilitated by fractional precipitations through the sequential addition of polar solvent to non-polar solvent in which nanoparticle are dispersed. The diameter of nanoparticles was evaluated by both TEM and XRD. The mean diameter of each fractionated nanoparticles gradually decreased with increasing polarity of solvent and the standard deviation of diameter was successfully reduced. An XRD peak originated from high diameter uniformity of nanoparticles was found at low angle region. The peaks show great sensitivity to small changes of mean diameter of nanoparticles. This indicates that this analysis is expected as one of alternatives to conventional TEM for diameter evaluation of the nanoparticles at small size region. We will show the result of CNTs grown by the fractionated nanoparticles.

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The influence of different growth conditions for the synthesis of single walled carbon nanotubes by alcohol catalytic CVD method using zeolite as a support material

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The yield and diameter distribution of single walled carbon nanotubes, synthesized by alcohol chemical vapor deposition method, is found to depend significantly on the ratio of metal catalyst-particles (Fe-Co) to zeolite (HSZ 390 HUA, Tosoh Inc). The diameters of the SWNTs were estimated to be in the range of 0.7 - 1.3 nm. We systematically studied the dependence of the total carbon-yield on the growth-temperature, which can crucially modify the distribution of chirality as well. The chiral distribution was determined by near-infrared fluorescence spectroscopy and Raman (radial breathing mode) spectroscopic measurements.

Trial for diameter-selective synthesis of SWNTs

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The diameter-controlled synthesis of single-walled carbon nanotubes (SWNTs) has been examined experimentally. The catalytic activities of the Rhodium and Palladium atoms have been confirmed at 950 °C in furnace temperature (approximately 800 °C in the reaction area) by blending with Cobalt atoms, though the Rh/Pd catalyst has not been available before in this temperature. Raman spectra indicate that the Rh/Co and Pd/Co catalysts can synthesize narrow-diameter SWNTs more selectively than the Fe/Co and Ni/Co catalysts, which can only synthesize SWNTs with slightly larger diameters. Referring to the results of Raman spectroscopy, the order of the strength of interaction between carbon atoms is revealed as Pd > Rh > Fe > Ni > Co. These results suggest that by changing the combination of catalysts, the longing problem of controlling the diameter of SWNTs can be solved without any expensive setup or complicated techniques.

Influence of the Co/Mo Ratio on the SWNT Synthesis from Carbon Monoxide

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By using carbon monoxide as carbon source, we have synthesized random, vertical and parallel aligned SWNTs on quartz substrates dip-coated with Co and Mo (COCCVD). In order to study the influence of the Co/Mo ratio in details, combinatorial method [1] with wide nominal thickness profiles of metal catalysts was employed. By the uniquely masked sputter-deposition technique, we prepared a 2-dimensional catalyst library with Mo (0.2 - 4 nm) and Co (0.2 - 8 nm) thickness profiles on a SiO_2/Si wafer [2]. After the CVD using hydrogen / carbon monoxide (500 / 500 sccm) (800 degC, 1 atom), SWNT formation region was confirmed by HRSEM observation and micro Raman analysis. The optimum Co/Mo ratio for the SWNT formation was larger in the order of COCCVD, ACCVD [2] and CoMoCAT [3]. The difference of the optimum Co/Mo ratio between COCCVD and ACCVD is suspected to originate in the relation between the activity of Co and the energy requirement for graphite precipitation in a thermodynamic equilibrium process. Furthermore, the effect of support materials, heating or reducing processes, catalyst preparations will be discussed.

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Single-walled carbon nanotubes from catalyst incorporating proteins

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Diameter control is the ultimate issue in maximizing the potential of single-walled carbon nanotubes (SWNTs). Recently, wet catalysts have been widely used for diameter control due to their predetermined size. To understand the growth mechanism and apply it to diameter or chirality control of SWNTs, we used catalyst containing proteins and systematically investigated the behavior of catalytic nanoparticles before and after chemical vapor deposition (CVD) using various techniques, such as AFM, SEM, TEM, XPS, and SIMS.

Ferritin [1] and Dps proteins [2] were used in order to obtain discrete Fe nanoparticles. Co-filled apoferritin yielding Co nanoparticles were used for comparison [3]. A size difference between catalytic nanoparticles and nanotubes was always observed [4]. The size difference between the active and poisoned catalysts was also observed after the CVD process. It should be noted that the mean diameter of the grown tubes was not changed significantly even though we used catalytic nanoparticles of different size. The present results provide useful information for diameter control of SWNTs.

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Selective Diameter Control of Single-Walled Carbon Nanotubes in the Gas-Phase Synthesis

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A selective diameter-control method in gas-phase synthesis of single-walled carbon nanotubes (SWCNTs) has been developed. Controlled synthesis of SWCNTs in the structural characteristics, i.e., diameter, length, number of defects and so forth, is an enabling step for realization of their many potential applications and fundamental studies requiring defined nanotube structures and properties. Above all, the controllability of the tube diameter would be the key to the chirality-controlled synthesis of SWCNTs. We designated this method as the enhanced direct injection pyrolytic synthesis (e-DIPS) method, in which two kinds of carbon sources were used simultaneously. The reversed micelles containing metallic ions were used as novel catalyst precursors. Our results suggested that this method could tune the mean diameter of SWCNTs at any point within the range of ca. 1.0 nm to 2.0 nm selectively.

Growing Carbon Nanotubes on Al_2O_3 Supported Metal Sulfate by Catalytic Chemical Vapor Deposition

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We report a series of novel catalysts to grow Multi-Wall Carbon Nanotubes (MWCNTs) by Catalytic Chemical Vapor Deposition. Fe, Co, and Ni sulfate are found could grow MWCNTs at mild temperature in the diluted CH_4 or C_2H_4. CNTs growing temperature stared at 600°C, the optimum temperature will locate in the range of 800 °C and 900 °C. When temperature is going above 1000 °C, the growing yield will dramatically reduce to near zero. In TGA and XRD measurements, showing the 61543;-type Al_2O_3 will transform into 61537;-type and metal sulfates also change crystalline phases result in suppressing the growth of CNTs. With the aid of SEM and TEM images, the diameter of MWCNTs observed in the range of 40~80 nm. $NiSO_4/Al_2O_3$ conduct better CNTs growing rate and near to three times than those of $FeSO_4/Al_2O_3$ and $CoSO_4/Al_2O_3$.

Controlled growth of high-purity DWCNTs using a catalytic CVD

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We have studied controlled growth of high-purity double-walled carbon nanotubes (DWCNTs) using a catalytic chemical vapor deposition (CCVD) method. Basically, to synthesize the DWCNTs, we used a gas phase carbon sources such as methane ethylene over Fe-Mo embedded MgO support material with different BET. The produced carbon materials showed high-purity DWCNTs free of amorphous carbon on the surface. The diameter and crystallinity of DWCNTs were dependent on growth temperature. Especially, we could control the type of CNT (SWCNT or DWCNTs) according to BET of support materials. We have evaluated field emission from DWCNTs. According to our experimental results, DWCNTs showed low turn-on voltage similar to SWCNTs but higher emission stability compared with SWCNTs.

Lower pressure effects on single-wall carbon nanotubes growth

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Single-wall carbon nanotubes (SWCNTs) have been grown with the alcohol catalytic chemical vapor deposition (ACCVD) at pressures down to 0.05 Pa using an ultra high vacuum chamber. A Co catalyst (0.1 nm) on a SiO2/Si substrate was used. To investigate the low pressure effects on the growth, SWCNTs were grown also with the standard pressure of 1.5 kPa using the conventional ACCVD system. The characterization of the SWCNTs grown at various temperatures and pressures has been carried out by Raman spectroscopy and scanning electron microscope measurements. It was found that the SWCNTs could be grown even at 0.05 Pa, which is much lower than that used in the conventional ACCVD (~1kPa). Moreover, the growth temperature with the maximum G+ Raman intensity was lowered at 0.05 Pa by more than 250 ^{o}C compared with the growth at 1.5 kPa.

Novel catalyst particle production method for CVD growth of single- and double-walled carbon nanotubes

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A novel chemical vapor deposition (CVD) method for the selective growth of single- or double-walled carbon nanotubes (CNTs) was developed. Unlike conventional methods, catalyst particles were produced in the form of an aerosol and ex situ or in situ deposited on different substrates via thermophoretic forces. The proposed method was demonstrated using Fe as the catalyst material and a mixture of CO and H_2 as the feeding gases. CNTs synthesized by the ex situ approach were large diameter (around 7.0 nm) double-walled CNTs, while the in situ method, depending on the operating conditions, resulted in the growth of either individual or bundles of single-walled CNTs (about 2 nm). The possibility to produce aligned and ultralong (up to 0.7 cm) nanotubes by this method was also demonstrated.

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Force Output and Control of Carbon Nanotube Film Structure by Applying Mechanical Pressure During Growth

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We demonstrate that a film of vertically-aligned multi-walled carbon nanotubes (CNTs) can exert mechanical energy as it grows, and in our experiments the average force output is approximately 0.16 nN per CNT. The film thickness after a fixed growth time and the alignment of CNTs within the film decrease concomitantly with increasing pressure which is applied by placing a weight on the substrate. The films adopt an ordered "serpentine" microstructure at pressures exceeding approximately 10,000 N/m^2. The mechanical energy necessary to deform CNT structures during growth is much less than the energies of the CNT formation process as well as the equivalent forces necessary to deform CNT structures after growth. This suggests that an oblique force on the catalyst particle causes the generation of structural faults in the CNT, which is confirmed by HRTEM imaging. However, the mechanical energy density of growth based on the film volume is comparable to muscle, and based on the volume of CNTs is comparable to hydraulic actuators.

We utilize this principle to fabricate three-dimensional structures of CNTs which conform to the shape of microfabricated templates. This enables growth of nanostructures in arbitrarily-shaped forms having sloped surfaces and non-orthogonal corners, and does not require patterning of the catalyst before growth.

Low Temperature On-Chip Growth of Carbon Nanotubes

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Chemical vapour deposition (CVD) is the method of choice for directly growing nanotube devices on-chip, providing the possibility of mass-production and controlled positioning via catalyst patterning. However, if nanotubes are to fulfil their promise in real applications it is essential to reduce the growth temperature to values that are compatible with CMOS processing.

Here we present a new experimental method for growing good quality, aligned single- or multiwalled carbon nanotubes on-chip at low ambient temperature. Localised ohmic heating at the catalyst allows controlled growth of nanotubes on metal electrodes. The surrounding silicon chip reaches an average temperature of 60 °C and no additional heating of the precursor gases is required. Heating of the catalyst site is extremely local - the temperature gradient at the catalyst is on the order of 100 °C/μm.

Being able to keep the sample temperature down during growth benefits the integration of carbon nanotubes with CMOS technology and also permits using low temperature materials as building blocks for nanoelectromechanical structures on chip. The resistive growth method presented here also opens up the possibility of sequential growth, with potentially large consequences for how future on-chip nanotube growth will be performed.

Three-dimensional alignment control of individual single-walled carbon nanotubes by diffusion-plasma CVD

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Individual single-walled carbon nanotubes (SWNTs), considered to be one of ideal one-dimensional material, have attracted a great deal of attentions owing to their outstanding electrical and optical characteristics. Although such an ideal one-dimensional structure provides abundant benefits in a basic science field, a difficulty of their manipulation causes a critical barrier to be applied to an industrial application. To overcome this significant problem, a precise growth direction control of the individual SWNTs is performed by a diffusion-plasma chemical vapor deposition method.

When energy of ions coming into a substrate decreases drastically, the individual SWNTs are found to grow in the form of vertically- and individually-aligned structure against the substrate surface. On purpose to heighten an accuracy of the alignment control, several effects of plasmas on the growth of the freestanding individual SWNTs are also investigated with detailed plasma measurements and simple calculations. These results give direct evidence that a plasma sheath electric field plays a crucial role in the control of individual-SWNT growth direction [1,2]. The technique developed can contribute to creating a novel-architecture device for individual-SWNT industrial applications.

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Direct Growth of Single-Walled Carbon Nanotubes on a Conducting Oxide Film and Its Field Emission Properties

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Surface layers on substrates for single-walled carbon nanotubes (SWNTs) growth by chemical vapor deposition are limited to non-conducting films such as oxides. Much effort for the direct growth of SWNTs has been not successful on metallic or conducting films of which thickness is large enough to be used as an electrode, despite the usefulness for nano-electronics and opto-electronics. The grown nanotubes were multi-walled, or graphite films were deposited on the conducting films, possibly due to large thickness of catalyst films or poisoning of catalytic activity on the surface of conducting films. Here, we report that SWNTs can be directly grown on a conducting oxide film by water plasma-enhanced chemical vapor deposition. The grown SWNT/conducting film was used as a cathode for field emission of electrons, to confirm the conducting capability of the oxide film.

Direct Growth of Single-Walled Carbon Nanotubes on Glass

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Direct growth of single-walled carbon nanotubes (SWNTs) on glass is required for display applications such as electron emitters for field emission display (FED) and network transistors to replace thin film transistors (TFTs) for liquid crystal display (LCD) and organic light emitting diode (OLED). However, the low strain temperature (~ 666 °C) of the best display glass is a crucial barrier to directly grow nanotubes on glass, since chemical vapor deposition (CVD) of SWNTs generally requires higher growth temperature than 700 °C. Here, we report that SWNTs can be directly grown on glass at the growth temperature range of 450°C ~ 650 °C by using water plasma CVD. The growth behavior of SWNTs on glass is not only influenced by the growth temperature, but severely also depends on a buffer layer. This success may facilitate future opto-electronic applications of SWNT-based active devices.

Synthesis of horizontally-aligned SWNTs with controllable density on sapphire surface and their polarized Raman spectroscopy

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Recently, we found that the horizontally-aligned single-walled carbon nanotubes (SWNTs) are formed on R- and A-faces of sapphire substrates, which is promising for nanoelectronics applications [1]. We used the colloidal particles of iron oxide with the mean diameter of 4 nm, but the SWNT yield was relatively low [1]. Here, we report on the facile synthesis of the aligned SWNTs on A-face sapphire with controllable nanotube density and the results of their polarized Raman spectra. The catalyst was prepared by simply dipping a substrate into the methanolic solution of iron and molybdenum salts where the addition of Mo improved the catalytic activity and reproducibility. The SWNT density was controlled by changing the metal concentration of the solution, and the high nanotube density of $> 20\ \mu\mathrm{m}^{-2}$ was achieved. This high SWNT density allowed us to measure the polarized Raman spectra. The spectra clearly indicate the formation of aligned and isolated SWNTs, not nanowires of metal or metal carbide.

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Precursor control for the growth speed of carbon nanotubes using CH_4/H_2 RF plasma

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We have synthesized vertically-aligned carbon nanotubes (CNTs) on $Al_2O_3/Fe/Al_2O_3$ thin films deposited on Si substrates by CH_4/H_2 RF (=13.56 MHz) plasma-enhanced chemical vapor deposition (PECVD). So far, we have evaluated the CNTs in terms of number densities, diameter and length, and analyzed the densities and fluxes of radicals and ions in CH_4/H_2 plasma using 1-dimensional fluid model[1]. These results showed that carbon atoms in the CNTs obtained and carbons supplied onto the substrate, which were calculated by the fluxes of carbon-containing species considering their sticking probabilities were in the same order[1]. In this model, main precursors for CNTs growth were carbon-containing ions such as CH_5^+. We think that controlling the fluxes of ions enable us to promote or suppress the CNTs growth. In this paper, the effects of bias voltage on control the growth speed of CNTs is taken into account to the model. It seems reasonable that bias voltage can control the ions fluxes onto the catalyst surface easily. When the substrates were biased to positive, CNTs got shorter. We will discuss the difference of CNTs growth speed by adjusting the ions fluxes.

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Growth and control of vertically aligned SWNTs

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Previous investigations [1,2] into the growth of vertically aligned single-walled carbon nanotube (VA-SWNT) films from alcohol have shown that the maximum achievable film thickness is largely determined by the initial catalyst activity, which is sensitive to the conditions at which VA-SWNT synthesis occurs. In this study, we have investigated the role of the ambient growth pressure, and report a significant enhancement of VA-SWNT growth by a slight increase in growth pressure. Using an *in situ* optical absorbance technique [1] to monitor the film growth, high-quality VA-SWNT films from 1 to 30 μm thick can be produced with accurate control over the final film thickness. Combining this thickness control with the hot-water assisted film-removal and re-attachment technique developed by our group [3] represents an important step in the controlled production of VA-SWNTs for various applications.

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'Super growth' of multiwall carbon nanotubes from camphor at 650°C

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In the last fourteen years, carbon nanotubes (CNTs) have been studied extensively; nevertheless, the exact growth mechanism of CNTs is yet unclear. CNTs can be grown in such a wide range of materials, methods and conditions that it is difficult to determine what is the key mechanism of CNT growth. Till date, the art of CNT synthesis lies in the optimization of the preparative parameters for a selected group of materials (carbon source, catalyst and support) on a particular experimental set-up. In our previous study, we reported 'selective growth' of single-wall nanotubes (SWNTs) and multiwall nanotubes (MWNTs) from an unconventional precursor: camphor, with Fe-Co-impregnated zeolite support by a simple chemical vapor deposition (CVD) method [1]. Using the same materials and method, we have now optimized the relative concentrations of camphor, catalyst and support material in the reactor to achieve very high growth rate of MWNTs at 650°C at atmospheric pressure.

In our small CVD reactor (an ordinary quartz tube: 1-m long and 26-mm wide), 1.2 g camphor is vaporized at 200°C under a mild argon flow of 50 sccm, and is pyrolyzed over 0.12 g Fe-Co-impregnated zeolite support at 650°C. Such a simple process for 10 minutes inflates the zeolite approximately 50× by volume, and nearly 5× by weight. Transmission electron microscopy of as-grown material reveals MWNTs of diameter ~10 nm with negligible amorphous carbon and absolutely no graphite particle. Thermogravimetric analysis of as-grown nanotubes also confirms the absence of amorphous carbon and graphite particles in our samples. Weight-gain calculation thus suggests a high produce of ~0.5 g MWNT in 10 minutes, which refers to an exceptionally high growth rate. Hence we call it 'super growth'. Camphor-to-CNT production efficiency is ~40%, which is much higher than that of any CNT precursor by any method. It may be debatable whether the key of 'super growth' lies in the source material: camphor, or in the optimization of the control parameters, or in both (as we believe); however, there is no doubt that this is a breakthrough in the utmost utilization of a carbon source for CNT growth.

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SYNTHESIS AND CHARACTERISATION OF METALL FILLED SINGLEWALL CARBON NANOTUBES

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In our study we use a highly efficient and simple methodology based on wet chemistry to fill single-wall carbon nanotubes (SWCNTs) with continues metallic (e.g. Ag, Fe) nanowire on a bulk cale. The research shown is unique in that it is the first experimental single-wall carbon nanotubes that have metal continuously within their core for extended length scale. The intercalation of metals within singlewall carbon nanotube structures is a significant step towards the realization of the potential applications using these materials. Here we present the structural, optical, and electronic study on the metal filled SWCNTs.

Direct synthesis of single-walled carbon nanotubes selectively suspended on tips of vertically-aligned silicon nanostructures

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Recently, suspended single-walled carbon nanotubes (su-SWNTs) have attracted a great deal of attention, because that (1) the perturbation from substrates is minimized to allow probing the natural properties of SWNTs; and (2) nanodevices using su-SWNTs exhibit enhanced performance. In this work, we present a method to synthesize su-SWNTs selectively suspended on tips of silicon based nanostructure (Si-ns) templates. An anisotropic hydrogen plasma etching is employed to fabricate vertically-aligned Si-ns, followed by thermal chemical vapor deposition technique to synthesize SWNTs. Nano-sized islands or particles as formed from multi-layered thin-films (Mo/Fe/Al) at high temperature are served as the catalytic nanomasks (CNMs) during plasma etching, where the remaining CNMs left at tips directly become the catalysts for SWNTs growth. As revealed by characterizations using scanning electron microscopy and resonance Raman spectra, su-SWNTs form networks interconnecting ns-Si templates. This methodology provides an accessible approach to assemble two different nanomaterials, i.e., ns-Si and su-SWNTs, together as a building block for future possible applications.

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A simple way of synthesizing single walled carbon nanotubes via a floating reactant method

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In recent years, single walled carbon nanotubes (SWNTs) have been intensely studied as an ideal nanomaterials because they exhibited very intriguing physical and chemical properties. Therefore, when considering their versatile applications, synthetic method for producing high purity SWNT at a relatively low cost has to be developed. Here we demonstrate the ability to synthesize SWNTs by spraying ethanol solution containing ferrocene into the conventional reactor without using hydrogen or sulfur. Resultantly, we obtained high-purity and relatively crystalline SWNTs with diameter of 0.9-1.2 nm containing small amount of double walled carbon nanotubes.

Exhaustive mapping of Co-Mo catalytic activity against their compositions in growing SWNTs from ethanol

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In the direct growth of SWNTs on substrates by CVD methods, preparation of the catalyst nanoparticles is a crucial issue. Co-Mo binary catalysts effectively grow SWNTs either from CO [1] and from alcohol [2]. However, different values are reported as the optimum Co/Mo atomic ratio; 1/3 for the former [1] and 1/1 for the latter [2]. The structure of catalyst nanoparticles should be determined not only by the composition but also by the load of catalyst metals, and optimum conditions should depend on the CVD conditions. In this study, by using a combinatorial method [3], the SWNT growth by alcohol catalytic CVD with Co-Mo catalyst was systematically investigated and the catalytic activity was mapped against the nominal thickness of these metals. Both of these two regions showed high catalytic activity. Furthermore, at high pressure and longer time, the third region with a larger catalytic activity appeared at a large Co/Mo ratio. The mechanism for this incubation is unknown but this catalyst may be practically important in growing SWNTs at least from ethanol.

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Enhanced Growth of Millimeter-long Vertically Aligned Single-walled Carbon Nanotubes by Edge Growth

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We have succeeded in synthesizing vertically aligned single-walled carbon nanotubes (SWNTs) by radical CVD. SWNTs were grown on Si wafers with a sandwich-like structure of Al_2O_3 (0.5nm) / Fe (0.5nm)/ Al_2O_3 (>5nm) by root growth mode [1]. Their lengths increased in the order of millimeters for long time deposition, 1.5 mm for 10 hours and 2 mm for 20 hours. Growth rate of SWNTs, however, decreased as they grew longer. In this study, we have found the enhanced growth of SWNTs and synthesized 3-4 mm SWNTs with good reproducibility by an edge growth method. When vertically aligned SWNTs are grown on patterned catalysts, carbon radicals can diffuse from sidewalls of patterned SWNTs, where the diffusion path lengths of carbon radicals can be shorten. As a result, SWNTs grow fast and can be longer than the homogeneously grown SWNTs by a factor of 2 at the same deposition time. A larger amount of carbon radicals could arrive at the catalysts on the substrate from sidewalls. We expect that our SWNTs can continue to grow as long as the catalysts are active by edge growth.

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Low temperature CNT synthesis in floating catalyst reactor

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Conventionally, CNTs are synthesized at high temperature. From both production and application points of view it is important to minimise CNT synthesis temperatures to allow broader use, better control of reactor conditions and reduce manufacturing costs. We have produced single-walled CNTs in an aerosol flow reactor based on the introduction of pre-made catalyst particles via the hot wire generator (HWG) method [1] with an average total residence time as small as 4 seconds in the reaction zone. Optimization of the experimental conditions, namely, the variation of the gas composition in the CNT nucleation and growth region have allowed us to reduce the synthesis temperatures from 900 to approximately 550 °C [2].

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Correlation between oxidation state of catalyst and growth of carbon nanotubes in plasma-enhanced chemical vapor deposition

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We have analyzed multi-layered catalyst thin films with X-ray photoelectron spectroscopy (XPS) and examined their influence on carbon nanotube (CNT) growth. Thin films of catalyst and support materials (Fe/Al_2O_3) with each thickness of 3 nm were reduced by 5-Torr H_2 plasma with an RF input power of 50 W at 550 degree C. After that, the films were immediately transferred to the XPS apparatus in N_2 gas ambient without exposing to air. CNTs were grown on the catalyst thin films by $CH_4/H_2/Ar$ plasma-enhanced chemical vapor deposition at 650 degree C. It was confirmed that the CNT length became maximum for the reduction time of 4 min and decreased over 4 min. The Fe 2p XPS spectra showed that Fe_2O_3 in the as-deposited catalyst was reduced to Fe by the 4-min reduction. However, excess reduction over 4 min resulted in the peak shift from Fe to Fe_3O_4. This result indicates that content of iron oxide in the catalyst plays an important role in growing CNTs, and CNT growth can be estimated by the Fe XPS spectra.

Structural control and growth mechanism of carbon nanotubes produced by a floating catalyst method

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We demonstrate the controllable synthesis of carbon nanotubes (CNTs) with different structures by a floating catalyst method. Single-walled (SWNTs) and double-walled carbon nanotubes (DWNTs) with different diameters were selectively produced and it was found that sulfur plays an important role in their nucleation and growth. Based on experimental studies, high resolution transmission electron microscopy (HRTEM) observations and theoretical analysis, a growth model was proposed to understand the growth of SWNTs and DWNTs by a floating catalyst method. These results open the possibility for the further structural control and applications of CNTs.

Direct synthesis of single-walled carbon nanotubes by pyrolysis of ferrocene

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Single-walled carbon nanotubes (SWNTs) were directly synthesized only by pyrolysis of ferrocene in an argon environment, without the addition of sulfur and additional carbon sources reported previously for the growth of SWNTs by a floating catalyst method, such as hydrocarbons, carbon monoxide and alcohol. High-resolution transmission electron microscopy (HRTEM) observations and Raman measurements reveal that the SWNTs have high quality and their diameters are in the range of 0.6 and 2.8nm. Moreover, it is worth noting that (1) the growth of SWNTs depends strongly on the sublimation rate of ferrocene, and (2) the size of catalyst particles (3-12 nm) is larger than those of SWNTs. These results provide some useful information for understanding the growth mechanism of SWNTs produced by a floating catalyst method.

In-situ observation of SWNT growth by Raman scattering

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Inside an atomic force microscope (AFM) with Raman scattering measurement capabilities, we have synthesized SWNTs on the sample stage by using a laser-heated cold-wall alcohol catalytic CVD method. Raman scatterings from the SWNT samples were measured in-situ during the CVD process. Mo/Co metal particles, which were directly loaded on the silicon substrate by a dip-coat technique, were used as the catalyst and a CW-Ar-ion laser (488.0 nm, 50.0 mW) was used as both the heating and Raman excitation laser. After the supply of the ethanol gas (0.02-0.2 Torr), there was a certain delay time before the G-band from SWNTs appeared in the in-situ Raman scattering spectra. The intensity of the G-band increased with time, however, the intensity increase stopped after several minutes. The incubation time between the supply of ethanol gas and the beginning of SWNT growth was nearly inversely proportional to the ethanol gas pressure, and was independent of the CVD temperature.

The role of catalysts oxidation degree on carbon nanotube growth: In situ photoelectron spectroscopy studies

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Using in-situ photoelectron spectroscopy (PES) we have followed the evolution of the chemical composition during annealing and CVD of different combinations of supported-catalyst and substrates (i. e. Fe/Al2O3/Si; FeMo/Al2O3/Si; and Fe/Si). The influence of chemical composition on CNT growth will be discussed, with focus on the role of the catalysts oxidation state. It is already known that different oxidation states of the same metallic catalyst imply different growth modes and characteristics of the nanotubes [de los Arcos et al, J. Phys. Chem. B 108, 7728 (2004)]. However, in the approach we have followed until now the catalyst particles were prepared by annealing of thin films onto different substrates (Al2O3, TiN, TiO2). Therefore, it was not possible to separate the final oxidation state from the nature of the substrate, or to disentangle the influence of the substrate in the growth from the catalyst. In order to deepen our understanding of the influence of the oxidation degree, we have applied different plasma treatments (oxidative and reductive) of the same catalyst onto identical substrates. We could prepare metallic and oxidized Fe particles onto Si covered with Al2O3 thin layers, and we have determined differences in the growth process in both cases. The PES study is complemented with HR-TEM, SEM and AFM characterization.

Supported Ni catalysts of nominal submonolayers grew single-walled carbon nanotubes.

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Fe, Co, and Ni are known catalytically effective to grow single-walled carbon nanotubes (SWNTs). However, when supported on oxide substrates, Ni tends to yield only multi-walled carbon nanotubes. Enhanced surface diffusion at the elevated growth temperature may cause coarsening of Ni catalyst nanoparticles, and adjusting the nominal Ni thickness should be crucial to control the particle size.

Using our combinatorial method [1], we screened the nominal thickness of Ni for a rather wide range (0.05-3.5nm) on SiO_2 and found that Ni nanoparticles did catalyze the growth of SWNTs by alcohol catalytic chemical vapor deposition [2] only when its nominal thickness was as thin as subnanometers. The yield of SWNTs was much smaller for Ni than Co although the optimum metal thickness is somewhat larger for Ni (~ 0.2 nm) than Co (~ 0.1 nm). This poorer catalytic activity may arise from the existence of inactive Ni nanoparticles or the growth of thinner SWNTs than Ni nanoparticles.

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Synthesis of carbon nanotubes from Ni nanoparticles formed with organic Ni complex

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The field emission performance of carbon nanotube (CNT) cathodes is affected by structural features of CNT such as size, density and alignment. In the growth of CNT by catalytic thermal chemical vapor deposition (C-TCVD), CNT structures are strongly related to catalyst nanoparticles. Therefore, control of their size and density is very important issue. We report a new C-TCVD growth method which is capable of carefully controlling the size and density of the catalyst nanoparticles. Formation of Ni nanoparticles and synthesis of CNT are successively carried in an identical growth chamber. To form nanoparticles, organic Ni complex gas was used as a precursor. Size and density of nanoparticles can be controlled by varying the molar flow rate, decomposition temperature and flow time. When nanoparticles were formed at a flow rate of Ni complex at 3.5 μmol/min and substrate temperature of 700 °C, the diameter and density of nanoparticles were 20-30 nm and 1.3×10^{11} cm^{-2}, respectively. Following the formation of nanoparticles, CNTs were successively grown by thermal CVD at 800 °C. Acetylene was used as a carbon source. The transmission electron microscopy observation confirmed the formation of Ni nanoparticles and the growth of multiwalled CNTs.

Surface reactions of Co catalysts in ethanol-CVD ambient at low-pressure studied by *in situ* photoelectron spectroscopy

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Since the growth mechanism of carbon nanotubes (CNTs) using CVD is the key to controlling the CNT structure, such as its chirality, it has attracted great deal of interest and has been hotly debated based on *in situ* analyses. In this work, we looked at the surface reactions of catalyst-nano-particles using *in situ* photoelectron spectroscopy (PES), which is one of the most suitable methods for the chemical analyses at surfaces.

For the *in situ* PES, we used a 2-nm-thick-Co thin film formed on an SiO_2 thin layer. The substrate was heated to 600°C under ethanol pressure of less than 0.1 Torr, which was introduced into existing photoelectron analysis system. Single-walled CNTs were obtained by this procedure (although the CNT density is very low) and this as-grown surface was analyzed without exposure to air. From this surface, single peaks of asymmetric C 1s and Co 2p spectra were observed. Also, a pi-plasmon-loss structure was observed on the C 1s. These results indicate that Co metal (not carbide) particles are covered with thin graphite or amorphous carbon layers. This means that Co carbides are not stable under the CNT growth atmosphere, although almost all photoelectrons were obtained from inactivated catalyst particles.

Molecular Dynamics Simulations of a Nucleation Process of an SWNT in Alcohol Catalytic CVD Technique

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The nucleation process of a single-walled carbon nanotube (SWNT) considering the dissociation of once-deposited carbon atoms from catalytic metal cluster is studied using classical molecular dynamics (MD) simulations. Experiments suggest that, in the alcohol catalytic CVD (ACCVD) technique, the dissociation of carbon atoms with dangling bonds through the reaction with oxygen atoms may play a key role. As a model system of the ACCVD method, based on the previously reported MD simulation technique [1], the current simulation takes the dissociation process into account. Following an interpretation of the experimental results, the dissociation process is expressed by removing one carbon atom with dangling bonds when three carbon atoms are attached to the metal cluster [2]. Since the dissociation of carbon atoms with dangling bond prevents from the formation of carbon shell around the catalyst cluster, continuous growth after the formation of initial cap structure is expected.

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Gas-Phase Synthesis of Single-Walled Carbon Nanotubes by Hot-Filament-Assisted Plasma CVD

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Single-Walled Carbon Nanotubes (SWNTs) have been successfully synthesized in gas phase by Hot-Filament-Assisted Plasma Chemical Vapor Deposition. Hot filaments of 1800-2000 °C were used for heating fine particles. 40 % ethylene diluted in hydrogen containing the vapor of ferrocene was flowed toward the hot filaments. The pressure in the chamber was maintained at 5.33 kPa (40 Torr). The plate of RF electrode was set 25mm downstream from the hot filaments and placed perpendicular to the flow. RF power was applied to the plate with the filaments grounded and heated for about one hour. Carbon fine particles on collecting plates put under and after a plasma were evaluated by Raman spectroscopy to be confirmed SWNTs. The fact that more SWNTs were obtained on the under-plate than on the after-plate suggests that fine particles were suspended in a plasma for a long time. While fine particles including SWNTs were synthesized, the streams of fine particles were observed by scattering of lights emitted by hot-filaments. By the observation of scattered lights, the control of synthesis processes will be possible.

CVD growth mechanism of single-walled carbon nanotubes from alcohol

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By using alcohol as carbon source, high-purity single-walled carbon nanotubes (SWNTs) can be generated at relatively low CVD temperatures. Based on these findings, we have proposed the alcohol catalytic CVD (ACCVD) technique for bulk and vertically aligned synthesis of SWNTs. In addition to the conventional metal particles supported on zeolite, we have developed a simple dip-coat method to directly disperse nano-particles on flat substrates such as quartz and silicon. The vertically aligned SWNTs film with about 30 μm is grown on quartz substrates by employing the most efficient activation of catalytic metals. In addition to molecular dynamics simulations, various experimental techniques have been employed to understand the growth mechanism of SWNTs: direct TEM observation of catalysts particles; in-situ Raman and AFM measurements during CVD; in-situ monitoring of laser absorption; combinatory spattering method to prepare catalysts. The chirality distribution of SWNTs measured by the near infrared fluorescence spectroscopy is quite unique for low-temperature ACCVD condition. The near armchair nanotubes are predominantly generated probably because of the stability of nanotube cap structure.

Separation and deposition of individual single-walled CNTs synthesized in CO-ferrocene system

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Single-walled carbon nanotubes (CNTs) are promising building blocks for nano-scale devices due to their unique structural and electronic properties. In order to fully utilize CNTs in their applications and accomplish their integration to new nanoelectronic devices, methods for the synthesis, isolation and manipulation of individual nanotubes are required. Here, we elaborate a novel approach for the separation of individual single-walled carbon nanotubes from bundles in gas phase and further deposition on any type substrates including temperature sensitive materials. The experimental results of the deposition of individual single-walled CNTs obtained on the basis of the TEM and AFM microscopy are presented.

Studies on mechanism of single-walled carbon nanotube formation

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We present detailed studies of the formation of single-walled carbon nanotubes by an aerosol method based on the introduction of pre-formed catalyst particles into conditions leading to carbon nanotube synthesis. Carbon monoxide and iron nanoparticles were used as a carbon source and a catalyst, respectively. The vital role of etching agents such as CO_2 and H_2O in CNT formation was demonstrated on the basis of on-line Fourier-transform infrared spectroscopy measurements. Hydrogen was shown to participate in the reaction of carbon release and to prevent the oxidation of the catalyst particles and the hot wire. The addition of H_2 and small amounts of CO_2 and H_2O led to an increase in the carbon nanotube lengths. The catalyst particle evaporation process inside the reactor was found to become significant at temperatures above 1100 °C, however, carbon nanotube growth was found to occur at a temperature of approximately 900 °C in the heating section of the reactor by in situ sampling and the growth rate was calculated to exceed 1.1 μm/s. A detailed analysis of possible processes during carbon nanotube formation revealed heptagon transformation as a limiting stage. A mechanism for carbon nanotube formation is proposed.

Highly aligned carbon nanotube synthesis by RF-plasma-assisted DC plasma CVD under high electric field

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Very highly aligned carbon nanotubes (CNTs) have been synthesized by the method of RF(radio-frequency)-plasma-assisted DC(direct current) plasma chemical vapor deposition, which was developed for the large-area growth of highly aligned CNTs under stable DC plasma without arcing. Three parallel electrodes, an RF electrode, a grounded electrode, and a DC cathode, were arranged in a vacuum chamber. The tip of a grown CNT was observed by a transmission electron microscope (TEM), and it was revealed that the top surface of CNT directly bombarded with ions is amorphous and the graphitic wall was etched at the top edge although the CNT was not seriously damaged. By an analytical consideration, it was found that, under the experiment conditions, ions are collisional in the sheath and that the condition of high DC voltage application in high pressure forms high sheath electric field to result in highly aligned growth of CNTs. It was also found that ion bombardment energy impinging on a cathode was less than 100 eV in the experiment. Such moderate energy ions should condition etching and growth without serious damage.

Analyses of Early Stages of Aligned Carbon Nanotube Growth by Surface-Wave-Excited Microwave-Plasma CVD

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Well-aligned Carbon nanotubes (CNTs) synthesized by plasma CVD are expected for electron emitters. However, the mechanism of the synthesis is not clarified enough. In surface-wave-excited microwave-plasma CVD, the analyses of early stages of aligned CNTs growth was done in this research.

The surfaces of iron foils were pretreated in hydrogen DC plasma. Then, CNTs were grown by methane addition. The specimens were taken out in the early stages of growth, and the surfaces of them were analyzed by SEM.

It was found from the result of the experiment that iron fine particles were coalesced after the dissolution of carbon into catalytic fine particles by methane addition. Then the fine particles became smaller, and the synthesis of CNTs started. The early stage of CNT growth is being investigated with the help of in-site ellipsometry.

Determination of the C^2 vibrational temperature from the molecular emission bands during PE-CVD growth of carbon nanotubes

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In order to optimise the growth conditions for forests of carbon nanotubes and individual vertically aligned carbon nanofibres we have used optical emission spectroscopy for monitoring the plasma and for determining the C^2 vibrational temperature from the molecular emission bands. The vibrational temperature can be quite decoupled from the translational and rotational temperatures.

We found a vibrational temperature of the C^2 radical in excess of 10000 K. The temperature is strongly dependent on the plasma current density. Carbon nanotubes are grown at different plasma conditions and their properties were correlated with optical measurements.

How Do Carbon Nanostructures Form on Nickel Surfaces ? A Tight binding Grand Canonical Monte Carlo study.

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The self-organization of carbon atoms close to a nickel surface, which is a process involved in the catalytic growth of carbon nanotubes, is analyzed using grand canonical Monte Carlo simulations based on a specifically designed tight-binding interaction model. This model (1) accounts for the competition between very different local configurations around carbon atoms and for the thermodynamics of the NiC bulk system. On crystalline (111) and (100) Ni surfaces, as well as on crystalline or liquid Ni droplets of different sizes, we show that a substantial excess of carbon chemical potential, as compared to the bulk equilibrium value, is necessary to grow nanostructures on the surface. The growth proceeds in the following three steps way : i) single C atoms are adsorbed on the surface or incorporated in interstitial sites; ii) chains creeping on the surface are formed, and iii) sp^2 C atoms formed at the intersections of the chains gradually build a layer that interacts weakly with the Ni surface.

(1) H. Amara, C. Bichara and F. Ducastelle, PHYSICAL REVIEW B 73, 113404, 2006.

Selective Growth of Vertically Aligned Single and Double-Walled Carbon Nanotubes on a Substrate by Hot-Filament Chemical Vapor Deposition

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Carbon nanotubes (CNTs) have been attracting a great deal of attention due to their electrical and mechanical properties. Many electronic devices such as transistors have been suggested using CNTs, especially single-walled and double-walled carbon nanotubes (SWNTs and DWNTs) [1]. For such applications, it is important to synthesize SWNTs and DWNTs on a desired substrate at a low temperature. In this presentation, we report on vertically-aligned SWNT and DWNT growth on a silicon substrate at temperatures lower than 600 °C. SWNTs and DWNTs were grown by hot-filament chemical vapor deposition, which is a powerful method for CNT growth at a low temperature. During the CVD process, acetylene was used as the carbon source, which was diluted by hydrogen. Iron and aluminum double layers were used as a catalyst. By optimizing the growth condition, we succeeded in growing vertically aligned CNTs consisting of 75% DWNTs or 100% SWNTs selectively. The results indicate that the average shell number of CNTs can be controlled by changing the ratio of the source gas to hydrogen.

[1] S.J. Wind et al., Appl. Phys. Lett. 80 (2002) 3817.

CVD synthesis, bonding environment and electronic properties of CNx single and double wall carbon nanotubes

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It is known that in layered sp2 carbon arrangements it is possible to modify the electronic, vibrational, chemical and mechanical properties by replacing some of the carbon atoms with nitrogen. Aiming a substitutional configuration, we have synthesized single and double walled CNx nanotubes by the chemical vapor deposition of pure benzylamine and ethanol with acetonitrile mixtures employing wet chemistry supported catalysts on substrates and directly using multilayer sputtered films of catalysts. Single and double walled nanotubes are obtained and later characterized regarding morphology by means of high-resolution transmission electron microscopy (HRTEM)and scanning electron microscopy(SEM). Optical probes such as Raman, infrared and optical absorption spectroscopy are used for the characterization regarding their diameter size and distribution, overall yield, morphology, alignment and crystallinity. In order to determine the nitrogen content on a local scale, TEM electron energy-loss spectroscopy (EELS) is performed by mapping individual tubes, which is complemented on a bulk scale by high resolution transmission EELS experiments in a purpose built machine. In addition this allows us to clarify details in the bonding environment as well as the internal charge transfer and electronic properties of the CNx nanotubes with substitutional doping in comparison to pristine nanotubes.

Overheated Carbon Source for High Yield and Low Temperature Carbon Nanotubes Growth

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We present a new technique to enhance the growth yield of carbon nanotubes (CNTs) and decrease the growth temperature of CNTs. Our catalysts are iron or alumina supported iron thin films, and our carbon source are ethylene or methane and ethylene mixture. In order to get the overheated carbon source, the carbon source first passes through the 900 ^{o}C reign for overheating and then goes into 600 ^{o}C reign for the CNTs growth. When the carbon source is cooling down in the 600 ^{o}C reign, a lot of carbon comes out and then becomes the source of the CNTs. Without this technique, the CNTs are barely grown at the same gas condition and temperature condition. This method can be used for low temperature growth and mass production of CNTs.

A Flexible, Controllable, and Observable Platform for Laboratory Studies of Carbon Nanotube Growth

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We present a benchtop apparatus for studies of carbon nanotube synthesis (CNT), where the growth temperature is locally maintained by resistive heating of a silicon substrate. The small thermal mass of the substrate and the suspended configuration enable rapid heating and cooling at ≈100 °C/s, using DC power (≈25 V, 4 A) in current-control mode. The substrate is a strip cut from a p^{++}-doped silicon wafer, and is electrically contacted using stainless steel blocks. By decoupling the gas and substrate temperatures we grow vertically-aligned MWNT monoliths to a thickness of 3 mm in just 15 minutes in a $C_2H_4/H_2/CO$ atmosphere, as well as tangled SWNT films in CH_4/H_2. Optical imaging during growth directly measures thickness versus time, and reveals how cracks develop in thick CNT films. Combining these results with Rutherford backscattering spectrometry measurements of the substrate surface, we study competing effects of catalyst migration and reactant diffusion limitation on the terminal film thickness.

Rapid heating of the reaction gases upon contact with the substrate facilitates high-precision studies of how thermal treatment affects reactant activity and growth progress. Further, a microchannel device for combinatorial flow studies of CNT growth is packaged on the substrate using spring clips.

Together, these technologies seek to overcome the limitations of tube furnaces which do not permit rapid adjustment of gas flow or temperature, moving toward spatial and temporal control of reaction conditions matching the dynamics of individual growth events.

High-Precision and Combinatorial Studies of Carbon Nanotube CVD Synthesis using Microchannel Arrays

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We present a system and methodology for combinatorial flow studies of nanomaterials growth using precisely-fabricated microchannel arrays as reactors, and its application to CVD growth of CNTs. Through a unique microchannel design which utilizes anisotropic etching of single-crystal silicon in KOH, an arbitrary velocity progression is achieved across the array, enabling dozens of simultaneous isolated flow experiments. For example, flow velocities across the array range from 0.001–1.0 m/s, with a differential flow between neighboring channels as low as 1×10^{-5} cm^3/min. The arrays are batch-fabricated on 6” wafers in a single etch step, and for growth an array is inverted over a second silicon substrate coated with a lithographically-patterned catalyst film. The substrate pair is clamped and placed in a tube furnace or on a resistively-heated substrate. Because of a reversible seal between a mating polished and non-polished surface, the catalyst pattern is easily removed for characterization, and the microchannel array is cleaned and reused.

Using CVD reactions which we have previously studied in tube furnaces [1,2], we observe transitions in CNT yield and quality along the microchannels, manipulate transitions between tangled and vertically-aligned growth morphologies, and grow CNTs which are aligned by the gas flows through the microchannels. Further, this technology generally enables direct growth of CNTs in microfluidic devices, for applications including sensing, filtration, and catalysis.

[1] A.J. Hart, A.H. Slocum, L. Royer. Growth of Conformal Single-Walled Carbon Nanotube Films from Mo/Fe/Al_2O_3 Deposited by Electron Beam Evaporation, *Carbon*, 44(2):348-359, 2006.

[2] A.J. Hart, A.H. Slocum. Rapid Growth and Flow-Mediated Nucleation of Millimeter-Scale Aligned Carbon Nanotube Structures from a Thin-Film Catalyst, *J. Phys. Chem. B*, in press, 2006.

Synthesis, purification, and optical properties of double-wall carbon nanotubes

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Previously, we demonstrated it is possible to control number of layers of carbon nanotube in an alcohol chemical vapor deposition technique by changing catalyst. Fe/MgO catalyst preferably produced double-wall carbon nanotube (DWCNT) as well as single-wall carbon nanotube (SWCNT). In this work, we have purified mixed soot of SWCNTs and DWCNTs and successfully removed SWCNTs in the soot. After the purification, typical resonance Raman peaks of radial breathing mode (RBM) originating from SWCNTs completely disappeared and some new peaks appeared. This means the observed RBM peaks are originating from nanotubes having the same diameters but having different electronic structures. Indeed, optical absorption spectrum and photoluminescence mapping from the inner nanotubes showed slightly modified electronic structures from that of SWCNTs. Interestingly, even thin film of the sample still indicates photoluminescence from the inner nanotubes, which suggests the inner nanotubes are well isolated with less interaction between outer nanotubes. By comparing excitation spectra of directly grown isolated SWCNTs, micelles of SWCNTs, and DWCNTs, we will discuss the effect of surrounding media on excitons in carbon naotubes.

The effect of process parameters in the growth of carbon nanotubes at atmospheric pressure using ferrocene-ethanol mist

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In this paper, we present the continuous growth of carbon nanotubes (CNTs) by chemical vapor deposition (CVD) at atmospheric pressure (~1 atm) using alcohol-ferrocene mist. An electrical ultrasonic vibration with high frequency of ~1.8 MHz was used for generating tiny mist. The effects of the position in the reactor, the growth temperature, the ferrocene/ethanol ratio, the gas flow rate and the reacting time on the formation of CNTs were investigated using scanning electron microscopy and Raman spectroscopy. The results showed that CNTs with narrow diameters could be formed outside the furnace even at low substrate temperature, instead of the center of the furnace. The high growth temperature could increase the diameter and impurity (intensity ratio of G-band to D-band) of the CNTs. The ferrocene/ethanol ratio did not affect the diameter, but strongly influenced the impurity of the CNTs. The gas flow rate also did not affect the diameter, but strongly influenced the impurity and the growth rate of the CNTs. The obtained CNTs had a narrow diameter of ~0.8-1.4 nm, evaluated from Raman spectra. The described method is simple, does not require vacuum and hazardous gases, and can be applied for producing continuous narrow nanotubes at a low temperature.

Effect of precursor chemistry on the direct spinning of fibres of carbon nanotubes

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We have previously introduced a continuous catalytic gas-phase process for carbon nanotube (CNT) formation and collection in bulk quantities (Li et al. Science 304, 2004, 276-278). The major benefit of this process is the ability to collect the CNTs continuously as pure fibres or films. Reaction chemistry controls both the formation of carbon nanotubes and the ability to continuously withdraw product. We will discuss the effect of ethanol and hexane as carbon sources, various catalyst compositions, concentrations and particle sizes as well as additives on the process. The use of different catalysts and additives results in the formation of different types of nanotubes and in changes on the conditions for continuous spinning. Raman spectroscopy and transmission electron microscopy were carried out in order to understand CNT formation, bundling and assembly as an aerogel. In-line mass spectroscopy showed that the carrier gas (H_2) and CH_4 are the main gaseous species at 1100°C, despite thermodynamic predictions. The presence of oxygen and sulphur seems to facilitate the formation of a continuous aerogel instead of soot. Mainly multiwalled CNTs form when ethanol is used as the carbon source, while under similar process conditions single/double walled nanotubes are more easily produced with hexane.

Single wall carbon nanotube synthesis from ferrocene and iron pentacarbonyl: Nanotube nucleation and growth in the gas phase

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Single walled carbon nanotubes (SWCNTs) were produced in the gas phase by the thermal decomposition of iron pentacarbonyl or ferrocene in the presence of carbon monoxide. Experiments were carried out in ambient-pressure laminar-flow reactors in the temperature range of 600-1300°C. In order to prevent growth of catalyst particles, and therefore the formation of nanotubes, it is beneficial to use a carbon source and a catalyst precursor that decompose at similar temperatures. Ferrocene was found to be a better catalyst precursor in the studied conditions since iron pentacarbonyl decomposes at a lower temperature resulting in excessive growth of catalyst particles. In situ sampling carried out at 1000°C showed that the SWCNT growth occurred from individual metal particles in the heating section of the furnace in the temperature range of 891-928°C, in which the growth rate was estimated to exceed 2 μm/s. FTIR measurements show that ferrocene does not decompose completely in the process. High-purity SWCNT product was confirmed with Raman spectroscopy and transmission electron microscopy. On-line aerosol number size distribution measurements were carried out to detect SWCNT formation and product morphology changes at different process conditions.

Continuous production of single/double walled carbon nanotubes as high performance fibres

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Pure fibres of single/double walled carbon nanotubes can be directly spun from the gas phase when an aerogel is pulled to a region outside a CVD reactor. The amount of iron catalyst dissolved in the feedstock solution was adjusted to below 0.01 wt% to form catalyst particles with suitable size for the growth of single/double walled nanotubes. The amounts of carbon and carrier gas in the reactor also had to be adjusted to ensure that enough nanotubes were available for the formation of a continuous aerogel and, therefore, the spinning of the fibres. At present these fibres are spun at a rate of ~5m/min, with the average linear density (TEX) of 0.25 g/km. Under optimum conditions two particularly interesting types of fibres were produced, namely high-strength (2.2 N/TEX) and high-toughness (125 J/g) fibres. Electron microscopy shows that the fibres are composed of bundles at least tens of microns long with an average diameter of 30 nm. The nanotubes found isolated from the bundles are double walled with remarkably large diameters, typically 5-9 nm.

Role of sulphur on the production of carbon nanotubes by chemical vapour deposition

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Sulphur has been extensively reported to act as a promoter for the growth of carbon nanotubes in chemical vapour deposition processes. We previously introduced a process for continuous spinning of fibres from individual carbon nanotubes (Li et al. Science 304, 2004, 276-278). In this process, ferrocene and thiophene dissolved in a liquid carbon source decompose during heating and form catalyst nanoparticles (< 20 nm) that act as nucleation sites for the growth of carbon nanotubes. Experiments were carried out with different sulphur concentrations with respect to iron. Optimal conditions were found at Fe/S = 0.7, although fibres could be spun continuously even when Fe/S is as low as 0.07. However, fibres could not be spun in the absence of sulphur. High-resolution composition mapping in a dedicated scanning transmission electron microscope has shown that sulphur is present as a thin layer at the ironcarbon interface. Based on these results it is suggested that sulphur favours the carbon nanotube growth through surface diffusion.

Numerical Predictions of the Chemical and Physical Conditions in Floating CVD Reactors Influencing the Nucleation and Growth of Carbon Nanotubes

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The evolution of iron catalyst particles during floating catalyst Carbon Nanotubes (CNT) Chemical Vapor Deposition (CVD) synthesis from CO is computed using a Computational Fluid Dynamics (CFD) model incorporating an aerosol method of moments (MOM) to describe their dynamics and a combined chemical kinetics and equilibrium model for catalytic production of CO_2. The influence of iron at the reactor walls, fed particle size, concentration and polydispersity and catalytic production of CO_2 at the reactor wall are studied. It is found that catalyst particle dynamics are essentially insensitive to wall effects and, for a wide range of particle sizes and concentrations, it is found that the catalyst particles are stable up to a window in which CNT nucleation and growth occurs. Concentrations of catalyst particles significantly above 1×10^{14} #/m^3 lead to poor control over catalyst particle size and polydispersity at the CNT nucleation front which, in turn, lead to poor control over CNT diameter. The growth window location is shown to be associated with the availability of catalytically produced CO_2 diffusing from the reactor walls. These results help to explain the large variations in CNT diameter and chirality and the inefficient use of catalyst material in many floating catalyst CNT processes.

Mass production of Single-walled carbon nanotubes using nanoporous catalyst by CVD method

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An economical production method for single-walled carbon nanotubes in large quantity using MgO nanoporous catalyst is developed. Co-Mo catalyst supported MgO nanoporous were prepared by sol-gel method[1]. Methane decomposition at 900- 1000°C over catalyst surface produced carbon nanotubes with single wall structure using a special rotary reactor. TEM, SEM, XRD, TGA and Raman Spectroscopy techniques were utilized to characterize the product and shows that Up to 180 wt % yield of high quality, SWNTs with inner wall diameter distribution close to 1.0-1.2 nm are obtained.

[1] A.M. Rashidi, M.M. Akbarnejad, A.A. Khodadadi, Y.Mortazavi,High yield and selectivity single wall carbon nanotubes synthesis on Co-Mo catalysts supported on Nanoporous MgOsubmited in journal of carbon

Ab initio calculation of cyclacene-based carbon nanotubular compounds

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We use *ab initio* Density Functional calculations to investigate the interplay between structural and electronic properties of a new class of one-dimensional nanowires, related to carbon nanotubes [1]. The cyclacene building blocks consist of phenyl rings, and can be viewed as the shortest segments of (n,0) zigzag nanotubes. The nanowires are formed by inter-connecting cyclacenes to a chain using biphenyl, tetrazine, or acetylene linkers. Depending on the nature and the orientation of the linkers, we find it possible to change the systems from narrow- to wide-gap semiconductors, and to modulate the band dispersion, suggesting the possibility of band gap engineering.

[1] Glen P. Miller, Shinya Okano, and David Tomanek, Toward uniform nanotubular compounds: Synthetic approach and *ab initio* calculations,
J. Chem. Phys. **124** , 121102 (2006).

Observation of Bamboo-liked Structure of Carbon Nanotubes Prepared via Pulsed Laser Ablation Technique

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The bamboo-liked carbon nanotubes were formed by laser ablation using a graphite target containing 10 weight percentage of NiCo catalysts. An Nd:YAG laser with 532 nm wavelength, 10.54 W was used to ablate the target to form the carbon nanotubes. The pressure inside the chamber was kept at 4 Torr and the bamboo-liked carbon nanotubes were formed on the substrate after 30 minutes of laser ablation. The TEM images showed that the diameter of the carbon nanotubes formed by NiCo catalyst were about 35 nm.

KEYWORDS: carbon nanotubes, Nd: YAG laser, pulsed laser ablation, bamboo-liked structure, catalyst.

Development of Fe-doped carbon electrode for mass-producing high-yield single-wall carbon nanotubes

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Macroscopic net of high crystallinity single-wall carbon nanotubes (SWNTs) with high-yield can be prepared by arc discharge evaporation of carbon electrode containing 1 at% Fe catalyst in hydrogen mixed gas [i.e., H_2-inert gas (Ne, Ar, Kr, Xe), or H_2-N_2]. However, the yield of SWNTs is strongly affected by the kind of carbon electrode materials. Here, we report the development of high-quality Fe-doped carbon electrode for mass-producing high-yield SWNTs. More than fourteen kinds of carbon materials have been used to prepare Fe-doped carbon electrode, and the Fe-doped carbon electrode have been also heat-treated at different temperature from 1473 to 3173 K. It has been found that only low-crystallinity carbon materials are suitable for preparing high-quality Fe-doped carbon electrode, and heat treatment also plays an important role. At present, the best carbon electrode containing 1 at% Fe catalyst is capable of generating $\sim$ 10 g/day of high-yield SWNTs in our laboratory. Moreover, these SWNTs can be easily purified by a liquid-phase and macroscale purification process, reflux treatment in H_2O_2 solution and rinsing with hydrochloric acid, to obtain SWNTs with purity higher than 90 at%.

Continuous Synthesis Single-Walled Carbon Nanotubes from Carbon Black

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High purity single-walled carbon nanotubes were synthesized continuously by injecting carbon black into electric arc. The process was optimized using DC electric arc in normal pressured argon. Since carbon black has similar structure to graphite, but less expensive and has some mineralelement, which can promote the growth of carbon nanotubes. We studied the catalysis effect of Fe,its oxide and salt. The best proportion of catalyst to carbon black (mass%) is 20~30%. The catalysis effect is $Fe \sim Fe_2O_3 > Fe_3O_4 > FeS > FeCl_2$.The single-walled carbon nanotubes coarse purity can reach 30%.The result was characterized by scanning electron microscope and transmission electron microscope.

The growth mechanism from carbon black to carbon nanotubes was put forward in this paper.

Draw out Carbon Nanotube from Liquid Carbon

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Carbon nanotube (CNT) is expected for much more important and broader applications in the future, because of its amazing electrical and mechanical properties. However, today, the prospect is detained by the fact that the growth of CNTs cannot be well controlled. In particular, controlling the chirality of CNTs seems formidable to any existing growth method. In addition, a systematic method for a designed interconnected network has not been established yet, which is focused particularly in nano-electronics field. Up to now, there is a strong need for novel synthetic method that is controllable for chirality and architecture and applicable to mass production. Recently, the experimental evidences were reported for the growth of pure carbon-arc-product nanotubes from a liquid precursor(W. A. de Heer, et.al,Science 307, 907 (2005)). Here we show the simulation results of elongated growth process of CNT by drawing out a well-formed nanotube from liquid carbon and discuss the mechanism and suitable synthesis conditions. The process is also simulated for creation of a Y junction from two isolated CNTs as first step to CNT network. We propose this novel synthetic method as a promising one for catalyst-free mechanical design of interconnected CNT network and CNT cloning. (http://arxiv.org/abs/cond-mat/0604043)

Fabrication of Carbon Nanotube Pattern on 6H-SiC(000-1) using Ti mask

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It has been reported that well-aligned zigzag-type carbon nanotubes (CNTs) could be produced with fairly uniform tube diameters by surface decomposition of SiC(000-1). To fabricate CNT-based device, it is important to form selectively CNTs on SiC surface. In this study, we used Ti as a mask for selective growth of CNT on SiC, since the melting point of Ti is higher than the decomposition temperature of SiC surface.

Equal line-and-space Ti patterns 10 micro-meters in width were fabricated on SiC(000-1) surface. The samples were heated at 1270°C for 30 min at 10^{-6} Pa, followed by annealing at 1700°C for 30 min at 10^{-2} Pa. After each treatment, the surfaces of the samples were investigated by SEM, STM, XPS and micro Raman spectroscopy.

At the open areas of the Ti mask, carbon nanocaps were formed at 1270°C by STM observations, and strong G band peak was observed after annealing at 1700°C in micro Raman spectroscopy. In addition, XPS spectra showed that Ti was still present even after annealing at 1700°C. From these results, the effectiveness of Ti mask was shown for the selective growth of CNT on SiC.

XPS and STM studies of the effects of oxygen ambient on carbon nanotube growth into SiC by surface decomposition

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It has been reported that well-aligned zigzag-type carbon nanotubes (CNTs) with fairly uniform tube diameters could be produced by surface decomposition of SiC(000-1). In this study, the effects of oxygen on CNT growth into SiC by the surface decomposition were investigated.

After HF etching, 6H-SiC(000-1) (Carbon-face) samples were introduced into ultra-high vacuum (UHV) chamber and annealed at 1270°C under various oxygen partial pressures (10^{-4} Pa , 10^{-3} Pa) by control of the supply of oxygen gas. For comparison, we also annealed several samples under UHV ($\sim 2\times10^{-8}$ Pa). The surfaces of the samples after annealing were investigated by STM and XPS.

After annealing for 30 min, STM observation showed that, irrespective of the oxygen pressure, carbon nanocaps were formed on SiC surface, indicating the formation of CNTs. C 1s XPS spectra showed that the ratio of the peak intensity of the sp^2 component to that of the SiC component became large, as the oxygen partial pressure increased. Our results indicate that oxygen enhances the decomposition of SiC surface, promoting the growth of CNTs into SiC. By estimating the thickness of CNT layers by angle-resolved XPS, the growth rates at various oxygen pressures were determined.

Synthesis of multiwall carbon nanotubes by pulsed laser irradiation of liquid

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In this work, a simple method has been developed for the synthesis of multiwall carbon nanotubes (MWCNTs) under room temperature and atmospheric pressure. In the proposed method, a pulsed Nd:YAG laser (355 nm, 10Hz) irradiates the mixture of ferrocene [$Fe(C_5H_5)_2$] and xylene [$C_6H_4(CH_3)_2$] solutions in which ferrocene plays the role of a catalyst while xylene is the carbon source for MWCNTs growth. Upon the completion of laser irradiation, typically for about one to two hours, the color of solution changes from transparent orange to dark brown. MWCNTs are found in the solution with co-existing other forms of carbon nanostructures. The characteristics of these carbon nanotubes and nanostructures analyzed with Raman spectroscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM) are presented.

Synthesis of SWCNTs by arc-discharge process using nonmagnetic catalysts

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We demonstrate that it is possible to grow SWCNTs large enough to accommodate larger fullerenes using nonmagnetic metal catalysts. The growth was performed in water-cooled dc arc-discharge Krätschmer generator with horizontally aligned electrodes. We used different catalysts such as Pt, Rh, Pd and their mixtures, as well as various buffer gases and additives. Different methods such as Raman and optical spectroscopy, TGA and TEM were used for characterization of the material produced at the various growth conditions. The highest yield of SWCNTs was obtained for Pt/Rh mixture. Both, the type and the pressure of the buffer gas strongly affect the yield of SWCNT webs, but they have only a small influence on the diameter of SWCNTs. In fact only a slight increase of diameters was observed with the decrease of the molecular mass of buffer gas and with the decrease of its pressure. The highest yield of SWCNT webs was obtained when helium was used as the buffer gas. The concentration of sulfur promoter strongly influences the yield of SWNTs and affects their diameter distribution. The addition of 0.5 at% sulfur into Pt/Rh/C anode gave the maximum yield of SWCNTs. Diameters of tubes increase with increasing sulfur concentration.

Toward low temperature growth of carbon fibers by means of reactive sputtering

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Carbon fibers and carbon nanotubes have long been considered as prominent candidates for wiring in information devices. Low temperature in-situ growth of carbon nanotubes onto silicon based substrate is important from the application point of view. Sputtering has been widely used in fabrication of electronic devices. Sputtered atoms normally have energy as high as several electron volts. Such high energy makes it is possible to fabricate well crystallized thin films at relatively lower temperature. In this study, reactive sputtering has been proposed to growth carbon nanotubes. Particular efforts have been paid to control the catalyst particle size and size distribution. Acetylene gas was used to increase the growth rate.

To prepare catalyst particles with uniform particle size, we have utilized the nano-porous structures of anodized aluminum oxide films. Aluminum films, with thickness around 50 nm, were first deposited onto thermally oxidized silicon wafer with a 10 nm thick W underlayer. The films were then anodized to obtain nano-porous structure. It is found that the size of the nano holes depended on the anodizing voltage. Lower anodizing temperature is suitable to prepare smaller nano-holes. Holes with diameter of 10 nm can be prepared at anodizing voltage of 10 V. The silicon wafer with catalyst particles were served as substrate to growth carbon nano-tubes. According to the experimental results, carbon nanotubes with diameter of about 40 nm were successfully prepared at temperature of 500 ^{o}C. After prearation ost particles have been deposited onto thermally oxidized silicon wafer. Anodized aluminum oxide films have been used to control the catalyst particle size and size distribution. After preparation of the Fe catalyst particles, acetylene gas, incorporated with the Ar sputtering gas, was introduced in to the sputtering chamber. The growth rate has been increase to about 10 times than only using carbon sputtering target.

In conclusion, carbon nano-tubes have been successfully prepared by reactive sputtering process at temperatures as low as 500 ^{o}C.

A novel method for the ambient temperature substrate deposition of individual single-walled carbon nanotubes based on gas-phase charging

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Spontaneous gas-phase charging phenomenon of single-walled carbon nanotube (CNT) bundles synthesized with an aerosol (floating catalyst) method (1) was discovered. CNT bundles were both positively and negatively naturally charged, whereas individual nanotubes remained electrically neutral. The origin of this surprising phenomenon was directly correlated to the bundling of the nanotubes. On the basis of the observed self-charging of CNTs, a novel method for the gas-phase separation of individual CNTs from bundles and their subsequent deposition on any solid substrate at ambient temperature was developed. This method opens new avenues for the direct integration of CNTs produced in gas phase into silicon-based electronics as well as into the rapidly developing area of flexible electronics (i.e. electronics based on the use of temperature sensitive materials).

(1) A. G. Nasibulin, A. Moisala, D. P. Brown, H. Jiang, and E. I. Kauppinen. Chem. Phys. Lett. 402, 227, 2005.

Characterization of Carbon Nanotubes Formed on Silicon Carbide Materials by Surface Decomposition

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Carbon nanotubes (CNTs) have been formed on the surface of silicon carbide (SiC) wafers during high temperature anneals (1400-1700°C) under moderate vacuum conditions (10^{-2} - 10^{-5} torr). No metal catalysts are required for this CNT growth method and the resulting CNTs are vertically aligned on the SiC substrate and have a high purity. Scanning electron and transmission electron microscopy along with Raman scattering measurements have confirmed the presence of both single-wall and multi-wall CNTs with a dispersion of nano particles of graphitic carbon.

In this work, we extend this growth technique to include CNT growth on 3C-SiC nano particles with diameters of 45nm and 38 μm. We also investigate CNTs formed on carbon foams and carbon fibers that have a chemical vapor deposited layer of 3C-SiC. Using scanning electron microcopy (SEM), Raman Spectroscopy, and transmission electron microscopy (TEM) the resulting CNT structures are characterized on these novel substrates. We also report on the use of these materials for electrochemical impedance spectroscopy (EIS) and anodic stripping voltammetry (ASV), due to chemisorption of gases onto the CNT arrays, and the subsequent development of sensors for aqueous and vapor phase chemical detection by these techniques.

Synthesis of carbon nanotubes with narrow diameter-distribution by spray pyrolysis of a natural precursor: Turpentine oil

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In this work we report the synthesis of carbon nanotubes (CNTs) with narrow diameter distribution using a natural precursor, turpentine oil as a carbon source on a high-silica zeolite impregnated with Co-Fe bimetallic catalyst. The spray pyrolysis method here we used, is a very simple and inexpensive method for synthesis of this type of CNTs.We characterized the structure of the grown nanotubes by SEM, TEM and Raman spectroscopy. Raman spectroscopy identified the formation of narrow diameter-distribution nanotubes through the presence of radial breathing mode in lower wave number region (100-550 cm^{-1}). The strong peaks observed at 202, 300, 487 and 509 cm^{-1} corresponds to CNTs with diameters ranging between 0.48 to 1.22 nm.The intense G-peak compare to D-peak represents well graphitic structure of as-grown CNTs.

Carbon nanowires prepared by arc plasma gun

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Carbon nanowire (CNW) made of a long linear carbon chain (C-chain) inside a carbon nanotube (CNT) is a new type of 1D carbon structure, and it has unique physical properties and potential applications. Here, we show a new method for preparing CNWs by using an arc plasma gun. In order to evaporate carbon rod containing 1 at% Fe catalyst easily, one end of this carbon rod was sharpened like a pencil, and placed it at the centre of Ar-H_2 plasma flame. Multiwalled carbon nanotubes (MWNTs) and CNWs (C-chain@MWNTs) were found on the surface of carbon rod inside the plasma flame. The characteristic Raman peaks of CNWs have been observed at approximately 1850 cm^{-1}, and strong peaks at 328 and 389 cm^{-1}, appear in the Raman spectra obtained by using two kinds of laser sources, 514.5 and 633 nm. These two peaks are the radial breathing modes from the inner-most tubes with diameters of 0.7 and 0.6 nm included in MWNTs, respectively. It can be concluded that the formation of CNTs with very thin central holes (~ 0.7 nm in diameter) is the essential condition for CNW growth.

Collision of highly-charged ion on graphite: Ab initio simulation for structural deformation

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Graphite-diamond transition attracted a lot of scientific (and economic) attention for long year. Recently, an experimental report [T. Meguro et. al., Appl. Phys. Lett. **79** , p3866 (2001).] shows formation of nano-diamond by collision of Ar^{+8} ion on graphite. In addition to the impact energy, positive charge injection by Ar^{+8} is also expected to play an important role for the nano-diamond formation based on a first-principles study for graphite-diamond transition [H. Nakayama, and H. Katayama-Yoshida, J. Phys.: Cond. Mat., **15** , R1077 (2003).]. Yet, real-time dynamics on a surface of graphite has not been clarified in both experimental and theoretical works. We have tested an influence of Ar^{+8} irradiation on the graphene layers by means of the time-dependent density functional theory (TDDFT) and molecular dynamics simulation, which enables us to treat both electron and ion dynamics. A computer code FPSEID (First-Principles Simulation tool for Electron Ion Dynamics) has been applied. We found fast but incomplete charge transfer from graphite to Ar ion and formation of sp^3-like bond network in graphene layers. In this presentation, we will discuss possible mechanisms of nano-diamond formation. All of present calculations have been performed using the Earth Simulator.

Filling carbon nanotubes with silicon nanocrystals formed by pulsed-laser fragmentation of electrochemically etched Si micrograins.

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Funcionalization of the carbon nanotubes (CNTS) is one hot issue nowadays research in this field. One promising application is stabilization of nanoparticles, molecules or nanocrystals in their cavity. On the other hand, luminescent silicon nanocrystals (Si-ncs) with quantum confinement effect (less than 10 nm diameter) apart the optoelectronic devices, biological and environmental application will also be possible by preparing Si-ncs in colloidal solutions. Recently it has been shown that stabilization such a colloidal Si-ncs in carbon nanotube cavity can largely increase both applications as Si-ncs and also CNTs [1]. Here, we report on cheap and effective way to fill carbon nanotubes through shock waves by pulsed-laser fragmentation of Si micrograins in silicon technology compatible spin on glass (SOG) solutions The Si grains are prepared by electrochemical etching and pulverizing of porous silicon wafers. Grains are dispersed in liquid SOG and fragmented by nanosecond Nd:YAG pulsed-laser (355 nm, 8 ns). Fine blue luminescent Si-ncs with quantum confinement size can be formed. With increasing laser fluences the optical absorption and generated plasma heat together with strong shock waves provoke grains fragmentation The shock waves produced mainly by breakdown of SOG is the driving force to bring the Si-ncs into inner cavity. Subsequently, influence of ablation laser power on fragmentation and filling of Si-ncs is reported in this work in detail.

[1] V. vrcek et al. Appl. Phys. Lett. 88 033112 (2006).

Band Structure Modification in Carbon Nanotubes Due to Crystal Encapsulation

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We report the modification of the band structure of single-walled carbon nanotubes (SWNTs) through encapsulation of the inorganic material manganese ditelluride ($MnTe_2$). Using photoluminescence excitation mapping we show that this leads to a global reduction of the E11 and E22 band gap energies by a similar percentage (up to 3.8%). Beyond a threshold diameter for filling of ∼1 nm the shifts increase with tube diameter due to the increased quantity of filled material. The direct relationship between the E11 and E22 shifts leads us to interpret this as due to a lowering of the carbon-carbon transfer integrals within the tubes. The radial breathing mode frequencies are also found to increase due to the tube filling, which is consistent with idea that the interaction between the tubes and the $MnTe_2$ filling becomes stronger with increasing tube diameter. The measurements suggest that crystal-filling enables a permanent, air-stable and large band gap modulation for carbon nanotubes. The development of local or modulated filling along length of the nanotubes therefore offers the opportunity for the development of longitudinal modulation of the band structure to produce one dimensional heterostructures.

Formation and Structural Changes of Carbon Nanofibers Having an Array of Conical Nano Cavities

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A catalytic chemical vapor deposition (CVD) method has been extensively investigated as a promising method for the growth of carbon nanofibers (CNFs) and carbon nanotubes. Recently, we found that CNFs having an array of conical nano cavities were formed by an alcohol CVD method using indium tin oxide (ITO) / Fe as metal catalysts. The CNFs contain the conical nano cavities in a one-dimensional array at uniform intervals. In this study, we explored the most effective growth condition of the CNFs and studied on the possible formation mechanism of the one-dimensional array of conical nano cavities. Moreover, we report that the CNFs are easily snapped at their nodes corresponding to the bases of conical cavities.

Electron microscopic observation revealed that the inner structure consisted of an array of periodic conical cavities with lengths of 300-800 nm. Nodes of the CNFs, which correspond to the bases of conical cavities, are fragile due to the very thin structure. The CNFs can be easily cut in 1-10 pitch at the nodes like snapping branches by mechanical force such as ultrasonic irradiation. We suggest that the snapping technique using our CNFs may be suitable for controlling the length of CNFs.

Growth of vertically aligned carbon nanoflags assembled by carbon nanofibers and nanowalls

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Self-assembled vertically aligned nano-carbons like carbon nanotubes, carbon nanofibers and carbon nanowalls have attracted considerable attention for bulk devices such as field emitters, energy storage, via-interconnection and heat sink and for estimation of mechanical, electrical and thermal properties of individual nano-carbons. Here we report the first synthesis of vertically aligned carbon nanofibers decorated with carbon nanowalls, so-called carbon nanoflags, by a plasma-enhanced chemical vapor deposition method. Raman spectroscopy and high resolution electron microscope (SEM, TEM) were used to characterize crystallinity of the carbon nanoflags. A vertically aligned carbon nanoflags film was formed under a plasma ion current of 0.23 A. Both density and average diameter of the carbon nanofibers increase with the increase in plasma ion current. The above studies suggest that carbon nanowalls are initiated on the defective lateral wall of carbon nanofibers.

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Spectroscopic study of linear-polyyne encapsulating carbon nanotubes: polyyne peapods

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A new hybrid material $C_{10}H_2$@SWNTs, linearly bonded sp-carbon atoms encased in single-wall carbon nanotubes (SWNTs), has been synthesized and characterized by Raman spectroscopy. The hybrid material exhibits a Raman signal at 2066 cm^{-1} attributable to the stretching vibration of the $C_{10}H_2$ molecules interacting with SWNTs. Being trapped inside the SWNTs, $C_{10}H_2$ molecules are shown to be stable well above 300 °C even under dry-air conditions.

Preparation of Fe_3O_4 / SnO_2Particle Catalysts for the Growth of Carbon Nanocoils

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Carbon nanocoils (CNCs) are expected to be used as electromagnetic absorbers, reinforcement materials, etc. because of their unique structure. In order to apply carbon nanocoils to these practical applications, the mass-production of carbon nanocoils is required. For this purpose, the Fe-In-Sn-O catalyst in powder form was synthesized [1]. However, the process to synthesize this catalyst is time-consuming because calcination and milling are required. To solve this problem, a new method to prepare powder catalysts is shown in this study.

Polyol process was used to prepare powder catalysts [2]. With this method, the Fe_3O_4 / SnO_2 composite catalysts in powder form could be prepared only by boiling mixtures of Fe ions and SnO_2 particles in polyol in a few minutes. It was also found here that structures of the catalyst particles depended on the composition ratios of Fe_3O_4 and SnO_2, and the difference in structures of the catalyst particles largely influenced to the probability of CNC growth. This result gives us important information on designing catalysts with other different methods and the growth mechanism of carbon nanocoils.

Acknowledgement:
This work was carried out for Osaka Prefecture Collaboration of Regional Entities for the Advancement of Technological Excellence, JST.

Reference:

[1] N. Okazaki et al., *J. Phys. Chem. B* , **109** , 17366-17371 (2005).
[2] F. Fievet et al., *MRS bulletin* , **14** , 29 (1989).

Shrinking Carbon Nanotubes

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We report a method to control the diameter of an individual carbon nanotube. Electronic transport measurements performed in situ reveal a striking dependence of conductance on nanotube geometry. As the diameter of the nanotube is reduced to near zero, we observe negative differential resistance.

Template-growth of self-assembly interconnected carbon nanotube networks

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we report a growth method for large-scale interconnected two-dimensional carbon nanotube (CNT) networks. From a well-prepared nano-channel network formed in porous anodic aluminum oxide (AAO) template, CNT network film was self-assembly produced by pyrolysis of hydrocarbon molecules. This network film is fully interconnected together by billions of nanotube segments, with centimeter-size large and only single-tube thickness, which would provide a novel route for the controllable growth of nanotube architectures and the development of nanotube-based integrated electronic devices.

Bridging Nano-Gaps in Nanotubes

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We report a method to fabricate highly reproducible nanometer scale gaps in multi-walled carbon nanotubes. Devices are fabricated in an architecture compatible with transmission electron microscopy, which allows the gap to be imaged with atomic resolution and correlated to electrical measurements. The gap can be bridged with individual molecules or nanocrystals to produce a variety of behaviors.

Graphitic tube formation induced by flush discharge with Ga

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We have found that an amorphous carbon pillar containing Ga, which originated from fabrication using focused-ion-beam induced chemical vapor deposition (FIB-CVD), transformed into a graphite tube with a flush discharge [1]. The as-grown amorphous carbon pillar prepared by FIB-CVD contained Ga in its core region. An instantaneous current injection, typically with 10 to 20 nC, induced quick movement of Ga vapor and/or liquid by Joule heating, and transformed the pillar into a multi-walled carbon nanotube that contained a characteristic structure with regular intervals of Ga droplets. The transformed pillar typically had about 100 nm in diameter, and several microns long. However, the inner graphitized tube was still covered with a thin amorphous carbon layer. Such an outer surrounding carbon residue has shown a very high resistivity about 100 Ωcm [2], however local resistivity in the core region was considerably lower around 1000 $\mu\Omega$cm. This double structure restricted the current flow passing through the core region so as to heat up the core rather than the outer, and thus the double structure seemed to be a key to induce the characteristic solid phase tube transformation. This work was supported by CREST-JST.

Synthesis of carbon nanocoils using organic metals as a catalyst

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The catalyst film of ITO/Fe [1] or Fe-In-Sn-O has been successfully used for the synthesis of carbon nanocoils, so far. In this study, the effectiveness of carboxylic acid metals as a precursor of the catalyst for nanocoils growth has been investigated. Carboxylic acid metals with the mole ratio of Fe/In/Sn =3/1/0.1 was dissolved into organic solvent. The Fe-In-Sn catalyst were formed by spin coating the solution on Si substrates and sintering at 450 °C. Carbon nanocoils are synthesized by the thermal CVD using acetylene as a reaction gas and He as a carrier gas. It is found that carbon nanocoils were synthesized uniformly all over the substrate. The line diameter of the grown nanocoils are ranged from 100 nm to 200 nm and the diameters of coils are several hundreds of nanometer. The average line diameter of the nanocoils can be controlled by adjusting the mole concentration of Fe/In/Sn in the solution. The yield of the nanocoils is as high as those synthesized by using ITO/Fe. It is revealed that carboxylic acid metals are efficient as a precursor of the catalyst for nanocoils growth.

[1] M. Zhang, Y. Nakayama and L. Pan, Jpn. J. Appl. Phys. 39 (2000) L1242.

Microstructures of Catalyst Particles at the Tip of Carbon Nanocoils Grown from Fe-In-Sn-O Catalysts

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To discuss the growth mechanism of carbon nanocoils from Fe-In-Sn-O catalysts experimentally, the microstructures of catalyst particles at the tip of carbon nanocoils and other carbon products have been investigated by transmission electron microscope (TEM). The statistical studies of TEM images proved that most of the catalyst particles at the tip of carbon nanocoils had anisotropic morphologies, while those of filament carbon products were isotropic. In addition, high-resolution transmission electron microscope (HRTEM) images revealed that each catalyst particle had surface phase, whose thickness was 5-30 nm. In many cases of the catalyst particles at the tip of carbon nanocoils, their surface phases were highly crystallized. The growth of carbon nanocoils is considered to be due to the nonuniformity of the carbon extrusion speed at different parts of the catalyst particle [1]. This nonuniformity was discussed at the viewpoint of the morphology and surface phase of the catalysts.

This work was carried out for Osaka Prefecture Collaboration of Regional Entities for the Advancement of Technological Excellence, JST.

[1] L. Pan et al., *J. Appl. Phys* , **91** , 10058-10061 (2002).

Isolation of Toroidal Aggregates of Single-Walled Carbon Nanotubes by Ultrasonic Atomization

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Although carbon nanotube (NT) bundles are usually known to align in parallel or tangle to fabricate complex textures, other superstructures of NTs, like rings and coils, attracted much attention due to their topologically interesting carbon structures at the curvatures and the potential for the characteristic properties especially in electromagnetics. Here a sonoprocess for the isolation of toroidal aggregates of single-walled carbon nanotubes (SWNTs) is reported. A black solid was recovered by blowing small droplets generated ultrasonically in a gas flow. This was found to exclusively consist of toroidal aggregates of SWNTs about 0.5 - 3 mm in diameter. These are round, oval and twisted tori in shape, and a few toroidal SWNTs might be interlocked. It is worth noting that wreath-shaped aggregates of SWNTs were observed, when much shorter SWNTs, oxidatively cut HiPco, were sonicated under the same conditions. The relatively small droplets, which can accommodate only the toroidal aggregates, are considered to be blown by the carrier gas, resulting in the isolation of the tori.

Vertically aligned conical amorphous carbon nanowires : Synthesis and Characterization

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Vertically aligned conical amorphous carbon nanowires were deposited on silicon coated with thin film of cobalt using pulsed discharge plasma chemical vapor deposition. FE-SEM observations indicate that they are vertically well aligned, with an average diameter of about 200 nm at the bottom and with a tip of about 70 nm to 100 nm in diameter and a length of about 2 microns. High resolution transmission electron microscopy and Raman study reveals that the nanowires has an amorphous structure. Formation mechanism and other studies will be discussed at the conference venue.

Lateral alignment of single walled carbon nanotubes by selective laser ablation

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In this work, we present the results on the selective ablation of single walled carbon nanotubes by use of femtosecond laser. After irradiation with laser, random networks of single walled carbon nanotubes are reconstructed to laterally aligned one dimensional nanostructure oriented perpendicular to the polarization direction with 100nm width. We believe that the linearly polarized femtosecond laser ablate only those tubes located along the polarization direction and the ablated nanotubes are sticked on other tubes located perpendicular to the polarization direction. The characteristics of these aligned carbon nanotubes are analyzed with UV-VIS-NIR absorption spectroscopy, polarized Raman spectroscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM).

Synthesis of GaN nanowires using NiI_2-filled carbon nanotubes

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We report the synthesis of GaN nanowires using single-walled carbon nanotubes (SWNTs) or graphite as the starting materials in the presence of Ni catalyst. The use of carbon source can efficiently promote the growth of long and straight GaN nanowires, and the presence of Ni catalyst is essential to the formation of GaN nanowires. The effect of the use of different carbon forms on the growth temperature of GaN nanowires was also investigated. It was found that the growth temperature of GaN nanowires can be lowered to 700°C; due to the curvature of SWNTs. Moreover, GaN nanowires synthesized from graphite reveal that the growth of GaN nanowires in the presence of Ni catalyst is template-independent (1). From the TEM observation, most of GaN nanowires have nickel particles on the tips and this result suggests the formation of GaN nanowires could be through Vapor-Liquid-Solid process (2).

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Novel Hybrid Nanomaterial: Fullerene-Functionalised Carbon Nanotubes

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Both fullerenes and single-walled carbon nanotubes (CNTs) are of great interest since they exhibit unique and useful chemical and physical properties. We have discovered a novel hybrid nanomaterial combining these structures, i.e. consisting of fullerenes covalently attached to the outside surface of CNTs, called fullerene-functionalised CNTs. The material structure was investigated by High Resolution Transmission Electron Microscopy (HR-TEM) together with optical spectroscopic and mass-spectrometric techniques. Two one-step continuous methods for their selective synthesis have been developed: using pre-made iron catalyst particles by a hot wire generator method and particles grown *in situ* via ferrocene vapour decomposition in the presence of CO and trace amounts of H_2O and CO_2 etching agents. This new material showed a high cold electron field emission efficiency thus making it attractive for many electronic applications, e.g., flat panel displays.

ORGANIC ACIDS ASSISTED SYNTHESIS OF TITANATE RELATED MATERIALS WITH VARIOUS SHAPES AND MICROSTRUCTURES

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In this poster, we report a novel synthesized strategy of titanate related materials with various morphologies assisted by organic acids such as acetic and formic acids. Using TTIP as precursor and organic acids as solvent, the mixture was refluxed in a three neck-flask at 90-150°C for 48 hours to synthesize titanate related materials. Morphologies and microstructures of the products are dominated by organic acid utilized and reaction temperatures, in our experiments, the wire-like materials will be acquired at 90 °C with either acetic acid or formic acid, however, the lath-like and petal-like products will be obtained at higher reaction temperature (150 °C) with acetic and formic acids, respectively. From the XAFS analysis, XANES shows the two structures both consisted of octahedral coordination around Ti atoms with the characteristic of triple peaks at near edge.

Carbon Nanotube Fabrication using HW-VHF-PECVD Method

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It is explained one of the carbon nanotube research progress in Indonesia. Plasma Enhanced Chemical Vapour Deposition (PECVD) method is one of the best method to growth Carbon Nanotubes. Various modifications of PECVD method are possible to do. It is being attempted a carbon nanotube growth using the modifications of PECVD method, which are Very-High Frequency PECVD (VHF-PECVD) and Hot-Wire VHF-PECVD (HW-VHF-PECVD). The fabrications, which are being done, are a catalytic growth process where Fe catalyst thin film is growth on the Silicon substrate, by using dc-Unbalanced Magnetron Sputtering method. By using two gas sources, which are methane as the source of carbon and diluted silane in hydrogen as the source of hydrogen, a carbon nanotube fabrication has been attempted at relatively low temperature, 250^{o}C. From the morphological characterization using Scanning Electron Micrograph, some sign of carbon nanotube has appeared even though the grain size or the nanotube diameter. From the composition characterization using Energy Dispersion Analysis using X-Ray (EDAX), carbon become dominant in the formed structure, with some signature of silicon from the substrate or defects. On the other hand, the carbon nanotube fabrication using HW-VHF-PECVD is being done by using only one single gas source, which is methane (CH_4). By using the Hot-wire, it is expected some of the methane will be dissociate to produce some free H radicals, which are needed in carbon nanotube growth process. From the growth process on relatively low temperature, 400^{o}C, some better signatures of carbon nanotube are present. From the characterization using SEM, EDAX and Scanning Probe Microscopy (SPM), their results show that the grain or nanotube size has diameters less than 100 nm, which make much convincing result of formed nanotube possibilities.

Simulating the X-junction formation of double-walled carbon nanotubes

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Double-walled carbon nanotubes (DWNTs) are thought to possess remarkable electronic and mechanical properties compared to single-walled carbon nanotubes. The progress in nanoelectronics requires various molecular connections among individual DWNTs. The X-junction nanodevice made by joining coaxial tubes can have great mechanical strength and unique electrical characteristics. This device can form a nanonetwork, can contribute to the simplification of electronic circuits, composites, and more. Therefore, the elucidation of X-junction formation by joining DWNTs is crucial. We studied the coalescence of X-junction of DWNTs using molecular dynamics (MD) calculation.

In the present poster, we will discuss the results on MD simulations on the coalescence of X-junction formation between DWNTs and the effect of defects in the tubes for the coalescence at the junction.

Contribution B.036 - Monday, June 19

Discovery and optical properties of the Thermal Conversion of Bundled Carbon Nanotubes into Graphitic Ribbons

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Raman scattering and optical absorption were used to study the thermal evolution of purified bundled single-walled carbon nanotubes (SWNTs), HiPCO and ARC, subjected to high temperature heat treatment (HTT) up to 2200°C in vacuum. After each HTT, the material was removed and characterized with transmission electron microscopy (TEM), Raman scattering and the optical absorption. Structural modifications observed in HiPCO and ARC SWNTs involved tube-tube coalescence (HTT 1300-1400°C), formation of multiwalled carbon nanotubes (HTT 1600-1800°C). At HTT 1800°C only ARC material was found to then evolve to Graphitic Nanoribbons (GNRs), a new form of filamentary carbon. Here, we present the details of these thermal transformations as seen in changes in the radial (R) SWNT band, the G-band (and its substructure), and the relative intensity of the disorder-induced D-band scattering. The large GNR D-band scattering intensity is tentatively assigned to K-point modes activated by the small lateral width of the GNRs that is estimated from TEM and Raman to be 6-8 nm. The changes of optical absorption bands from semiconducting and metallic tubes were also observed.

Contributed abstracts

June 20 (Tuesday)

Dispersion of Carbon Multi-Walled Nanotubes in Organic Solvents by Modifications with Oleic Acid

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Owing to the superior electrical, thermal and mechanical properties of carbon nanotubes (CNTs), many potential applications have been proposed for them. However, untreated CNTs is surface inactive and hard to form good adhesion with other materials. In order to improve its compatibility with others, surface treatments of non-covalent and covalent methods have been widely used. In this investigation, we propose a novel two-step approach, combining functionalization with hydrogen peroxide and then modification with oleic acid, to increase the dispersibility of carbon multi-walled nanotubes (MWCNTs) in organic solvents. The surface properties of the two-step treated MWCNTs were characterized by analysis of zeta-potential, FT-IR and TGA, and its corresponding dispersion behaviors in organic solvents were examined through measurements of rheology and sedimentation. The results show that the two-step treated MWCNTs can be well dispersed in various polar organic solvents.

Solubilization of Single-Walled Carbon Nanotubes using Polycyclic Aromatic Compounds - Toward Selective Nanotube Chirality Index Discrimination-

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Strategic approaches toward the solubilization of carbon nanotubes by debundling are important for the applications of CNTs [1-4]. We describe the design of polycyclic aromatic compounds with high performance that dissolve single-walled carbon nanotubes (SWNTs) [1-2]. Synthetic amphiphiles, trimethyl-(2-oxo-2-phenyl-ethyl)-ammonium bromide (**1**) and trimethyl-(2-naphthalen-2-yl-2-oxo-ethyl)-ammonium bromide (**2**) carrying a phenyl or a naphtyl moiety were not able to dissolve/disperse SWNTs in water. On the contrary, trimethyl-(2-oxo-2-phenanthren-9-yl-ethyl)-ammonium bromide (**3**) solubilized SWNTs, while the solubilization ability was lower than that of trimethyl-(2-oxo-2-pyrene-1-yl-ethyl)-ammonium bromide (**4**). Compound **4** was found to solubilize both as-produced SWNTs (raw-SWNTs) and purified SWNTs. Near-IR photoluminescence measurements revealed that the chiral indices of the SWNTs dissolved in an aqueous solution of **4** were quite different from those using micelles of sodium dodecyl sulfate, that is, the intensity of the (7,6), (9,5) and (12,1) indices were strong in aqueous solution of SWNTs/**4** , and the chirality distribution was narrower than those of the micellar solutions.

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Optical pH Response of Micelle-encapsulated and Polymer-wrapped Single-Wall Carbon Nanotubes

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The solution stability and spectroscopic characteristics of isolated single-walled carbon nanotubes (SWNTs) dispersed in various aqueous surfactant and polymer solutions were investigated by optical spectroscopies: the UV-vis-NIR absorption, near-IR fluorescence, and Raman shift. Some polysaccharides (polymers) such as carboxymethylcellulose (CMC) and chitosan with different charge features were used as dispersion agents together with typical surfactants such as sodium dodecyl sulfate (SDS, anionic) and n-dodecyl trimethylammonium bromide (DTAB, cationic). The interband optical transition originated from van Hove singularities were affected by dispersion agent species and pH. The absorption peaks in the first semiconductive band range disappeared with decreasing pH below 5 in the case of SDS-SWNTs dispersion, whereas a small decrease in the peaks was observed in case of DTAB. On the other hand, the CMC- and chitosan-SWNTs dispersion did not exhibit peak quenching. The foregoing results implies that the discrepancy of the quenching of interband transition induced by protonation between the surfactants and polysaccharides comes from the difference in the structural characteristics, that is, micelle-like for the surfactants and wrapping for the polysaccharides, which prevent the SWNTs from protonation. Also, the protonation effect appears to be strongly affected by the electrical charge of the dispersion agent.

Dispersion and separation of thin multi-wall carbon nanotubes

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Different surfactants, such as Triton X-100, SDS, PVA, PVP were used to solubilize thin multi-wall carbon nanotubes (t-MWCNTs) in aqueous solutions. About 30 g of t-MWCNTs were prepared by methane pyrolysis at 940 °C in continuous regime and have been used for the study. Dispersions were produced by sonication of t-MWCNTs in aqueous surfactant solution followed by mild centrifugation (30 min, 1100 g). To estimate the concentration of t-MWCNTs in the dispersion, supernatant liquor was subjected to coagulation after decantation. The solid materials were analyzed by means of TEM, X-ray diffraction and characterized using nitrogen adsorption measurements (BET). A few hundred of individual t-MWCNTs were involved in the determination of their diameter and length distribution in the stable dispersion. An enrichment of the dispersion with small diameter and length t-MWCNTs was reviled: the diameter of 92% tubes did not exceed 4 nm. The solubility depended on their diameter and length. The optimal t-MWCNTs:TritonX-100 and t-MWCNTs:SDS ratios corresponding to the highest FWCNT concentrations (1.67 and 1.35 g/L, respectively) have been found. The solubility of t-MWCNTs in surfactant solutions was compared with the behavior of covalently functionalized tubes. The synergetic effect of surfactant pairs will be discussed.

Oxidation of SWNTs Decorated with Significant Amount of a-C

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In this study, the air oxidation of single-walled carbon nanotubes (SWNTs) decorated with significant amount of amorphous carbon (a-C) is presented. The novel carbon fibers we synthesized are suitable for realizing the removal of a-C from SWNTs by oxidation treatment. The oxidation temperature was controlled from 540 °C ~ 580 °C for 30 min. The average thickness of a-C on SWNTs roughly decreased with increasing the oxidation temperature. The formation of porous and bread-like structure of a-C on SWNTs was observed. Although the oxidation of a-C in air is better controllable than the wet chemical methods, our results suggest that the a-C could not be uniformly removed by air oxidation method.

Thin films of metallic carbon nanotubes prepared by dielectrophoresis

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Separating metallic from semiconducting carbon nanotubes by dielectrophoresis [1,2] is advancing towards a bulk separation method and allows now to produce thin films of metallic single-walled carbon nanotubes [2]. We provide the first optical absorption spectra of dielectrophoretically separated SWNTs, which demonstrate that the technique is operative independent from the diameter distribution of the starting material. The data confirms previous results obtained on smaller quantities by resonant Raman spectroscopy. We further provide electrical transport measurements on separated nanotube material.

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Dielectrophoretic Deposition of Surface Conductivity Modulated Single Walled Carbon Nanotubes and Their Sensor Applications

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Dielectrophoresis has received much attention for separating nanotubes according to electronic types. In this work, we examine the effects of surface conductivity of semiconducting single walled carbon nanotubes (SWNT), induced by ionic surfactants, on the sign of dielectrophoretic force. The crossover frequency of semiconducting SWNT increases rapidly as the conductivity ratio between the particle and medium increases, leading to an incomplete separation of ionic surfactant suspended SWNT at an electric field frequency of 10 MHz. In order to reduce the conductivity ratio, the surface charge of SWNT is neutralized by an equimolar mixture of anionic surfactant sodium dodecyl sulfate (SDS) and cationic surfactant cetyltrimethylammonium bromide (CTAB), resulting in negative dielectrophoresis of semiconducting species at 10 MHz. Dielectrophoretically deposited nanotubes were used to detect ions and radicals in their sensor applications.

Dielectrophoretic assembly of carbon nanotubes

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Single-wall carbon nanotubes (SWNTs) are assembled between nanopatterned gold electrodes by alternating current (AC) dielectrophoresis. Integration of the structures is made possible by the use of lift-off photolithography and gallium focused-ion beam (FIB) milling. Potential future applications of this work are as a method of separation of metallic and semiconducting SWNTs, and in the production of nanoelectronic devices such as an SWNT field effect transistor.

For dielectrophoresis of individual nanotubes, we have suspended the tubes in sodium dodecyl sulfate (SDS) surfactant as the electrolyte. However, the electronic properties of SWNTs are affected by the presence of SDS. Hence we have used a rinsing technique to remove SDS from the tubes. The SDS-treated SWNTs were investigated by x-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. After dielectrophoresis, we have observed growth of an SWNT bundle between nanopatterned gold electrodes using scanning electron microscopy (SEM). The current-voltage characteristics measured between the electrodes were consistent with those of metallic SWNTs.

Diameter-Based Separation of Carbon Nanotubes by Extraction with Diporphyrin Tweezers

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Molecular tweezers, comprising two porphyrins and rigid spacer in between, have been found to solubilize carbon nanotubes (NTs) into organic solvent to reduce the impurities and enrich specific range of diameters. Although monoporphyrins have large solubility to organic solvents, only a small amount (<1 %) of NTs was extracted. On the other hand, the extraction yields improved remarkably with diporphyrin. The large difference in their ability for solubilization of NTs is considered to be attributed to the difference in stability of the complexes. That is, the concave gable structures complementary to convex surface of NTs formed much more stable complex as compared to those of NTs with monoporphyrins. TEM analysis of the extract obtained with diporphyrin revealed reduction in the amount of impurities as compared with the raw tube and residue. The diporphyrin serves as an efficient extracting agent that discriminates NTs from metal impurities. It is noteworthy that diporphyrin tweezers with naphthalene spacer showed much higher extraction ability towards DWNTs than those with m-phenylene spacer, indicating that the larger accomodation space of the diporphyrin with naphthalene spacer can accept DWNTs. From TEM, Raman and absorption spectroscopies, specific diameters of NTs were found to be extracted preferentially.

Anomalous Dispersing Agents for Carbon Nanotubes

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Many surfactants and polymers are available to stabilize CNT dispersions, mostly in water. Surfactants usually form self-aggregates, such as micelles, to encapsulate CNTs and polymers adsorb strongly onto CNTs. Here, we report a dispersing agent that show chemical selectivity and physical properties that are not usually found in previously known compounds.

Chemically, with a help of light sonication, it disperses CNTs only in polar halogens and not in other organic solvents and water. The concentration dependence shows that, at a particular concentration, the dispersed amount relative to that of a pure solvent increases linearly with the duration of sonication, crossing zero at a finite time; this means that the dispersibility becomes worse than pure solvent at short sonication time, then improves as the sonication time is extended.

Optical study of the SWNT dispersion after dielectrophoresis

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It was proposed that metallic SWNTs (M-SWNTs) can be selectively deposited on electrodes by dielectrophoresis (DEP) [1]. The DEP force is strongly dependent on permittivity of SWNT, which is inversely proportional to square root of the band gap of the nanotube. Thus, M-SWNTs having infinite permittivity are suggested to be attracted more strongly to the electrode as compared with S-SWNTs [1]. One major issue of the DEP separation is the reliability of the Raman spectra observed for the SWNTs deposited on electrodes, because a Raman spectrum is very sensitive to an aggregated state of SWNTs [2]. Therefore, other analyses, such as an optical absorption measurement, are necessary to discuss the metal-semiconductor separation. Here, we report on the optical absorption measurements of the SWNT dispersion obtained after a DEP process. Effects of the formation of an electric double layer around a SWNT are also discussed.

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The ultrasonication time and power density effects on the dispersion of single-walled carbon nanotubes in aqueous solutions

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The process of debundling by ultrasonication is based on powerful cavitation effect and subsequent substitution of nanotube-nanotube Van der Waals forces by surfactant micelles or polymer wrapping. In this work we are investigating the effect of ultrasonication parameters on single-walled nanotubes (SWNTs) dispersion in aqueous solutions in order to understand the side reactions and their effect on nanotubes properties. The SWNTs dispersion properties are dependent on horn type, cup geometry, power density, total energy, electrochemical character of the dispersion agent, and maximum temperature reached during the ultrasonication. The temperature and pH were monitored during ultrasonication process while absorption, emission, and Raman spectroscopies have been carried out after nanotubes dispersion. The length distribution of SWNTs colloidal dispersions was investigated by dynamic light scattering for different power density ultrasonication. We found that ultrasonication power density is a key parameter for SWNTs dispersion. The pH of dispersion is decreasing during mild ultrasonication in relation with the electrochemical character of the dispersion agent and is affecting the optical spectra without changing the chiral distribution. For the same energy density delivered by ultrasonication, the nanotube length distribution is proportional with the power density.

Dispersion and Characterization of Carbon Nanotubes and Carbon Nanofibers in Water

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An effective process for dispersing multi-walled carbon nanotubes (MWNTs) and carbon nanofibers (CNFs) in water up to 5wt% by treatment with peroxide and then dispersion with dispersant of ammonium polyacrylic acid (PAA-NH_4) was acheived in this study. The surface chemistry and the morphology of H_2O_2-treated MWNTs was characterized respectively by Fourier transform-infrared (FT-IR) spectroscopy and transmission electron microscopy (TEM), while the amount of functional groups was quantified by temperature programmed desorption (TPD) technique. For comparison, MWNTs or CNFs were also treated with concentrated acids of HNO_3 and H_2SO_4 with volume ratio of 3:1. It was found that the MWNTs with H_2O_2-treatment had less microstructure defects than those with acid-treatment. The dispersion stability of as-prepared aqueous suspensions was analyzed by rheology and settling experiments

Dispersion effect of carbon nanotubes for direct methanol fuel cell performance

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The dispersion effect of carbon nanotubes (CNTs) used as a support material of Pt impregnated catalyst for a direct methanol fuel cell (DMFC) was investigated. Several different dispersion methods were applied. They are sonication using a tip sonicator, beads mill treatment with and without dispersing polymers, and cryogenic crushing treatment. The deposition of Pt nanoparticles to impregnate 60 wt % of Pt in CNTs was performed by refluxing the dispersion-treated carbon nanotubes in a mixture of ethylene glycol and water containing Pt precursors. The produced Pt particle sizes are in the order of 3 to 5 nm depending on the treatment method. The electrochemical activities of the Pt/CNT catalysts as a cathode electrode for DMFC were measured by cyclic voltammogram in 0.1M $HClO_4$ solution under oxygen gas purging. The electrode was prepared by painting the Pt/CNT catalyst paste containing 30 wt % Nafion on a carbon paper. The highest activity was obtained from the Pt/CNT sample employing sonication. The treatments of beadsmill and cryogenic crushing led a negative effect to the electrode activity, probably due to the damage of CNTs during mechanical collision process. The damage of CNT structure induces the increase of electrical resistance, which causes the decreasing performance of DMFC. Here, we report that the dispersion process of CNTs should be properly optimized for the best performance of electrode activity, allowing the production of a desired value of uniform 2~3 nm Pt nanoparticles without structural degradation.

Photoluminescence mapping of length-separated single-walled carbon nanotubes

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We present near-infrared photoluminescence (PL) mapping of individual single-walled carbon nanotubes (SWNT) in water-surfactant dispersions length-sorted by size exclusion chromatography1. Furthermore, we investigated the ultrasonic induced scission of different SWNT materials by AFM, Raman and absorption spectroscopy. The influence of different parameters on the scission rate was studied. We predict a mechanism for the cavitation-induced scission process and simulate length distributions with a model.

1 Heller, D. A.; Mayrhofer, R. M.; Baik, S.; Grinkova, Y. V.; Usrey, M. L.; Strano, M. S. J. Am. Chem. Soc. 2004, 126, 14567-14573.

Purification of Double Wall Carbon Nanotubes by a Novel Oxidation Method

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Purification of Double wall carbon nanotubes (DWNTs) has been achieved by high temperature air oxidation [1]. However, it is still difficult to realize high yields and selectivity because of the bundling effect. Here, we present a novel purification method with dispersion and oxidation techniques to minimize the bundling effect and maximize the purity and the yield of DWNTs, respectively.

DWNTs synthesized by the pulsed arc discharge [1] were dispersed into sodium dodecyl sulfate solution by sonication. The solution was mixed with excess of fumed silica and was dried to powder. This powder was oxidized to remove SWNTs and amorphous carbon under following conditions: (a) heating at 500°C in air, (b) reflux at 120°C in H_2O_2, and (c) a combination of (a) and (b). The purified DWNTs were obtained from the powder eliminating metal particles and fumed silica. The purity was evalated by TEM and Raman spectroscopy.

The results show that the purity of DWNTs becomes more than 95% by the combination method (c), whereas it reaches only 50% by each method of (a) and (b). It suggests that each oxidation method removes different SWNTs complementarily.

[1] T. Sugai, et al., Nano Lett., 3, 769 (2003)

Purification of Single Wall Carbon Nanohorns by Gravitational Sedimentation

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Single wall carbon nanohorns (SWNHs) are produced with higher purity (>85 wt%) and yield (>75 wt%)[1] than single-wall carbon nanotubes through CO_2 laser ablation of pure graphite rods without metal catalysts. But SWNHs thus produced are always mixed with micrometer-order graphite-based particles, named GG (Giant Graphitic) balls (<15 wt%)[2] which are the obstacle for various applications of SWNHs. We investigated the methods of purifying SWNHs on large scale, and found that the gravitational sedimentation method was useful.

In the gravitational sedimentation method, SWNHs were first dispersed in ethanol using ultrasonication, and then left at rest for 12 hours. During this period, the GG balls precipitated at the bottom of the container due to natural gravitational effect, while SWNHs remained in the supernatant. SWNHs in the supernatant were evaluated and characterized by means of thermo gravimetric analysis, X-ray diffraction, and adsorption isotherms of N_2. They were also observed with scanning electron microscope and high resolution transmission electron microscope. As a result, the SWNHs in the supernatant were found to be completely free from the GG balls in such an easy way. The high-purity SWNHs thus obtained will enhance progress of studies on the properties and applications of SWNHs using will be developed.

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Purification and Opening of Carbon Nanotubes

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A vast amount of research has been focused on the preparation of high purity carbon nanotube samples, either during their synthesis or in a post-growth purification process. Typically amorphous carbon, graphitic particles and metal particles (catalyst) are the main impurities in as-made carbon nanotubes. Although several procedures have been used to purify as-made SWNTs, nitric acid has become the standard reagent for purification of carbon nanotubes and constitutes one of the steps in many different purification schemes. Recent studies have shown that acid purification leads to partial oxidation of SWNTs themselves and sometimes to an extensive disruption of the tubular structure. We have explored the use of a new oxidizing agent which allows a better control of the opening and removal of the carbonaceous fragments, neither functionalizing the SWNTs nor damaging their tubular structure. Addition of an aqueous solution of uranyl acetate to the purified SWNTs gives uranyl acetate@SWNTs (HRTEM), which provides direct evidence of the opening of the SWNTs. IR and Raman spectra of the purified samples are also presented.

Diameter and chirality dependent oxidation of semiconducting single-wall carbon nanotubes in hydrogen peroxide

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Previously, we have reported an effective enrichment of metallic single-wall carbon nanotubes (SWCNTs) by the selective oxidation of semiconducting SWCNTs in hydrogen peroxide. [1] In this presentation, we demonstrate a chirality dependent oxidation process of semiconducting SWCNTs in hydrogen peroxide. We have measured Raman spectra of SWCNTs heated in hydrogen peroxide with changing a heat treatment time. It is well known that the thinner SWCNTs are more fragile, which is understood as a curvature effect. Indeed, in most cases, intensity of higher frequency radial breathing mode (RBM) peaks decreased more rapidly than the lower frequency ones. This indicates smaller diameter SWCNTs burned faster. However, some RBM peaks showed non-diameter-dependent burning behavior, which suggests some additional driving force on burning process. If the chemical stability of SWCNTs is affected by their electronic structures, selective oxidation process in hydrogen peroxide could be explained consistently including our previous work. Correlation between the chemical stability and the electronic structure of SWCNTs will be discussed.

Purification and Purity Evaluation of Single-Walled Carbon Nanotubes Produced by Arc Discharge

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Arc-produced SWCNT soot contains carbon impurities including amorphous carbon, graphitic nanoparticles, etc. This study does not only aim to develop efficient, less damageable purification processes, but also evaluate their purity using TGA. The carbon phases can be moderately differentiated in TGA derivative curves if knowing thermal stability of each constituent. We prepared the soot samples which compositions were varied by oxidizing the soot at different temperatures of 275∼425^{o}C; for 20h, then analyzed by TGA, SEM, TEM. Deconvoluted derivative curves showed systematic variations with the temperatures, and each of them could be assigned to a corresponding constituent based on microscopic observations. Their compositions were calculated by measuring the areas under the deconvoluted curves. Our purification processes were composed of acid treatment, functionalization, soxhlet extraction. The carboxylated soot was functionalized by hexadecyl amine forming ionic bonds with carboxyl groups on carbon impurities as well as SWCNTs. Long-chain alkyl groups of the functionalized carbon impurities made them soluble in solvents, in particular, tetrahydrofuran. During the extraction, carbon impurities could be easily expelled through a filter without any significant loss of CNTs. The functionalized CNTs were well dispersed for 6 months, and organic groups in the CNT bulky paper were easily burned out.

Design of a Dispersant for Carbon Nanotubes in Organic Solvent

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Poly-thiophene was used to design a dispersant for nanodispersion of single-walled carbon nanotubes (SWCNTs) in organic solvent by varying the orientation of the head group (thiophene) and the ratio of head to tail length (hexyl group). The mixture of SWCNTs / dispersant (1:1) in 1-methyl-2-pyrrolidinone (NMP) solvent was sonicated in a bath type sonicator for 10 hours at 240 W and centrifuged with 8,000 rpm for 10 minutes. The SWCNTs were well macrodispersed. The supernatant was measured with both Raman and UV-Vis-NIR spectroscopies. We found that sulfur atoms in the head group enhanced interactions between thiophene and the CNT walls evidenced by the x-ray photoelectron spectroscopy. Furthermore, their alignment of head groups, rather than their random orientation, plays an important role in dispersing SWCNTs. The strong correlation between the subband peak shifts in the absorption spectra and the peak shifts of the G-band and radial breathing modes in the Raman spectroscopy were discussed in detail in conjunction with designing parameters of dispersant.

Purification of Single-walled Carbon Nanotubes Using Zirconia Beads and Polymer Wrapping

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SWCNTs produced by arc discharge were purified through two different processes, zirconia beads and polymer wrapping. Various diameters (10mm, 5mm and 1mm) of zirconia beads were packed together with the as-produced (AP-) SWCNT soot inside a vertical quartz tube to enhance the air flow uniformity through the SWCNT soot during thermal oxidation in air. For smaller diameters beads, more carbonaceous impurities burned out, producing purer SWCNTs. A subsequent HNO_3 treatment and the second thermal oxidation were also engaged to improve further the purity of SWCNTs. While in the polymer wrapping process, the AP-SWCNT soot was first treated with 3M HNO_3 in order to remove metal catalysts and introduce carboxyl groups to carbon impurities as well as SWCNTs. The carboxylated soot was then wrapped with 10 wt.% of poly(2-ethyl-2-oxazoline) in ethanol. Finally the polymer-wrapped soot was oxidized in air. In a control experiment, the SWCNT soot was purified by the conventional processes which consisted of the gas phase oxidation (of course, without zirconia beads) and the HNO_3 treatment. The three purification processes of SWCNT soot were compared in term of their yields and purities. SWCNTs were characterized using thermogravimetric analysis, scanning electron microscopy, transmission electron microscopy, and Raman spectroscopy.

Introduction of COOH on MWCNT by Friedel-Crafts acylation

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When multi-walled carbon nanotube (MWCNT)/polymer composites are prepared through melt compounding for the improvement of mechanical strength, the surface modification of MWCNT becomes important. There is several possibilities, depending on the structure of MWCNTs, about chemical modification on the surface of MWCNT. MWCNTs are categorized into two structures. One is tubular type and layers of grafensheets are rolled, commercially available as VGCF®. The other is six-membered rings arranged like cup are stacked up (Carbere®). VGCF® has the defect part where six-membered ring is lacked on the surface, and many edges of graphites located on the surface are thought to be terminal with hydrogen for Carbere®. In this study, COOH groups are introduced by using the Friedel-Crafts reaction on the defect parts of VGCF® surface and Carbere® surface. The introduced amount of carboxyl groups were determined by neutralizing titration. The results suggested that about 17 carboxyl groups existed per 100 carbons on VGCF® surface, and about 22 carboxyl groups on Carbere®. Moreover, the further modification of VGCF® surface was examined by graft reaction of polymer.

Synthesis of Boron Nitride Nanotubes in large quantity and their functionalization

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Boron nitride nanotube (BNNT) has a constant band gap, exhibits excellent mechanical properties, high thermal conductivity and superb resistance to oxidation. Therefore, BNNTs are thought to be primarily useful as nanoscale semiconductors working in hazardous environments or additives in composites to improve mechanical and thermal properties of the matrix. However, to date, many unsolved problems, such as BNNT high-yield production, adjustment of BNNTs electronic structure, dispersibility of BNNTs in solvents etc., have hampered their real practical applications.

Here we report that highly pure BNNTs may be synthesized at high yield via a chemical vapor deposition method using a metal oxide and a boron powder as reactants. For the first time, BNNTs were perfectly dispersed in various organic solvents by wrapping them with a polymer or due to covalent functionalization. The functionalized BNNTs were investigated by cathodoluminescence and UV-vis absorption experiments. The results reveal drastic changes in BNNT band structure and strong interactions between BNNTs and a polymer. Our studies indicate that chemical functionalization may be a promising way to adjust the electronic structure of BNNTs. In addition, soluble BNNTs may be highly useful for the polymer composite materials.

Controllable n-type doping of carbon nanotubes via plasma fluorination and amino functionalization

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Functionalization of carbon nanotubes with fluorine-based plasmas for short durations at low bias voltages affords a reliable and controllable method of doping nanotubes. By tailoring the plasma conditions the structural integrity of the nanotubes can be preserved and consequently the capability for electron transfer is maintained. We have exposed single-walled carbon nanotubes to CF_4 and SF_6 plasmas as a method of controlling the degree of functionalization before further functionalizing with 1,2-diaminoethane. The degree of amino functionalization is dependent on the degree of initial fluorination rather than oxygen or carbon defects and thereby presents a replicable route to n-type doping. We have investigated different types of fluorine CNT-F bonding produced by the plasma processes (e.g., covalent, semi-ionic) and the effect of different plasmas on the doping process. An additional step to remove residual fluorine using hydrazine gave a significant improvement in the n-type character of the devices. Reaction at both ends of 1,2-diaminoethane was observed to increase with fluorine content. Electrical characterization using back-gated SWNT devices have shown p-type semiconducting behavior for CF_4-functionalized SWNTs and n-type semiconducting behavior for amino-functionalized SWNTs. The degree of n-type behavior increases with the amount of nitrogen attached to the SWNTs.

Introduction of COOH on MWCNT by ligand exchange reaction

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Carbon nanotube (CNT) has chemically stable and inactive surface, so dispersibility in solvents generally is poor due to the weak interfacial interaction between CNT and polymer matrix. To improve the dispersibility and interfacial interaction in solvent or polymer matrix, the surface modification by ligand-exchange reaction between ferrocene containing carboxyl groups and VGCF® or Carbere® , which has stacked-cup structure, was investigated. Carboxylated multi-walled carbon nanotube (MWCNT-COOH) was synthesized by stirring of MWCNTs in tetrahydrofuran at 50°C for 24h in the presence of $AlCl_3$ and Al powder under nitrogen. MWCNT-COOH was carefully purified by filtration and soxhlet extractor. The amount of carboxyl groups introduced onto MWCNTs surface was determined by titration with sodium hydroxide solution using phenolphthalein as an indicator. Further modification was carried out by grafting reaction between copolymer containing oxazoline groups and VGCF including carboxyl groups. Dispersibility of MWCNT-COOH was investigated by optical microscope. The agglomerated structure of MWCNTs was effectively destroyed by the introduction of carboxyl groups, and MWNT-COOH gave homogeneous dispersion in solvent.

Transparent and flexible Carbon Nanotube/Polyaniline pH Sensor

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Thin film carbon nanotube networks are used as a conductive, transparent and flexible backbone structure for electrochemically deposited polyaniline. Such a device is sensitive to pH allowing the potentiometric determination of pH values ranging from pH 1-13. The excellent performance in terms of linearity, selectivity, stability and fast response makes this device suitable for pH sensor applications. In addition, the extremely simple preparation technique allows the conversion of any user defined substrate into a pH sensor. Since this technique is not limited to polyaniline only, the deposition of various polymers on carbon nanotubes in general offers a great potential for demanding sensor applications.

DNA-CNT interaction from density functional theory

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DNA-coated carbon nanotubes (CNT) represent a hybrid system which unites the biological regime and the nanomaterials world. They possess features which make them attractive for a broad range of applications, e.g., as an efficient method to separate CNTs according to their electronic properties [1], as highly specific nanosensors [2], or as an in vivo optical detector for ions [3]. It is therefore certainly worthwhile to obtain a detailed understanding of the binding between the bases in DNA and the surface of CNTs, preferably from ab initio. To this end, we are carrying out a systematic study of the interaction between single-stranded DNA and single-walled CNTs (SWCNTs) using density functional theory. More specifically, we are interested in assessing the subtle differences in the interaction of the four DNA bases, and how important the underlying structure of the CNT is for the equilibrium geometry of the bases on the outer tube surface. We will present results from our investigations for the interaction of adenine, cytosine, guanine and thymine with SWCNTs of varying tube diameter and chirality.

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Functionalization of suspended single-walled carbon nanotubes with gold nanoparticles and DNA: Synthesis and characterization

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Biomolecules or metal nanoparticles have been used as a functional species since they enable us to develop nanotubes for sensors, fuel cells, and catalyst applications. We have performed single-walled carbon nanotubes (SWNTs) functionalization using gold nanoparticles and DNA.

SWNTs were synthesized using on both flat and pillar-patterned substrates [1,2]. After introducing amine groups to the SWNTs by covalent coupling, gold nanoparticles and thiolated single-strand DNA were immobilized on suspended SWNT. From the gold-functionalized suspended SWNTs, we observed enhanced Raman scattering phenomena, which were suppressed after DNA functionalization. To address electronic transport properties during functionalization processes, we performed measurements at each functionalization step using the field effect transistor configuration. We found that the transport behavior was significantly changed during the amide coupling processes, and electron injection from the DNA to the functionalized SWNTs was observed.

G. -H. Jeong et al., [1] JACS 127 (2005) 8238 and [2] JAP 98 (2005) 124311.

Covalent Attachment of a Protein Molecule to the Tip of Carbon Nanotube

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We have investigated trapping of protein molecules on the tip of open-ended multiwall carbon nanotubes (MWNTs) in aqueous buffer solutions. The open-ended MWNTs were prepared by the oxidation of arc produced MWNTs in air at 700 ^{o}C on a SiO_2 wafer. Chemical reaction using carbodiimide (EDC) forms a chemical bond between an open-end tip of MWNT and a protein molecule, GroEL. After the chemical reaction, the products on the substrate were rinsed by pure water. The remained materials were characterized by atomic force microscopy. Since the size of the protein is lager than the tip diameter of open ended nanotubes, only one protein is expected to attach the open-ended tip. The AFM observation revealed that only one protein attached to the open-ended tip of nanotube. It is noted that proteins attached to the un-oxidized nanotubes were hardly detected. This indicates that the proteins made a covalent bond to the open-ended tip of nanotubes and the binding energy between the protein and the nanotube tip is larger than that of the van der Waals interactions between the protein and the side wall of the nanotubes.

In-situ Potassium doping into SWCNTs synthesized by a hydrogen arc-discharge method and their field emission properties

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Potassium-doped single-walled carbon nanotubes (SWCNTs) were directly synthesized by a hydrogen arc-discharge method using only Fe catalyst. The potassium-doped carbon materials indicated high-purity SWCNTs about 90% without amorphous carbon materials. The potassium-doped SWCNTs had the diameters of 1.4 - 2.0 nm from TEM observation. With a simple purification method which consists of a thermal oxidation in air ambient and acid treatments, amorphous carbon materials and metal catalyst particles on the surface of SWCNTs were effectively removed. For the field emission properties of SWCNTs, potassium-doped SWCNTs showed much lower turn-on voltage of 0.7 V/um and the higher emission current density of 1 mA/cm^2 at an applied field of 1.5 V/um compared with the undoped SWCNTs. Moreover, the potassium-doped SWCNTs indicated stronger emission stability than that of undoped SWCNTs

A study on effective doping and characterization of DWCNTs synthesized by a catalytic CVD method

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We have investigated doping and characterization of DWCNTs using nitrogen, potassium, and boron materials. High-quality DWCNTs were synthesized using MgO/Fe-Mo catalysts by chemical decomposition of CH_4. To achieve effective doping of nitrogen into DWCNTs, we controlled CH_4/NH_3 flow rate and reaction ambient during CNT synthesis. To incorporate potassium into DWCNTs, we performed a post-treatment such as evaporation of potassium solution at the preheater zone. For boron doping into DWCNTs, we used evaporation of boron oxide. Electronic structure was examined by x-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. High resolution transmission electron microscopy (HR-TEM) was also conducted for the study of structural and morphological behavior of doped DWCNTs.

Lipid Bilayer Coating of Multiwalled Carbon Nanotubes

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Unfunctionalized carbon nanotubes are not biologically compatible because their hydrophobicity causes immediate aggregation in water. Both single-walled carbon nanotubes (SWNTs) and multiwalled carbon nanotubes (MWNTs) can be easily dispersed in aqueous solution by non-covalent binding of surfactant molecules that consist of a single hydrophobic chain and a polar headgroup. But since these detergents dissolve biological membranes and unfold proteins, the use of their double-chain equivalents (specifically phospholipids), the main component of biological membranes, is much more desirable. However, SWNTs can only be coated with phospholipids when the SWNT diameter has been increased with polyelectrolyte layers, and lipid coating of raw MWNTs in the absence of detergent could not be demonstrated.

We show here that acid-treated MWNTs can be coated with synthetic phospholipids without the need of detergent or polyelectrolyte components. Phospholipid vesicles (liposomes) were allowed to fuse on acid-treated MWNTs, which were subsequently studied by atomic force microscopy. A smooth coating with occasional defects or transitions to a second layer was observed. These discontinuities are consistently 4-5 nm deep, the typical thickness of a lipid bilayer. Moreover, when fluorescently labelled lipids are included in the vesicles, the MWNTs can be observed with a fluorescent microscope, clearly indicating successful lipid coating.

NEW 1,3-DIPOLAR CYCLOADDITION OF A NITRILE OXIDE TO SWNT. PHOTOCHEMICAL AND ELECTROCHEMICAL STUDY OF A PYRIDINE-SWNT COMPLEX WITH A ZINC PORPHYRIN.

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Chemical processing and solubility can play an essential role in the applications of SWNTs. Along the last years, interest has focused on their chemical properties and functionalization of SWNTs is actually a field of great interest. Covalent chemistry on the walls of the SWNTs is a viable route to functionalize SWNTs and cycloaddition reactions have proved to be a powerful tool.

In this communication we show the new cycloaddition of a nitrile oxide to SWNT. (The benefits of microwave irradiation as source of energy in these reactions are presented as well).

The resulting Pyridine-SWNT forms a complex with a zinc porphyrin (Zn-Por) in a similar way to that reported for pyridyl functionalized [60]-fullerenes. Photophysical and electrochemical studies have been carried out.

Bio-Directed Assembly of Carbon Nanotubes for Molecular Electronics

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The miniaturization of devices for electronical and biological applications requires the development of new assembly strategies that allow their precise localization and interconnection at the nanometric scale. The most promising mechanism for accomplishing this is self-assembly. Thus, the exceptional recognition properties of DNA molecule make it an ideal candidate for realizing a site-controlled implementation of nanocomponents, particularly single wall carbon nanotubes, one of the main building blocks of future nano-electronics. Within this context, an advanced strategy is proposed to design and develop novel SWNT-based devices bio-assembled with DNA.

In this paper, we will discuss three of the main key points required to perform SWNT circuits templated onto DNA : (i) the control of SWNT-DNA binding (ii) the DNA scaffold itself and (iii) the metallization of DNA to get conductive nanowires. Thus new tools will be presented that we developed to specifically target and bind SWNTs to DNA, using both covalent (bio-directed) and non covalent chemistry. Complementary characterizations by gel electrophoresis and AFM demonstrate the efficiency of the binding methods, which allowed us for example to bridge two SWNTs by a DNA molecule or to specifically attach DNA to SWNT extremities. In addition, SWNTs bound to DNA can be aligned on a substrate using the combing properties of DNA strands, bringing a new tool into the toolkit for self-assembling SWNTs onto surfaces. These methods were next applied to precisely address a SWNT on a μm-scale three-armed DNA scaffold, as a starting point for the assembly of a simple electronic device such as a transistor. Finally, to fully utilize DNA not only as a positioning scaffold for nanodevices but also as a conducting element, DNA is metallized by electroless plating techniques. We will present our last results on the production of thin (50 nm in mean diameter) and conductive palladium coated-DNA nanowires.

Synthesis of polyethylene glycol grafted single-walled carbon nanotubes through silanization of carbon nanotubes

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The synthesis of water-soluble single-walled carbon nanotubes (SWNTs) is an important topic because such materials have potential applications in biology and materials science. It has been reported that water-soluble carbon nanotubes can be produced by functionalization with carboxylic acid groups(1), polymers(2), proteins(3), and through sidewall functionalization(4). In this report, we demonstrate the first example of the functionalization of single-walled carbon nanotubes with polyethylene glycol (PEG) through silanization of SWNTs. Three PEGs with different chain lengths were covalently attached to the sidewall of carbon nanotubes. Dispersions of these different PEG-grafted SWNTs were prepared in order to understand the influence of PEG chain length on the dispersion of carbon nanotubes in water.

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The interaction of lung surfactant proteins A and D with carbon nanotubes; potential for damage to lung immune defense mechanisms

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To date, pulmonary toxicity of carbon nanotubes is a research area that has received attention. Inhalation probably constitutes the highest risk as it is difficult to deal reliably with suspension in air of extremely small particles. Surfactant protein A and D (SP-A and SP-D) are collectin proteins that are secreted by airway epithelial cells in the lung. They play an important role in firstline defense within the lung. The aim of this study was to investigate the interaction between carbon nanotubes and proteins within lung surfactant.

By using Sodium dodecyl sulphate-polyacrylamine gel electrophoresis (SDS-PAGE), Western Blotting, and a novel technique of affinity chromatography based on carbon nanotube-Sepharose matrix [Salvador-Morales, C. et al]1 it was shown that SP-A and SP-D bound to carbon nanotubes. The binding was Ca^{2+} ion dependent, and was variable between batches of nanotubes. It was therefore likely to be mediated via surface impurities or chemical modifications of the nanotubes. Thus, the sequestration of SP-D and SP-A by carbon nanotubes would induce susceptibility to lung infection and emphysema

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Electric Fields Induced Inside Modification of Carbon Nanotubes Using Negatively Charged Single-Stranded DNA

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Inside modification of carbon nanotubes has great potential to be applied to carbon nanotube based electronic devices because encapsulated functional materials are shielded by its sidewall. However, the encapsulated functional materials are limited to simple molecules, such as fullerenes, alkali metals, and low-molecular-weight organic materials, so far. Here we demonstrate the insertion of single-stranded DNA into carbon nanotubes using two kinds of electric fields. Experiments are performed by applying direct current (DC) and radio frequency (RF) fields to the DNA solution through nanotube-coated anode and cathode electrodes which are submerged in the DNA solution. In this procedure, motion and conformation of DNA are controlled by the DC and RF electric fields, respectively. As a result, the DNA encapsulated nanotubes are confirmed by several analyses and the electric field strength is found to play an important role in the insertion process. According to the Raman spectrum analysis, the downshift of G-band and the change of radial breathing mode are observed to depend on the length and the base sequence of DNA, respectively. In order to investigate the base sequence effects on the encapsulation, electrical characteristics of the DNA encapsulated nanotubes are currently measured.

Suppression of fullerene polymerization inside the single-wall carbon nanotube: Effect of hydrogen gas

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C_{60} molecules encapsulating in the single-wall carbon nanotubes (SWNTs), so-called peapods, have been transformed into smaller tubes inside the host tubes after high temperature annealing at ~1200^{o}C. [1]. In this study, we carried out the annealing in H_2 flux and investigated polymerization of C_{60} molecules in such a confined nano-space of SWNT. Rates of the polymerization were evaluated by the yield of inner tubes formation using Raman scattering measurement. After annealing the peapods in H_2 flux, it was found that the C_{60} molecules slightly transformed into the tubes. The yield of the inner tube formation for the H_2 annealed peapods was well below a half of the conventional Ar-annealed ones. In addition, when once having annealed the peapods in H_2 environment, the rate of the C_{60} polymerization becomes considerably lower in subsequently conducting conventional high temperature treatment in Ar flux. Further extended duration of annealing in Ar flux (~10 times longer) makes the polymerization gradually progress and recover the yield for formation of the inner tubes. We suspect that the hydrogen molecules penetrate into the interior spaces of nanotubes and weakly interact with the C_{60} molecules. This may be a reason for preventing the polymerization.

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New Synthetic Method of Silica-Coated Carbon Nanotubes with Controllability of Coating Thickness

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Multi-walled carbon nanotubes (MWCNTs) coated with an insulation sheath of silicon oxide (SiO_2) have a potential as excellent heat-removal materials for electrical and electronic devices. To date, SiO_2-coated CNTs have been commonly prepared by sol-gel methods in combination with cationic surfactants (*e.g.,* polyethyleneimine: PEI). However, the conventional methods have the difficulty of controlling the coating thickness and the problem of a high production cost caused by the use of the specific surfactants. In this work, we have developed a novel surfactant-free SiO_2-coating method by using the mixture of triethoxyphenylsilane (PhTEOS) and tetraethoxysilane (TEOS) as SiO_2 precursors. The heterocoagulation of the hydrophobic SiO_2 precursors with MWCNTs enables the selective gelation of SiO_2 on the surface of MWCNTs. Furthermore, the adjustment of the mixing ratios (Si/C molar ratios) of the SiO_2 precursors and MWCNTs allows for the control of the coating thickness, which significantly influences the electrical and thermal conductivities of SiO_2-coated CNTs. As a consequence, the SiO_2-coated MWCNTs synthesized by this novel synthetic method (at the molar ratio of Si/C = 2/1) have exhibited the high insulation property of 2.3 Ω·m (at R.T., 100 kgf/cm^2, 1.13 g/cm^2).

Temperature dependence of the reaction of O_2AsF_6 with cup-stacked carbon nanotubes and graphite to form intercalation compounds C_xAsF_6

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Cup-stacked carbon nanotubes (CSNTs) have a fibrous structure with piled-up conical cups made of graphene layers. Although CSNTs have many open channels on the inside and outside of the tube walls, it is not certain whether the nanotubes can form intercalation compounds similar to those of graphite. In the course of the invstigation on the reactivity of CSNTs with AsF_5, AsF_5+F_2, or O_2AsF_6 to form intercalation compounds C_xAsF_6, it was found that the reactivity of O_2AsF_6 with cup-stacked carbon nanotubes and with graphite is highly temperature dependent. Solid-solid reaction of O_2AsF_6 with graphite proceeds very rapidly above 30^{o}C, but slowly below 20^{o}C. Temperature dependence of the reactivity of O_2AsF_6 with heat-treated CSNTs and graphite was investigated. Jander-type equation was used to elucidate the reaction mechanism. The reaction was found to be diffusion-controlled and the activation energy was estimated to be *ca.* 60 kJ/mol for heat-treated CSNTs and *ca.* 150 kJ/mol for graphite.

Electrochemical synthesis and characterization of carbon nanotube-supported metallic nanoparticles

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Carbon nanotubes (CNTs) have many practical and potential applications due to their outstanding physical and electrical properties. Recently, there has been great interest to exploit the application of CNTs in the area of catalysts, where nanotubes can function as supports of heterogeneous catalysts. Various methods such as impregnation, sol-gel and hydrogen reduction have been developed to prepare well-dispersed metallic nanoparticles supported on CNTs that can be used as the heterogeneous catalyst in the hydrogenation reaction and the advanced electrocatalyst in fuel cells.

We aimed to design an electrochemical route to prepare highly-dispersed metallic nanoparticles supported on the CNTs. For this purpose, we designed an pretreatment procedure and the electrodeposition and electroless methods to prepare the metallic nanoparticles supported on the sidewall of carbon nanotube. The present study introduced an effective electrochemical deposition process for the preparation of metallic nanoparticles supported on the surface of CNTs, which involves a pre-treatment step and electrochemical deposition process. The resulting metallic nanoparticles were dispersed homogenously on the surface of CNTs with finely spherical morphology and a narrow distribution of particle diameter.

Nanotube Network Capacitors for Protein Detection in Serum

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Current methods for protein detection rely on optical techniques, involving fluorescent markers or enzymatic color change reactions. We have fabricated disposable carbon nanotube devices that eliminate the need for optical detection and instead offer direct electronic detection of proteins, while still exploiting the welestablished methods currently used for clinical bioassays. The novel device configuration is a capacitor with a carbon nanotube network as one conducting plate immersed into a liquid buffer along with a standard reference electrode acting as the second plate of the capacitor. While other nanotube based biosensors are expensive to fabricate and require completely new sensing procedures, our devices utilize protein assay technologies used in clinical research throughout the world. A standard method, ELISA, detects a specific protein by immobilizing antibodies onto a plastic substrate and then exposing the substrate to human serum. Our devices utilize the same plastic substrate and immobilization technique, but also incorporate a nanotube network, thus enabling us to electronically probe the plastic substrate used in an ELISA procedure. Our research represents the first time carbon nanotubes have been incorporated into an existing biosensing technology along with the first successful detection of a specific protein in human serum using carbon nanotube devices.

Zinc Phthalocyanine Incorporation into Single-Wall Carbon Nanohorns for Photodynamic Therapy

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Single-wall carbon nanohorns (SWNHs) have large inner nanospaces, unique physicochemical properties, and an appropriate size as a single aggregate. They are free from potential toxicity, thus their medical application for example, as a drug delivery system (DDS) has been considered. Recently, the possibility of using SWNHs as an anticancer drug carrier was demonstrated [1]. We, in this study, entrapped a photosensitizer of zinc phthalocyanine (ZnPc) inside SWNHs for a possible application of photodynamic therapy. Our results showed that a large amount (40-50 wt.%) of ZnPc was incorporated inside the SWNHs. Fluorescence spectra confirmed that ZnPc within the SWNHs (ZnPc@NHs) rapidly quenched fluorescence of 9, 10 dimethylanthracene. This indicated that the ZnPc in SWNHs retained its photo-physical property of singlet oxygen generation, which is critical for photodynamic therapy. We also confirmed that ZnPc@NHs attracted bovine serum albumin. Since the albumin is known to have a targeting function to tumors, ZnPc@NH-albumin should selectively reach tumors.

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High performance EDLC assembled with highly-oriented CNT sheet electrodes

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A highly-oriented carbon nanotube (CNT) sheet has been investigated in order to apply it to a polarizable electrode in an electric double layer capacitor (EDLC) containing a typical organic EDLC electrolyte system, triethylmethylammonium tetrafluoroborate (TEMABF4) in propylenecarbonate (PC). Observed discharge capacitance of the CNT sheet electrode increased with an increase in the length of the CNTs oriented vertically on an electrode substrate, aluminum sheet current collector. This would correlate with variation in important properties, such as density, number of walls, of the CNT sheet with an increase in the CNT length. It is noteworthy that the CNT sheet electrodes can provide a practical discharge capacity: e.g., 10-15 F g^{-1} (of the oriented CNTs) even at an extremely high current density, 200 A g^{-1} (of the oriented CNTs), while typical high-performance activated carbon electrodes cannot discharge with such a high current density.

Carbon Nanocable Composed of Orthogonal Graphene Arrangement

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A novel carbon nanocable has been successfully synthesized. The carbon nanocable with singular composition includes double layers with two different orientations of graphene laminations. The outer layer is synthesized by reduction of C_6Cl_6 with metal Na in the channels of anodic alumina template. After desalination process, the liquid phase pitch would fill the channels and be solidified by pyrolysis treatment. After graphitization treatment at 2450 °C, a distinguishable structure of double layers composed of orthogonal graphene arrangement could be observed by high-resolution TEM. According to the studies on the microstructure, the graphitic orientation of outer layer is parallel to the cable axis and the graphitic orientation of inner layer is inclined to the cable axis. The thickness of outer layer is about 5 nm. The result shows that we can combine two kinds of synthesis methods to produce the carbon nanocable with adjusted graphene arrangement. It is expected that the novel cable structure will reveal particular electronic property.

Fabrication and modification of the carbon nanotube tip for AFM

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We developed a method for fabricating a carbon nanotube (CNT) tip for an atomic force microscope (AFM). To assemble the CNT on the top of Si tip, we used dielectrophoresis (DEP) which is caused by a non-uniform electric field. After dropping the CNT solution and applying an AC electric field between an AFM tip and an electrode plate, CNTs were deposited directly on the tip so that they protruded from the tip. We fabricated tips with individual multi-walled carbon nanotube and found the experimental conditions that give high fabrication yields. In addition, to make the CNT tip that slant vertically, we developed the new technique by the focused-ion-beam (FIB). The directionality of the CNT was changed according to the beam direction of FIB. Moreover, the straightness of the CNT was greatly improved by the ion beam. From the AFM measurements of 15 nm gold particles, we showed that the CNT tip assembled by DEP produces higher resolution images than those of a conventional Si tip.

Single-wall carbon nanohorns for various applications

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Single-wall carbon nanohorn (SWNHs), a type of single-wall carbon nanotube, form spherical aggregates with diameters of about 100 nm [1]. Their production achieved the purity of 95Inside spaces of SWNHs are known to be useful to store materials. We found that anticancer drugs could be incorporated inside SWNHs and released slowly in biological culture medium [3]. For the possible drug-carrier use of SWNHs, the residence time of SWNHs in the blood should be increased as indicated by magnetic resonance imaging and histopathological studies [4]. For this, hydrophilic property of SWNHs was enhanced by physical [5] and chemical [6] modifications. The rough outside-surfaces of SWNH aggregates are useful to load nano-particles of catalysts, leading to the high catalyst-performances. We also show in this report that EuPt/SWNH enables the high-rate generation (practical level) of hydrogen gas from methane and water at such a low temperature of 300°C [7].

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Application of a peptide aptamer to functionalization of single-wall carbon nanohorns

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Peptide aptamers are short peptides that have selected based on their ability to bind target molecules. Various peptide aptamers have been selected for a variety of target molecules including inorganic materials. We have previously reported the selection of NHBP-1, which can bind to the surface of single-wall carbon nanohorns (SWNHs) [1].

SWNHs have been found to be loaded with small drugs on their surfaces or within their inner spaces, and then slowly release them [2, 3], indicating the possible use of SWNHs as a novel drug carrier. For such a biological application, functionalization of the surfaces of SWNHs is very important. In this presentation, we report the modification of the surface of SWNHs using NHBP-1. We synthesized polyethylene glycol (PEG) derivatives conjugated with NHBP-1 motif. The PEG-NHBP conjugates non-covalently bound to SWNHs and endowed SWNHs with dispersibility in aqueous media. The complex of SWNHs and PEG-NHBP has been loaded with the anticancer drug, doxorubicin, and showed apoptotic effect on tumor cells.

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Microreactors utilizing vertically-aligned carbon nanotubes

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Carbon nanotubes are one of promising materials as catalyst support, because of their high surface area, feasibility to chemical modifications, and mechanical/chemical stability [1]. However, there are severe limitations in the use for catalyst support due to their high cost and poor solubility. Recently, microreactors have attracted a great interest as efficient and highly-controlled reactors. We have applied carbon nanotubes to the catalyst support by growing them inside a microreactor. The nanotube-incorporated microreactor has many advantages; (i) nanotubes are fixed inside the channel so that dispersion of nanotubes in solvent is unnecessary, (ii) large contact area is expected because the nanotubes cover the whole channel, and (iii) collection of nanotubes after a chemical reaction, such as filtration, is not required. We grew vertically-aligned multi-walled carbon nanotubes inside the channel and modified them with Pt nanoparticles. Hydrosilylation of olefin, which proceeds in the presence of Pt catalyst, was performed as a model reaction of catalysis. Our microreactor showed >99 % yield for 10 hr. We believe that our idea of incorporating nanotubes into microfluidic devices may find promising applications, because a small amount of nanotubes work uniquely and efficiently.

Reference

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Carbon nanotube-supported hydrous ruthenium oxide: A highly active catalyst for aerobic oxidation of alcohols

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Carbon nanotube(CNT)-supported hydrous RuO_2 nanoparticles were prepared via a green oxidation method using metal salts as starting material. Using hydrogen peroxide as both oxidant and precipitant, hydrous RuO_2 nanoparticles were formed on the surface of CNTs at room temperature. High-resolution transmission electron microscopy (TEM) and X-ray diffraction patterns (XRD) showed that hydrous RuO_2 nanoparticles were highly dispersed on the outer surface of CNTs with a mean size of 1.35nm. The structure of supported hydrous RuO_2 has also been investigated by XPS and TGA. In a preliminary catalytic study, it was found that the RuO_2 nanoclusters exhibited extraordinarily high activity and selectivity in the aerobic oxidation of (activated and unactivated) alcohols under mild conditions using molecular oxygen. CNTs showed the most preeminent supporting property to form highly dispersed nano hydrous RuO_2 among a variety of supports investigated, indicating their great potential for catalyst support. This simple and novel technique for preparing CNT-supported metal oxide nanocatalysts raises the prospect for various catalytic applications in chemical syntheses.

Functionalized Single-walled Carbon Nanotubes as an Effective Solid Acid Catalyst

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Since their discovery in 1993, researchers have paid extensive attention to functionalize single-walled carbon nanotubes (SWNTs) due to the requirements from dispersion and further chemically grafting. Recently, treating SWNTs with superacids has been recognized as an efficient method for decoration of SWNTs. In this study, we present that the functionalized SWNTs can be used as a novel protonic acid catalyst with high catalytic activity, which is potential to replace unrecyclable and difficult-to-separate “liquid acid“ catalysts. By treating them with concentrated sulfuric acid at 525K, SWNTs was succeeded to be functionalized by a hybridization of protonation and sulphonation. The nature and efficiency of this functionalization were explored by XPS, TGA, IR and Raman spectra. The surface of functionalized SWNTs was single-layered covered by about 3/5 H_2SO_4 and 2/5 SO_3H. These groups were highly thermalstable below 400^{o}C. The catalytic activities of the functionalized SWNTs were demonstrated by esterification and alkylation. In the formation of ethyl acetate, the functionalized SWNTs were more active than some typical acid catalysts, including Nafion, zeolite, sulphonated mesoporous organosilica, etc. Thus, the functionalized SWNTs are potential for catalytic applications.

Chemical Modification of Carbon Nanohorns by Microwave Irradiation

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Microwave irradiation is able to heat various forms of carbons quite efficiently. We have applied the microwave irradiation to chemically modify carbon nanohorns. As a simplest example, CNHs are irradiated in air for various periods at different powers. The dispersibility in organic solvents and XPS analyses consistently indicate that only a small irradiance is necessary to oxidize CNHs. Compared with oven-heating or acid-treatment methods, in which either high powers or unwanted chemicals are involved, the microwave method requires less than several % power of a home-use microwave oven and uses no chemicals. For applications, Pt particles are loaded onto CNH by applying microwave chemistry.

Effects of Gravity on Dissipative Structures of Dispersed CNT under Electric Field

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Acid-treated CNTs possess negative zeta-potentials in water. Applying DC electric field to the CNT dispersion sandwiched between two ITO plates moves CNTs toward anode by electrophoresis. Under certain conditions, CNTs distribute non-uniformly over the anode plane, exhibiting geometrically regular patterns that change slowly with time. It first forms cell-pattern that consists of space-filling polygonal cells, then changes to butterfly pattern in which CNTs gather toward the nodes where the neighboring cells touch each other. Cell-pattern is shown to be closely related with Benard convection. In contrast, butterfly-pattern is strongly affected by the relative direction of the electric field and the gravitational field.

Detection of DNA Sequence-Specific hybridization Using Single-walled carbon nanotube field-effect transistors

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One-demensional nanostructures have been demonstrated as good candidates for ultrasensitive, miniaturized molecular sensors in many applications. Among them, carbon nanotube based sensors are quite promising for highly sensitive sensors. Here we demonstrate the detection of DNA (deoxyribonucleic acid) hybridization by using single-walled carbon nanotube FETs (field-effect transistors) fabricated by patterned growth technique. When the target ssDNA (single stranded DNA) hybridize with the probe ssDNA immobilized on CNTFET, abrupt decrease of conductance observed from the CNTFET. Since DNA has negatively charged backbones, the observed decrease of cnductance can be explained either by the charge transfer from DNA bases or the effect of counterions. We will demonstrate that CNTFETs can be employed for label-free, direct real-time electrical detection of DNA hybridization.

Air-bridge and vertical CNT switches for high performance switching applications

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Carbon nanotubes are attractive for switching applications since electrostatically-actuated CNT switches have low actuation voltages and power requirements, while allowing GHz switching speeds. We describe the fabrication and characterization of two types of nanoelectromechanical (NEM) switches based on CNTs. Our first NEM structure is a CNT air-bridge switch which consists of single walled nanotubes suspended over shallow trenches in a SiO_2 layer, with a Nb pull electrode beneath. The nanotube growth is done on-chip on Fe-catalyst islands using a methane chemical vapor deposition (CVD) process. Electrical measurements of these devices show well-defined ON and OFF states as a dc bias up to a few volts is applied between the CNT and the Nb pull electrode. The CNT air-bridge switches were measured to have speeds that are 3 orders of magnitude higher than MEMS based electrostatically-driven switches, with switching times down to a few nanoseconds. Our second NEM structure, the vertical CNT switch, consists of nanotubes grown perpendicular to the substrate. Vertical multi-walled nanotubes are grown directly on a heavily doped Si substrate, from 200 - 300 nm wide, $\sim 1\ \mu$m deep nanopockets, with Nb metal electrodes to result in the formation of a vertical single-pole-double-throw switch architecture.

A facile way of shortening cup-stacked type carbon nanotubes via sonication

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Recently, large-scale production system of carbon nanotubes has been established through the development of the floating reactant system which allows a three-dimensional of hydrocarbon with the catalytic particles. One of reason for limiting widespread application of carbon nanotubes would be their low dispersionability due to their physical entanglement between long tubes. In this study, we will report a simple way of shortening cup-stacked type carbon nanotubes by subjecting the optimally air-oxidized tubes to the ultra-sonication for a short time. Then, we will discuss their morphological changes with the oxidation temperature varied and their possible application as filler in hybrid nanocomposite.

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 and will be presented. As an example, we also present two-terminal nanotube electromechanical switches based on singly clamped, self-assembled and suspended MWNTs. The self-assembly techniques relies on the chemical modification of a patterned substrate. This local functionnalization 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 around a low (<3V) voltage threshold compatible with applications. The key physical parameters and routes towards high frequency operation will be discussed.

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Cell proliferation of osteoblasts on carbon nanotubes with different diameter

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The developments of carbon nanotubes (CNTs) for tissue engineering have attracted a great deal of attention. The present *in vitro* study investigated cell proliferation of osteoblasts (the bone-forming cells) cultured on single-walled carbon nanotubes (SWCNTs) or multi-walled carbon nanotubes (MWCNTs) with various diameters. CNT scaffolds were formed on polycarbonate membranes by filtration. Cell proliferation and morphology were investigated by using a scanning electron microscopy and a ELISA kit for detecting transforming growth factor-beta 1 (TGF-beta 1). Osteoblasts on CNTs showed excellent proliferation with extension of cell morphology in all direction. The effect of diameter on cell proliferation of CNT scaffolds will be reported in detail.

Oxygen Plasma Ion Irradiation Effect on Modification of Carbon Nanotubes

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Carbon nanotubes (CNTs) are modified by energetic ion irradiations in oxygen plasma and oxygen-argon plasma. According to the previous study [1], the MWNTs were modified by sputter-etching due to nitrogen plasma ion irradiation without chemical reaction. In this study, in order to observe the chemical reaction effect on modification of CNTs, oxygen was fed into reactor and oxygen plasma ions were irradiated to CNTs. The modification of CNTs using oxygen plasma was compared with that of argon plasma. The ions are irradiated to CNT target through the plasma sheath formed on CNT target and the energy of incident ions were controlled by the sheath potential. The irradiated ion dose was controlled by plasma density and treatment time. The plasma sheath potential and density were monitored by emissive probe and Langmuir probe, respectively. The target CNTs was multi-walled carbon nanotubes (MWNTs) grown by thermal chemical-vapor deposition and the single-walled carbon nanotubes (SWNTs) grown by arc discharge. Preliminary results show that, under the condition of same ion irradiation energy and dose, the intensity ratio of D to G band of Raman spectrum of CNTs treated by oxygen plasma is larger than that of CNTs treated by argon plasma. It is possible that the carbon monoxide and dioxide is created on surface of CNTs by covalent bond between oxygen radical and carbon atoms [2], which may be enhanced by the energetic oxygen ion irradiation. The oxygen plasma treatment was carried out with and without energetic ion irradiations. The variation of amount of oxygen radicals and ions was monitored by intensity ratio of optical emission spectroscopy (OES). Modifications of CNTs with various ratios of oxygen radicals and oxygen ions will be presented. Also, physical and chemical etching effect on the modification of CNTs was studied. The surface morphology of modified CNTs was observed by scanning electron microscope (SEM) and transmission electron microscope (TEM).

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PtRu Supported on CUP-Stack Typed Carbon Nanotubes as an Electrode for Fuel Cell Applications

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The potential of cup-stacked type carbon nanotube (CSCNTs) supports for platinum-ruthenium (PtRu) catalysts as an electrode for direct methanol fuel cell (DMFC) applications was investigated using the electrochemical oxidation of methanol at various temperatures. PtRu supported CSCNTs shown an anomalously high power density, as high as twice that compared to when the bimetallic catalyst was dispersed on Vulcan carbon (XC-72). The characterization of the CSCNT features before and after the catalyst loading were demonstrated by scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), and X-ray diffraction (XRD). The PtRu bimetallic electrocatalysts were very homogeneously dispersed on the CSCNTs, and the electrocatalyst particle size was about ~5 nm. A DMFC using CSCNTs showed a better performance than one using the Vulcan XC-72 carbon.

EDLC properties depend on the Diameter of Mass Produced Multi-walled Carbon Nanotubes

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Two types of mass produced multi-walled carbon nanotubes (MWNTs, which is generally known as a VGCF) with different diameters (the trade mark of the thicker one is VGCF® and of the thinner one, VGNF®) have been investigated for their potential for use in electric double layer capacitors (EDLCs). The variation aspects of the two MWNTs by KOH activation depend on their diameters. The capacitance enhancement and specific surface area (SSA) on KOH activation is more drastic for the thicker MWNT (VGCF®). The VGCF-KOH 500 exhibits a capacitance enhancement as much as 30 times greater (37.2 F/g) than that of the as-grown materials (1.2 F/g), under the conditions of charging up to 3.5V and discharging at a current density of 10mA/cm2. Interestingly, only for the case of the thinner MWNT (VGNF®), selective attack on its amorphous carbon impurity has also been observed, but only the case of thinner MWNT (VGNF®) as demonstrated from both SEM observations and Raman spectra. Consequently, the results of this study will provide the insight into the potentiality of using MWNTs for EDLC electrodes, which would enable cheapest production cost among the various types of carbon nanotubes.

Fluorine storage by single-wall carbon nanohorns

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We have been doing extensive studies on fluorination of nanocarbons using elemental fluorine, and have reported that fluorination is effective for property control and functionalization of nanocarbons. In the course of the study on fluorination reaction of single-wall carbon nanohorns (SWNHs), we have found that SWNHs have the ability to both absorb and release fluorine at practical pressures and temperatures. When SWNHs exposed to 1 atm fluorine in the temperature range 35-300^{o}C for 24 h, they absorb fluorine gas to give fluorinated nanhorns (F-SWNHs) CF_x (x =0.1-0.75). In the case of hole-opend nanohorns(h-SWNHs), they absorb large quantities and yielded fluorinated h-SWNHs CF_x (x =0.5-1.2). Elemental fluorine was generated from the F-SWNHs ($CF_{0.66}$) by a RT treatment subsequent to initial 400^{o}C treatment under a reduced pressure; a total amount of 40 mg of fluorine was generated from 63.4 mg of the sample $CF_{0.66}$. The generated fluorine contained only ppm impurities such as CF_4, HF, and SiF_4. The nanohorn and dahlia structures are mostly preserved after the fluorine generation indicating that SWNHs enable storage and transport of fluorine in a solid-state form.

Formation of Multi-Walled Carbon Nanotube Sheets

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Carbon nanotube (CNT) sheets, so-called “bucky papers“, have been proposed as promising materials for actuators, membrane filters, catalyst supports, and energy storage devices. For obtaining the CNT sheets, several structural parameters of the CNTs are recognized as key factors. The most important factors are flexibility, length, bundling, and entanglement of the as-grown and post-treated CNTs. CNT sheets derived from single- and double-walled CNTs have been easily fabricated by filtration process, due to their tendency to form a bundled assembly structure. On the other hand, formation of the sheet by filtration process from the as-grown powder of entangled multi-walled CNTs (MWCNTs) has been known difficult, prohibiting potential applications to electrodes of batteries, supercapacitor, and fuel cell. We found a solution for this issue by a simple fabrication of MWCNT sheets by ultrasonication-assisted filtration process. Two types of the MWCNTs with different bulk density were selected to elucidate the formation mechanism of MWCNT sheets. Morphology and structure of MWCNT sheets were investigated by transmission electron microscope, field emission scanning electron microscope, Raman spectroscopy, bulk density measurement, and nitrogen adsorption at 77 K. We expect that the MWCNT sheets fabricated in this study can find useful applications to energy storage devices.

Application Possibility of Sing-Wall Carbon Nanohorns to Supercapacitors

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Recently, several attempts have been reported on application possibilities of carbon nanotubes as electrode materials for supercapacitors. In this study, we report for the first time fabrication of electrodes for supercapacitors using the single-wall carbon nanohorns (SWNHs). We also investigated the hole-opening effect of the SWNHs on their capacitive properties. In addition, capacitance behaviors of SWNH electrodes were compared for the aqueous and non-aqueous electrolytes to elucidate dependence of electrolyte ion size in specific capacitance. Oxidation treatment of SWNHs with oxygen gas developed predominantly microporosity by opening the internal spaces of individual SWNHs. When using the aqueous electrolyte, the specific capacitance of SWNH electrode for supercapacitors dramatically increased as a result of oxidation treatment of SWNHs. On the other hand, for the non-aqueous electrolytes used in comparison with the aqueous one, opened SWNH electrodes did not give pronounced enhancement in specific capacitance, compared to as-grown SWNHs, which should be associated with larger solvated ion size of non-aqueous electrolytes. Therefore, our study clearly revealed that the nanowindow size of the SWNHs is an important parameter for improving the performance of supercapacitors.

Structural Changes of Single-Wall Carbon Nanohorns by Supercritical CO_2-Treatment

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Single-wall carbon nanohorns (SWNHs) have been proposed as a promising material for gas storage, catalyst support, and drug delivery. Therefore, various attempts to control the porosity and structure of SWNHs by chemical and mechanical methods have been reported. Supercritical carbon dioxide (CO_2) has been applied in various nanotechnological fields, due to its peculiar characteristics such as high diffusivity, low surface tension. In this study, we report structural changes of SWNHs by supercritical CO_2 treatment. The morphological and structural changes of SWNHs as function of supercritical CO_2 pressure and treatment time were investigated by transmission electron microscope, field emission scanning electron microscope, Raman spectroscopy, and nitrogen adsorption at 77 K. Treatments with supercritical CO_2 considerably altered the interstitial spaces between individual SWNHs, resulting in changes of pore structures determined by gas adsorption technique. This structural changes of SWNHs strongly depend on supercritical CO_2 pressure and treatment time.

Development of Bio-Nano Sensor Based on Carbon Nanotube Hybrid Materials

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We are developing research on the development of bio-nanosensors using nanocarbon materials such as fullerene or carbon nanotubes, with the aim of investigating application of these new devices in the field of biomedical engineering. Characteristic evaluation of bio-nanosensors based on single-walled carbon nanotubes (SWNTs) is demonstrated by using biotin (vitamin B_7) which binds in the peculiarity with avidin, a glycoprotein.

We fabricated a FET-chip with Al-Si electrodes as source and drain using back-gate electrode. The SWNT network, which is dropped onto between source-drain electrodes in the FET-chip, is composed of a mixture of avidin-modified SWNTs and polyethylene glycol (PEG)-grafted SWNTs (PEG-SWNTs).

An increase in impedance, resulting from a change of state of the SWNT network surface due to avidin-biotin binding, is observed when biotin is injected. On the contrary, injection of other vitamins results in decrease in impedance of the solution. In contrast, when only PEG-SWNTs is fixed on the electrodes, impedance decreases after injection of all vitamins. It is thought that the vitamins do not bind directly with PEG-SWNTs because impedance recovers almost to its initial value when the electrode is washed with distilled water.

Oxidation of embedded iron clusters in CNTs under photoflash exposure

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The phenomena of single wall carbon nanotubes (SWNTs) exposed to photoflash have been investigated and the corresponding response which is called photoacoustic effect was studied. In this work, five carbon materials including as-synthesized SWNTs, purified SWNTs, multi-walled carbon nanotubes (MWNTs), carbon nanocapsules, and carbon fibers were photoflash-exposed and their results were compared. All the carbon materials except carbon fibers were synthesized through the floating catalyst chemical vapor deposition (CVD) method which used xylene as the carbon source and the ferrocene as the catalyst. The results showed that the raw SWNTs and the MWNTs were oxidized when they were exposed to photoflash. Increase in temperature of the carbon nanotubes (CNTs) over 475^{o}C due to photoflash exposure was attained, which causes oxidation of both the CNTs and embedded iron catalysts in such a high temperature. Moreover, ignition occurred when the CNTs containing numerous carbon nanocapsules were photoflash-tested, and the residual products may contain Fe_2O_3 or Fe_3O_4 depending on the degree of ignition. However, no reaction occurs for the purified SWNTs and the carbon fiber. In this study, X-Ray, FE-SEM, and HRTEM were used to identify the composition of residual products and to study the variation in microstructures of the CNTs. The study reveals that ignition of the CNTs under photoflash exposure is significantly influenced by the amount of iron catalysts embedded in the CNTs.

Influence of purification procedure on the pore opening of SWCNT for hydrogen storage

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Influence of purification procedure on the pore opening of SWCNT for hydrogen storage

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Abstract:

A modified purification procedure is undertaken in order to study the influence of pore opening vs. the hydrogen storage capabilities of SWCNT, prepared in this laboratory (1).

The material were characterized by Scanning Electron Microscopy, Raman spectroscopy, and X-ray diffraction (XRD) respectively and tested for adsorption of hydrogen in variety of conditions.

The results indicate any damage to carbon nanotubes structure and the high purity of the products. The purified SWCNT under isothermal adsorption condition demonstrated to have high hydrogen capability, which depends to the purification extend of the material. The results interrelated as the indication of the influence of carbon nanotube pore opening on the hydrogen storage capability of the structure.

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Raman spectra of (n,m)-identified individual single-walled carbon nanotubes

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We have developed a procedure that allows the determination of the structural indices (n,m) by electron diffraction and of the features of the phonon modes by Raman spectroscopy on the very same individual and isolated free-standing SWCNT [1]. The precise and independent determinations of both structure and Raman features allow answering at several important questions.

1-A relation between the diameter and the radial breathing mode (RBM) frequency is determined. The comparison with previous RBM frequency vs diameter relations obtained on SWCNTs grown on a substrate, or wrapped in a surfactant allows discussing the role of the environmental effect on the Raman response of SWCNT.

2-The profiles of the tangential modes with respect to the structure of the tubes are reported. The dependence of the frequency and line shape of the tangential modes are compared with the predictions of different models.

3- The comparison between the incident excitation energies for which an intense Raman signal is observed and the calculated transition energies allows us to determine precisely the values of the optical transition energies for SWCNTs in a broad diameter range [3]

4-In the debate concerning the dominant process at the origin of the first-order Raman scattering in SWCNTs: single resonance process against double-resonance process, the ensemble of our results are well understood in the framework of a single resonance approach [3]

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Raman spectroscopic analyses of fullerene nanotubes and nanowhiskers

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Fullerene nanotubes and nanowhiskers composed of C_{60}, C_{70} and fullerene derivatives were prepared by the liquid-liquid interfacial precipitation method [1,2]. The C_{60} nanotubes prepared by use of pyridine and isopropyl alcohol (IPA) and dried in air exhibited Raman spectra very close to those of pristine C_{60} crystals, while the C_{60} whiskers prepared by use of quinoline and IPA showed Raman spectra similar to those of one-dimensionally polymerized C_{60} and C_{60} dimers. The whiskers prepared by use of C_{60}(6,7-dimethoxytetralin), toluene and IPA showed Raman spectra with clearly splitted peaks in the Raman shift range of 200-800 cm^{-1}. The C_{60}-C_{70} two-component whiskers prepared by use of a pyridine solution of C_{60}-24mol% C_{70} powder and IPA showed a mean composition of C_{60}-60mol%C_{70}, analyzing their Raman profiles. However, the C_{60}-C_{70} two-component nanowhiskers prepared by use of m-xylene solutions of various $(C_{60})_{(1-x)}(C_{70})_x$ mixed powders and IPA showed the compositions nearly close to those of the mixed powders. This result shows that the composition of C_{60}-C_{70} two-component nanowhiskers changes depending on the solvent species.

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Relative Humidity sensitivity of DNA-SWNT hybrids

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Many unique properties of DNA are very attractive for functionalization of novel nanoscale materials. One of the most exciting applications of DNA for the materials functionalization is the production of DNA-wrapped single-walled carbon nanotubes (DNA-SWNT hybrids) dispersed in aqueous solution. The production of DNA-SWNT hybrids have led to a big advance for separation of SWNTs that is required for many applications. However, relatively little is known about physical and chemical properties of DNA-SWNT hybrids in air.

We show here that the DNA-SWNT hybrids in air are sensitive to the humidity. The behavior of the humidity sensitivity is clarified by means of Raman spectroscopy. The Breit-Wigner-Fano (BWF) line, which derives from metallic nanotubes, in Raman spectra of DNA-SWNT hybrids strongly depends on the relative humidity, namely drying. The change in the BWF is reversible, depending on the humidity. The humidity-dependent of the BWF can be attributed to coupling of a phonon to the electronic continuum in metallic nanotubes associated with the interaction between DNA and water vapor in air. These results suggest that such DNA-SWNT hybrid with modification is a promising material for various applications, such as humidity sensors, not only in solution but also in air.

Real-Time Observation of Lattice Vibrations in Single-Walled Carbon Nanotubes

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Time-domain oscillations were generated in individual micelle-suspended single-walled carbon nanotubes (SWNTs) dispersed in aqueous media using ultrafast excitation pulses from a Ti:sapphire laser over the range of 710-860 nm. Fast Fourier transform of such oscillations reveals the observation of coherent phonons (CP) corresponding to the radial breathing mode lattice vibration (RBMs) of 16 distinct (n,m) SWNTs with phonon lifetimes on the order of 10 ps. Comparison to Resonance Raman scattering (RRS) experiments indicates excellent agreement with observed RBMs, with significantly narrower linewidths and no lower frequency detection limit seen for CP. Additionally, similar RBM intensity behavior is observed within 2n+m families as compared to RRS but exhibit different intensity behavior between 2n+m families. Finally, we have directly observed band-gap modulation of SWNTs in the form of two-peak maxima, separated by tens of meV, in the excitation profile for a given RBM. Therefore CP spectroscopy is a modulation spectroscopy providing information on the lineshape of the excitonic interband absorption peaks. This technique represents a novel, easy, and powerful method for (n,m) characterization as well as electronic structure probing.

Raman study on laser-induced defects in single-wall carbon nanotubes

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Evaluating and controlling of defects in single-wall carbon nanotubes (SWNTs) are very important for characterizing their physical properties. In the Raman spectra of SWNTs, a disorder-induced mode (so-called D band) is observed at about 1350 cm^{-1}. It is known that the D band is activated by defects. However, there are very few studies on the D band associated with specific defects in SWNTs. In this paper, we report the feature of the D band with specific defects produced in SWNTs by laser irradiation.

Laser irradiation was carried out with pulsed KrF excimer laser. The Raman spectra were acquired on a micro-Raman system. The spectra excitation was provided with a Nd;$\mathrm{YVO_4}$ laser (532 nm).

Raman spectra of SWNTs including RBM, D band and G band were obtained after irradiation. It is found that the D band consists of four components. The width of the most intense component at 1345 cm^{-1} remains unchanged due to irradiation while the intensity increased significantly. This indicates that specific defects were introduced into the SWNTs by laser irradiation. The characteristic of defects will be discussed by both Raman spectra and TEM images.

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Chirality and energy dependence of first and second order resonance Raman intensity

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We present our overall theoretical results on resonance Raman intensity for first and second order processes. By conbining with (1) optical processes matrix elements, (2) electro-phonon matrix elements, (3) elastic scattering matrix elements, and (4) exciton binding energy calculations, we can now calculating relative Raman intensity for different phonon modes as a function of laser energy, (n,m) and length. Further an excitonic effect on Raman intensity is a new important issue that we should clarify. Using the exction wavefunction, we modified the formula of exciton-phonon interaction matrix element for Raman intensity. Pressure effect will show an interference effect on Raman processes for metallic carbon nanotubes.

Environmental effects in position-selected PL/Raman spectra from suspended SWNTs

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Suspended single-walled carbon nanotubes (SWNTs) do not make contact with foreign materials such as a substrate, and environmental interactions affecting SWNT optical properties are therefore expected to be reduced significantly. In this work, we examined the environmental effects due to SDS wrapping, interaction with substrates, and bundle formation, based on PL and Raman spectra obtained from an identical suspended SWNT.

The chirality of a specific SWNT between a pair of SiO_2 pillars can be strictly determined by the combination of Raman and PL signals from the identical suspended SWNT. The RBM frequencies from the suspended SWNTs can be better fitted using the equation RBM freq. w[cm^{-1}]=223.5/diameter d[nm]+12.5, which is based on the results for SDS-wrapped SWNTs, rather than the equation w=248/d, which is derived from Si oxide substrates. In other words, environmental effects in Raman spectra are very strong for oxide substrates enough to cause higher frequency shifts, but are negligible for SDS wrapping, which causes a considerable shift in PL spectra. The environmental effects due to bundle formation were also examined based on systematic shifts of Raman and PL signals around pillars. These results indicate position-selected PL/Raman measurements are very powerful tools for evaluating the environmental effects.

Two phonon Raman intensity of single wall carbon nanotubes and graphite

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We calculate two phonon Raman spectra of single wall carbon nanotubes (SWNTs) and graphite. The Raman intensity and spectra are calculated by electron phonon matrix elements [1] and extended tight binding method [2]. The spectral range between 600 and 1100 cm^{-1} in the bundles of SWNTs is associated with the intermediate frequency modes (IFMs) which have the step-like dispersive peaks [2]. The negatively dispersive IFMs are considered the combination of the creation of oTO phonon and the annihilation of iTA phonon, and the positively IFMs are considered of the creation of both oTO and iTA phonon. The Raman intensity of the disorder-induced D -band in graphitic materials is calculated as a function of the in-plane crystallite size (L_a) and as a function of the excitation laser energy. The electron-defect interaction is calculated by considering the elastic scattering at the armchair edge of graphite [3]. We compare the calculated results with the experimental results obtained from the spectra for different laser lines and L_a.

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Temperature-dependent Raman features of individual suspended single-walled carbon nanotubes crossing deep trench

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In this study, resonance Raman spectroscopy (RRS) is employed to probe the structural information of CVD-synthesized single-walled carbon nanotubes (SWNTs) [1] in ambient environment at various temperatures ranged from 300 K to 700 K. SWNTs are fabricated crossing as-formed deep trench on SiO_2/Si to avoid the interferences from surrounding media such as the substrates. Furthermore, the enhanced RRS from suspended SWNTs (su-SWNTs) also helps to observe the slight changes of principal peaks as the temperature increased. We specially use the well-established Si Raman thermology to monitor and determine the accurate surface temperature of the measured su-SWNTs. Non-resonant Si Raman peaks intensity ($\sim$ 520.6 cm^{-1}) are also used for the normalizing of RBM and G-band peak intensity. The frequency of G^{+}-band peak is found downward shifted with the increase of temperatures due to the softening of C-C bonding strengths, where the changes are reversible during different temperature cycles. Temperature coefficients ($\alpha = d\omega/dT$) of the characteristics peaks are estimated respectively. We also compare the temperature-dependent Raman features of individual su-SWNTs with that of bulk SWNTs (containing bundles of SWNTs and probably some amount of amorphous carbons) to explore the bundling effects.

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The Raman fingerprint of graphene

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Graphene, a single, one-atom-thick sheet of carbon atoms in a honeycomb lattice, is the two-dimensional (2D) building block for carbon allotropes of every other dimensionality. It can be stacked into 3D graphite, rolled into 1D nanotubes, or wrapped into 0D buckyballs. Only very recently graphene has been produced in its free state [1]. This has fuelled research in 2D carbons and highlighted their remarkable electronic properties [2,3]. Graphene is a ballistic conductor in which electrons mimic the behaviour of massless, relativistic particles [2,3].. Electron transport is governed by the (relativistic) Dirac equation (rather than the Schrödinger equation) and this allows access to the rich and subtle physics of quantum electrodynamics in a condensed matter experiment Here we present the first Raman measurements of an isolated graphene layer [4]. These are supported by the definitive identification of free-standing single and bi-layers by transmission electron microscopy and electron diffraction. We show that graphenes electronic structure is uniquely captured in its Raman spectrum. We identify the unique features of its Raman spectrum, which fingerprints graphene amongst all other carbon allotropes. We compare its spectrum to that of n graphene layers having the same stacking as graphite, with n=2 to 28. We demonstrate that the Raman spectrum evolution with increasing number of layers uniquely reflects the evolution of the electronic structure and electron-phonon interactions. This makes Raman spectroscopy is a quick, high-throughput, non-destructive technique for the unambiguous identification of graphene layers. Finally we discuss the implications for the interpretation of the Raman spectra of single and double wall nanotubes.

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The first optical transition in carbon nanotubes: a resonant Raman study

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Resonance Raman spectroscopy on the second optical transition and photoluminescence excitation are the most commonly used techniques to obtain the chiral indices in carbon nanotube samples [1]. These techniques were also used to probe the relative abundances of different tubes in nanotube ensembles produced by different growth methods. In both techniques light is absorbed by exciting excitons into the second subband E_{22}. The absorption into E_{22} is suspected to be strongly affected by exciton resonance [2]. We performed resonant Raman spectroscopy on the first optical transition E_{11} in single-walled carbon nanotubes separated in solution. Comparison to luminescence data shows that we observe three tubes not seen in luminescence. Our results on the signal strength show that the intensity difference between nanotube families $\nu = (n - m) \bmod 3$ is much smaller than for the E_{22} transition. Both results support the theory of exciton resonance taking place only when exciting higher subbands. Our observed dependences of the Raman intensity on the chiral index (n, m) are in good agreement with predictions on the electron-phonon coupling from *ab-initio* calculations. We suggest resonance Raman spectroscopy on E_{11} to determine (n, m) abundances, since it is not affected by processes including additional subbands.

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Spatially-resolved Raman Spectroscopy of Single poly (3-methylthiophene) Nanotubes

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We present Raman spectra of isolated single poly (3-methylthiophene) nanotubes fabricated by electrochemical method. Using a high-resolution confocal microscope combined with an atomic force microscope (AFM), nanoposition-correlated Raman spectra are obtained. Characteristic polythylthiophene peaks are well observed, which indicates solid formation of polymer chains to the level of individual nanotubes. However minor differences in Raman spectra are observed depending on the nanotubes and on the locations of the same nanotube, perhaps due to the variation of doping rates in the nanotubes. Doping rates are estimated by measuring the intensities of corresponding Raman peaks. Our result shows that AFM-correlated confocal Raman microscopy is a powerful tool to study the nanosized system of conducting polymers.

Anomalous scaling and a new ratio problem in the optical transitions of carbon nanotubes.

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Using resonance Raman spectroscopy, we assigned (n, m) indexes for 94 carbon nanotubes. We studied the relation between the radial breathing mode frequency (ω_{RBM}) and the tube diameter (d_t), obtaining $\omega_{RBM}(\mathrm{cm}^{-1})=\frac{219}{d_t(nm)}+15$. Furthermore, we studied the many-body effects in the carbon nanotube structure. Understanding many-body effects (electron-electron repulsion and electron-hole attraction) in carbon nanotubes is important for carbon nanotube optics. We measured E^S_{33} and E^S_{44} transition energies for carbon nanotubes and saw that their nature are different from the E^S_{11} and E^S_{22} transition energies. While the E^S_{11} and E^S_{22} transitions happen from excitonics levels, in E^S_{33} and E^S_{44} transitions these excitonic effects are strongly suppressed. In fact, we saw that many-body corrections for the E^S_{11} and E^S_{22} and for the E^S_{33} and E^S_{44} follow different scaling laws. We observed a new ratio problem"where the $\frac{E^S_{33}}{E^S_{22}}$ ratio goes to 1.9 instead of 1.75, as expected in the excitonic model. We also proposed two polynomial functions, one for describing E^S_{11} and E^S_{22} transitions, and another for E^S_{33} and E^S_{44}. One differs from the other by a function that describes the exciton binding energy.

In-situ Raman Study on Lithium Insertion into Double walled Carbon Nanotubes-derived Bucky paper

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We carried out the Li^+ storage behaviors of highly pure single wall carbon nanotube (SWNT)- and double walled carbon nanotubes (DWNT)-buckypapers (consisting of entangled tube bundles) as an anode material in lithium ion batteries (LIBs) using an in-situ the Raman technique. The fabrication of these SWNT- and DWNT-buckypaper via a filtering process resulted from entangled long nanotube bundles of either SWNTs or DWNTs, in which the nanotubes are packed into hexagonal arrays. These thin, flexible and mechanically tough SWNT- and DWNT-foils exhibit an analogue behavior to hard carbons upon Li ion insertion at different voltages. From our studies, we mainly suggest the interstitial space in bundled nanotubes as the Li^+ storage sites in nanotube-foils. In detail, Raman changes as a function of Li^+ addition will be discussed.

Raman Study of Carbon Nanotubes on Line-Patterned Substrates

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Single-walled carbon nanotubes (SWCNT), confined to lines of a few micron widths on line-patterned substrates, are studied using Raman spectroscopy. The tangential mode (G-band) as well as the radial breathing mode (RBM) Raman intensity shows distinct anisotropy with changing the polarization directions of the incident and the scattered photon with respect to the direction along the patterned line. The anisotropy is more distinct for samples with line patterns of narrower line-width, which indicates an increasing degree of alignment of SWCNT's along the patterned line direction with decreasing line width. Surface-enhanced Raman scattering (SERS) effect on SWCNT's with Au nanoparticles and SWCNT's on a thin Au-film is also studied.

Dispersive Raman Feature of SUrfactant Solubilised SWNT

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Raman investigation of carbon sp2 materials, e.g., Graphite and single wall nanotubes, has revealed that the D-band and its overtone, G´ band, exhibit a dispersive character. For 2D graphene sheets the electronic interband transition as well as the phonon frequency varies linearly (close to the fermi energy) with the wavevector of the electrons and the phonons, respectively. Hence, the strong coupling between the electrons of wave vector k, measured from the K-point in the Brillouin zone, to phonons of wave vector q (=k) is responsible for the frequency dependence of the D-band and the G´ -band features in the Raman spectra of sp2 carbon. However, this explanation is probably an over simplification when the 2D structure is folded into a 1D tube structure and it appears that there is no consensus on the explanation. Here the dispersive features of G´ for surfactant solubilised SWNTs is presented.

Non Adiabatic effects on the phonon dispersions and Raman spectra of nanotubes

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Density Functional Perturbation Theory (DFPT) [1] is the most accurate ab-initio computational tool for the investigation of phonons and electron-phonon coupling. In tri-dimensional systems phonon calculations are done within the adiabatic approximation, which neglects the terms in the dynamical matrix recursively depending on the phonon energies, since these give negligible corrections. So far phonons in nanotubes have always been calculated within the adiabatic approximation. Here we demonstrate that non-adiabatic effects play a major role in determining the optical phonons, and, thus, the Raman spectra, of carbon nanotubes. These induce significant change in the shape and occurrence of the Kohn anomalies [2] in metallic nanotubes [3]. The correct assignment of the G+ and G- peaks in metallic nanotubes requires the inclusion of non-adiabatic effects [3]. We present the experimental dependence of the G+ and G- peaks of metallic and semiconducting nanotubes on the electronic temperature. We show that these data can only be reproduced within the non-adiabatic approach, while the common adiabatic approximation gives completely different trends with respect to the experimental data. To the best of our knowledge, nanotubes are the first material for which such behavior has been experimentally identified and theoretically explained.

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Complex Permittivity of Carbon Nanotubes Filled with Metallic Silver Nanowires

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The multi-walled carbon nanotubes (MWNTs) were prepared by catalytic decomposition of benzene using floating transition method at 1100-1200 °C. Benzene was used as carbon source and iron as catalyst with sulfur. The carbon nanotubes had an inner diameter in the range of 20-40 nm and an outer diameter in the range of 40-60 nm with lengths of 5-15 μm. The filling of multi-walled carbon nanotubes with metallic silver nanowires via wet chemistry method was investigated. The carbon nanotubes were filled with long continuous silver nanowires. The carbon nanotubes were almost opened and cut after being treated with concentrated nitric acid. Silver nitrate solution filled carbon nanotubes by capillarity. Carbon nanotubes were filled with silver nanowires after calcinations by hydrogen. The diameters of silver nanowires were in the range of 20-40nm, and lengths of 100nm-10mm. We studied the micromorphology of the silver nanowires filled in carbon nanotubes by transmission electron microscopy (TEM) and X-ray diffraction (XRD). Based on the experimental results, a formation mechanism of the Ag nanowire-filled carbon nanotubes was proposed. And the microwave permittivity of the carbon nanotubes filled with metallic silver nanowires was measured in the frequency range from 2 GHz to 18 GHz. The loss tangent of the carbon nanotubes filled with metallic silver nanowires is high. So the carbon nanotubes filled with metallic silver nanowires would be a good candidate for microwave absorbent.

Complete structural determination of single-walled carbon nanotubes by electron diffraction

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Keywords: SWCNTs, electron diffraction, intrinsic layer-line spacings

Abstract: We introduce a novel nondimensional **intrinsic layer-line spacing** concept to perceive new insights into the electron diffraction nature of single-walled carbon nanotubes (SWCNTs). Accordingly, we develop an efficient and unambiguous method for direct identification of chiral indices (n, m) of the carbon nanotubes from their electron diffraction patterns (EDPs). The new method is absolutely calibration-free. Uniquely, errors due to the nanotube inclination are specified. The tilt angle of the carbon nanotube with respect to the incident electron beam is simultaneously evaluated, thus the effect of the tube tilting is totally compensated for in the determination of chiral indices (n, m). Based on the new perceptions of the electron diffraction patterns (EDPs) of SWCNTs, several independent procedures are available for cross-checking the results by taking full advantage of abundant information contained in the EDPs. Therefore, the determination is free of ambiguity. In particular, the present method is easy-to-use and has no significant limitations. Tedious trial-and-error simulation procedure, which is currently popularly used, is not anymore needed. It is very promising to apply the proposed method to accurately mapping the (n, m) chiral indices distribution in carbon nanotube samples. The efficiency of the method is convincingly demonstrated on both simulated and experimental diffraction patterns from single-walled carbon nanotubes. The technique is readily extended to structural analysis of nanotubes of other materials with structures analogous to carbon nanotubes, such as boron nitride nanotubes.

A robust Bessel-function-based method for (n, m) chiral index determination of single-walled carbon nanotubes by electron diffraction

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Keywords: SWCNTs, electron diffraction, Bessel function analysis

Abstract: We report a calibration-free method for direct identification of chiral indices (n, m) of single-walled carbon nanotubes (SWCNTs) from their electron diffraction patterns (EDPs) based on Bessel function analysis of the diffracted layer-lines. A novel approach has been developed for confident identification of the orders of the Bessel functions from the intensity modulations of the diffraction layer-lines, to which (n, m) are correlated. In particular, we critically evaluate the effect of nanotube inclination on the validity of the method and show that the layer-lines governed by high-order Bessel functions tolerate higher tilt angles than those of low-order Bessel functions and thus are favored for (n, m) evaluation. The new method is of particular significance in that it considerably enhances the precision of chiral indexing and makes possible the analysis of high-order Bessel functions, especially when electron diffraction patterns are of relatively low pixel resolution. The technique can be applied to structural analysis of double-walled carbon nanotubes.

3D TEM observation of metallic nanoparticles in carbon nanotubes

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For the last decade, carbon nanotubes were thouroughly studied for their amazing properties in several fields : nanoreactors, supports for catalysts, ... The most popular characterisation technique used for the study of nanotubes is high-resolution electron microscopy (TEM). With such a technique, one can access the location, size and morphology of deposited particles by 2D projections of the 3D solid structure. However, all structural features of the solid are overlapped in the resulting 2D image which doesnt allow to know the exact location of the particles (i.e. inside or outside the tube channel). To resolve this problem, 3D-TEM characterisation (i.e. electron tomography) has been developed. The principle of this technique is to reconstruct a 3D representation of the solid from hundreds of 2D images of the sample tilted at various angles.

The aim of our work was to investigate the distribution and morphology of palladium nanoparticles deposited onto and into carbon nanotubes. 3D-TEM allowed us to determine the exact location of the particles and to study their morphology after thermal treatment. It is expected that such technique will become an useful tool for the understanding and observation of nanoparticles or nanowires in the catalysis field.

Electronic properties and nature of the metallic ground state in functionalized single wall carbon nanotubes

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The electronic properties of SWCNT are determined by the local one-dimensional arrangement of their sp2 hybridised carbon atoms, such that their character can be insulating, semiconducting or metallic. The latter exhibits a Luttinger liquid behavior.

Examples of our recent work on how one can analyse these electronic properties using high energy spectroscopy (electron energy-loss, photoemission and x-ray absorption spectroscopy) and optical techniques (Raman and UvVis absorption spectroscopy) as a probe will be given. Furthermore, we report on how to functionalise the SWCNT in order to modify their electronic structure in a controlled manner including examples of three alternative doping routes, namely, substitution, intercalation and endohedral doping. For metallic nanotubes and those filled with fullerenes doping induced changes will be discussed in the framework of a dimensionality crossover which causes a change from an one-dimensional metal to a normal Fermi liquid. The detailed understanding of these fundamental electronic properties of functionalised SWCNT is key to their future success.

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Change of CD4$^+$/CD8$^+$ ratio and cytokines after subcutaneous implantation of various carbon nanotubes in mice

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Nano-sized carbon nanotubes are expected to be utilized explosively in versatile fields including bio- ad medical devices [1, 2]. In this sense, it is imperative to investigate the bio-compatibility of carbon nanotubes systematically [3]. In this study, we will report one of the simple but powerful methods to evaluate the biological responses to various types of carbon nanotubes by measuring CD4$^+$ and CD8$^+$ T-cells, and a few cytokines in plasma in peripheral blood after subcutaneously implanted carbon nanotubes.

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Low-temperature scanning tunneling microscopy of single wall carbon nanotubes at metal surfaces

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The scanning tunneling microscope (STM) is a powerful tool for investigating the geometry and electronic properties of single wall carbon nanotubes (SWCNT) at the atomic scale, and has therefore been already widely used. In general, the electronic state of the CNT remains close to what is found for a gas phase material. However, in the particular case of STM, the nanotubes are individually adsorbed on a metallic substrate and interact with it, leading thereby to fine electronic effects. In particular, due to the difference in the work functions of the nanotube and of the surface, charge transfer occurs and induces a shift in the density of states of the nanotube with respect to the Fermi level. By analyzing the different cases obtained on Au(111) and on Cu(111), we show that the electronic coupling of a SWCNT to a surface is closely related to its geometry, to the local adsorption configuration, and to the surface nature.

Selective removal of metallic single-wall carbon nanotues using high power microwave radiation

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We report new method for selectively removing the metallic CNTs from semiconducting CNTs in a powder using high-power microwave radiation in the infrared and radio frequency range of the electromagnetic spectrum. SWNTs in a powder film were heated in a 2.5-GHz microwave oven for a few minutes, and the metallic nanotubes burned more rapidly than the semiconducting nanotubes. Raman data showed that the ratio of metallic to semiconducting nanotubes decreased dramatically after exposure to microwave radiation. Using their more rapid absorption of the radiation energy of the microwaves, we achieved the selective removal of metallic SWNTs from semiconducting SWNTs. This method results in the high purity of semiconducting SWNTs necessary for sensor and electronic applications.

Contribution D.026 - Tuesday, June 20

Electronic properties of a pair of narrow-gap carbon nanotubes

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A pair of (3m,0) narrow-gap zigzag carbon nanotubes, with the intertube interactions, are studied for the low-energy electronic properties within the tight-binding model. Energy dispersion, band symmetry about the Fermi level, state degeneracy, subband spacing, energy gaps, and density of states are dominated by the nanotube radius and the relative azimuthal angle between two nanotubes. The intertube interactions could destroy double degeneracy. Moreover, they could effectively reduce energy gaps, or change narrow-gap systems into gapless systems. The above-mentioned electronic properties are strongly modulated by the transverse electric field. Such field could induce new band-edge states.

Water-induced effects on the electronic properties of SWCNTs

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We report results from electrical characterization of single-wall carbon nanotube (SWCNT) field-effect transistors (FET) as a function of water pressure from 10^{-5} Torr up to 17 Torr, near the vapor-liquid equilibrium at room temperature (18.8 Torr). Long (4-5 um) SWCNTs were grown catalytically from 2 nm Fe seeds, patterned onto a 400 nm thick SiO_2 layer. The water used in the experiments was triply purified, deionized and outgased. Charge traps in the oxide caused large I-V hysteresis with marginal pressure dependence for various gasses, as well as for water under 12 Torr. Surprisingly, between 12.8 Torr and 16.5 Torr the water reduces the hysteresis width approximately six-fold. The most plausible hypothesis at this time considers (1) interaction of the water molecule dipole with the applied electric field, which can reduce the field strength at the CTN surface, and/or (2) the orientation of the molecule with respect to the CNT surface, which can influence the charge exchange with the CNT. Further experiments with other polar molecules are warranted.

Contribution D.028 - Tuesday, June 20

Pore structure and oxidation stability of double walled carbon nanotubes

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Recently much attention was paid on double-walled carbon nanotubes (DWNT) because it is expected that they exhibit different physicochemical properties compared to single walled carbon nanotubes and multi-walled carbon nanotubes, due to their coaxial morphology. Therefore, it is important to evaluate oxidation stability of DWNTs as compared with that of SWNTs when considering their basic science and various applications. In this study, we investigated oxidation behaviors of the DWNTs in detail by using Raman spectroscopy and thermal gravity analysis and scanning field emission microscopy and transmission electron microscopy.

X-ray photoelectron spectroscopy study of vertically aligned carbon nanotube films

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Vertically aligned carbon nanotube (CNT) films composed of two to three layers of MWNTs are attractive for applications like the FED. The electronic properties of CNT films, such as field emission, depend on the surface properties of the MWNTs, which are sensitive to gas exposure. In this study, the chemical state and the adsoption of the production (C_2H_5OH, Ar, H_2) and atmosphere gases were investigated by x-ray photoelectron spectroscopy (XPS).

The CNT film was grown by alcohol CVD and comprised of two to three layers of 0.2-mm-long MWNTs. In C1s, three components were found, while only a single peak attributed to intrinsic CNTs existed after annealing at 600 ^{o}C. The component of the peak at the highest energy, 0.7 eV higher than the intrinsic one, was attributed to hydrogen adsorption [1]. This assignment is supported by the result that the other peaks were scarcely detected in the XPS spectra in the wide energy range. Our result suggests that chemisorption of the production gases occurs in the production process and can influence to the CNT properties.

[1] A. Nikitin et al., Phys. Rev. Lett 95, 225507 (2005)

Sodium Chloride-Catalyzed Oxidation of Multi-Walled Carbon Nanotubes for Environmental Benefit

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The easy availability of multi-walled carbon nanotubes (MWCNTs) in a large scale (approx. 100 ton/year) through the development of a catalytic chemical vapor deposition method has established new areas of chemistry and physics for nanometer-sized carbon materials. We report here the use of sodium chloride (NaCl) as a catalyst for facilitating the oxidation reaction of graphitized MWCNTs. The reaction mechanism of the NaCl-catalyzed oxidation of MWCNTs has been investigated by the kinetic, spectroscopic and microscopic analyses. The results imply that the lowering of the oxidation temperature in the presence of NaCl originates from the introduction of disorder into the MWCNTs, thus increasing the facility of the oxidation reaction of the disorder-induced nanotubes. An accelerated oxidation process using the NaCl catalyst is important for contributing to facilitate the disposal of nanotubes for environmental considerations. This work has clearly demonstrated the effectiveness of NaCl as a catalyst for the oxidation of well-graphitized MWCNTs that exhibit a relatively high oxidation resistance. From the viewpoint of material costs, this approach has the advantage that the NaCl catalyst required for the large-scale treatment of MWCNT-based products could be available from abundant seawater, making the practical use of this approach very appealing.

Carbon nanotubes as a new future for bone tissue engineering.

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Carbon nanotubes as a new future for bone tissue engineering.

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In our experiments the terpolymer was mixed with single- or multi-walled carbon nanotubes, because it is believed that the structure of materials containing nanotubes can resemble the architecture of the natural extracellular matrix (ECM). A terpolymer of polypropylene, polytetrafluorethylene and polyvinyldifluoride (PTFE/PVDF/PP, density 1.600, purchased from Aldrich Chemical Co., USA, Cat. No. 45 458-3) was dissolved in acetone (POCh SA. Gliwice, Poland, Cat. No. 102480111; 5g of PTFE/PVDF/PP polymer resin per 50 ml of acetone) the terpolymer was mixed with single- or multi-walled carbon nanotubes (NanoCraft Co.

Inc., Renton, WA, U.S.A.) in concentrations of 2 or 4 wt%. Quantitative data were presented as means ± SEM (Standard Error of Mean) from 8-18 measurements obtained from 3 samples for each experimental group). On day 7 after seeding, the cell colonization was markedly improved and the maximum cell number and cell area was achieved when the terpolymer was modified by addition of 2 or 4wt% of multiwalled-nanotubes.

Acknowledgements

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Effects of External Fields on Electronic Structures of Finite Carbon nanotubes

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Electronic states of finite-length carbon nanotubes in the presence of electric and magnetic fields are calculated by the tight-binding model. Electronic properties such as state energy, energy gap, and density of states are mainly determined by the transverse electric field, the magnetic field, the Zeeman splitting, the nanotube length, as well as the transverse geometric structure. The electric field could induce the destruction of state degeneracy, produce more low-energy states, and lead to significant changes in energy spacing. The strong influences of the external fields on the band structures are investigated.

Direct observation of six-membered rings in a single wall carbon nanotube by spherical aberration-corrected HRTEM

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High-resolution transmission electron microscope (HRTEM) images of a single-wall carbon nanotube (SWNT) taken by a conventional HRTEM are the moiré patterns of two graphene sheets perpendicular to the incident electron beam, which correspond to the top and bottom portions of a rolled-up graphene-sheet constituting the SWNT [1, 2]. Appearing the moiré patterns is due to the large value of spherical aberration coefficient (Cs: ~0.5mm). However, aberration-corrector system has developed in recent years [3]. HRTEM mounting a Cs-corrector (Cs-corrected HRTEM) can control the value of Cs for the objective lens down to sub-microns order, which is lower by 0.1~0.2% than conventional one. In this study, we observed a SWNT by using a HRTEM (JEOL, JEM-2100F) mounting a hexapole-type Cs-corrector [3]. To reduce electron irradiation damages and obtain high-contrast image of SWNTs, the Cs-corrected HRTEM was performed with an acceleration voltage of 120kV [4]. By taking advantages of Cs-correction, graphitic network of a graphene-sheet constituting a SWNT was successfully visualized with atomic resolution. This result enables us to directly determine the chiral indices (n, m) of individual SWNTs and their handness, only by taking HRTEM images without any digital processing such as Fourier filtering. The detail will be discussed in the presentation and the following papers [4].

[1] A. Hashimoto, K. Suenaga, et al., Nature 430 (2004) 870.
[2] J. M. Zuo, I. Vartanyants, et al., Science 300 (2003) 1419.
[3] M. Haider, H. Rose, et al., Ultramicroscopy 75 (1998) 53.
[4] K. Hirahara, Koh Saitoh, J. Yamasaki, et al., submitted.

[5] The authors thank M. Haider et al. of CEOS for technical support, and T. Sugai for sample preparation.

Carbon Nanotube Material Quality Assessment

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The nanomaterial activities at NASA-Johnson Space Center focus on carbon nanotube production, processing, characterization and their applications for aerospace systems. Single wall carbon nanotubes are produced by CVD, arc and laser methods. Characterization of the nanotube material is performed using the NASA-JSC protocol developed by combining analytical techniques of SEM, TEM, UV-VIS-NIR absorption, Raman, and TGA [1]. Possible addition of other techniques, such as XPS and ICP, to the existing protocol will be discussed. Changes in the quality of the material collected in different regions of the arc and laser production chambers are assessed using the original JSC protocol. The observed variations seem to indicate different growth conditions in different regions of the production chambers.

Ref.: 1) Arepalli S., Nikolaev P., Gorelik O., Hadjiev V. G., Holmes W. A., Files B. S., and Yowell L., Protocol for the Characterization of Single-Wall Carbon Nanotube Material Quality, Carbon, Vol. 42, pp. 1783-1791 (2004).

Using Magnetic Carbon Nanocapsules as Support Architecture in Synthesizing of Cisplatin

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Here we report a unique synthesis method of Cisplatin (Cis-dichlorodiaminoplatinum) utilizing the magnetic metal filled carbon nanocapsules (M@CNCs) as support architectures. Cisplatin is one of the most widely used anticancer drugs. However, traditional preparation methods of Cisplatin were complicated and lower product yield. In this study, we using Fe@CNCs as a carrier which is facilitating only cis-form product located on its surface, as well as be effectively collected under magnetic field to get high yield (86%) of Cisplatin. The system utilizes malonic acid derivates of Fe@CNCs that can be coordinated with platinum complex used for synthesizing Cisplatin. Driven by the magnetic field, Fe@CNCs can be effectively collected and reused for the synthesis of Cisplatin. We might be able to use this technology plate in developing a serious of Cisplatin analog in the future.

Electronic structure and stability of BCN bulk and nanoscaled structures

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We investigate the stability of boron-nitride nanocones, using first-principles calculations. Our results indicate that nanocones with an antiphase boundary (an APB: a line defect with either B-B or N-N bonds) can be more stable than those without one, and that doping the APB's with carbon enhances their stability, and creates localized states in the bandgap. The structure with the smallest energy is a nanocone with a carbon-doped APB with a spin splitting of $\sim$ 0.5eV at the Fermi level. We also addres the relative stability and electronic structure of several $B_xC_yN_z$ layered structures. Twenty structures are considered, derived from a graphite layer by placing carbon, nitrogen, or boron atoms on each site. Interestingly, a $B_3C_2N_3$ structure is found to be more stable than the eight BC_2N structures in our study. The BCN compositions considered present a wide range of electronic behaviors. In general, we observe that structures with large values of the electronic band gap have a B/N (x/z) ratio of one. We also identify composition patterns that lead to the formation of metallic BCN layers.

Contribution D.037 - Tuesday, June 20

Energetics of Ordered Ice Encapsulated in Carbon Nanotubes

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We report first-principles total-energy calculations within the density functional theory that provide energetics and atomic structures of ice nanotubes (ice-NTs) encapsulated by carbon nanotubes (CNTs). We have examined several structures for ice-NTs: stacked-polygon (pentagon, hexagon, heptagon and octagon), helix-polygon and double-helix-polygon structures. We find that energy gain upon encapsulation ($approx$ 10 meV/H_2O molecule) is almost the same for those ice-NTs, CNT thus acting only as a mold. However, the cohesive energy for each ice-NT ranges from 0.42 eV to 0.54 eV per H_2O molecule. It is found that the most stable form is the stacked-polygon structure. This cohesive energy difference is found to originate from difference in hydrogen bond strength, i.e. bond lengths and bond angles, among the structures.

Chemical Peeling and Branching of BN Nanotubes in Dimethyl Sulfoxide

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We report that BNNTs can be effectively peeled off in a highly-polar dimethylsulfoxide (DMSO) solution under solvothermal conditions. The cycloaddition of DMSO to BNNTs is suggested to weaken the B-N covalent bonds and ease the hydrolysis process. Interestingly, peeled shells were found to form Y-junctions with trunk tubes. This is the first example that Y-junction BNNTs could be fabricated through a chemical method. The formation mechanism of Y junction BNNTs is discussed and explained in terms of rollup and self-catalyst fashions. These findings broaden the allowed chemistry on BNNTs and will stimulate further studies on BNNT engineering. Moreover, as evidenced by the previous theoretical and experimental works, Y-junction BNNTs composed of two segments with varying diameters are promising for electromechanical and optoelectronic devices. We think this work will stimulate broad interest in multidiscipline fields.

Refractive properties of Boron Nitride nanotubes in high electric field.

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Recent studies have shown that the boron nitride nanotubes demonstrate the giant Stark effect in the high transverse electric field. In particular, it was shown that the band gap of the boron nitride nanotube can be dramatically reduced in the electric filed as high as 1-10 V/nm. Such effect can be used in utilizing these structures as nanometer size switches, whose electronic properties can be changed in the wide range from dielectric to metallic.

In this experiment individual boron nanotubes were bent and positioned into transverse electric field using the STM-TEM holder inside the TEM column. The applied electric field was controlled by both: the applied bias and adjusted by the piezo-stage distance between the STM electrodes. The band gap characterization has been performed using low energy EELS spectroscopy combined with Kramers-Kronig analysis.

Low Temperature Growth of Boron Nitride Nanotubes

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Boron nitride nanotubes (BNNTs) are recognized as the candidate that will complement the uses of carbon nanotubes (CNTs) in nanoscale science and engineering. However, high growth temperatures (>1100 ^{o}C), low production yield, and impurities have prevented effective synthesis and applications of boron nitride nanotubes (BNNTs) in the past ten years. For the first time, we have succeeded on the growth of pure BNNTs on substrates at 600 ^{o}C [1]. This was realized based on our phase selective growth model, where energetic growth species play an important role on controlling the phases of BN solids. We verified that BNNTs can be grown in a total resputtering region, where other BN phases were suppressed. Bundles of BNNTs can be grown vertically aligned in regular patterns. These BNNTs can be used for applications without purification. Tunneling spectroscopy indicates that the BNNTs are having energy band gaps of ~4.4-4.9 eV. Results generated by plasma-enhance pulsed-laser deposition (PE-PLD) and chemical vapor deposition (PE-CVD) will be discussed in the conference.

YKY acknowledge supports from NSF CAREER award, the Dept. of the Army, Michigan Tech Research Excellence Fund, and CNMS at ORNL. [1]. Wang et al., Nano Letters.5, 2528 (2005).

Direct Growth of Vertical ZnO nanotubes without Catalysts and Templates

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Nanotubular structures of oxides materials have gained attention for their hydrophilic properties. These nanotubes are attractive for biological applications including nanofluidic devices for single DNA molecule sensing, rapid diseases diagnosis, and DNA sequencing. Here, we show that nanotubular cavities of ZnO can be directly grown on substrates without the use of catalysts and templates. Our experiments were conducted by thermal chemical vapor deposition (CVD) with ZnO/graphite powders as the source materials. We have detected ZnO nanowires, nanobelts, nanocombs, etc. at various growth conditions. In these processes, we found that vertical ZnO nanotubes can be grown on Si or oxidized Si substrates at a temperature of ~650 ^{o}C when appropriate cooling procedures were applied. These ZnO nanotubes was characterized by X-ray powder diffraction, high-resolution transmission electron microscopy (HRTEM), Field-emission scanning electron microscopy (FESEM), Raman spectroscopy, and photoluminescence (PL). Result indicates that these ZnO nanotubes were single crystals of the wurtzite phase.

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Structure, Stability and Electronic Properties of Aluminium Oxide based Nanotubes

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Among numerous oxide nanostructures alumina nanotubular materials are of interest due to their mechanical properties, large surface area, catalytic activity non-toxicity and low production cost. Furthermore, alumina has a high dielectric constant, low permeability, high thermal conductivity and nanotubular alumina has therefore a considerable potential for application as capacitor and gate electrode in nanoelctronics. We have studied the structural properties, the stability and the electronic properties of various nanotubular structures based on the layered $Al(OH)_3$, gamma-AlO(OH) hydroxides and alpha-Al_2O_3 using the density-functional based tight-binding method (DFTB). The single walled (n,0) and (n,n) $Al(OH)_3$, (n,0) AlO(OH) and (n,n) Al_2O_3 nanotubes show a similar size (diameter) dependence as other tubular structures, e.g. carbon and metal chalcogenide nanotubes. (0,n) AlO(OH) nanotubes were found to be unstable, whereas (n,0) Al_2O_3 nanotubes are stable but have a rasp like surface. All alumina based nanostructures investigated, are insulators independent from their chirality with band gaps of 10-14 eV for $Al(OH)_3$, 6-10 eV for AlO(OH) and 6-7 eV for Al_2O_3.

First Principles Study of structural and electronic properties of single-walled elemental boron nanotubes

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The results of a first principles study of the structural, electronic, mechanical and optical properties of single-walled elemental boron nanotubes (SWBNTs) are presented. Calculations are performed in the framework of density functional theory using the periodic ab initio program (CRYSTAL03). The predicted variations in the properties of different configurations and chiralities of SWBNTs are found to be associated with the unique features of mixed covalent and multicentered bonds present in the nanotubes.

Electronic structure and stability of aluminate nanotubes and bundles

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Since the discovery of carbon nanotubes, one dimensional nanomaterials and other various tubular forms have attracted considerable attention due to a wide variety of applications in nanoelectronics, fuel cells, and catalysis. Recently, lithium containing aluminate nanotubes have been synthesized by a surfactant templated hydrothermal process. In this work, we study the structural and electronic properties of aluminate nanotubes and bundles through first-principles theoretical calculations [1]. We propose a tubular structure in the form of AlO_2, which is energetically stable with fewer strain energies, compared with MoS_2 nanotubes with similar diameters. The AlO_2 nanotubes are all metallic with pseudogaps, independent of chilality. For small diameter zigzag tubes, electron conduction mostly occurs through the outer O shell with longer Al-O bonds, while the whole tube wall contributes to electron conduction for large diameter zigzag tubes or armchair tubes, which have similar inner and outer Al-O bond lengths. The stability of AlO_2 nanotubes is also maintained with Li doping inside the tube cavity and these nanotubes can be semiconducting when heavily doped. On the other hand, nanotubes in the form of AlO are disintegrated into clusters, not forming tubular structures. When AlO nanotubes are positively charged, the stable semiconducting nanotubes are obtained, similar to BN nanotubes. For a bundle structure of aluminate nanotubes, we find that inter-tube interactions are much stronger due to both ionic and covalent bonds.

[1] H.-M. Hong, Y.-J. Kang, C.-Y. Moon, K. J. Chang, and H. J. Kim, Phys. Rev. B 72, 205435 (2005).

Growth of SiO_x Nanowires on Ge Nanodots

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A metal-free direct growth has been developed for silica nanowires (SiONWs) on Ge nanodots. From high-resolution TEM, field-emission SEM, and energy-dispersive spectroscopy, the fabricated nanowires are identified as SiONWs with diameter in range from 10 to 50 nm and length around 1 μm.

The Ge dots were prepared by CVD on Si wafers subsequent to the growth of a thin Si buffer layer. The height of the dots ranged from 10 to 25 nm and the diameter ranged from 20 to 250 nm. These substrates were doped by carbon ion implantation and chemical oxidation was carried out. The thicknesses of GeO_x on Ge dots and SiO_x on Si substrates were estimated to be around 1.9 nm and 0.5 nm. Finally, SiONWs were synthesized with argon and hydrogen at 1000°C for 10 min by using conventional furnace.

The Ge dots with lower melting point (938°C) changed into small nanodots (around 10 nm) during the annealing with argon at 1000°C, which acted as nuclei of the SiONWs. It was found that Ge nanodots, a chemical oxidation, and the presence of carbon were essential. We believe that the growth of SiONWs is attributed to the vapor-liquid-solid mechanism through the carbothermal reduction of GeO_x.

In-situ monitoring of iron nanoparticles movement in amorphous carbon wall

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Solid phase nanotube growth induced by migration of iron nanoparticle seems to give an useful information for understanding the nanotube growth mechanism. Here we report the origin of the driving force would be resulted from the temperature gradient that was generated in the amorphous carbon specimen.

We prepared samples for real-time scanning transmission electron microscopy (STEM) study by using focused ion beam chemical vapor deposition(FIB-CVD) combined with phenanthrene and ferrocene precursor. We prepared an amorphous carbon wall on a extremely thin tungsten wire by FIB-CVD, where the wall typically have 100 nm thick, 1 micron wide, and several microns high, and a thin iron doped region was sandwiched locally at the mid point of the wall. Heating of the wall induced the segregation of iron nanoparticles that have 3 to 10 nm in diameter, and spread over fluctuating with Brownian like motion. However the majority of the nanoparticles tended to shift toward the wall top, where the temperature should be lower then that of the bottom of the tungsten heater. This fact suggested that the temperature gradient seems to be the possible candidate for the driving force. This work was supported by CREST-JST.

The Density Functional Tight Binding (DFTB) Method for Large Scale Finite Size Model System Calculations of Nanotube Growth, Reactions, and Properties

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We are discussing the performance and application of the density functional tight binding (DFTB) method for large scale finite size model system calculations in important areas of quantum chemical carbon nanotube modeling. In the first application, we use direct on-the-fly quantum chemical molecular dynamics (QM/MD) simulations comparable to CPMD accuracy to study the metal-catalyzed SWNT formation mechanism from carbon vapor feedstock model systems on Fe/Co/Ni catalyst nanoparticles. We also present studies of the catalyst-free, chirality-specific growth of SWNTs on SiC surfaces. In the second application, we examine the linear relationship between tube diameter/curvature and reaction energies of chemical functionalization reactions on armchair and chiral nanotube sidewalls, and identify the 1/d dependence of the orbital mixing energy contribution as origin of the linear relationship of the total reaction energy using energy decomposition analyses. In the third application, we present Raman and IR spectra of pristine and oxidized finite size SWNT fragments, as well as of linear polyyne chains encapsulated in SWNTs, and compare our findings with perviously published periodic boundary condition vibrational spectra and experiment. We note that the D band is exaggerated in finite size model systems, very much like in finite size graphene models where experiment agrees with our calculations.

Direct observation of superstructures of double-wall carbon nanotubes(DWNTs) by UHV-STM

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Carbon nanotubes (CNTs) have attracted much attention by virtue of their one-dimensional structure and of unique electronic properties induced by rolling-up of the graphene sheets. Scanning Tunneling Microscopy (STM) is a powerful tool for analyzing surface electronic structures of atoms, molecules and nanomaterials such as carbon nanotubes. Direct observations of multi-wall carbon nanotubes (MWNTs) by STM have revealed the presence of super-structures in the honeycomb lattice images induced by inter-layer interaction. Recently, progress on CNT synthesis has enabled us to prepare high-quality double-wall carbon nanotubes (DWNTs). However, high resolution surface images of DWNTs by STM have not been reported yet.

Here, we present the clear lattice images and super-structures of DWNTs by UHV-STM at room temperature. We observed not only the lattice images corresponding to the outer graphene sheet of DWNTs but also some periodic superstructures. Similar to the periodic super structures observed for MWNTs and atomic overlayers on graphite, we propose that the superstructures are explained by the inter-layer interaction between the inner and outer tubes of the DWNTs.

Kinetics of defects on carbon nanotube walls as studied by Monte Carlomethods

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The behavior of point defects such as vacancies and adatoms in carbon nanotubes is not yet fully understood, although the kinetics of these defects may govern nanotube growth, reactivity and local electronic properties.

We employ a kinetic Monte Carlo method for studying the migration, annihilation and coalescence of these defects at macroscopic time scales. As realistic simulations require accurate knowledge of transitions and activation energies, we use density functional theory-based methods to calculate these characteristics. In particular, because carbon adatoms can penetrate through the nanotube wall, we calculate the activation energy of this process for nanotubes with various radii. As defect complexes are formed during the migration, we also study the energetics of multi-vacancies on the nanotube walls.

The tests of our method give results which agree qualitatively with experiments on annealing of irradiation-induced defects in nanotubes at room temperature. Our method can be used to simulate the time evolution of defected carbon nanotubes on realistic, macroscopic, time scales. It allows studying the behavior of carbon nanotubes under irradiation and the mechanism of their self-healing. Underway are simulations to get more insight into the nanotube growth process and into the experimentally observed welding and shrinkage of irradiated nanotubes.

Diffusion Barrier Calculations for Mono-Vacancy on Carbon Nanotube

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For applications of nanotubes to nano-scale devices, the influence of atomic defects on the electronic and optical properties and on toughness is crucial. Recently the atomic structures of defects have become observable using TEM technique [A. Hashimoto et al, Nature 430,870 (2004).], so better understanding of atomic structures and dynamics of defects (as well as their electronic properties) can be achieved by combining theory and experiment.

Here, we discuss diffusion mechanisms of mono-vacancies in nanotubes with various chiarlities based on calculated diffusion barriers. Since mono-vacancies are stabilized due to C-C dimer formation particularly on curved graphene sheets, the diffusion barrier on nanotube walls is expected to be higher than that on planar graphene sheets. Nevertheless, we found some short cut paths on nanotube walls which lower the diffusion barrier. We will also discuss the diffusion anisotropy depending on the chirality.

Contribution D.051 - Tuesday, June 20

Energetics and electronic structures of nanotubes with topological line defects

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We report first-principles total-energy electronic-structure calculations in the density functional theory performed for carbon nanotubes with a topological line defect consisting of pentagon and octagon rings. We find that the ground state of the nanotubes with the topological line defect is ferromagnetic with small but finite magnetic moment of about $0.04 mu_B$/AA irrespective to the tube diameter. Detailed analyses of energy bands and spin densities unequivocally reveal the nature of the ferromagnetic spin ordering which is associated with the peculiar edge-localized states of graphite flakes.

Atomic and Electronic Structure of Divacancy in Carbon Nanotubes

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We report atomic and electronic structure of divacancy in carbon nanotubes (CNTs), calculated within density functional theory. Divacancy in a CNT is unstable, and self heals by reconstructing into a single stable geometry. The formation energy of divacancy could be as low as ≈3.2 eV in moderate diameter CNTs, suggesting higher probability than monovacancy. Divacancy formation energies strongly depend on the angle between tube axis and the new bonds that are formed during self healing. The electronic-structure of divacancy in a not semiconducting CNT exhibits a flat band, and increased density of states near the Fermi level. For particular divacancy configurations, we predict small net spin polarization because of the magnetic instability of the flat band. Semiconducting CNTs develop mid-gap bands, which have the potential to influence the functionality of CNT transistors.

Energetics of Plastic Bending of Carbon Nanotubes

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Plastic deformation of single-wall carbon nanotubes (SWNTs) is analyzed using nudged elastic band minimum energy path calculation with a bond-order potential. Two SWNTs of (5,5) armchair type and (8,0) zigzag type were examined under homogeneous bending for obtaining the activation and formation energies of Stone-Wales 5-7-7-5 defect, its dissociation pathway into 5-7 and 7-5 defects and migration of the two decomposed defects. The final formation energy of the two decomposed defects becomes negative at a critical bending curvature ρ_{yield}, which is 0.11 and 0.13 nm^{-1} for (5,5) and (8,0) SWNT, respectively, and roughly inversely proportional to the SWNT diameter. These calculations demonstrate that plastic deformation is thermodynamically favorable above a threshold “yield curvature” ρ_{yield}, and is also kinetically feasible above 1500K, which agree with our experimental observations. A deformation mechanism map for bending SWNT is constructed.

Orientation dependence of vacancies interaction in defective carbon nanotube

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Semi-conducting (10,0) defected single-walled carbon nanotubes (SWCNTs) were studied by density functional theory (DFT). Our results indicate that the orientation and distance between the vacancies influences the band-gap of semi-conducting SWCNTs. The energy barriers of the vacancy migration are studied with and without an external transverse electric field. The electric properties of carbon nanotube field effect transistors with vacancy-defects change when vacancies migrate under the electric field. We believe this study should be able to shed some light on the basic and complex defect processes in these devices.

Selective etching of metallic single-wall carbon nanotubes with hydrogen plasma

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We present Raman scattering and scanning tunnelling microscopy (STM) measurements on hydrogen plasma etched single-wall carbon nanotubes (SWNTs). Interestingly, both the STM and Raman spectroscopy show that the metallic SWNTs are dramatically altered and highly defected by the plasma treatment. In addition, structural characterizations show that metal catalysts are detached from the ends of the SWNT bundles. For semiconducting SWNTs we observe no feature of defects or etching along the nanotubes. Raman spectra in the radial breathing mode region of plasma-treated SWNT material show that most of the tubes are semiconducting. These results show that hydrogen plasma treatment favours etching of metallic nanotubes over semiconducting ones and therefore could be used to tailor the electronic properties of SWNT raw materials.

In $AlPO_4 - 5$ grown Single Wall Nanotubes are defective

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We present a Grand Canonical Monte Carlo simulation study of carbon adsorption in $AlPO_4 - 5$ (AFI) zeolites. An order N simplified tight binding model is used for carbon-carbon interactions and the carbon - matrix interactions, is assumed to be weak, in the physisorption range. Comparing the almost perfect tubes formed in smooth cylindrical channels and those numerically grown in $AlPO_4 - 5$, we can assess the role of the carbon-wall interaction. In $AlPO_4 - 5$, we obtain defective single wall nanotubes with a diameter of ~ 4 Å in good agreement with experiment. The tube is thermally stable and presents a mixture of (4,2) and (3,3) patterns. The energy cost associated to the defects is about 0.2 eV/atom, indicating that the probability of obtaining defective tubes is large.

Study of an isolated, individual and (n,m) labeled carbon nanotube

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Understanding the genuine properties of carbon nanotubes requires to study a well defined object. Unfortunately, usual product contains, beside various contaminant, a random mixture of nanotube with different chiral indexes (n,m) that makes difficult, if not impossible, to extract intrinsic properties.

We turn our research effort to produce isolated single-walled carbon nanotubes [1]. Several interesting results have already been extracted from this approach [2,3].

An other step has been made with the identification of the (n,m) indexes of a given nanotube thought electron diffraction [4]. The characterized nanotube, which position is known thanks to lithographic process, can then be studied with other tools such as Raman spectroscopy. Our goal is to produce an all-experimental catalog of properties corresponding to n,m indexes.

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Defect engineering of graphene layers

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Here, we describe the formation of dislocation dipole in graphene layers, which is the primary defect formed in the later stage of irradiation [1-3]. The nucleation of dislocation dipole occurs by the reconstruction of di-vacancies, making eightfold ring and two fivefold rings [1]. One more knock-on produces trivacancies, which reconstructs into a structure consisting of eightfold, sevenfold and fivefold rings. Successive knock-ons at the ends of the dislocation dipoles induce their growth along the zigzag line. In-situ observation of a topological defect in a graphene layer induced by electron irradiation [4] supports the formation of dislocation dipole. Irradiation induced amorphization of highly oriented pyrolytic graphite (HOPG) [5] can be explained by the accumulation of dislocation dipole. Strong barriers on the recombination probability between interstitials and vacancies, which lead to the stored energy (Wigner energy), have been revealed [1,2].

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Vacancy concentration and Raman intensity ratio of graphite

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The Raman intensity ratio of the disorder-induced D-band and the graphite G-band is known to increase with decreasing the in-plane crystallite size of La [1]. On the other hand, the intensity ratio of highly oriented pyrolytic graphite (HOPG) also increases under high energy particle irradiation at room temperature. The increased Raman intensity ratio remarkably decreases on annealing at 473 K. We estimate 98 % of the damage is repaired on annealing at 873 K and, then, conclude that the Raman intensity ratio relates to the concentration of single vacancy for the low damaged case [2,3]. The relation between the vacancy concentration and the Raman intensity ratio for 488 nm argon laser Raman measurements is deduced from the dislocation accumulation model [4] as follows,

$C_v = 0.0016 (I_D/I_G)^2$.

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Quantum electromechanics of singly and doubly clamped nanotubes

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We investigate theoretically the quantum mechanical motion of singly and doubly clamped suspended carbon nanotubes. For the singly clamped tubes we focus on macroscopic quantum tunneling between two different mechanical configurations and discuss the possibility to affect and detect the tunneling by electrostatic means. For the doubly clamped nanotubes we investigate the rotational motion of a buckled nanotube, and discuss the conditions under which the quantization of the rotational motion may be observable.

Raman spectroscopy in nanographite

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In this presentation, new advances in the study of the Raman spectroscopy of nanographite will be shown. We will present a Raman study of nanographite ribbons on HOPG, where the existence of quantum confinement of the electrons in their 1D band structure is detected, and a study of step edges in graphite with different atomic arrangements, showing that Raman spectroscopy can be used in the structural analysis of these systems. These works were the first evidences for the anisotropy of light absorption in 2D graphite.

A systematic analysis of the dependence of the Raman cross sections on the in-plane crystallite size of nanographite (L_a) and on the excitation laser energy will be also presented. These experimental data allow us to study the dependence of the Raman scattering matrix elements on the excitation laser energy and on the crystallite size of nanographite. We developed a very accurate determination of L_a by Raman spectroscopy, and two relations for determination of the crystallite thickness (L_c) and interlayer distance [$d_{(002)}$] of nanographites by Raman spectroscopy.

Process chain for fabrication of products containing metallic single-wall carbon nanotubes

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Single-wall carbon nanotubes (SWCNTs) possess outstanding electromechanical properties and are thus good candidates to develop actuators with remarkable performance features. For realization of such actuators with macroscopic length changes and forces, a novel actuator concept has been developed. The core of this concept is a microsystem (microelectrodes) with aligned metallic SWCNTs arranged sequentially and in parallel. Furthermore, all tubes are connected electrically and mechanically. In order to fabricate and commercialize such SWCNT-actuators a process chain with industrial potential is needed. The main steps within this chain are suspension and purification of SWCNT-materials, deposition, alignment and contacting of individual metallic SWCNTs. For preparation of suspensions containing individual SWCNTs a novel suspending process in combination with an appropriate SWCNT-material is used resulting in suspensions with long (> 5 μm) SWCNTs. Aligned metallic SWCNTs are deposited via AC-dielectrophoresis on microelectrodes patterned with state-of-the-art lithography. Electrodeposition of nickel on the electrodes will be used to contact the deposited tubes. The different fluids (suspension, electrolyte, DI water) are handled with a miniature fluidic system. The outlined process chain is also suitable for fabrication of other potential products containing metallic SWCNTs. Amongst others, these comprise data memories, flow rate sensors, light sources and voltage generators.

Atomic and electronic structures of carbon nanotubes on Si(001) stepped surfaces

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We report first-principles total-energy calculations that provide energetics and electronic structures of adsorbed carbon nanotubes (CNTs) on stepped Si(001) surfaces. We find that adsorption energies strongly depend on directions of CNT, and that there are several metastable adsorption sites both on terraces and near step edges. We also find that electronic structure of adsorbed metallic CNT becomes semiconducting or remains metallic, depending on the adsorption site. Charge redistribution upon adsorption is prominent mainly at CNT-surface interface.

Activation barrier reduction of Stone-Wales transformation in endohedral metallofullerenes

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Using ab initio calculations, we examine effects of encapsulated metal atoms inside a C_{60} molecule on the activation energy barrier for the Stone-Wales transformation. The encapsulated metal atoms we study are K, Ca, and La which nominally donate one, two, and three electrons to the C_{60} cage, respectively. We find that isomerization of the endohedral metallofullerene via the Stone-Wales transformation can occur more easily than that of the empty fullerene owing to the charge transfer. When K, Ca, and La atoms are encapsulated inside the fullerene, the activation energy barriers are lowered by 0.30, 0.55, and 0.80 eV, respectively compared with that of empty C_{60} (7.16eV). The lower activation energy barrier of the Stone-Wales transformation implies the higher probability of isomerization and coalescence of metallofullerenes, which required a series of Stone-Wales transformations.

Intrinsic and irradiation-induced defects in carbon nanotubes as studied by computer atomistic simulations within the Born-Oppenheimer approximation and beyond

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Intrinsic and irradiation-induced defects in carbon nanotubes dramatically affect their mechanical and electronic properties. Despite a common believe, defects not always play a detrimental role. In fact, defects in nanotubes can be useful, for e.g., nanotube band engineering, improving mechanical properties of macroscopic nanotube-based materials and nanotube functionalization.

As irradiation is a powerful tool to produce defects in a controllable manner, we simulate collisions of energetic particles such as electrons and ions with nanotubes and other carbon systems by atomistic computer simulations within the Born-Oppenheimer approximation [1] and beyond [2] to understand the defect production mechanisms. We also study the structure and properties of irradiation-induced defects, their annealing and interaction with each other.

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In situ characterization of surface structure of acid-treated carbon nanofibers using 1-aminopyrene as a fluorescent probe

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Oxygen-based functional groups produced on surface of acid-treated carbon nanofibers (CNFs) were characterized by UV-Vis absorption spectroscopy and measurements of fluorescence spectra using 1-aminopyrene (1-AP) as a probe molecule.

Non-treated, HNO_3-treated, and HNO_3 + H_2SO_4-treated CNFs are designated as N-, A-, and AA-CNF, respectively. The N-, A-, and AA-CNF were dispersed in 1-AP solution containing water and ethanol (8:2) by ultrasonic irradiation. These CNF samples were centrifuged to obtain the supernatant suspensions.

Both the adsorption and fluorescence spectra hardly changed in the N-CNF suspension, indicating that 1-AP hardly interacted with the CNF surface. On the other hand, in the A- and AA-CNF suspensions, the absorbance assigned to 1-AP decreased with increasing in the amount of the 1-AP adsorbed on the CNFs. In the fluorescence spectra for the A- and AA-CNF suspensions, the 1-AP cation-like band was observed, indicating that 1-AP was tightly immobilized by the interaction between its amino group and the oxidized groups on the CNF surface. The fluorescence intensity observed in the AA-CNF suspensions was stronger than that in A-CNF suspensions. Harder acid treatment caused the chemical modification to generate the larger amounts of the oxygen-based functional groups on the CNF surface.

Formation of multiwalled carbon nanotubes, graphitic- and alpha-C_3N_4 fine particles in space by dc arc discharge

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Multiwalled carbon nanotubes (MWNTs), graphitic-C_3N_4 (g-C_3N_4), and alpha-C_3N_4 fine particles were successfully prepared by dc arc discharge evaporation of pure carbon electrode in NH_3 gas. This is the first report for the formation of MWNTs without metal catalyst in the space, not in cathode deposit by dc arc discharge. The diameter of hollows vary from 1 to 5 nm, and those of the outer diameter of MWNT, are from 6 to 60 nm. G- and alpha-C_3N_4 fine particles were also formed with MWNTs. The formation of g-C_3N_4, the ground state, is also firstly reported. Synthesized nanotubes and particles were studied by transmission electron microscopy. The g-C_3N_4 particles were observed on the graphite or independently in a dispersed state on the collodion film, and alpha-C_3N_4 fine particles were observed in a coagulated form. The lattice parameters of g- C_3N_4 are $a = 0.416$ nm, $b = 0.478$ nm, and $c = 0.295$ nm, and those of alpha-C_3N_4 are $a = 0.647$ nm, and $c = 0.472$ nm

Structural, Electronic and Thermal Properties of Diamond-basedStructural, Electronic and Thermal Properties of Diamond-based Nanowires and Nanotubes by DFTB Calculations

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Recently much progress has been achieved in fabrication and investigation of properties and potential applications of two main classes of quasi-one-dimensional (1D) nanostructures. One of them represent the well-known nanotubes of cylindrical morphology related to cooresponding layered material (graphite, hexagonal phases of BN, BxCyNz, CNx, as well as metal chalcogenides, halides, some oxides, hydroxides, etc). The extended monolytic nanostructures constitute a second important class of quasi-one-dimensional (1D) nanosystems; among them the nanowires, nanorods and nanobelts are known. At present, a lot of inorganic nanowires with a single crystalline structure have been successfully fabricated via various synthetic routes. Meanwhile, in some cases the formation of both forms, tubes and wires, for the same material was realized.

For example, the well-known graphite-like nanotubes with sp2 carbon configurations and the monolytic diamond-like carbon nanowires (DNW) with sp3 atomic configurations have been synthesized. Very recently the novel type of single crystalline diamond-like hollow nanostructures (nanotubes - DNT) were synthesized on a polycrystalline diamond substrate using microwave plasma enhanced CVD.

In this work we present the first results of comparative studies of electronic and structural properties for these novel quasi-one-dimensional diamond-based materials: the monolytic nanowires (DNW) and the hollow nanotubes (DNT). The optimized geometries, energetics, stabilitiy and the electronic sturcture were calculated and analyzed as a function of the morphology and size of these nanostructures, using the density functional-based tight binding (DFTB) method.

Alignment of Carbon Nano-coils using Dielectrophoresis

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We have investigated the alignment of carbon nanocoils (CNCs) using dielectrophoresis. The cabon nanocoils synthesized by chemical vapor deposition were suspended in iso-propyl-alcohol (IPA) using the ultrasonic dispersion. After the suspension was dropped on a pair of coplanar electrodes formed on glass substrate, AC or DC electric field was applied to the electrodes. After the evaporation of IPA, the surface between the electrodes was observed using a scanning electron microscope (SEM). In the case of DC electric field, most of all CNCs were moved toward the cathode. On the contrary, in case of AC electric field with the frequency higher than 100 Hz, CNCs were aligned along the electric field and connected each other. It is noted that the CNCs made bridges between the electrodes, when the CNC concentrations in IPA was high. At a higher electric field, the degree of the alignment was improved. The Debye length around the colloidal CNCs was estimated to be ~ 500 nm from the conductivity of the dispersion. This range is comparable to the coil diameters. As a result, the CNCs act as rods with a diameter of ~ 500 nm during the dielectrophoresis.

This work was carried out for Osaka Prefecture Collaboration of Regional Entities for the Advancement of Technological Excellence, JST.

Preparation of twisted carbon nanotubes

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We have already reported that maltiwalled carbon nanotubes (MWCNT) had been prepared by very simple method. Solutions of ferrocene and some straight chain alkanes such as hexane were directly injected into a silica reaction tube preheated at 800 to 1000 °C. Array of MWCNTs formed a sheet with around 20 μm of thickness and the MWCNT-aligned sheets also deposited on the silica glass substrate. Here, we are to report about the preparation of twisted carbon nanotubes (TWCNTs) with less than 100 nm in diameter. They were prepared from mixture of ferrocene and thermosetting resin called as COPNA resin, instead of straight chain alkanes. The existance of iron particles formed by pyrolysis of ferrocene was investigated from TEM images. Conditions for preparation of twisted carbon nanotubes would be discussed.

Characterising the dc and high frequency properties of carbon nanotube NEMS

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Carbon nanotubes and nanofibres are very promising nanostructures for producing nanoelectromechanical systems that can be integrated with silicon technology. Due to their small size and intrinsically high resonant frequencies, carbon nanotubes may be expected to have interesting high frequency properties [1].

In this contribution we report results of the experimental investigations of the power sensitivity, DC, low frequency and RF properties of individual metallic carbon nanotubes or nanofibres in the double contacted regime as well as singly-clamped two and three terminal relay structures [2].

Results of the growth of vertically and horizontally aligned MWCNTs for three-terminal relay devices are given and the two geometries are compared from the eventual device point of view.

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Defect-derived localized states in semiconducting single-wall carbon nanotubes

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We study the effect of defects on the electronic structure of semiconducting single-wall carbon nanotubes based on the first-principles calculations. Monovacancy and vacancy-adatom structures are relaxed by the conjugate gradient method. For monovacancy cases, a deep level is present between the HOMO and LUMO levels. Vacancy-adatom comlex defects result in two well-localized deep levels in the energy gap. The stability of the vacancy-adatom complex structure and the magnetic moment near the defect are also investigated.

Contributed abstracts

June 22 (Thursday)

Alignment of MWCNT in polymer film under low and high magnetic field

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Multi-walled carbon nanotube (MWCNT) has outstanding mechanical, thermal, and electric characteristics, and it has strong anisotropy. To take advantage of the enhanced properties, the orientation control of MWCNT should be important. We have performed the magnetic processing of polymer composite films including Vapor-grown carbon fiber (VGCF) by using magnetic processing apparatus with permanent magnets (1T) and superconductive magnet (10T). In addition, alignment behavior of VGCF was examined and compared between under low (1T) and high magnetic field (10T). We have studied the orientation of VGCF along the thickness direction of the film. It was demonstrated that the oriented VGCF / polymer composite films were successfully produced even by permanent magnets (1T). Moreover, when treated under high magnetic field (10T), not only alignment of VGCFs but also their aggregation was observed. The volume resistivity (Ω cm) of the film (vertically oriented VGCF by using permanent magnets (1T), 1.0wt.%, 10μm thickness) showed 3.2×10^{12} and 2.1 Ω cm along surface and thickness direction, respectively. Vertically oriented VGCF / polymer composite film could be utilized as an alternative material having anisotropic electric conductive property.

Aligning MWCNT in polymer using magnetic or dc electric field

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Orientation control of MWCNT in polymer is important for producing functional composites. Here, vapor-grown carbon fiber (VGCF) is used as MWCNT. A trace amount of VGCF, which had aggregated lump form as received, was completely dispersed in polydimethylsiloxane, non-polar viscous liquid at room temperature by mechanical stirring. By using the uniform dispersion as the starting material, the application of dc electric or magnetic field was used to induce the formation of aligned structure. In-situ transmission optical microscope observation was carried out to observe structural development of VGCF in polydimethylsiloxane under dc electric or magnetic field, which was given parallel and perpendicular to the observation direction. Aligned ramified network structure of VGCFs was finally developed between electrodes. The network structure was formed by connecting both ends of VGCFs one another, followed by rotation and orientation. On the other hand, magnetic field only generated the orientation of VGCF by rotation without networking. The rotation speed of VGCF under dc electric field was compared with that under magnetic field. The electric resistivity of the network structure under magnetic or dc electric field was evaluated. Additionally, the influence of viscosity in polydimethylsiloxane matrix on the structural formation process was examined.

Characterization of DNA(RNA) - Carbon Nanotube Nanocomposites

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The combination of carbon nanotubes and DNA is of interest to many chemical and biochemical areas in both fundamental and application [1-3]. We have already reported that double-stranded DNA dissolves SWNTs in aqueous solutions[2]. Here we report the detail about the preparation and characterization of DNA-solubilized SWNT aqueous solutions as well as the preparation of RNA/SWNTs ultra thin films on solid substrates. RNA/carbon nanotube films were successfully formed by the alternating adsorption of two different RNA/SWNTs solutions onto a quartz substrate [3]. UV-vis-near IR and Raman spectroscopies, TEM, SEM and AFM were used to characterize the solutions and thin films of DNA (RNA)-SWNTs nanocomposites.

The effect of near-IR laser irradiation onto the SWNTs solutions dissolved by DNA was examined. The laser irradiation acted as a trigger of flocculation of SWNTs.

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Individual dissolutionof carbon nanotubes and gel formation using totally aromatic polyimides

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Carbon nanotubes (CNTs) have a high potential for applications in energy, electronics, IT and materials. However, their insolubility in solvents has hindered chemical approaches using CNTs. Our interest is focused on the fundamental properties and applications of soluble carbon nanotubes in aqueous and organic systems. Polymer wrapping is a powerful technique to construct CNTs-polymer composite materials. Polyimides are based on stiff aromatic backbones, and total aromatic polyimides are especially suitable polymers having unusual mechanical strength and high resistanve to heat and chemical reactions. Combination of carbon nanotubes and polyimides is expected to play an important role in the development of novel nanocarbon composite polymers with high performance. We found that some polyimide results in individually dissolved SWNT solutions. Here, we describe the individually dissolution of SWNT and the formation of a gel of SWNTs/polyimide.

Higher concentrations of SWNTs in polyimide solutions form a gel composed of individually dissolved SWNTs. The visible-near IR spectra of SWNTs/the polyimide showed characteristic features assignable to individually dissolved SWNTs. We also report fluorescence behaviors in the near-IR region, at the meeting.

Optical Properties of Aligned Single Wall Carbon Nanotubes

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In this work, stable suspensions of DNA wrapped SWCNTs were mechanically aligned by dispersing them in amorphous polymer films, and their intrinsic optical anisotropy measured through a combination of polarized light spectroscopy, polarized resonant Raman spectroscopy (RRS), and small-angle neutron scattering (SANS).

Conventional measures of nematic alignment in the stretched polymer films typically varied from 0.7 to 0.9. Nematic alignment was also investigated as a function of tube chirality, using RRS.

We obtain the intrinsic optical anisotropy of the SWCNTs over a broad range of photon energies, with a number of well-resolved absorption peaks corresponding to specific SWCNT chiralities.

Characterization of Reactive Carbon Nanotube Solubilizers Carrying Anthryl Groups

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We report a new carbon nanotube (CNTs) solubilizer based on a novel concept, that is, reactive carbon nanotube solubilizers that are compounds carrying a reactive moiety for the introduction of the desired functional groups. In this study, the anthracene moiety-carrying poly(styrene-alt-maleic anhydride) copolymer (Anth-P) was synthesized by a one-pot synthesis. It was found that the copolymer acts as excellent CNT solubilizers. The vis-near spectrum of single-walled carbon nanotubes (SWNTs)/Anth-P in solution showed characteristic structural spectral features, suggesting the individual dissolution of the SWNTs and the atomic force microscopic image showed a wrapping of SWNTs by Anth-P. To demonstrate the concept of a reactive nanotube solubilizer, a SWNTs/Anth-P solution was reacted with amino compound, and the introduction of the amide bonding was confirmed. Fundamental properties of SWNTs/Anth-P solutions including near IR absorption and photoluminescence behaviors will be reported.

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Molecular design of nanotube-based ultralow-k dielectrics

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It is one of the urgent problems in microelectronics to develop insulating materials with dielectric constants of less than 2 for future applications in semiconducting circuits.Here we predict a new class of interlayer dielectrics based on fluorinated carbon nanotubes using density-functional theory based methods. A chemical derivatization of single wall carbon nanotubes (SWNT) may open possibilities for tailoring the electronic properties of nanotubes. An ethylene like decoration pattern of carbon nanotubes can open a rather large gap and reduce also the dielectric constant considerably. In this way it is proposed that fluorination of carbon nanotube based material may be used for ultralow-k materials.

C_{60}-carbon nanotube composites - a search for ultrahard, light materials

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Carbon nanotubes have excellent elastic properties and are already used as a strengthening ingredient in various composite materials. In this work we present the recent results on high pressure high temperature treatment of C_{60} mixed with different types of carbon nanotubes (SWCNT, DWCNT, MWCNT). The raw mixtures and resulting carbon-only composite materials are characterized by means of Raman spectroscopy.

C_{60}-carbon nanotube composites benefit both from the fullerene ability to create covalently bond polymers (hard but brittle) and nanotube elasticity and strength. This study is a first step towards creation of ultrahard and at the same time light materials, based on low density, hollow carbon nanostructures.

High Strength Extra Super Duralumin Reinforced by MWCNTs

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Carbon nanotubes (CNTs) are very attractive material for reinforcing metal matrix composites due to their remarkable properties such as extremely high strength, elastic modulus and high electric and thermal conductivity. However, due to its intricate entanglement of long and fine CNTs uniform dispersion of CNTs in Al alloy matrices is quite difficult. Further the poor wettability of CNTs for Al alloy has been a great troublesome problem to produce the composite. Original mechanical mixing technique to form the composite powders of extra super duralumin and MWCNTs was introduced. Composite powder was hot pressed to form a dense bulk piece. The bulk composite piece was deformed in a rod by extrusion process. Consequently, composite rod specimen containing 1.0 mass % of MWCNTs subjected to artificial aging of T6 was found to have a tensile strength above 600MPa. The original procedure and other mechanical properties will be reported.

Growth of carbon nanotubes and nanofilaments on fibrous fabric to improve C/C composite tribological properties

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Carbon nanotubes or nanofilaments were directly grown on the surface of a 2D fabric made of PAN-based carbon fibers. It was performed by catalytic decomposition of ethylene over catalytic particles, themselves deposited on the surface of the fibers. Through judicious selection of transition-metal catalysts, amount of catalyst, experimental conditions during catalytic decomposition of ethylene and appropriate chemical treatment of the carbon fibers surface, it is possible to grow either carbon nanotubes or carbon filaments which form a sheath surrounding individually the carbon fibers of the fabric. The influence of the experimental parameters on the yield (ranging from 15 to 150%), homogeneity and density of the carbon sheath is reported, together with TEM investigation of the microtexture of the nanotubes or filaments, which remain firmly anchored on the fibers.

The interest of such multiscale C/C composites lies in the change in reinforcement scale of nanotubes and nanofilaments relative to carbon fibers, which offers possibility to combine benefits of nanoscale reinforcement with well-efficient fibrous skeleton at the micrometric scale.

Then, the carbon nanotube/carbon fiber preforms were densified by chemical vapour infiltration. The influence of this nanoscale reinforcement on the mechanical and tribological properties of C/C composites is presented.

Aluminum matrix composite containing pitch-based carbon fiber (CF) and vapor grown carbon fiber (VGCF)

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Carbon fiber (CF)/ carbon nano fiber (CNF)/ aluminum (Al) matrix composites were synthesized using pulse current sintering method to modify the thermal properties. Pitch based CF and vapor grown carbon fiber were used for the composites as CF and CNF respectively. CFs were laid unidirectional in aluminum matrix. CNFs were doped in aluminum matrix. The composites showed high thermal conductivity over 700W/(mK) along CF direction and suppressed thermal expansion around 15ppm/K (at RT to 373K) in perpendicular to CF direction.

Numerical Simulation for Mold Press Forming of CNF/Resin Composite

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In the present study, press forming of the resin-based composite is investigated by numerical and experimental process. The composites are made by a twin screw extruder for mixture process of resin pellets and CNF powder, and an injection molding machine to obtain the test specimens, where vapor grown carbon fiber VGCF and polycarbonate PC have been employed for the filer and matrix, respectively.

One dimensional compression tests were applied to estimate creep functions of the composites in the several temperature environment. The creep functions are transformed into relaxation functions using Duhamels convolution integral law according to the linear thermo-viscoelastic theory. The effect of the temperature is converted to the reduced time which is estimated by shift factor defined by Narayanaswamys equation.

Using thermo-viscoelastic modulus of the PC/CNF composites, finite element analysis has been carried out to simulate the press forming process using a V-shape die. The profiles of the press-formed specimens are compared with those obtained by experimental pressing tests. The characteristics of press formed PC/CNF composite are investigated from various perspectives.

Carbon nanofibers as solid glue for the elaboration of advanced carbon composites

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Carbon nanofibers (CNFs) were synthesized on both carbon cloth and felt : CNFs synthesis was carried out at relatively low temperature by a catalytic route (CVD) using transition-metal as growth particles and ethane as gaseous source of carbon. Catalysts, metal loading and ethane/hydrogen ratio were changed in order to investigate the impact of CNFs growth, with reported yields of up to 400%. The formation of the CNFs layer generated numerous micro/nano-bridges, and acted as a solid glue which allowed control of the macroscopic shape and significant improvement of the mechanical strength of the final composites.

Further C/C/C composite elaboration from the previous micro/nanoscale composite has also been reported : a carbonaceous matrix was generated via a phenolic resin infiltration followed by a carbonization step. It has been demonstrated that the previously synthesized CNFs heightened resin infiltration and gave a better wrapping of the carbon precursor owing to numerous anchorage points. With moderate weight increase but considerable improvement of the load transfer, it is expected that CNFs will replace pyrolytic carbon in the elaboration of advanced composites : low weight, high mechanical resistance at lower synthesis temperature and with complete control of the final shape.

Electrically Conducting Composites of Carbon Nanotubes and Poly(vinyl chloride) Microspheres

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In this study, the electrically conducting polymeric microspheres were prepared from composites of carbon nanotubes (CNTs) and suspension-polymerized poly(vinyl chloride) (PVC) particles which have an average diameter of ~100 micrometer. Cetyl trimethylammonium bromide was selected as a surfactant to stably disperse CNTs in water. Adsorbed CNTs on surfaces of the PVC microspheres with strong adhesion were observed from images of field emission scanning electron microscopy. The amount of adsorbed CNTs on microspheres was approximately 0.5~3 wt %, which was calculated from thermogravimetric analysis. Electrical conductivity of these microspheres was remarkably increased to $\sim 10^{-1}$ S/cm due to the CNTs on their surfaces, while that of the pure PVC microspheres was $\sim 10^{-8}$ S/cm.

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Electrically Conducting Nanofiber/Carbon Nanotube Composites

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Recently, carbon nanotube(CNT)-filled nanofibrous membranes have been produced by electrospinning to improve their performance characteristics. Although the nanofibrous membranes showed a significant enhancement in their mechanical properties, their electrical properties were inferior to those of typical semiconductors or conductors. In this study, we demonstrate a new and simple processing route which can be used to incorporate CNTs into a polymer matrix by adsorption. The CNTs were adsorbed on the surface of nanofibers electrospun from an aqueous solution of silk fibroin with poly(ethylene oxide) by dip-coating the nanofibrous membranes in a bath containing CNT dispersion. The dispersion of the CNTs was prepared by the sonication of the CNTs in an water containing a surfactant. The CNT adsorbed membranes not only have good electrical properties ($\sim 10^{-4}$ S/cm), but also retain the inherent characteristics of the nanofibrous membranes, such as their high porosity and flexibility.

Acknowledgements. The authors of this work would like to thank the Korea Science and Engineering Foundation (KOSEF) for sponsoring this research through the SRC/ERC Program of MOST/KOSEF (R11-2005-065).

Bacterial Cellulose/Carbon Nanotube Composites for Electromagnetic interference shielding

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In this study, multilwalled carbon nanotubes (MWCNTs) were incorporated uniformly into the microbial cellulose membranes using an aqueous MWCNT dispersion with a surfactant. Acetobacter xylinum bacteria are known to produce cellulose extracellularly. This microbial cellulose is expected to become a new industrial material, because of its unique structure and properties in terms of its purity and high crystallinity. To minimize the damage to the inherent properties of the individual MWCNTs induced by the chemical modification, we chose to use a surfactant for the purpose of dispersing the MWNTs in water. We also investigated the morphology and electrical conductivity of the cellulose membranes containing well-dispersed MWNTs. The composites films showed good electrical conductivity (~10^{-1} S/cm) and electromagnetic interference shielding efficiency, when the content of MWCNTs was about 9.6 wt%.

Acknowledgements. The authors of this work would like to thank the Korea Science and Engineering Foundation (KOSEF) for sponsoring this research through the SRC/ERC Program of MOST/KOSEF (R11-2005-065).

Alignment of SWNTs using SWNT/supramolecule composites

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We have been developed the alignment of signle-walled carbon nanotubes(SWNTs) using SWNT/supramolecule composites. SWNT/supramolecule composite could be prepared by mixing SWNT suspension with solutions of the supramolecules and then evaporating the solvents. SWNTs are pretreated chemically to facilitate solubilization. By preparing well mixed composites, the behavior of SWNTs in the composites and the effect of SWNTs to the composites have been investigated. SWNTs can be aligned by the effect of oriented supramolecules. POM and SEM were used to analyze the behavior of supramolecules and SWNTs.

Aluminum and Carbon Nanotube Composites Fabricated Using High Pressure Torsion Process

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In this study, aluminum and carbon nanotube (CNT) composites are fabricated using a process of high pressure torsion (HPT). Aluminum powders in 99.99% purity with an average powder size of 75 mm were mixed with 5 vol% of single wall CNTs (SWCNTs) in ethanol while the solution in ultrasonic vibration. The solution was dried in air at room temperature. The dried mixture was then subjected to a process of HPT with an applied pressure of 2.5 GPa, where the mixture was inserted between the upper and lower anvils with depressions of 10 mm in diameter and 0.25 mm in depth on each anvil. While applying the pressure, the lower anvil was rotated for up to 30 turns with respect to the upper anvil with a rotation speed of 1 rpm. Microstructure observations were undertaken using scanning electron microscopy (SEM). Vickers microhardness was measured across the diameter of the sample. It is shown that the hardness of the sample containing SWCNTs is twice as high as the sample without SWCNTs. SEM observation revealed that the SWCNTs are uniformly dispersed in the aluminum matrix and the grain size is smaller for the sample with SWCNTs than the sample without SWCNTs.

Tribological Properties of Binder-Free Single-Walled Carbon Solids

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Binder-free single-walled carbon nanotube (SWCNT) solids were evaluated for solid lubrication applications. Carbon-derived materials such as diamond-like carbon (DLC) and graphite have the outstanding lubrication properties, which have been widely used as lubricants for many years. Here we report preliminary results on the tribological properties of the binder-free SWCNT solids solidified using a highly pure SWCNTs only. Tribological properties of the SWCNT solids were investigated using a ball-on-plate tribometer which provided an unidirectional sliding friction motion under dry conditions. The silicon nitride ball of 7.1 mm in diameter was used as a counterpart. The steady-state friction coefficients for the SWCNT solids were found to reach values as low as 0.18-0.22. In the most of the sliding interface, a colored tribofilm that differ from the original SWCNT structure was observed by the SEM observations. These experimental results may imply that some part of SWCNTs that existed in the sliding interface was transformed to SWCNTs-derived thin transfer film during sliding, which may be a possible reason for the low friction coefficient of the SWCNT solids. The experimental results obtained in this study may show a promise in application as a solid lubricant.

Energetics and dynamics of nanopeapod

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We present encapsulation dynamics and various ordered phases of fullerenes in elastic carbon nanotubes by temperature-controlled molecular dynamics simulation with covalent-bond and van der Waals interactions. Atomic relaxation of circular edge to maximize van der Waals attraction energy is crucial to insert fullerenes into open-ended carbon nanotubes. A peristaltic movement of elastic nanotube assisted by finite temperature effect helps fullerenes form various ordered phases inside nanotubes that have been observed in experiments. As a result, volume fraction of fullerenes in ordered phase in nanotube interior space remarkably increases by nanotube deformation. The results on fullerene doping into double-walled and bundled nanotubes will also be presented. A conclusion obtained through the simulation is that the van der Waals long-range attraction in competition with the short-range covalent-bonding of carbon atoms not only generates a variety of fullerene packing arrangement, but changes carbon nanotubes into “nano-worms“.

Carbon Nanotube Polymer Composites - The Influence of Polymer Polarity

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There has been a large body of work published over the last decade on the reinforcement of polymers with CNTs. However from this literature it is difficult to make conclusions about the effect polymer polarity has on the interaction between carbon nanotubes and a polymer. It is hard to compare the different studies as they use CNTs of varying quality that are then purified and/or functionalised using a diverse range of treatments. The composites are then produced using various processing techniques and characterised using an assortment of testing procedures.

In this work, a selection of thermoplastics, of varying polarity, were blended with MWCNTs. The mechanical properties of the composites were investigated via tensile testing. In all cases MWCNTs provided a greater increase in stiffness and tensile strength than either VGCFs (vapor grown carbon fibers) or carbon black. The fracture surfaces were then analysed using SEM to asses the degree of polymer/nanotube bonding. Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Thermal Analysis (DMTA) were also used to investigate the interactions between the polymer and the nanotubes.

Mechanical properties of carbon nanotubes with continuum analysis incorporating interatomic potentials

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Carbon nanotubes (CNTs) have attracted great attention due to their exceptional mechanical, thermal and electrical properties. Since carbon nanotubes (CNTs) are extremely small, direct measurement of their mechanical properties is quite difficult. Especially, it is rather difficult to understand the effect of the chirality on the mechanical properties of CNTs because of experimental error. Computational simulation has been regarded as a powerful tool in view of the experimental difficulties. In this study, we present a theoretical study on the mechanical properties of CNTs based on the elastic continuum analysis incorporating interatomic potentials. The mechanical properties of CNTs with different structures, such as strain, tensile modulus and bulk modulus, are investigated as a function of nanotube diameter.

Synthesis and Characterization of Single-Walled Carbon Nanotube-Silicon Carbide Nanocomposites

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The main objective of this research is to coat single-walled carbon nanotube (SWCNT) bundle surface with SiC nanoparticles in view of an alternative for traditional fibrous materials used as reinforcing components. The effective utilization of SWCNTs in composites depends strongly on the ability to achieve strong interfacial bonding between the SWCNTs and the matrix in order to ensure load transfer. Here we introduce a simple and effective method of homogeneous coverage of SWCNTs with SiC nanoparticles using polycarbosilane (PCS) as the source of SiC. Unlike conventional ceramics obtained by sintering powders, polymer-derived ceramics are synthesized by direct thermal decomposition of polymeric precursors, by which strong bonds may be realized between the SWCNTs and SiC nanoparticles. Results obtained from XRD, TEM and EDS analyses indicated that ?-SiC nanoparticles with about 20 nm in diameter homogeneously distributed on the sidewall of the SWCNT bundles. By adjusting the ratio of SWCNTs to PCS, SWCNT/SiC nanocomposites with different density distribution of SiC nanoparticles are obtained. The nanocomposites may have potential applications as ideal reinforcements in composites and starting materials for sintered ceramics because SiC is chemically stable and the SiC nanoparticles on the SWCNTs provide an anchor effect.

Observation of dispersion of nanotubes in polymer by electron microscopy and optical microscopy

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Effects of nano composites of nanotubes (CNTs) and polymer for mechanical, electric and thermal properties depend on dispersion of the nanotubes in the polymer. In general, study using high resolution microscopy and low resolution microscopy is carried out individually. In this study, in order to clarify the dispersion of CNTs, the CNTs and the composite of CNTs and polymers were observed microscopically and macroscopically by transmission electron microscopy (TEM), scanning electron microscopy (SEM) and optical microscopy (OM). The interaction between CNTs and interface-boundary activator is important for dispersion of CNTs. The structure of nanotubes and the interface boundary between carbon nanotubes and activator were observed by high resolution transmission electron microscopy (HRTEM). SEM was used for macro observation of CNTs and polymer composite. The surface and fracture surface of the composites were observed by SEM. In order to observe inside of the composite, the polished sections of them were observed by polarization OM which could recognize orientation of texture of carbon materials. That the orientation of CNTs reflects macro texture was shown by the series of microscopy observations. The observation method of combination of microscopes is useful for analysis of distribution of CNTs.

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SWNT/POLYMER COMPOSITES

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Polymer and single wall carbon nanotube (SWNT)composites have been inspiring the development of new high performance materials due to the unique combination of mechanical, electrical and thermal properties and density of SWNTs. The critical challenge of polymer/SWNT composites is how to control nanotube dispersion and alignment in the matrix. In this study, homogenous, well-aligned arrays of SWNTs were synthesized using alcohol catalytic chemical vapor deposition (ACCVD)and a monomer was infiltrated into the arrays, followed by in situ polymerization. This synthesis process is adaptable to various polymers. The pre-aligned single-wall carbon nanotube arrays were infiltrated with methyl methacrylate (MMA) and the MMA was then polymerized. Once polymerized, the PMMA/SWNT composite had higher thermal stability. Mechanical, electrical and thermal properties of SWNT- and MWNT-reinforced polymer composites have been studied and compared.

Electrodeposition of platinum-ruthenium nanoparticles on carbon nanotubes directly grown on carbon cloths for the anode of a direct methanol fuel cell

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Platinum-ruthenium (Pt-Ru) nanoparticles were successfully electrodeposited on dense carbon nanotubes (CNTs) directly grown on carbon cloths in ethylene glycol (EG) containing sulfuric acid solutions. EG enhanced dechlorination of the Pt and Ru precursor salts to form the respective nanoparticles and acted as a stabilizing surfactant to prevent the particles from agglomeration during the electrodeposition processes. Relatively well dispersed Pt-Ru nanoparticles (2 to 5 nm) on CNTs (Pt-Ru/CNTs) were verified by transmission electron microscopy. The electrochemical characteristics of methanol oxidation on the prepared specimens were analyzed by cyclic voltammetry in mixed methanol and sulfuric acid solutions. The physical chemistry performance of the Pt-Ru/CNTs electrode in the aspects of mass activity (normalized current density of methanol oxidation vs. Pt loading), 542.6 $A/g{\cdot}cm^2$, and i_f/i_b value (the ratio of forward peak current density to reverse peak current density), 13.36, was superior to that of the commercial Pt-Ru/C one with a mass activity of 168.3 $A/g{\cdot}cm^2$ and an i_f/i_b value of 10.66. Furthermore, the power density of a direct methanol fuel cell (DMFC) using Pt-Ru/CNTs as the anode was ~65% greater than that of another DMFC with a commercial Pt-Ru/C anode, clearly indicating a significantly improved catalytic activity of the new Pt-Ru/CNTs electrode.

Keywords: Ethylene Glycol, Anode, Cyclic Voltammetry, Methanol Oxidation

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Characteristics of carbon nanotube/polymer composite materials prepared by direct mixing method

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Carbon nanotube (CNT)/polymer composite materials are expected as useful new functional materials. In this research, CNTs were directly mixed with various polymers using simple and easy mixing method. Predetermined quantities of granulated polymer and CNTs were mixed by rapid rotating blade. The mixing process was carried out under a condition of the blade rotated at 25,000 rpm and 120 sec. Mixed powder materials were observed by scanning electron microscopy (SEM). Some of CNTs stuck or entered the polymer. The rise of temperature by high speed collision of powder, about 70-90 °C during mixing, is thought to cause the softening of the polymer, and accelerating the mixing. This simple and easy method has possibility to mix up the powders uniformly which have different size and properties. In order to make plate-shaped samples, The mixed powder was heated under pressure. The electrical conductance and capacitance of the samples measured by AC impedance meter increased with the increase of CNTs ratio in the polymer. The DC resistivity measured by 4 probe method was in the order of 10 Ω-m or lower.

Transparent, flexible and conductive CNT containing polymer thin films for electronic applications

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We have developed a simple and direct method for the preparation of CNT mats with different thicknesses to be easily integrated in polymers. The nanotubes were synthesised by an aerosol method based on the ferrocene vapour decomposition in CO atmosphere and collected directly from the gas phase via the filtering through silver and nitrocellulose filters. We proposed a simple thermo-compression method for transferring the CNT layers from the filters to polyethylene polymer films. As a result, we were able to manufacture transparent, conductive, and flexible CNT containing polymer films. The optical and electrical measurements demonstrated their excellent properties suitable for many electronic applications.

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Conducting and transparent SWNT/polymer composites

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Transparent, electrically conductive layers based on indium-tin-oxides (ITO) are currently used for electrode applications. Unfortunately the ITO layers are brittle and cannot be deposit on flexible substrate such like plastics. Additional difficulty lies in the preparation of the thin ITO films which requires a vacuum sputtering technique. An alternative to ITO is offered by the transparent polymer matrix filled with single wall carbon nanotubes. This contributions shows flexible, transparent and conducting poly(methyl methacrylate) (PMMA) composites films prepared using $SOCl_2$ functionalized SWNTs. Optical absorption spectra measured on composite films confirm that the composite preparation procedure conserve the electronic properties (position of the Fermi level) of the p-doped nanotubes in polymer matrix. Due to the doping effect of $SOCl_2$ the electrical conductivity of the composites is improved by factor of 5. The light transmission of the composite films depends on the film thickness and the nanotube concentration. For the films of about 20 μm thick the transmission between 92 % for 0.1 wt % SWNT content and 46 % for 0.5 wt % of SWNT is measured at 500 nm wavelength. The conductivity of the thin films measured by the four point method is 3.5×10^{-3} S/cm and 4.7×10^{-1} S/cm, respectively.

Carbon MWNTs as transparent conductive layer on glass and polymeric substrates

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A suspension of multi-walled carbon nanotubes (MWNTs) previously dispersed in a cationic surfactant using a microfluidizer has been prepared and added in different concentrations to two organic-inorganic hybrid materials. In the first case, 10g of MPTS or GPTS were hydrolysed using HCl under the presence of the MWNT suspension and in the second case, the suspension has been added to a sol made of antimony doped tin oxide (ATO) nanoparticles. Both new suspensions have been deposited at RT on glass and polymeric substrates by spin coating and cured at temperature ranged between 100 and 150°C. Dispersions of MWNT in ATO matrix lead to sheet resistance about 56 times lower than that of MPTS matrix under polycarbonate substrates while dispersions of MWNT in ATO matrix lead to sheet resistance 2.8 times lower than pure ATO films in borofloat substrates. A minimum sheet resistance of 54 kΩ is obtained for layers on PC substrates heated at 130°C for 1h and 28 kΩ for layers on glass substrate heated at 250°C. The transmission in the visible range of all films is greater than 85%. The layers have passed the tape test procedure for adhesion as well as the pencil test for hardness.

SWNT polymer nanocomposites based on P3OT, TPU and a blend of P3OT/TPU

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Purified and debundled single walled carbon nanotubes (SWNTs) were used to prepare nanocomposites based on poly(3-octylthiophene) (P3OT), thermoplastic polyurethane (TPU) and a blend of them. Stable dispersions of SWNT in solvent were obtained by non-covalently interaction with the polymers dissolved. The blending of 10 wt% of P3OT with TPU allowed the preparation of a self sustained membrane with separated domains of conjugated polymer. Composites exhibited glass transitions, melting temperatures and heat of fusion which changed in relation to pure polymers. This behavior is discussed as associated to interactions between nanotubes and polymers. TPU interaction with carbon nanotube is probably mainly through the functions introduced in the selective oxidation and acid digestion. On the other hand, P3OT may interact with the graphene structure of the tubes. In the heterogeneous polymer blend the SWNT behavior may be dominated by one type of interaction. Conductivity and spectroscopic studies are in progress.

Organometallic compounds encapsulated in single wall carbon nanotubes

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One-dimensional nanostructure of single wall carbon nanotube (SWCNT) is of great interest as it gives us an opportunity to testify issues of the fundamental physics in one dimension as well as for applications in nanoelectronic devices. Specifically, filling of the inner space with atoms and molecules is promising means to modify the electronic properties of SWCNT. We report on our recent study of the filling factor and the electronic structure of SWCNT filled with endohesdral fullerenes and metallocenes using photoemission, x-ray absorption, electron energy-loss spectroscopy as probes. We demonstrate that x-ray and resonance photoemissions are reliable means to evaluate the filling factor and Dysprosium valency of $Dy_3N@C_{80}$-filled SWCNT. From the valence-band photoemission of high-purity SWCNT filled with metallocenes, we show direct evidence of a charge transfer from the metallocene to SWCNT. The electronic structure of the metals inside SWCNT is discussed with the results of the x-ray photoemission and electron energy-loss spectroscopies. A proof of the filling is given by a transformation of the filled SWCNT to double wall carbon nanotubes using high-temperature annealing.

Effect of VGCF on Mechanical Properties of ABS Thermoplastics

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In the present work, mechanical properties of the carbon-nano-fiber reinforced plastics were investigated. Two kinds of carbon-nano-fiber are employed for the filler of the composite, which are vapor grown carbon fiver (VGCF) and cups-stacked type carbon nanofiver (CS). For the matrix of the composites, two kinds of thermoplastic resin are used which are Acrylonitrile Butadiene Styrene (ABS) possesses the different tensile strength. For the 5wt% VGCF and ABS composites, the tensile strength of the wire specimen in 0.5 mm diameter by the extrusion molding has doubled compared with that of the sheet specimen in 0.5 mm thickness.

Properties of Polycarbonate/Multi-walled Carbon Nanotube Composites

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Electrical, thermal and morphological properties of the polycarbonate (PC) / multi-walled carbon nanotube (MWNT) composites were studied. The MWNT was functionalized by treating with the hydrogen peroxide (H_2O_2) under the sonication process. And then, the mixture of the MWNT and hydrogen peroxide was dried by thermal and freeze-drying methods. For the preparation of the PC/MWNT composites, the PC/MWNT mixture, ranged from 1.0 to 7.0 wt% MWNT, was dissolved in tetrahydrofuran (THF) under the sonication process. The functionalization of the COOH and OH groups of the MWNT by treating with the H_2O_2 were confirmed by the measurement of FT-IR spectra. The effect of the MWNT functionalization by H_2O_2 was observed by SEM and TEM image. For measuring the electrical conductivity, the four-probe method was used. From the electrical properties of the PC/MWNT composites, the electrical conductivity of the PC/MWNT (H_2O_2 untreated) showed the percolation threshold at about 5 wt% MWNT content. For the PC/MWNT (H_2O_2 treated and freeze dried) composites, the electrical conductivity showed the percolation threshold at about 2 wt% MWNT content.

Metal matrix composites reinforced with arc-discharged carbon nanotubes

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Carbon nanotube / aluminum matrix composites have been processed by powder metallurgy. Blends of metal powder and CNTs have been prepared by ball milling. Both commercially pure aluminum and prealloyed powders were used. Composite powders where obtained with nanotube embedded in the metallic matrix. Disk shaped specimens where consolidated by hot compaction of the composite powders. Appropriated sintering conditions allowed to obtain sound mechanical properties. The main drawbacks are related with uniform dispersion of nanotubes in the metal matrix and CNT-metal interface strength. Preliminary results show that compared with unreinforced sintered aluminum (Al 99.5%), CNT-aluminum composites exhibit fibrous fracture instead of fragile fracture, which suggests that nanotubes can support load even after matrix failure.

The effect of nanotube quality on the mechanical properties of vertically aligned carbon nanotube array-polymer composites

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The major challenge in carbon nanotubes (CNT)-polymer composites is how to gain control of CNT quality, dispersion, and alignment inside the composite.

Here we will investigate the effect of nanotube quality on the mechanical properties of CNT-epoxy composites, while keeping other factors (CNT alignment and dispersion) unchanged. This was achieved using vertically aligned carbon nanotube arrays (VANTAs) grown with chemical vapor deposition technique. The alignment of CNT in VANTAs was preserved after infiltration of arrays with epoxy. Two samples of VANTAs with high and low concentration of defects were used in this study, and the anisotropy of mechanical properties of nanocomposites has been tested using nanoindentation technique.

The Youngs modulus of VANTAs-epoxy composite showed largest improvement, 174% compared to epoxy, for VANTA-epoxy composite made from CNT with the low density of defects, and CNT orientated parallel to indentation direction. High-defect-density-VANTA-composite showed smaller, 120%, improvement in Youngs modulus compared to epoxy. The anisotropy of mechanical properties of is more pronounced for CNT with high density of defects. The hardness of the nanocomposites was improved moderately by 10-20% with higher values for VANTA-epoxy composite made with high-defect-density of CNT.

The mechanism explaining changes in mechanical properties of nanocomposites will be discussed.

Transfer and Reinforcement of Carbon Nanotube Structures with Epoxy

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We present a simple and robust method of transferring and reinforcing carbon nanotube structures grown with CVD method. The process allows transfer of pillars with a cross-section of as small as 50μm × 50μm. Columns of vertically aligned multi-walled CNTs are grown from a catalyst layer of 1.2/10 nm Fe/Al_2O_3 film deposited by e-beam evaporation, which is then patterned using lift-off prior to growth. C_2H_4 is used as hydrocarbon source for CVD. The epoxy and curing process during the transfer process causes the columns, which have initially a very low density due to the large spacing between individual nanotubes, to shrink approximately to 80% of their original width. The cross-section of the reinforced structures indicates strong densification which results in regions with highly dense CNT bundles as well as hollow regions.

We also present electromechanical test data where columns are compressed and electrical resistance is measured with a 4-point measurement configuration along with force displacement and time. We observe reduction in electrical resistance with compression and discuss possible reasons for the collective behavior of CNTs. We also observe interesting mechanical behavior such as very large permanent deformation and force relaxation, and note that the columns reinforced with epoxy are 100 times stronger than as grown columns.

Critical behavior in SWNT-polymer composites: polymer dynamics, electrical transport and orientation percolation

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SWNT/PMMA nanocomposites prepared by a coagulation method exhibit uniform dispersion at different length scales, as determined from optical microscopy, Raman imaging and SEM. The linear viscoelastic storage modulus becomes almost independent of frequency as the SWNT loading is increased from 0 to 2 wt%, indicating the onset of terminal solidlike behavior. The data is well-represented by power law, or critical behavior, with a rheological threshold of 0.12 wt %, well below the percolation threshold 0.39 wt %. This difference is a manifestation of the requirement for smaller intertube separation to form a percolated resistor network relative to that required to impede polymer coil mobility by adding rigid rods.

Percolation through a network of conducting rods also depends on the degree of rod alignment, or preferred orientation, as well as on concentration. SWNT alignment and concentration can be varied independently in this composite family, and both dependences exhibit critical behavior. We used x-ray fiber diagrams to study the orientational threshold in detail. Quite surprisingly, we find that the highest composite conductivity is obtained with slightly aligned, rather than completely isotropic, rods. The experimental results are fully borne out by Monte Carlo simulations.

Effect of HIP treatment on microstructure and mechanical properties of VGCF/MgO-Al_2O_3 spinel ceramic composites

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The VGCF/MgO-Al_2O_3 spinel ceramic composites have been prepared by the sintering of magnesia, alumina, mica-composition ($KMg_3AlSi_3O_{10}F_2$) glass and VGCF powder mixtures. VGCF was dispersed in the polyvinylalcohol solution and the tangled VGCF was removed by elutriation. Such dispersed VGCF was used. The mixing ratio of the magnesia and alumina powders corresponded to a stoichiometric spinel composition and the additions of the mica-composition glass powder and VGCF were 40 mass% and 1-3 wt%, respectively. The powder mixtures were compacted by a cold-isostatic pressing at 98 MPa. The green compacts were embedded in SiC powder and fired in the air. The composite with the content of 1.2 wt% VGCF became dense at 1550°C. However, as the content of VGCF increased, the many pores appeared in the composites. As the result, the bending strength was lowered. Then, in order to improve the mechanical properties, the composites were treated with HIP (hot-isostatic pressing) after firing in the air. The HIP treatment decreased the volume and the size of pores in the composites and increased the bending strength. However, it did not have any effects on the fracture toughness. On the other hand, electrical resistance was decreased drastically by HIP treatment.

Production of Micro Mechanical Components with Cup Stacked Type Carbon Nanotubes by Micro Injection Molding

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Carbon nanotubes have good potentials as fillers in their composites because of their excellent physical properties. It is accepted that additions of small amounts of nanotubes provide good improvements in mechanical, thermal and electrical properties to composites. Especially, their polymer-based composites are suitable for making micro-scale components by means of highly-established injection molding techniques with ultra precisions. This paper reports several practices of molding processes to produce micro components with cup stacked type carbon nanotubes / polymer composites. The research involves qualifications of rheological parameters in nanotubes / polymer melts to decide the molding conditions. The results show additions of nanotubes require no significant modifications in the molding parameters of polymer melts as long as the quantity of nanotubes is less than 10wt%. After determining the blending and molding conditions, several injection techniques are applied to produce nanotube components. The techniques are based on micro-molds obtained from discharge machining and LIGA processes. Mechanical components such as micro-gears can be successfully produced and assembled to show improved frictional, thermal and electrostatic properties in a planetary-gear system. Fine products with higher aspect ratios can also be produced with LIGA molds, and their size variations are effectively reduced by increasing the nanotube quantity.

Shape Memory Effect of Nanocomposite with CNT/Shape memory Polymer

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Shape memory polymer (SMP) as one of smart materials is characterized with its remarkable recoverability and shape memory effect, but its mechanical property such as strength and elastic modulus is not high enough. In this study, Carbon nanotube(CNT)/SMP nanocomposites were developed with the typical CNTs of the vapor growth carbon fibers (VGCFs). A fine and homogeneous dispersion of VGCF throughout the SMP matrix is obtained. The specimens with different VGCF weight fraction, such as SMP bulk, 0.5wt%, 1wt% and 1.5wt%, were prepared, and their dynamic mechanical properties and shape recovery behavior were investigated. It was found that storage elastic modulus is improved obviously with increment of VGCF weight fraction, and the CNT/SMP nanocomposites showed a good shape memory effect. It is indicated that the recovery stress of CNT/SMP nanocomposites with only 1 % weight fraction of carbon nanotubes will reach almost twice of that in SMP bulk.

Properties of CNT/NiTi/UPR Three-phase Composites

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In this work, the three-phase composites of CNF/NiTi/UPR, carbon nanofiber (CNF), shape memory alloy particles (NiTi) and unsaturated polyester resin (UPR), are innovated, and their electrical properties are investigated. It is found that the CNF/NiTi/UPR composite materials are of very low electrical percolation threshold due to CNF. Their electrical resistance increases with increasing NiTi particles in spite of being significant percolation threshold. The effect of the filler content on the electrical conductivity is discussed as a function of temperature. Moreover, the three-phase composites express a positive temperature coefficient (PTC), and its intensity increases around the percolation threshold because of the contribution of NiTi particles of 5wt% and 10wt%. The electrical resistance reduces with the increment of thermal cycle number. For the time dependence of electrical property, there exist the characteristics of a dynamic percolation and overcurrent protective effect with current attenuation. It is shown that the relation between current and voltage is linear and the electrical conductivity obeys an Ohmic law for these three-phase composites

Novel Microcatheter from Carbon Nanotube-Incorporated Nanocomposites

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Carbon nanotubes can be visualized as rolled up graphene layers [1], and exhibit excellent physical and chemical properties that make them potentially useful in wide range of applications [2]. Among their versatile applications, they are expected to be promising as bio/medical devices due to their nano-sized diameter and their expected good biocompatibility. Here we report one of the carbon nanotube applications toward medical device: microcatheter. We successfully fabricated black-colored, mechanically strong microcatheter by extruding molten nylon polymer containing homogeneously dispersed high-purity (iron content < 20 ppm) carbon nanotubes [3]. Interestingly, there were no exposed carbon nanotubes on the outer surface of microcatheter. In addition, our novel microcatheter exhibited highly reduced thrombogenicity and blood coagulability. Thus, it is expected that these system will be widely utilized in various medical devices.

Anchoring molecule guided self-clustering of transition metals on the sidewalls of single walled carbon nanotubes

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Functionalization of 2,2:6,2-terpyridine (Terpy) on single walled carbon nanotubes (SWNTs) via non-covalent interaction as well as their thermal stability have been studied by UV-Vis spectroscopy. Terpy functionalized SWNTs (Terpy-SWNTs) have reacted with transition metal ions, such as Ru(III), Cu(II), Zn(II), and Sn(II) in solution phase to spontaneously create discrete nanoparticles on the sidewalls of SWNTs. Electron transfer during the Terpy functionalization as well as transition metal formation has been investigated by monitoring significant conductance changes using SWNT -FET devices. Atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS) and conductance measurement studies have suggested that the elevated Fermi level of SWNT after Terpy coating is responsible for the spontaneous electron transfer from Terpy-SWNT to transition metal ions, resulting in the formation of nanoparticles containing electronically reduced species.

Characteristics of composite film with highly orientated vapor grown carbon nanofibers

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To manufacture the highly functional micro devices by plastic forming, mechanical properties and volume resistivity of polypropylene (pp) / vapor grown carbon nanofiber (VGCF) composite film with orientated VGCF in matrix by rolling and extrusion methods were investigated. In composite film reinforced with 30wt% VGCF at 80% rolling reduction, high tensile strength equivalent to an engineering plastic (PEEK) was obtained. This was due to the existence of orientated VGCF and decreasing of defects, which exist on surface of composite film and at the interface between VGCF and pp matrix. Also, volume resistivity was decreased with increasing of VGCF content.

Development of Al Infiltrated VGCF/C Porous Prerform Composites

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In the recent years, composites of vapor grown carbon fiber (VGCF) have been developed as high-strength structural material and high thermal conductive materials. In case of Al/VGCF composite, It is well known that we have some difficulties on the disperse of nano-filler in the matrix. So we have employed VGCF/C preforms composed of VGCF and AR-pitch, and the vacancy of the porous structure is infiltrated melting Al alloy. The preforms, which has high strength toughened by VGCF, are constructed of interconnected open cell network of VGCF and graphitic ligaments with high degree of graphitization. It was exhibited that thermal conductivity of Al/CNT/C composites reached about 130 W/mK which is higher than that of Al alloy as a matrix (121 W/mK).

Carbon nanotube/carbonized cedar wood hybrid multiscale composites

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This work is part of our continuous effort to produce advanced carbon materials based on biomass resources. Such application requires the creation of hybrid multiscale material in order to control their organization and property at all scales.

To this end Japanese cedar was carbonized in electric furnace at 700 °C for one hour, with initial heating rate of 4 °C /min under a flow of dry nitrogen. The carbonized material was milled and soaked in 40 % isopropyl alcohol solution of Al-triisopropoxide, dried and heated in a pulse current sintering device at 1300 °C for 5 min. Subsequently, the samples were impregnated with ferri ions and brought in a nitrogen/hydrogen or nitrogen/ethylene atmospheres at 650 °C.

These turned out to be the ideal conditions for carbon nanotubes or nanofilaments to be produced by catalytic decomposition of ethylene or acetylene. Such complex materials made of carbonized wood on which carbon nanotubes are grown offer opportunity to combine two different types of microtexture at different scales to create multiscale composites, and are now tested for potential application in energy storage.

Effect of carbon nanotubes on the structures and properties of mesophase pitch-based nanocarbon composite fibers

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In this paper, the structures and the properties of mesophase pitch-based nanocarbon composite fibers were studied in detail. The multi-walled carbon nanotubes as filler were pre-treated by nitric acid, and then were mixed with mesophase pitch by two ways: melt method and ball miller method. Hydroxyl and carbonyl groups were introduced on the sidewall of inert multi-walled carbon nanotubes after modified by nitric acid. The acid-treated multi-walled carbon nanotubes were mixed with mesophase pitch to prepare the nanocarbon composite fibers through a fabrication procedure including melt spinning, stabilization and carbonization. The results show that the ball miller method can homogeneously disperse carbon nanotube into mesophase pitch. The carbon fibers obtained from pure mesophase pitch have a typical radical or open wedge texture, whereas the nanocarbon composite fibers have a random texture. The mechanical properties of nanocarbon composite fibers show good performance compared with those of carbon composite fibers from pure mesophase pitch.

Manufacture of parallel PAN/MWCNT composite nanofibers by electrospinning

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Polyacrylonitrile (PAN) and PAN/MWCNTs composite parallel nanofibers with a diameter distribution from 100nm to 300 nm were prepared by electrospinning technology. Scanning electron microscope (SEM) and transmission electron microscope (TEM) were used to determine the diameter and the morphologies of nanofibers. The thermal properties of the nanofibers were analyzed with the help of DSC and TG. The effect of MWCNT content on the mechanical properties of nanofibers was investigated. SEM and TEM observation indicated that the MWCNTs were well-aligned along the axes of the nanofibers with the increase of the MWCNT content. The nanofibers became rougher and the diameter distribution got non-uniform because of the variety in MWCNTs shapes. DSC and TG results showed that the addition of MWCNTs accelerated the thermall decomposition of PAN-based nanofibers. The tensile properties of PAN nanofibers were promoted by the addition of MWCNT fillers. However, as the MWCNT content is 10%, the tensile strength of the composite nanofibers dramatically decreased.

Bending Tests of Tungsten Disulfide Mulitwall Nanotubes

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The mechanical properties of WS_2 Nanotubes are of great interest from both scientific and applicative point of view. Their perfect crystalline structure results in superior mechanical properties compared to bulk materials. In former studies we have shown that these nanotubes have Young's modulus of 150GPa, tensile strength of 16GPa, elongation of 14% and completely elastic behavior under axial tension and compression. Bending tests of WS_2 nanotubes with atomic force microscope (AFM) were conducted lately. Nanotubes were suspended on trenches and then force was applied to a suspended nanotube by means of lateral deflection of the cantilever. Analysis of the bending by using Timoshenko's equation takes into account tension, compression and shear of the nanotube. Since the shear stress is believed to facilitate sliding of the layers, the shear modulus which is measured is probably the elastic constant c44. The average value of the c44 is 2.9±0.8 GPa, this value is in good agreement with the calculated and measured c44 for bulk MoS_2 which is 4GPa.

Gauge Factor of Carbon Nanotubes

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Sensing of mechanical strain is one of the applications for which carbon nanotube (CNT) is investigated as a potential replacement of the existing technology based on silicon piezo resistor. In this research, gauge factors of different types of ideal CNTs were investigated by quantum mechanical calculations to get an understanding of the maximum which could be achieved.

Current-voltage characteristics of the CNTs were calculated by using the software Transiesta which incorporated first principle calculations based on DFT and Non-Equilibrium Greens Function Method. The simulation model consisted of an infinitely long CNT with a central region through which current was driven in response to a voltage applied to left and right regions which were treated as electrodes. The central region had a width equal to an integer number of unit cells of the CNT. Left and right electrodes were defined as semi-infinite CNTs which had the same unit cell as the central region. Strain was applied to the CNT by stretching the unit cell in the axial direction. Resistance of the CNT was calculated as a function of strain to obtain the gauge factor.

Resistance of three basic types of CNTs (14,14), (12,0), and (13,0) were calculated as a function of axial strain. Resistance values of (12,0) and (13,0) CNTs increased with increasing strain, whereas those of (14,14) CNT did not exhibit any change. Variation of resistance as a function of strain was found to be greater for (13,0) CNT than for (12,0) CNT. Gauge factor of (13,0) CNT was approximately 2 times greater than that of (12,0) CNT. Gauge factors of both CNTs increased as a function of increasing strain. The gauge factor of (13,0) CNT ranged from a value of about 400 at 0.01% strain to over 1000 at 0.5% strain.

Diameter dependence of formation and healing of defects in single-walled carbon nanotubes induced by low-energy electrons and photons

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Low-energy (20 eV to 20 keV) electron and photon irradiation causes damage to single-walled carbon nanotubes (SWNTs) and extinguishes their characteristic optical, chemical, and electric properties [1]. In this study, the damage was found to strongly depend on the diameter: thinner SWNTs were more severely damaged. The activation energy for healing of the defects was evaluated to be of the order of only several ten meV, so that there is competition between formation and healing of the defects even at room temperature. The activation energy was also found to strongly depend on the diameter. Our results show that the strain energy in the sidewall plays an essential role in stabilizing the defects. It is also suggested that the damage is characteristic of thin nanotubes such as SWNTs and does not occur in thick multi-walled nanotubes (MWNTs) or graphite, at least at room temperature.

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Finite element modeling of single-walled carbon nanotubes with introducing a new wall thickness

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A three-dimensional finite element (FE) model for armchair, zigzag and chiral single-walled carbon nanotubes (SWCNTs) is proposed. By considering the covalent bonds as connecting elements between carbon atoms, a nanotube could be simulated as a space frame-like structure. Here, the carbon atoms act as joints of the connecting elements. To create the FE models, nodes are placed at the locations of carbon atoms and the bonds between them are modeled using three-dimensional elastic beam elements. Using a linkage between molecular and continuum mechanics, and Morse atomic potential, we calculate the elastic moduli of beam elements and a new wall thickness (=bond diameter) equal to 0.1296 nm. In order to demonstrate performance of FE model and new wall thickness, the influence of tube wall thickness, diameter and chirality on the Youngs modulus of SWCNTs is investigated. It is found that the choice of wall thickness significantly affects the calculation of Youngs modulus. For the values of wall thickness used in the literature, the Youngs moduli are estimated which agree very well with the corresponding theoretical results and many experimental measurements. We also obtain dependence of elastic moduli to diameter and chirality of the nanotubes. The larger tube diameter, the higher Youngs modulus of SWCNT. The Youngs modulus of chiral SWCNTs is found to be generally larger than that of armchair and zigzag SWCNTs. The presented results demonstrate that the proposed FE model and wall thickness may provide a valuable tool for studying the mechanical behavior of carbon nanotubes.

Buckling of multiwall carbon nanotubes with different inner diameters

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We have investigated the axial buckling of a multiwall nanotube under the axial compression by nanomanipulation experiments and molecular dynamics (MD) simulations. Experimentally, Youngs moduli of nanotubes with different inner hollow diameters with the same outer diameters are consistent with the Eulers buckling model based on the continuum analysis. The MD simulations for the buckling behaviors of triple- and double-walled nanotubes are also consistent with the continuum analysis. This good agreement indicates that the Eulers buckling model is applicable to the analysis of the axial buckling behaviors of the multiwall nanotubes.

Phonon transport in finite length single-walled carbon nanotubes using a non-equilibrium molecular dynamics method

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SWNTs are expected to possess high thermal conductivity due to the quasi-one-dimensional structure and strong carbon bonds. An important feature of the SWNT thermal conductivity in terms of both physics and engineering is its length dependence [1], which occurs because the length-scale of phonon quasi-ballistic transport is usually longer than the tube-length in practical situations. In this study, we calculate the length dependence of the thermal conductivity of SWNTs for a range of nanotube-length up to 3.2 μm using a non-equilibrium molecular dynamics method. The simulation gives us access to detail pictures of phonon transport such as the dispersion and relaxation [2]. The results indicate two length-regimes with different trend of thermal conductivity; (1) the shorter tube-length regime (<200 nm) with contribution of diffusive-ballistic phonon transports from a wide range of phonon branches including optical phonons, and (2) the longer tube-length regime (>200 nm) with dominant contribution from the key low frequency phonons with mean free path well longer than the tube-length. In the latter regime, the thermal conductivity exhibits exponential divergence on the length with the exponent somewhat smaller than the available one-dimensional models. The phenomena will be discussed in terms of detailed pictures of phonon transport.

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Relation between mechanical strength and maximum allowable current of carbon nanotubes

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A relation between mechanical strength and maximum allowable current (MAC) for multiwall nanotubes has been investigated. Nanotubes examined were grown by a thermal CVD process and annealed at a temperature over 2000 ^{o}C. The mechanical strength of the nanotubes was measured from the resonant frequencies of nanotube cantilever vibrations in a scanning electron microscope (SEM). The Young's moduli of the nanotubes were widely spread in a range of 0.1 ~ 1.5 TPa. The values of MAC of the same nanotubes were also measured inside the SEM. The nanotubes with a higher MAC show a higher Young's modulus. The value of MAC saturates to 3μA/nm (circumferential density), when the Young's modulus is higher than 1 TPa. Whereas highly graphitized nanotubes synthesized by arc discharge show similar Young's modulus, the value of MAC is around 7μA/nm. This indicates that the defects affecting the mechanical strength are different from those affecting the electrical conduction. It is noted that the Young's modulus was measured in a small deflection limit. The molecular dynamics simulation in this region predicted that pinhole defects in nanotubes do not affect the resonant frequency. 1) Therefore, the defects in the examined nanotubes might be mainly the pinhole defects.

Thermal conductivity measurement of vertically-aligned single-walled carbon nanotubes by 3 omega method

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Thermal conductivity of single-walled carbon nanotubes expected from molecular dynamics simulations varies between 300~3000 [W/mK]. The quasi-ballistic phonon dominated length-dependence is also discussed [1]. Hence, the reliable experimental measurement of the finite length SWNTs is desired. By using the high-purity vertically aligned single-walled carbon nanotubes [2], the reliable measurement of thermal conductivity can be possible. The 3 omega method commonly used for thin film thermal conductivity measurements, was employed.

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Frictional Characteristics of Carbon Nanotube powders and their composites

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Carbon materials like Diamond or Graphite(Gr) have been used for their superior frictional characteristics. Carbon nano-tubes(CNTs) have also been expected to have good frictional characteristic. Therefore, we first compared the basic frictional characteristics of CNTs as solid lubricants in powder form with those of Gr and MoS_2.[1,2] We then measured frictional characteristics of some resins with and without CNTs. In experiment, powder samples of MWCNTs, Cup Stack CNTs(CSCNT), Gr, and MoS_2 were spread on horizontal plate and a slider was slid one way on it. The sliding speed was 0.5mm/s. The lowest coefficient of friction of MWCNT was about 0.1, while that of Gr was about 0.05.[3] We made MWCNTs composite sliders with Epoxy(EP), POM, and PEEK resins. The coefficients of friction of pure EP, PEEK, and POM were 0.5, 0.2, and 0.12 respectively. With the addition of a MWCNTs, COF of EP decreased, while those of PEEK and POM changed little. We considered that EP is a thermohardening resin and that its sliding surface did not melt by frictional heating. On the other hand, POM and PEEK are thermoplastic resins and these resins covered up MWCNTs by frictional melting.

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Site-Dependent Combustion Mechanism of Single-Wall Carbon Nanotubes

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The combustion of carbon nanotubes (CNT) has been a powerful tool for purifications and evaluations of CNT. However, the detailed combustion mechanism such as dependence on the number of layers and bundles, have not been elucidated yet. In this work we have succeeded in tracking of combustion processes of individual single-walled carbon nanotubes (SWNT) by observing with atomic force microscopy (AFM).

SWNTs (HiPco) were dispersed in 1,2-dichloroethane and were spin coated on SiO_2 substrates scratched with a diamond pen for eye markers. Those mm-sized eye markers enable us to rescan the same positions after combustion in a furnace outside the AFM. The structural changes of SWNTs were observed with a tapping mode AFM (Nanoscope IV, Dimension 3100, Veeco Digital Instruments), and then were oxidized in air at various temperatures. The observation and oxidation steps were repeated alternately.

The results show that SWNTs burn mainly from sidewalls not from ends, which have been believed to have higher reactivity than sidewalls. The results also reveal the presence of very slow combustion processes, where a few carbon atoms of SWNTs are removed every second.

Force Measurement of the Bond between the Joined Carbon Nanotubes

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To create nano-sized devices with carbon nanotubes (CNTs), we have explored the junction formation of CNTs. In this report we have measured the bonding force between the two ends of CNTs at a very early stage for forming the junction.

An individual nanotube was manipulated using a nanomanipulator system installed in a transmission electron microscope. A double-walled or triple-walled CNT was cut down to get the two protruded closed ends of inner single-walled CNTs which had the same diameter. Then the both ends were manipulated to contact together again and the current was flowed through the contact. We have confirmed the carbon-carbon bond creation and obtained the threshold current density for the bond creation.

The one side of the cut single walled CNT set on the cantilever was pulled away against the other side which was fixed. We measured the tensile force acted on between the two CNTs from the bending of the cantilever. We found out that the measured force increases stepwise with increasing the current. The each step of the measured force is corresponding to a number of the carbon-carbon bond recreation.

Transfer and Dissipation of Mechanical Energy Between Single Walled Carbon Nanotubes

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The equilibrium vibrational properties of single walled carbon nanotubes (SWNT) have been well studied and are known to exhibit unusual behaviour that arise from the quasi-one-dimensional nature of the tubes, such as ballistic thermal transport and negative thermal expansion. This work focuses on the non-equilibrium vibrational behaviour of nanotube systems, that is, understanding the pathway by which vibrational energy is redistributed towards thermal equilibrium.

In particular coupling and energy transfer between radial modes in adjacent SWNTs is considered. Surprisingly it is found that energy can transfer from an excited breathing mode in one tube to its resonant counterpart in the adjacent tube before there is significant dissipation into other modes. The time-scale for this energy transfer is set by a beat frequency that arises from the resonant modes in each tube and the inter-tube oscillations. Several tube-tube orientations are considered, and we find that, although the amount of energy transferred depends on orientation in all cases enhanced energy transfer occurs between modes in resonance.

This work has significance for understanding the operational limits of nanomechanical devices, such as suspended nanotube resonators, and hints at the possibility of new application for SWNTs based on the selectivity of resonant coupling.

Study of Single Wall Carbon Nanotube Structural Behavior by a Modified Space Frame Model

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Carbon nanotubes, since their discovery in 1991, due to their mechanical and electrical characteristics, are attractive to researchers and industries. Many applications have been found and nanotubes are nominated for many further applications too. To find their characteristics' to explain their mechanical behavior, many models and methods have been introduced. One of the most important methods is Molecular Dynamics (MD), which has great disadvantage; its restriction to small models and expense. Therefore, many researches have attempted to develop continuum models which have equal effective characteristics. In this regard different approaches have been hired like; elastic thin shell, truss, space frame, etc. One method which is able to show chemical characteristics of bonding and none bonding interactions of carbon atoms and presents them as effective mechanical properties, is space frame model which hires frame element with different mechanical properties, representing bonding and none bonding interactions. This model contains extra six beam elements to consider none bonding interactions which makes it difficult to build 3D model in a Finite Element Analysis software. Also, some space frame models are introduced which only consider bonding interactions. Introducing lower elastic modulus and other effective characteristics, are their essential weak point.

In present study, a new space frame model is introduced, which combines precision of considering all bonding and none bonding interactions and simplicity of usage of hexagonal frames. In other words, the introduce frame elements, which make up the carbon nanotube lattices, have effective mechanical properties, which considers none bonding interactions, too. In this way, carbon lattice force field constants were used. The obtained model, yields results which have good agreement with MD and other empirical results released through papers. Also, carbon nanotube elastic modulus has been developed as a function of tube diameter and length. Therefore when precision solution is needed, the presented space frame gives results with satisfactory expense and for other cases, the nanotube could be considered as one structural element.

In the last part, single wall carbon nanotube structural behaviors, which introduced model is able to present, has been reviewed, using Finite Element Analysis software. In this review, in every stage, distinguished effects of loading type are mentioned.

Electrical Transport of Single Wall Carbon Nanotube/GaAs Junction

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Transport properties of single wall carbon nanotubes (SWCNTs) and GaAs junctions have been studied. Both p-type and n-type GaAs were used to make SWCNT/GaAs devices and showed very different characteristics. P-type GaAs/SWCNT junctions showed ohmic-contact behavior, however, strong rectifying current was observed in n-type GaAs/SWCNT devices. To understand the details of the contact of GaAs/SWCNT junctions, temperature-dependent measurement was applied. Results showed the electronic transport through GaAs/SWCNT junction is very sensitive to the difference of Fermi levels between carbon nanotubes and GaAs.

Influence of phonon-defect scattering on thermal transport in carbon nanotubes

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We investigate thermal transport in defective carbon nanotubes using a new theoretical formalism based on the nonequilibrium phonon Green's function technique. The universal quantization of low-temperature thermal conductance in carbon nanotubes can be observed even in the presence of local structural defects such as vacancies and Stone-Wales defects, since the long wavelength acoustic phonons are not scattered by local defects. At room temperature, however, thermal conductance is critically affected by defect scattering since incident phonons are scattered by localized phonons around the defects. We find a remarkable change from quantum to classical features for the thermal transport through defective CNTs with increasing temperature.

Quantum Dephasing, Resonances and Decoherence in Carbon Nanotubes : Role of Electron-Phonon coupling and Chemical Disorder

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In this talk, the role of electron-phonon coupling on quantum transport is addressed in clean and disordered carbon nanotubes. Defects and impurities are modelled by a static short-range disorder, whereas the dynamical fluctuating potential associated with phonon vibrations is encoded by a time-dependent coupling between pi-pi nearest neighbour orbitals. On the basis of the Kubo framework in the coherent regime, the conductance scaling properties in the weak localization regime are explored numerically, and the energy-dependent coherence length and coherence times are derived from a phenomenological approach. The strong disturbance of the electronic structure due to optic modes is also investigated conductance scaling properties of both metallic and semiconducting nanotubes. Anomalous magnetoresistance behaviour due to chemical impurities and applicability range for simulation carbon nanotubes field effect transistors on the basis of the Fermi golden rule are discussed.

Electronic transport in carbon nanotubes: From individual nanotubes to thin and thick networks

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We measure the electronic transport properties of individual single-wall carbon nanotubes (SWNTs) and SWNT networks of varying thickness. The thinnest SWNT networks, like the individual semiconducting SWNTs, show nonlinear current-voltage (I-V) characteristics at low temperatures with a current that can be tuned by a gate voltage. The overall temperature dependence of conductance in the transparent networks changes systematically as the thickness of the network increases and is consistent with hopping conduction. On the other hand, the thickest SWNT networks (free-standing buckypaper) show more metallic behaviour: their I-V characteristics are linear with no gate-voltage effect, and a large fraction of their conductivity retained at very low temperatures, consistent with tunnelling through thin barriers separating metallic regions. For this thick network, the conductance reaches a maximum value near room temperature with a changeover to metallic temperature dependence at higher temperatures. We obtain an excellent fit to the data taking the energy of the backscattering phonons as 160 meV, in good agreement with the energies of the zone boundary phonons in SWNTs. We have also proposed another mechanism that could lead to reduction of the conductance in SWNT networks at higher temperatures, namely the softening of the van der Waals intertubular interactions, which leads to a reduction in intertube transfer of carriers.

Electrical conductance and breakdown in individual CNx multiwalled nanotubes

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Doping of carbon nanotubes with nitrogen during growth strongly modifies their electronic structure. The n-type doping by N within the lattice is expected to produce metallic behavior. To date, electrical measurements on individual nitrogen-doped multi-walled nanotubes (CN_x MWNTs) have reported low conductances. Here we present high conductance ($1.0 \pm 0.3 G_0$) measurements at low bias for individual CN_x MWNTs, which show metallic behavior. The conductance increases linearly with voltage at a rate of $0.7 \pm 0.2 G_0/V$ until the threshold for electrical breakdown is reached. Discrete current steps with a magnitude of $20 \pm 10 \times 10^{-6}$A are observed during electrical breakdown.

Charge transport in CNT driven by surface acoustic waves

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The need of devices able to produce utilizable currents with very hight precision lead to several solutions. These devices are based either on a single electron transport through a static quantum dot, or on GaAs-2DEG where the electrons are confined by the electrical potential of the applied surface acoustic wave (SAW).

Lately a new SAW-related effect has beeen predicted and investigated where the function of the 1D conducting channel is taken over by a single-walled carbon nanotube.

The aim of the work is to present an overview of theoretical predictions and existing experimental work.

The device suitable for detecting the predicted effect will be presented and the experimental progress will be reported.

Electromigration Forces on Ions in Carbon Nanotube Transistors

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Due to their unique structural and electronic properties carbon nanotubes (CNs) are promising candidates for future nanoelectronics. Recently, field-effect transistors (FETs) from single-wall CNs have been a research focus. In particular, ballistic transport has been demonstrated and key transport parameters compare well with state-of-the-art silicon FETs. Doping with alkali metals has been a main route to improve transistor performance. However, current-induced, electromigration, forces on such alkali ions may lead to ion diffusion and alter the device properties.

Here, we report calculations of ballistic transport in carbon nanotube transistors using the non-equilibrium Greens function formalism within a tight-binding approximation. We use a cylindrically device setup [for details, see S. Heinze, N.-P. Wang, and J. Tersoff, Phys. Rev. Lett. 95, 186802 (2005)] and calculate the current-induced forces on ions located either inside or outside the CN. The forces are largest in the turn-on regime of the transistor, and much smaller in the on- and off-state. The electromigration forces are mainly due to momentum transfer from the charge carriers, i.e., due to the wind force. The sign of the effective valence Z^* is independent of the actual charge sign, but can be reversed with gate voltage.

Current breakdown and transport measurements on individual multi-wall carbon nanotubes

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CNTs have been predicted to show extremely high electrical and thermal conductivity and are expected to display a 1-dimensional (1D) phonon density of states. The measurements reported here aim to investigate a number of issues relating to the 1D band-structure of individual CNTs. An arc-grown bundle of multiwalled nanotubes (MWNTs) is mechanically attached to a thermal probe. Then the bundle is advanced towards a graphite substrate until a single protruding tube contacts. The heat flow down individual MWNTs is recorded as a function of the temperature difference across them. We show that the current carrying capability of single electrically conducting nanotubes is unusually large (with a breakdown current density greater than 1013A/m^2). The tube behaviour at breakdown has also been measured and we attempt to explain this behaviour with a simple model. As part of our study of the thermal properties of CNTs [1] we report the tube thermo-electric properties over a wide temperature range. We will discuss our results in the light of the tube band-structure which is revealed by the observation of van Hove singularities, even in the room temperature current-voltage behaviour.

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Intraband electron-phonon matrix elements of single-walled carbon nanotubes

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We use a symmetry-adapted non-orthogonal tight-binding model to calculate the intraband electron-phonon matrix elements of all single-walled carbon nanotubes in the radius range from 3.5 Å to 12 Å. We considered only the massless bands of metallic tubes and the lowest-energy massive bands in all nanotubes, as well as all six phonons, allowed by selection rules. The calculations reveal that the matrix elements for massless bands are non-zero either for forward or backward scattering, while the matrix elements for forward and backward scattering in massive bands tend to the same value for final electronic states at the band bottom. The obtained matrix elements show radius and chirality dependence. For tangential optical phonons, they tend to 12.8 eV/Å (intravalley), 18.1 eV/Å (armchair, intervalley) for massless bands, and to 9.2 eV/Å (intravalley) and 13.4 eV/Å (armchair, intervalley) for massive bands in the large-radius limit. For twist and longitudinal acoustic phonons, the limiting matrix elements depend on the chiral angle as well. By means of the matrix elements, we estimated the intraband scattering length in the massless bands of medium-radius metallic tubes as 1.0-1.6$\times10^{-6}$ m (acoustic phonons), 0.16$\times10^{-6}$ m (tangential optical phonons), and 0.06$\times10^{-6}$ m (A1' K-point phonons).

Phonon-assisted tunneling in interacting suspended single wall carbon nanotubes

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Transport in suspended metallic single wall carbon nanotubes in the presence of strong electron-electron interaction is investigated [1]. We consider a tube of finite length and discuss the effects of the coupling of the electrons to the deformation potential associated to the acoustic stretching and breathing modes. Treating the interacting electrons within the framework of the Luttinger liquid model, the low-energy spectrum of the coupled electron-phonon system is evaluated. The discreteness of the spectrum is reflected in the differential conductance which, as a function of the applied bias voltage, exhibits three distinct families of peaks. The height of the phonon-assisted peaks is very sensitive to the parameters. The phonon peaks are best observed when the system is close to the Wentzel-Bardeen singularity. The results are compared with the recent experiment [2].

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Electromechanical instabilities of suspended CNTs

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We have theoretically investigated electromechanical instabilities of suspended carbon nanotubes when using an STM-tip to probe the suspended part of the tube. A coupling between the vibrational modes of the nanotube and tunneling electrons may lead to a pumping of energy into the mechanical subsystem, resulting in large amplitude vibrations of the CNT. This effect is related to the ”shuttle instability” and changes the transport properties of the system. In the present study, instability of different bending modes have been investigated.

We show that, with respect to the instability, different modes can be treated independently in the limit of weak electromechanical coupling. Also, we show that excitations of different modes are controlled by their vibration frequency and tunneling rates. Tunneling rates of the order of the frequency are found optimal for an instability to occur. Hence, a selective excitation of a single mode is possible. We analyze the limit cycle behavior in this case. Another scenario is simultaneous excitation of several modes, leading to a complex behavior in stationary regime.

A simple suspension of individual multi-walled carbon nanotubes based on a deep trench electrode

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We report the suspension of an individual multi-walled carbon nanotube (MWNT) from the bottom substrate using deep trench electrodes that were fabricated using optical lithography. By drying the solution during dielectrophoretic assembly, the capillary force pulls the MWNT toward the bottom substrate, and the MWNT then remains as a deformed structure adhering on the bottom substrate after the solution has dried out. Thin electrodes with large gaps could not suspend small diameter MWNT but thicker electrodes could. Thin MWNT could be suspended only when the electrode gap was reduced. We present the statistical experimental results for successful suspension as well as the feasible suspension condition of MWNT based on theoretical approach.

LSI via interconnects made of multi-walled carbon nanotubes grown from size-controlled Co nanoparticles

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We propose a novel approach to fabricate LSI via interconnects from bundles of multi-walled carbon nanotubes (MWNTs). The approach utilizes preformed catalyst nanoparticles to grow MWNTs in a controlled manner. For this purpose, a newly-designed impactor was employed for providing size-controlled Co particles, and a particle deposition system using differential pumping was developed to inject the particles into via holes down to 40 nm in diameter. MWNTs were grown from 4-nm Co particles at the via hole bottom by thermal chemical vapor deposition at 510 °C using acetylene. The number density of the resultant MWNTs in the via holes was as high as 9×10^{11} cm^{-2}, being approximately one order higher than that in the former studies using sputtered catalyst films. The CNT-via resistance was 0.59 Ω for 2-micrometer vias, which is the lowest ever reported, improved from the previous studies using catalyst films. The resistance is of the same order as that of W plugs, and is expected to improve further by enhancing the growth probability of MWNTs from the catalyst particles. This work was partly completed under JFCC management as part of an METI RD program (Advanced Nanocarbon Application Project) supported by NEDO.

Four-Point Resistance of Individual Single-Wall Carbon Nanotubes

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We have studied the resistance of single-wall carbon nanotubes measured in a four-point configuration with noninvasive voltage electrodes[1]. The voltage drop is detected using multiwalled carbon nanotubes while the current is injected through nanofabricated Au electrodes. The resistance at room temperature is shown to be linear with the length as expected for a classical resistor. This changes at cryogenic temperature; the four-point resistance then depends on the transmission coefficients between the different electrodes and can even become negative due to quantum-interference effects, as expected from the Laudauer-Buttiker theory.

[1]Phys. Rev. Lett. 95, 196802 (2005)

Transparent and Electrical Conductive Carbon Nanotube Films

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Transparent and electrical conductive thin film electrodes can be applied for lots of modern technologies such as flexible display devices, touch panels, sensors, and solar cells. We describe single-walled carbon nanotube (SWNT) thin films which show high optical transmittance in the visible light region and low sheet resistance. SWNT conducting arrays were constructed via consecutive amidation reactions with the aid of a linker molecule and a condensation agent on an amine-terminated glass substrate[1]. Conducting nanoparticles were deposited on the SWNT films by the electroless deposition method[2]. We discuss the optical properties (the visible light transmittance of the films) as a function of immobilization of the nanoparticles. The scanning electron microscope (SEM) and the high-resolution transmission electron microscope (HRTEM) were used to observe the nanoparticles formed on SWNT surfaces.

[1] D.-H. Jung et al., Chem. Commun., (2004) 526-527.
[2] H.C. Choi et al., J. Am. Chem. Soc., 124, (2002) 9058-9059.

Current-induced improvement of contact resistance between carbon nanotube and Pt electrode

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We have investigated the current-induced improvement of contact resistance between carbon nanotubes and electrodes. An individual double walled carbon nanotube was suspended between a pair of Pt electrodes. Current-voltage (I-V) characteristics were measured at temperatures from 4K to 295K with a limitation of the maximum applying current. At a low current limitation less than 4 μ A, the two terminal resistance was almost constant around 4 MΩ at room temperature. This resistance mainly comes from the contact resistance consisting of Schottky barrier and Ohmic resistance at the interfaces. At a low temperature, the Fowler-Nordeheim plot of the I-V characteristics well fell on a straight line in a high-electric field region. This implies that the carriers mainly tunnel through the barrier with the height of 0.26 eV. However, the barrier height is lowered to 0.17 eV at the current limitation of 4 μ A. When the current limitation increases to 5 μ A, the contact resistance was improved to 2.7MΩ at room temperature with the tunnel barrier of 0.16 eV. Thus, at first, the Joule heating at the interface lowered the barrier height. Further heating reduces the Ohmic resistance at the interface. The origin of this change seems to be the de-hydration of a-C at the interface during the Joule heating.

Contribution F.017 - Thursday, June 22

Carbon Nanotube Interconnection for Full 6-inch Integration

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Carbon nanotube (CNT) has been considered as a good electrical conductor, because of its unique shape with one dimensional graphene tubular structure, ballistic transport property and strong stability. These properties enable CNT to be a promising candidate for vertical interconnection material in a nano-scale feature competing with copper for the future memory devices. In this work, vertical interconnection using multi-wall carbon nanotubes (MWCNTs) is implemented into the full 6-inch Si wafer for semiconductor device integration. Integration processes are implemented by following sequential steps of conventional semiconductor processes; (1) Formation of bottom electrode lines covered with ultra thin CNT catalyst layer having sub 5 nm thickness (2) Patterning 240 nm diameter via hole using conventional dry etch process (3) CNTs are grown on the exposed catalyst surface at the bottom of the via hole by decomposing methane gas at 600 deg. C. using remote type microwave-PECVD system. (4) Planarizing over-grown CNTs using chemical mechanical polishing using capping layer (5) Ohmic contact layer and top metal lines formation. The via resistance is measured at a single contact of CNT via. The via resistance of several hundred Ohm with CNT density of ~ 5×10^{10} /cm^2 is obtained with small resistance variation within a wafer, which corresponds to ~ 10 kOhm per one MWCNT of the diameter of 10 nm. This result demonstrates that CNT via-module can be implemented into the conventional manufacturing process with compatibility. However research to improve the electrical properties should be investigated intensively.

Via contact etching using SiN stopper layer for carbon nanotubes growth

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Carbon nanotubes(CNTs) have inspired wide interests in current nanoscience and nanotechnology because of their excellent properties. For an application of CNTs growth in via contact, conventional direct via contact etching(without stopper layer for etching process) gives rise to several problems such as sidewall deposition of catalyst material(Ni, Fe, CoFe, NiFe, etc.) byproduct and difficulty in keeping catalysts thickness by low selectivity. In this work, silicon nitride was used as a stopper layer for via contact etch. High selectivity(to catalyst material) and low re-deposition(to via sidewall) rate were achieved by controlling etching gas condition. Fluorine gas chemistry was helpful to enhance selectivity to catalyst material. However, oxygen gas chemistry caused low selectivity and sidewall re-deposition. The via hole diameter and depth was 240 nm and 3000 Å. And via contact etching was done by following two steps; First, silicon dioxide layer etching stopped on the silicon nitride layer. Second, etching of silicon nitride layer stopped on the catalyst layer with minimum thickness loss of catalyst layer. The effect of via contact etching process which has high selectivity to catalyst material was confirmed by CNTs growth yield. CNTs synthesis was performed by decomposing methane gas at 600 °C. using remote type microwave-PECVD system. MWCNTs synthesized in our system had the diameter of 10nm with 6 to 8 walls.

Multiple Andreev reflections and reentrant behavior in network-like carbon nanotubes

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We have fabricated network-like carbon nanotubes with superconducting NbN electrodes on SiO_2/Si substrates. The carbon nanotubes were found to have the characteristics of single-wall carbon nantubes by measuring Raman spectra and scanning the diameter. We obtained sufficiently good contact between the single-walled carbon nanotubes and the NbN electrodes by infrared annealing at heater temperature of 700 °C for 15 min in vacuum. We observed dip structures in the differential resistance due to multiple Andreev reflection processes at dc bias voltages of $2E_g/e$ and E_g/e below 7 K, where the superconducting energy gap of NbN, E_g/e, is about 6 meV. Moreover, reentrant behavior of nonequilibrium effects was observed below superconducting critical temperature T_c. The proximity correction to the conductance disappears at low energies and reaches a maximum conductance around temperature Tmax which was observed to be at 8K, and is related to the correlation energy (Thouless energy). The magnetoconductance of reproducible aperiodic oscillations was also observed to have the maximum amplitude around 8 K, and these oscillations are due to Andreev interference. This variety of the amplitude of oscillations also demonstrates the reentrant behavior. This reentrant behavior of the amplitude of the oscillations has been predicted by nonequilibrium effect theory. These experimental results indicate that we can further study Andreev interference in carbon nantubes by using crossed junction structure and with superconducting and normal electrodes

First-principles study of charge transport across carbon nanotube - metal contacts

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Understanding the nature of semiconducting carbon nanotube (CNT)-metal electrode contacts represents a major difficulty toward CNT-based nanoelectronics applications. Performing large-scale first-principles matrix Greens function calculations, we investigated the coherent charge transport properties of finite (8,0) CNTs (up to 8.4 nm) and (10,0) CNTs (up to 5.0 nm) end-contacted to Au (111) electrodes at varying CNT-electrode gap distances. We find that the conductance of (8,0) and (10,0) CNTs show quite different behavior and conclude that the diameter of CNTs is an important variable in controlling the characters of charge transport across CNT-metal junctions.

Observation of magnetization drop in superconductive multi-walled nanotubes

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Superconductivity (SC) in carbon nanotubes (CNTs) is attracting a significant attention from viewpoints of both SC in one-dimensional conductors and SC in carbon-related materials. From the former viewpoint, only three groups have reported SC in CNTs including our report [1]-[3]. From the latter one, it has been found that highly B-doped diamond [4] and C_6Ca [5] could exhibit SC, interestingly.

Here, we report measurement results of magnetization in superconductive multi-walled CNTs (MWNTs). We measured magnetization in arrays of MWNTs that exhibited a sign of SC, in which resistance gradually drops from T_c with decreasing temperatures but does not saturate even at low temperatures. We found that most of such samples exhibited gradual and unsaturated drops in magnetization as temperature decreases. We will discuss correlation of this drop with Meissner effect.

[1] J.Haruyama et al., Phys. Rev. Lett. 96, 057001 (2006)
[2] M. Kociak, et al., Phys. Rev. Lett. 86, 2416 (2001)
[3] Z. K. Tang, et al., Science 292, 2462 (2001)
[4] E.A.Ekimov et al., Nature (London) 428, 542 (2004)
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Contribution F.022 - Thursday, June 22

Electronic conduction in metallic carbon nanotubes under external strain

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We have calculated conductance of finite-length metallic carbon nanotubes (CNs) containing randomly distributed long-range impurities under external strain. The conductance quantization is realized under no strain reflecting the suppression of the backward scattering due to the impurities [1,2]. We have found that the conductance is quite suppressed by the strain and shows exponential decay as the tube length increases in twisted armchair CNs and stretched zigzag CNs. This is because strain-induced modulation of electronic states around the Fermi energy gives rise to the impurity scattering. The change in the conductance suggests that the electronic conduction in metallic CNs is sensitive to external strain.

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Hot phonon generation in carbon nanotubes under electronic transport.

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We study the charge transport in carbon nanotubes on substrates using a combined Boltzmann approach for the description of electron and phonon population [1]. The scattering times involving electrons and phonons are deduced from experiment and/or from density functional theory calculations. We reproduce, without adjustable parameters, the experimental transport measurements. We find a huge increase of the optical phonon population (hot phonons) at high bias that explains the increase of differential resistance observed in the measurements.

[1] M. Lazzeri, F. Mauri, cond-mat/0603046 (2006)

Towards integrating carbon nanotubes with low-dimensional electron devices in GaAs

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We have fabricated devices with single-wall carbon nanotubes dispersed and contacted on a gallium arsenide HEMT heterostructure. A one-dimensional channel defined within the two-dimensional electron gas (2DEG) in the heterostructure can be used to probe and detect local charge transport, such as in a quantum dot [1]. We intend to use this to detect transport through the nanotubes, and similarly 1D conduction in the nanotubes may be used to detect transport within the 2DEG. This will be a new tool for making new and more complex devices to investigate low dimensional electron transport. We will report experimental progress and present data from these devices, including observations on the dispersion of nanotubes onto GaAs.

[1] M. Field et al. Phys. Rev. Lett. 70(9), 1311 (1993)

Quantum multi-connectivity in phase coherent SWNT electron transport

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As the sensitivity of nanoelectromechanical devices approaches the limits set by the laws of quantum mechanics it becomes increasingly important to consider the coherent quantum mechanical behaviour of individual devices. Here we present a theoretical study of a suspended single-wall nanotube in the fully quantum coherent regime with respect to both mechanical and electronic degrees of freedom. We show that coherent nanotube vibrations can induce an effectively multi-connected electron path through the tube. In the presence of a transverse magnetic field this gives rise to an Aharonov-Bohm type of effect and a negative magnetoresistance that can be detected through its characteristic, slow (1/T) temperature dependence. We propose that this is but one example of how employing quantum coherence in both the electronic and mechanical degrees of freedom may lead to new functionality and novel applications.

Modelling the effect of dispersed doping agents in carbon nanotubes

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Theoretical studies of how the electronic properties of a nanotube are affected by one isolated doping agent is commonly done by ab-initio electronic structure calculations. Although these calculations are essential to understand how the system responds to doping, they are by no means sufficient, since, in reality, a large disordered array of doping agents must be considered. It is then necessary to combine ab-initio techniques with less-computationally-demanding methods if one wishes to describe the real effect of doping on the electronic properties of nanotubes. Here we propose a method that makes use of ab-initio results for single impurities as an input to generate the parameters of the less-demanding tight-binding technique. The method is based on suitable sum rules for the Green functions of the impurity-free nanotubes and does not rely on any fitting scheme. The resulting parametrization allows us to describe disordered systems without losing the important contributions due to charge transfer and screening. Transport properties are subsequentially investigated.

Simulation of Carbon Nanotube Metal-Semiconductor On-Tube Heterojunction

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It is explained one of the carbon nanotube research progress in Indonesia. It is being investigated the theoretical construction of nanometer size carbon nanotube metal-semiconductor on-tube heterojunction. It is being modeled a heterojunction which consist of two Single-Walled Carbon Nanotube (SWNT) with different chiralities and electronic properties, that are coaxially connected. It has been chosen a CNT (10,10) as metallic CNT and pyridine-like n-doped CNT (17,0) as the semiconductor CNT. By using universal density of states and the way how to calculate the charge distribution in one-sided carbon nanotube p-n junction, it has been calculated the charge distribution of the heterojunction as well as its potential profile. The transmission coefficient calculation of the electron tunneling through the heterojunction is being performed in order to obtain its current-voltage characteristics.

Electrical characterisation of free standing multiwall carbon nanotubes

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Two terminal electrical measurements of freestanding multiwalled carbon nanotubes employing tunnelling contacts have been made. Previous electrical characterisation on both single and multiwalled carbon nanotubes revealed a zero bias anomaly, in which the current is characterized by a power law (V^{a+1}). In the case of single wall nanotubes this was explained within Luttinger liquid theory, the strong repulsive electron-electron interactions found in one dimension causing Fermi Liquid theory to break down. The origin of the power law in the characteristics of multiwalled nanotubes is less clear and is the subject of considerable debate e.g. [1].

Our measurements employing free standing nanotubes are quantitatively very different to all previous reports and are explained using environmental quantum fluctuations, which can give rise to power law in single junction Coulomb blockade. The size of the quantum fluctuations is strongly influenced by the high frequency impedance of the nanotube. The unique high frequency impedance in the freestanding geometry is caused by reflections, giving rise to the large quantitative difference in our results when compared with measurements made on-substrate.

[1] Kanda, A. et al. Phys. Rev. Lett. 92, 036801 (2004).

Experiments on electron transport in multi-wall carbon nanotube

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Electron transport in multi-walled carbon nanotube (MWNT) is one of the recent hot topics in the field of nanoelectronics. Most of previous experiments showed both ballistic and diffusive transport at room temperature, depending on the conditions and environment of MWNT (e.g. synthetic, contact resistance and measurement methods). Unfortunately, electron transport of a single MWNT has been not clarified because of their complex factors. Here, we have measured both freestanding and substrate-supported MWNT devices. The tungsten electrodes contacts attached to a substrate-supported MWNT were prepared using focused-ion-beam deposition technique. In case of freestanding device, we observed nonlinear current-voltage curves, corresponding to ballistic regime. In contrast, substrate-supported MWNT focuses on diffusive regime. We will discuss difference of resistivity between individual MWNT (quasi-1D or 2D) and bulk (3D) in detail.

Contribution F.030 - Thursday, June 22

Aharonov-Bohm Effects on Boltzmann Conductivity in Carbon Nanotubes

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The Boltzmann conductivity is calculated for carbon nanotubes in the presence of an Aharonov-Bohm magnetic flux with taking into impurity and electron-phonon scatterings.[1] We show that effects of strains or curvature manifest themselves as a prominent conductivity peak as a function of the flux.

A small gap is induced in metallic carbon nanotubes by the strain or curvature effects, which is incorporated in the effective mass theory as an effective flux. In the presence of magnetic flux the band gap diminishes and linear bands are restored, when the applied magnetic flux cancels with the effective flux.

A prominent peak appears in the calculated magneto-conductivity. The appearance of the peak corresponds to the absence of backscattering in metallic linear bands. The effective flux is so small that the peak can be observed easily using a conventional magnet. Various information on the curvature and strain effects and a relative amount of short-range scatterers can be obtained by careful measurement of the conductivity in the presence of the magnetic flux and by changing the electron density through a gate voltage.

Reference

[1] T. Nakanishi and T. Ando, J. Phys. Soc. Jpn. 74 (2005) 3027.

Encapsulated Vertically Grown Carbon Nano-Tubes for Submicron and Nano-Lithography

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We report a novel method of nano-lithography using electron emission of encapsulated nickel seeded carbon nano-tubes grown on Si substrate. The carbon nanotubes are vertically grown on silicon substrates using a PECVD method. The use of a plasma-enhanced chemical vapor deposition yields a well-aligned growth of carbon nano-tubes. Carbon nano-tubes are grown from the Ni catalyst islands at a pressure of 3.5 torr with a mixture of C_2H_2 and H_2 gases with 5 and 30 sccm flow, respectively. The growth occurs at temperatures ranging from 500^oC to 650^oC. The outer diameter of the tubes ranges from 50 to 100 nm in different samples and the inner diameter ranges between 5 and 8 nm. At firtst, we use standard photolithography technique to pattern Ni for CNT spot growth. The CNTs are encapsulated in a field emission transistor like structure [1]. At the next step the current emitted from CNTs is used for patterning Ni on a silicon substrate. The number of grown CNTs becomes less using electron emission from patterned CNTs for Ni patterning. After a few iteration of this procedure we could go down to the growth of only a single CNT. We then used this CNT as a tip for electron beam writing for submicron and nano lithography. For realization of emission from tips we cut them by using of chemical-mechanical polishing.

Keywords: Carbon Nano-tubes, vertical growth, patterned growth, tip growth, nano-lithigraphy

References;

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Effect of graphitic order on the electron field emission stability of carbon nanotube

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Carbon nanotubes (CNTs) are known to have excellent properties for electron field emission. However, the fundamental factors that contribute to the emission stability have not been well studied. Here, we found that stability of emission current from CNTs is directly related to their graphitic orders. We have tested various types of CNTs grown by thermal Chemical Vapor Deposition (CVD) and plasma enhanced CVD (PECVD). The field emission measurements were conducted in planar diode configuration at a vacuum level of 2.0×10^{-7} mbar. We found that the emitted currents from CNTs grown by PECVD degraded by as much as 70% within 20 hours. In contrast, randomly distributed CNTs grown thermal CVD can emit electrons at a threshold electric field as low as 1.3 V/micron. Furthermore, the initial emitted current was maintained for at least 20 hours. Both Raman spectroscopy and transmission electron microscopy indicate that the graphitic order of CNTs determines their emission stability. From these results, the upper performance limits of these CNTs for stable electron emission are determined.

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Investigation of Nanoimprint Lithography for the fabrication of carbon nanotube field emitters

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There is considerable interest in the use of multiwalled carbon nanotubes (MWCNTs) as cathodes in field emission electron sources. However, the feasibility of CNTs as field emitters requires the controlled growth of individual CNT arrays, spaced at least twice their height, directly onto an electrode/surface. This is currently achieved by means of dc-plasma CVD and electron-beam lithography (EBL) methods. The problem with EBL commonly used is that it is not suitable for mass production of the microcathodes on a wafer/large scale due to the high cost of a high throughput EBL instrument. In this work, Nanoimprint Lithography (NIL) is investigated as a simple low-cost alternative fabrication route. The resulting array of individual spaced carbon nanotube field emitters exhibited a high emission site density of $4{\times}10^5$ cm^{-2} which is well within the specification of the cathode for a field emission display. Moreover, the measured field enhancement values from the geometry of the CNTs were in reasonable agreement with the values obtained through electrical measurements. We also show that the distribution of field enhancement factor is Gaussian which is indicative of the presence of well ordered arrays of field emitters.

Field emission property of a standalone carbon nanotube encapsulated with Fe

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Carbon nanotubes encapsulated with Fe (Meta-Carbo) dispersed on the substrate show excellent field-emission properties than the conventional multiwalled carbon nanotubes (MWNTs).[1] For investigating its mechanism, the field emission properties from standalone Meta-Carbo, double walled carbon nanotube (DWNT), MWNT have been studied by a field emission microscopy (FEM). The diameters of examined DWNT, MWNT and Meta-carbo are approximately 3 nm, 10 nm and 20 nm, respectively. The turn-on voltage of Meta-Carbo is a little larger than that of DWNT but lower than that of the conventional MWNT even though the diameter of Meta-Carbo is lager. The FEM image also shows that many emission sites are distributed on the tip surface of the Meta-Carbon. The analysis of the voltage-current curves suggests that the Meta-Carbo has a lower work function value than those of MWNT and DMNT, which seems to be resulted from the formation of Fe-C in the surface layers of Meta-Carbo. It is also found that a current of as large as 10^{-5} A can emitted from the Meta-Carbo without large changes of the emission sites at the tip, suggesting a structural stability of Meta-Carbo.

[1] H. Nishino *et al* ., Proc. NT'05, p89, 2005.

Effect of series resistance on current saturation in field emission property of nano-carbon emitter

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A current saturation in current-voltage characteristics of field emission cathodes cold be explained in consideration of a series resistance of the current path. The voltage drop at the series resistance results in the rise of the electrical potential at the emission site. This causes the change in the field distribution around the emission site, and results in the decrease in the field enhancement factor β. The decrease in the potential difference between the anode and the emission site is negligible. The current increase is suppressed mainly by the change in the field distribution around the emission site. The experimental results obtained in nano-carbon emitters were well explained by this model using an appropriate value of the series resistance. These results showed that the series resistance was one of the serious limiting factors to obtaining the high current density in the field emission cathode fabricated with nano-carbon materials.

Thermal annealing effect on field emission properties of double-walled carbon nanotubes

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Three kinds of double-walled carbon nanotubes (DWCNTs) were synthesized using a catalytic CVD and a hydrogen arc discharge method. In order to grow DWCNTs by catalytic CVD, methane and THF were used as a carbon source. To synthesize DWCNTs by arc discharge, Fe catalyst and FeS promoter were used in hydrogen ambient. The as-synthesized DWCNTs were purified using a thermal oxidation in air ambient at 400^{o}C and acid treatment at room temperature. After purification, some of DWCNTs was further treated using high temperature annealing at 1300^{o}C in the vacuum chamber of 10^{-5}Torr in order to improve the crystallinity of DWCNTs.

Field emitters were fabricated on planar silicon substrates using the purified and the annealed DWCNT samples. The field emission properties showed that the emission performance of the DWCNTs grown using CVD was improved significantly after the high temperature annealing, while that of the DWCNTs synthesized using arc discharge was almost the same. The improvement of field emission performance of the CVD DWCNTs can be explained by the fact that the crystallinity of CVD DWCNTs is enhanced after the high temperature annealing. On the other hand, the emission properties of arc discharge DWCNTs reveals that the change of crystallinity of DWCNTs is negligible after the high temperature annealing because the arc discharge DWCNTs were synthesized at a high temperature.

Field emission characteristics of single- and double-walled carbon nanotubes attached on the AFM tip using a dielectrophoresis method

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The bundles of single walled carbon nanotubes(SWCNTs) and double walled carbon nanotubes (DWCNTs), which were synthesized by a hydrogen arc discharge, were attached on the tip of AFM probe using a dielectrophoresis method in order to fabricate the SWCNT or the DWCNT emitter. To dielectrophoretically attach the SWCNT or the DWCNT bundle on the AFM tip, alternating bias between the AFM tip and the planar counter electrode was applied to a solution of CNT bundles. After attaching a bundle of CNTs on the AFM tip, field emission of an individual SWCNT or DWCNT bundle was measured and investigated. The Fowler-Nordheim plot of the measured field emission current could be fitted to 2 lines with different slopes, which are corresponding to two kinds of CNT groups with different field enhancement factors. The field enhancement factor of the SWCNT emitter was nearly the same as that of the DWCNT emitter, but the density of emission site of the SWCNT emitter was higher than that of the DWCNT emitter. This result indicates that the emission current per an operating SWCNT emitter should be smaller than that of the DWCNT emitter when the same emission current is extracted from the SWCNT and DWCNT emitters. It reveals that the lifetime of the SWCNT emitter fabricated on the AFM tip may be expected to be longer than that of the DWCNT emitter. This expected behavior was observed experimentally from the lifetime measurement result of planar field emitters fabricated using SWCNTs and DWCNTs.

Investigation of field emission from multiwalled carbon nanotube yarn

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The field emission properties of multiwalled carbon nanotube (MWCNT) yarn made by a thermal CVD method were demonstrated. The MWCNT yarn was drawn from the super-aligned array of very long MWCNTs. The field emitter was fabricated by cutting the MWCNT yarn into a small segment and attaching it on a sharp metal tip. The gap between the anode and the MWCNT yarn was about 1 mm. The maximum field emission current, which can be extracted just before the destruction of MWCNT yarn emitter, was in the range of mA per one MWCNT yarn emitter. The emission current of 10μA could be extracted from the MWCNT yarn emitter up to 20 hr without any significant degradation. The emission properties of the MWCNT yarn emitter were changed during the initial subsequent voltage sweeps, and this change of emission properties can be explained by the effect of the adsorption and desorption of adsorbates on the MWCNT yarn.

Characterization of field electron emission using exfoliated carbon fibers

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Exfoliated carbon fibers (ExCFs) were prepared by rapid firing through carbon fiber-intercalation compounds. Applications of ExCFs have been studying, and unique morphology of its ExCFs has derived interesting characteristics. One of applications of its ExCFs was examined emitter. The ExCFs prepared from mesophase-pitch- and PAN-based carbon fibers electrolyzed in a 13.0 mol dm^{-3} nitric, and sulfuric acid solution were used for electron emittion. Comparison in I-V characteristics of the ExCFs and multi-wall carbon nano-tubes (MWNT) was carried out. The I-V characteristics depended on the length of ExCFs as electrodes. The results clearly indicate that the ExCFs have better current emission characteristics than MWNT. This may be due to the concentration of electric field at the tip of the ExCFs, leading to large currents.

Highly Aligned Magnetic Particles functionalized SWNTs by Magnetic Fields

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SWNTs have emerged as one of the most promising electron field emitter due to their high aspect ratio, high emission current and chemical stability. [1] For such applications, it require that CNTs be aligned over large-scale. The assembly of CNTs attached magnetic particles is one of the most challenging tasks in alignment of CNTs attached magnetic particles by magnetic field, field effect transistors, and field emission devices. Here, we present a novel method for aligning SWNTs by magnetic fields on the SWNTs-attached magnetic nanoparticles. The magnetic particles were constructed via thermal decomposition in high boiling solvent by metal chloride and sodium oleate. [2] The magnetic particles were attached to the CNTs during termal reaction precess. Electron microscopic results show that the magnetic particles functionalized SWNTs align perpendicular to the surface. We discuss the emission properties of those materials as a function of alignment. fabricated the CNTs attached magnetic particles and fixed the CNTs attached magnetic particles to use metal, such as titanium, gold, and molybdenum. Transmission electron microscope(TEM) certified that the magnetic particles are attached to CNTs and Scanning electron microscope(SEM) revealed alignment of MP-CNTs by magnetic field. We measured the field emission about alignment of carbon nanotubes attached magnetic particles. We expect that the attachment of metal particles to CNTs play an important role in the future devices applications.

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Effects of pentagons arrangement on field emission patterns of capped nanotubes

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The capped carbon nanotubes with high chemical stabilities even under strong external electric field are one of the most promising materials for making field emission devices [1] and scanning probes [2]. The sharpness of tip of the capped carbon nanotube is controlled by the number of the created pentagon rings and their relative positions at the tip. According to Eulers rule, presence of 12 pentagon rings is enough to make a carbon cage. Consequently, a carbon nanotube can be closed by presence of six pentagon rings. Depending on the diameter of the nanotubes, there are many different tip morphologies resulting from different possibilities of the pentagon rings confinements. Theoretically, it is observed that each cap structure has a specific electronic structure.

It means that the topology of the cap affects the strengths and positions of the peaks observed in density of states spectra near the Fermi energy [3-5]. Due to large curvature of the nanotubes at cap regions, in STM techniques using cone-shaped probes, the experimentalists cannot achieve a resolved atomic configuration of the cap precisely.

In our previous work, we introduced a general formalism to obtain field emission properties of any kind of nanostructures based on first principles local density of states and effective potentials [1]. The method could excellently reproduce the field emission patterns of capped carbon nanotubes observed in experiments [6,7]. It revealed that the experimental field emission images have the shape of the local density of states at the structure-vacuum barrier weighted by probability of electron tunneling. There are many different experimental field emission patterns of capped carbon nanotubes available in literatures. In present work, we explain that different patterns results from different distribution of pentagon rings. It is worth mentioning that our method gives a possibility to predict the precise atomic coordinates of the cap in the experiments by comparing the theoretical field emission images of different cap geometries with the observed ones in experiments.

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Enhanced field emission characteristics of carbon nanofibers on glass substrates by plasma treatment and multi-stage growth process

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In previous work, we have successfully synthesized vertically-aligned carbon nanofibers (CNFs) on Si substrate in an inductively coupled plasma chemical vapor deposition (ICP-CVD) system and demonstrated the improved field emission (FE) characteristics via energetic argon (Ar) plasma post-treatment [1]. Such process technique can be easily integrated with micro-fabrication process and can be scaled up for large size substrates. In this study, this process is extended on glass substrates, which are crucial for commercial applications. After plasma post-treatment, we have found that the tip-encapsulated catalytic nanoparticles are size-reduced and may re-deposit on CNFs surface through the co-sputtering/deposition mechanism [1]. This makes it possible to use post-treated CNFs (PT-CNFs) as the templates for subsequent re-growth of CNFs with smaller diameters; which enhanced FE characteristics, in the same reactor. In addition, dense CNF emitters may exhibit poor FE characteristics due to the field screening effects, which can be eliminated by decreasing the density via plasma pre-treatment. After the optimization of plasma pre-treatment (CNF density), post-treatment (sharpened CNF tips), and the multi-stage growth (re-grown CNFs of small diameters) conditions, CNFs based emitters with low turn-on field and high emission uniformity are achieved on glass substrates by this approach, which are desired for display application.

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Double-gated field emitter array with self-aligned carbon nanotubes grown by chemical vapor deposition

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We fabricated 4.75 inches diagonal field emitter array with double-gated structure in which the carbon nanotubes were synthesized by chemical vapor deposition using a gas mixture of CO and H2 at 420 °C. By using chemical vapor deposition, we were able to prepare carbon nanotube emitters inside the small gate holes with a size of 4 mm in diameter, resulting in a large number of gate holes in the pixel. It was found from current-voltage measurements that neither anode voltage nor focus gate voltage had a strong influence on the anode current. The pixel-to-pixel uniformity of the fabricated structure was measured to be about 91 %. Considering that the structure has only vertical resistive layer, it can be said that the fabricated field emitter shows quite a good uniformity. It is believed that these advantageous properties result from the small size and large number of gate holes. The fabrication of such small gate holes was possible through the use of self-aligned carbon nanotubes grown by chemical vapor deposition.

Enhancement factors of the electric field around a metallic, end-capped cylinder

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We have calculated the electrical field enhancement factor for a metallic cylinder with a hemispherical endcap in a plane capacitor geometry. The numerical results, which cover a range of different ratios of cylinder lengths and anode distances, show an important dependence of the separation between the emitter tip and the anode which is not accounted for in previous reports in the literature.

Our results can be fitted with simple functional expressions, which provide a useful scaling for calculations of field emission currents from, for example, closed cap carbon nanotubes. A comparison between the existing models in the literature and our model indicates that our formula gives better values for the field enhancement factor when the separation between the emitter tip and the anode is small compared to the emitter length.

Field Emission Properties of carbon nanotubes and carbon fibers prepared by thermal chemical vapor deposition

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Carbon nanotubes (CNTs) and fibers (CNFs) with different microstructures were adopted for field emitters which were fabricated through screen printing methods. Carbon materials with different morphologies such as entangled, straight and bundle structures were obtained from the floating catalyst method under different growth conditions and carbon sources. CNT paste for screen printing was prepared by mixing the carbon materials with solvent and silver paste. The paste was then screen printed onto the Ag electrode which was pre-patterned on an alumina substrate. After sintering in H_2+Ar atmosphere, the field emission properties of the electrode were measured. The results revealed that the emission performance of the carbon materials is bundle CNTs > straight CNTs > entangled CNTs > CNFs, which is corresponding to the crystallization of graphite layer of the tested carbon materials. The microstructures of CNTs and CNFs were studied using FE-SEM, TEM, and Raman spectroscopy, and the edge effect of cathode was investigated with different cathode configurations. In this work, a simple method to achieve lower turn-on and threshold voltages was demonstrated.

Field Emission of Carbon Nanotubes Grown by Thermal Chemical Vapor Deposition and Etched Back by dc Plasma

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We investigated the effect of NH_3 upon the synthesis of CNTs using thermal CVD, which has still been controversial. The CNTs were grown on an Invar layer coated on Si 650^{o}C using C_2H_2. The CNT synthesis seems to occur mainly through two steps, clustering of catalyst during annealing and growth of CNTs. Thus NH_3 was introduced during either annealing or growth step. For NH_3 fed only during annealing, CNTs grew longer and more highly crystalline with diameters unchanged. An addition of NH_3 during growth, however, resulted in shorter CNTs with lower crystallinity while increased their diameters. NH_3 seems to be beneficial to the synthesis of CNTs in the annealing step likely due to the etching effect of catalyst, but not in the growth stage probably due to simultaneous incorporation of N atoms into the CNT lattices. Vertically aligned, highly populated CNT samples showed poor field emission characteristics, leading us to apply post-treatments onto the CNT surface. The CNTs were treated by adhesive tapes or etched back by dc plasma of various gases to reduce the population density and the radius of curvatures of CNTs. We will discuss the morphological changes of CNTs and their field emission properties with surface treatments.

Carbon Nanotube-Based Components for High-Frequency Sources and Sensors

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Both multi-walled nanotubes (MWNTs) and single-walled nanotubes (SWNTs) are being employed in the development of high-frequency (tens of GHz to a few THz) sensors and sources. For sources, vacuum micro-tube oscillators and amplifiers are being developed using arrays of MWNT bundles as high-current-density electron sources, and for sensors, detectors are being developed using high cut-off frequency SWNT-Schottky diodes.

On the field emitter front, the previously reported high-current-density CNT bundle arrays have been successfully integrated with extraction grids using either molybdenum or conductive silicon-on-insulator substrates. The recent Mo-gate samples have produced current densities > 4 A/cm^2 at the anode with emission efficiencies up to 95%. Further electron beam optics design and fabrication considerations will be shown.

In the CNT-Schottky diode development, we have produced devices with Pt or Pd Ohmic contacts and Ti Schottky contacts using angled evaporation technique. After annealing the devices have exhibited ideality factors (n) of 1.3 to 1.5. They still suffer from hundreds of kOhms series resistance and the aging effect when tested after a prolonged storage. Again, annealing was seen to restore/improve the device performance. Details of these results along with preliminary results on alternate device fabrication schemes, and high frequency detection performance will be presented.

Fabrication of carbon-nanotube field emitter using a dip coating method

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A simple and robust dip-coating method for fabricating the carbon-nanotube (CNT) field-emitters has been proposed. The thin-multiwalled carbon-nanotubes (t-MWCNTs) synthesized by chemical vapor deposition (CVD) were dispersed in various solutions such as N,N-dimethylformamide (DMF), isopropanol (IPA), N-methyl-2-pyrrolidinone (NMP), and dichloroethane (DCE). The weak adhesion between CNTs and substrate, which was a serious drawback of the dip-coating approach, was resolved by anchoring CNTs to the substrate via melting of indium-layer. We found that uniformity and density of the CNTs could be optimized by controlling the degree of dispersion of CNTs in solvents. The field-emission characteristics were also further discussed.

Electron emission of CNTs/polymer

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Photoemission and field emission of polymer-coated carbon nanotubes (CNTs) were observed. Single-walled CNTs were positioned on the substrate either by dripping CNT-alcohol solution or coating CNT-containg paste and subsequent firing. On CNTs, MEH-PPV Photoemission was measured using visible light with wavelength variation in a vacuum chamber. Photoemission current of polymer-CNTs was greatly enhanced for the case of the single component, i.e., MEH-PPV only or CNT only. The strong electric field around CNTs may cause electron avalanche in the CNT-polymer composite resulting in high emission current. The underlying mechanism for this large photoemission will be explained in the poster.

Field emission properties of CNT/conducting polymer composite prepared by electrophoresis

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We have developed the very low cost preparation technique of the field emission cathods from conducting polymer/ fuctionalized SWCNT composite by electrophoresis. Positively charged functionalized SWCNTs and poly (3-octyl thiophene), which is denoted as P3OT, were successfully coated on the cathode with the resolution of higher than 0.01mm. We investigated the field emission properties of the above mentioned composites and discussed the biasing conditions of electrophoresis by either DC or AC coupled DC voltage. Higher current density are obtained by AC coupled DC biasing technique during the electrophoresis reproducebly. The turn-on field of the functionalized SWCNT/ P3OT composite is about 2V/μm, whereas the current density exceeds 1mA/cm^2 at about 6V/μm.

Stable Multi-Walled Carbon Nanotube Electron emitter for scanning electron microscope

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We have fabricated an individual multi-walled carbon nanotube (CNT) field emitter which can operate at low extraction voltages at a pressure of 10-3 Pa, and have investigated its emission properties. Even though the emission current reached 1.0 μA at 70 V and indicated linear behavior in Fowler-Nordheim (F-N) plots, its current fluctuation and lifetime were more than 30% and less than 5 hours, respectively. Changes in the CNT length were observed before and after field emission experiments indicating CNT evaporation. This clearly demonstrated that it is necessary to develop a new way to realize stable electron emission over a long time period. Then we attempted inserting a high ohmic resistance between the electron emitter and the power supply. As a result, the current fluctuation decreased from 30% to 2% at 0.1 μA, and the lifetime increased from 5 to 50 hours. The insertion of a high resistance was thus very effective for a long-term stable CNT emitter. Finally, in order to demonstrate the effectiveness of this procedure, we constructed an actual field emission scanning electron microscope (FESEM) optimized for a CNT emitter, and obtained a stable FESEM image with a resolution of 30 nm. We believe that a new electron microscope equipped with a CNT emitter such as our CNT-FESEM will be developed in the near future.

Simulation Study of the Beam Focus Effect for CNT Emitter based X-ray Source

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An X-ray source, which is based on the field emission electron source, is being currently developed by using carbon nano-tubes (CNTs) for the applications to biological, medical and material technology fields. In the design of triode type X-ray sources, the fine beam focus is important to acquire high resolution X-ray image. Therefore, the geometrical parameters such as electrode shapes and distances between each part must be optimized. In this study, four different shapes of triode structures were simulated and the beam focusing performances were presented according to voltage conditions of the each triode parts. Results show that the concave shape cathode structure shows the best spot size and structural simplicity among the tested in this study.

Magnetoconductance of Carbon Nanotubes with ferromagnetic contacts

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We present our results on experiments on carbon nanotubes (CNTs) with ferromagnetic contacts made from PdFe alloys.

The magnetic properties of the contacts has been studied by Lorentz-Microscopy and Squid Magnetometry.

CVD-grown CNTs were characterized by nanodiffraction in a TEM: with this technique we are able to identify singlewall and doublewall nanotube as well as small bundles.

In addition, the chirality of the bubes can be determined.

Preliminary magnetransport measurements on individually contacted CNTs were performed for different gate voltages.

The low field magnetoconductance showed a hysteretic switching. The amplitude of the low field magnetoconductance was found to be gate dependent.

In the high field magnetoconductance of multiwall CNTs we observed weak localization, from which a signature of the band structure can be extracted.

Field Emission Microscopy and in situ Transmission Electron Microscopy Studies of Carbon Nanotube Field Emitters

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Application of carbon nanotubes (CNTs) to electron emitters in field emission displays (FEDs) is now attracting considerable attention. Electron emitters in FEDs are required to provide low threshold voltages for electron emission, emission stability and uniformity. In order to seek for CNTs those satisfy the above requirements, we studied emission properties of individual CNTs by field emission microscopy and in situ transmission electron microscopy.

Contributed abstracts

June 23 (Friday)

Carbon Nanotube Biosensor for the Assessment of Personal Quality of Life

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The aim of this study is to provide home medical care facilities in distant places; this system could assist in assessing the quality of life. This system that provides medical care facilities in distant places is termed Personal QOL. Protein sensing is the key technology required for the construction of the Personal QOL system. A carbon nanotube field-effect transistor (CNT-FET) has potential for use as the above mentioned biosensor.

There are several problems associated with the use of a CNT-FET biosensor as an industrial product, namely, reliability, yield, and sensitivity.

The CNT-FET biosensor that was designed and made by us had a top-gate structure that improved its sensitivity and reliability. Moreover, the top-gate structure can function as a nondisposable biosensor.

This CNT-FET biosensor was tested for real-time sensing of pig serum albumin (PSA). PSA was detected on the basis of an antigen-antibody reaction. For PSA sensing, anti-PSA (a-PSA) was immobilized on the top-gate of the CNT-FET by physical adsorption. PSA was dissolved in buffer ($pH = 8.0$) and then reacted with the immobilized a-PSA. Our CNT-FET biosensor sensed PSA by a change in the drain current. These results will be reported in our presentation.

Gate-Position Effects on Tunable Conduction-Type Carbon Nanotube Field Effect Transistors

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In this report, we demonstrate a conduction-type-tunable carbon nanotube field effect transistor (CNT-FET) with double-gate structure (DG CNT-FET). In this DG CNT-FET, a specially designed narrow top-gate is created to modulate the energy band. In the proposed DG device structure, the top-gate and bottom-gate biases exhibit independent modulation behaviors. Depending on whether a positive or negative bias is applied to the top-gate, the CNT-FET can be operated in either n- or p-type conduction. In order to understand the extra top-gate bias effect, the FETs narrow top-gate is located at different positions, including the middle region of a single CNT, CNT the drain electrode (bias terminal) interface and the CNT-source electrode (ground terminal) interface. In these FETs, only the part of conduction path is modulated by top-gate bias and the FETs show different transfer characteristics. Based on above results, an energy band diagram conducive to the physical mechanisms of the proposed DG CNT-FET device structure is proposed and the critical portion of CNT-FETs conduction path is found. Based on the proposed model, ambipolar CNT-FETs can indeed be converted to n- or p-type-like behaviors.

Quantum dot manipulation in a single-walled carbon nanotube using a carbon nanotube gate

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A cross junction of carbon nanotubes (CNTs) separated by a thin oxide layer has been fabricated in which the top CNT is used as a local gate to control the electron transport through the lower CNT. Coulomb oscillation was observed on the lower CNT at T = 1.9 K. The gating field from the upper CNT is seen to modulate the band structure in the lower CNT, producing a double quantum dot. The ability to modulate the electronic structure of CNTs in such a way opens up many possibilities for novel electronic and logical nanodevices.

Origin and Modelling of Hysteresis in Gate-Modulated Transport in Single-Wall Carbon Nanotubes

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Transfer characteristics of gate-modulated transport in single-wall carbon nanotubes show significant hysteresis. This hysteresis has been previously attributed to a screening of the gate voltage due to movement and trapping/de-trapping of mobile charges/ions within the gate architecture. From a temperature dependence study of the hysteresis behavior, we provide experimental evidenc of an alternate mechanism, where the screening charges are injected from the nanotube itself into the surrounding dielectric. Any trapping/de-trapping mechanism does not appear to play a significant role and the experimental results can be understood in terms of a capacitive charging of the surrounding dielectric. We present a simple yet effective model to understand and analyze this phenomenon, wherein the charge injection and its subsequent redistribution has been modeled as a series RC circuit. A set of experiments validates this model, and also fits previously published data by other groups. Our work provides an in-depth picture of various parameters, which play a crucial role in modifying the transfer characteristics in nanotube FETs under different experimental conditions.

Surface Potential Measurement of Carbon Nanotube FETs using Kelvin Probe Force Microscopy

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Surface potential of carbon nanotube field effect transistors (CNT-FETs) was measured using Kelvin probe force microscopy. A clear potential image of the CNT channel with a diameter of about 1 nm was obtained by the measurement in air. The measured potential image was dependent on the sequence of the gate bias. For instance, the potential images at $V_{GS}=0$ V were different from each other depending on whether V_{GS} was changed from negative side or positive side. In addition to that, the potential showed transient behavior with a time constant of several-tens minutes. These behaviors were consistent with the drain current transient and the hysteresis of the current-voltage characteristic of the CNT-FETs.

Electron and hole injection into single-walled carbon nanotubes by using electrode metals with small and large work function

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Single-walled carbon nanotubes (SWNTs) are expected to be applied to optical and optoelectronic devices, because optical properties, e.g. photoluminescence, are clearly observed due to direct band gap. In addition, it was recently reported that optical emission from SWNT field effect transistors (FETs) due to the recombination of electrons and holes that are simultaneously injected at the opposite contacts into a SWNT was observed. In this study, we fabricate SWNT film FETs with large (Ni) and small work (Mg) function metal as source and drain electrodes, respectively, and electrons and holes are injected from source and drain electrodes. When the FETs with same kinds of metals as source and drain electrodes, unipolar characteristic is obtained; i.e., p-type and n-type characteristics are obtained for the devices with large (Ni) and small (Mg) work function metal, respectively. On the other hand, for the devices with Ni and Mg metals as source and drain electrodes, respectively, electrons and holes are injected at the opposite contacts. There is possibility that this device can be applied to simultaneous injection of electrons and holes into SWNTs.

Mechanism of metal-semiconductor transition in the electric properties of single-walled carbon nanotubes induced by low-energy electron irradiation

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Our previous study showed that low-energy electron irradiation converts the electric properties of metallic single-walled carbon nanotubes (SWNTs) to semiconducting [1]. That is, an off-region appears in the drain current-gate voltage characteristic after irradiation, although initially the device shows an almost gate-independent characteristic. Moreover, the off-region width can be tuned by controlling the irradiation dose. In this work, the mechanism of the metal-semiconductor transition was studied.

Low-energy electron irradiation causes damage to SWNTs [2]. We found that the defects act as an energy barrier of several ten meV for carriers. We also showed that gate-induced band bending of several ten meV can easily occur even in a metallic SWNT, owing to the low density of states at the Fermi level. The metal-semiconductor transition can be reasonably understood in terms of the formation of the energy barriers and the barrier height control by the gate-induced band bending.

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Conversion of p-type nanotube field effect transistors to n-type by a simple treatment in air

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Single-walled carbon nanotube field effect transistors (SWNT-FET) usually show only p-type characteristics in air. We found that a very simple amine-treatment can convert them into n-type characteristics. The mechanism of the conversion was also studied.

Twenty one SWNT-FETs with Ti/Au or Pd drain and source electrodes and a back-gate electrode were fabricated by using conventional lithography techniques. The Ti/Au and Pd electrodes form a medium and a high energy barrier for electrons in the SWNTs, respectively. Initially, the devices showed p-type characteristics in air, as usual.

The APTES ($NH_2(CH_2)_3Si(OEt)_3$) solution was dropped onto the devices and then the sample was rinsed in toluene. After this simple treatment, all the devices showed n-type or ambipolar characteristics in air. A shift of the threshold gate voltage with increasing doping concentration was observed. On the other hand, from the temperature dependence of the device characteristics, the barrier height at the contact was found not to be significantly lowered. These results mean that the conversion is mainly due to electron transfer from APTES molecules to the SWNTs.

Fabrication of carbon nanotube sensor for toxic gas under clean air

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We report the technique for assembly of carbon nanotube sensor using dielectrophoresis and characterization for gas detection at room temperature. The position and number of multi-walled and single-walled carbon nanoatubes for device were controlled by applied magnitude of frequency and voltage based on the solution density, and kinds of applied current. We compared sensing results with sulfur dioxide and nitrogen dioxide gas under both N_2 and clean air environment. This sensors detected those gases to sub ppm level. The response time of the sensor was generally about 50~200s.

Preferential Growth of Semiconducting Carbon Nanotubes Using Grid-Inserted PECVD

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Single-walled carbon nanotubes (SWNTs) were grown using grid-inserted plasma-enhanced chemical vapor deposition (PECVD). The field effect transistors (FETs) were fabricated using the PECVD-grown SWNTs. Many FETs showed good pinch-off I-V characteristics even though they have many SWNT channels bridging between the source and drain electrodes. This result suggests the preferential growth of the semiconducting SWNTs. Based on the electrical breakdown of the metallic nanotubes and the SEM observation, the probability of growing the semiconducting nanotubes has been estimated to be more than 90 %.

Memory effect in carbon nanotube based devices

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The ongoing race to implement nano-scale materials such as single walled carbon nanotubes into logic devices is steadily making progress. One of the interesting applications of nanotubes would be to utilize their exceptional properties to create high density memory elements. We are studying the possibilities to create such a memory element by placing charge traps in the vicinity of a nanotube device. The aim is to place the charge traps at well calibrated distances from the nanotubes, so that they can be addressed in a controlled way with high device reproducibility. The project is made in collaboration with Esko Kauppinens group at HUT.

High performance n-type single-walled carbon nanotubes with magnetic-metal encapsulation

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Magnetic Fe particles with diameter less than 1 nm have successfully been filled in single walled carbon nanotubes (SWNTs) by using ferrocene as the staring material. The encapsulation of Fe particles in SWNTs has been confirmed by transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDX), X-ray photoelectron Spectroscopy (XPS) and Raman spectroscopy. Magnetic properties of Fe-filled SWNTs are characterized by means of a quantum design MPMS-5 superconducting quantum interference devices (SQUID) magnetometer in the temperature range of 5~300 K. Electrical properties of Fe-filled SWNTs are studied by fabricating them as the channels of field-effect transistors (FETs) devices. Our results reveal that Fe-filled SWNTs are found to exhibit high performance unipolar n-type semiconducting characteristics with on/off ratio of $\sim 10^6$. In contrast, ferrocene-filled SWNTs show an interesting ambipolar behavior. Moreover, a Coulomb blockade phenomenon is significantly observed on Fe-filled SWNTs when the temperature is cooled down below 120 K, which indicates that they exhibit excellent single-electron transistor (SET) characteristics due to the Fe particle encapsulation. Our current results demonstrate that it is possible to make ferromagnetic semiconducting SWNTs which are anticipated to be a promising candidate for new spintronic devices.

Synthesis and electrical transport properties of Cs-encapsulated double-walled carbon nanotubes

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In this study, the synthesis of Cs-encapsulated double-walled carbon nanotubes (DWNTs) is realized for the first time through a plasma irradiation method. The formation of Cs-filled DWNTs is confirmed by transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDX), and Raman spectroscopy. Electronic transport properties of both pristine and Cs-encapsulated double-walled carbon nanotubes are investigated by fabricating them as the channels of field-effect transistor (FET) devices. Our results indicate that Cs-filled DWNTs can exhibit high performance n-type characteristics in contrast to ambipolar behavior of pristine DWNTs. Coulomb blockade oscillations are observed on the Cs-encapsulated DWNTs at low temperatures. In addition, we have made a comparison between the electronic properties of Cs-encapsulated DWNTs with different filling level obtained by adjusting the plasma irradiation conditions, and find high DC bias voltages applied during the plasma process can lead to forming unipolar n-type semiconducting DWNTs.

Electronic transport properties of single-walled carbon nanotubes modified by alkali-metal encapsulation via a plasma ion irradiation method

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Single-walled carbon nanotubes (SWNTs) have strong potential in fabricating novel nano electronic devices by combination with other foreign molecules and atoms, owing to their unique one-dimensional structure and electronic properties. Here, we present electronic transport properties of SWNTs modified by filling (encapsulating) alkali-metals or alkali compounds, such as Cs, Li, Na, K, KCl and CsI, via a plasma irradiation method. Our results indicate that the SWNTs electronic properties are greatly modified by the alkali-metal encapsulation. Compared with p-type pristine SWNTs, ambipolar or unipolar n-type SWNTs (even in air) are obtained due to the charge transfer between these electron donors and SWNTs at room temperature. The property conversion of SWNTs from p-type to n-type can be controlled by adjusting the plasma irritation time. In addition, a Coulomb oscillation phenomenon is clearly observed for the n-type SWNTs at low temperatures, and the quantum dot size is estimated to be about 20 nm. More importantly, in our case, p-n junctions in SWNTs tend to be created by means of selectively doping electron donors (such as Cs) and electron acceptors (such as I) though the alkali-halogen plasma irradiation method.

Carbon Nanotube and Silicon Nanowire Molecular 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 and Si NWs were grown using CVD from patterned catalysts, followed by deposition of Ti/Au electrodes. The nanotube and Si nanowire devices have been integrated with a PDMS-based microfluidic sample handling system to enable controlled delivery of microliter to nanoliter sample volumes to the sensors. Chemical functionalization processes were developed using oxysilane APTES linker molecules to attach amino acid oxidase (AAO) receptors to Si/SiO_2 nanowire surfaces, as well as the oxide surfaces adjacent to the CNTs. Microfluidic measurements show that both bare and functionalized Si NWs operate as sensitive nanoscale pH sensors. The AAO-functionalized Si nanowires have been used to measure amino acid levels down to 1 μM concentrations. The CNT devices with AAO receptors attached to the adjacent oxide surface were also found to act as sensitive detectors of amino acids.

Non-volatile Memory Operation in Ferroelectric gate carbon nanotube transistors

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Nanoscale electronic devices using carbon-nanotubes are expected as future sensing or computing applications. In this study, we describe the fabrication and electrical characteristics of single-wall carbon nanotubes field effect transistors (CNT-FETs) with ferroelectric thin films as gate insulators. The ferroelectric-gate CNT-FETs were fabricated using single-wall CNTs synthesized from alcohol by catalytic chemical vapor deposition and sol-gel derived $PbZr_{0.5}Ti_{0.5}O_3$ thin films. The ferroelectric-gate CNT-FETs showed modulation of the drain current with the gate voltage and the threshold voltage shift (memory window) on the drain current-gate voltage characteristics. This result indicates that carriers in CNTs are controlled by spontaneous polarization of the ferroelectric films. Because ferroelectrics exhibit complex couplings between their electrical, structural, mechanical, thermal, and optical properties, and because CNTs have unique mechanical and electrical properties, ferroelectric-gate CNT-FETs offer promise as potentially useful nanoelectronics devices not only for nonvolatile memory elements but also for high-sensitivity sensors.

Growth of SWNTs lying on substrate by double-layered catalytic configuration and devices characterizations

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The double-layered catalytic configuration1 including of nickel (Ni) and silicon dioxide (SiO_2) was used to grow single-walled carbon nanotubes (SWNTs) lying on substrate in a thermal pyrolysis CVD system at 800-900 ^{o}C fed with a mixed gas flow of methane (CH_4) and hydrogen (H_2) [1]. The SiO_2, as the upper layer on Ni pads, was observed not only to play a role as a barrier to prevent vertical growth, but also to serve as a porous medium for Ni catalyst nanoparticles to be embedded. Using the conventional photolithography technique followed by a thin film evaporation and lift off, three kinds of device structures with as grown SWNTs were fabricated to be back-gated carbon nanotube field-effect-transistors (CNTFETs). The CNTFET structure with a thin oxide shows ambipolar transport. However, the undesirable ambipolar transport can convert to unipolar transport by using the other symmetric and asymmetric field-effect-free-on source and drain structures [2]. These unipolar characteristics were consequently resulted from the structure electrostatic engineering. Recently, the selective diameter distribution of as-grown SWNTs by changing the condition of upper oxide layer of double-layered catalytic configuration was also observed [3]. The variability of the diameter distributions of SWNTs and its mechanism as well as its impact in the SWNTs-based nanoelectronics will be also important.

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The fabrication of suspended single-walled carbon nanotube electronic devices directly on vertically-aligned carbon nanofiber templates and the electrical characteristics

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In our previous work, we have developed a new method to directly synthesize suspended carbon nanotubes (su-SWNTs) crossing the tips of vertically-aligned carbon nanofibers (CNFs) which were sharpened by energetic argon plasma [1]. Via this approach, here we demonstrate the fabrication of electronic devices of novel su-SWNTs-on-CNFs structure and investigate the nano-sized contact between su-SWNT and CNFs as well as the electrical characteristics. Highly n-doped (phosphorous) poly-Si, due to its similarity to p-type single-crystalline Si substrate we used before, is demonstrated a good choice of under-layered electrodes for the fabrication of su-SWNTs-on-CNFs electronic devices. The electrical characteristics, including two (source/drain), three (source/drain/bulk-gate), and four (source/drain/bulk-gate/local-gate) terminal measurements reveal the electronic device features, such as hysteresis-free electrical transport, negative differential conductance, etc. Furthermore, we use multiple nano-probes to exert electrostatic forces, and in-situ observe the deformation of su-SWNTs in a scanning electron microscope to investigate the contact between su-SWNT and CNFs.

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GHz operation of active self-assembled Carbon Nanotube Field-Effect Transistors analysed by S-parameters measurement

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Carbon nanotube field-effect-transistors are expected to operate at extremely high frequencies up to the THz. Yet, their high impedance makes difficult the evaluation of their dynamic behaviour. Using a dedicated wet self-assembling technique we prepared Field-Effect Transistors consisting of a number of carbon nanotubes in parallel in a back-gate configuration using a very thin gate insulator. We succeeded in measuring the scattering parameters of those CNTFET with a good accuracy up to a few GHz. The active AC properties of CNT-FETs are indeed demonstrated up to at least 8-10GHz establishing a new state of the art. We demonstrate in particular a ft above 8GHz and a Maximum Stable Gain of 10dB at 1GHz. From these measurements, a small signal equivalent circuit is established for the first time for the CNTFET in the dynamic regime. The extraction procedure and the determination of the intrinsic AC elements of CNT-FETs are detailed1 and routes for improving practically the frequency range of active operation of the CNTFET are proposed.

1 J.M. Bethoux et al IEEE trans. Nano 2006 in press.

poster or oral

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We present temperature and tip-nanotube overlap area dependence of I-V characteristics of scanning tunneling microscope tip (metal)-carbon nanotube (semiconductor) junction by developing an algorithm for its I-V characteristics. The temperature and tip-overlap area parameters are varied within experimental range and their specific effects are described. The results reveal that the forward threshold voltage increases with decrease in temperature and decreases with large tip-nanotube overlap area. The current increases with increase in tip nanotube area, and is pronounced at high temperatures. The dependence of I-V characteristics on temperature is mere and the increase in current is more pronounced at large surface overlap area between tip- and nanotube.

Surface Potential Measurements of CN-FETs with Two Different Metal Electrodes Studied by Kelvin Probe Force Microscopy

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Since the electrical characteristics of carbon nanotube field effect transistors (CN-FETs) are dominated by the electronic states at the interface between the SWNTs and the metal electrodes, the analysis of these states are essentially important. We fabricated back-gate type CN-FETs by use of a dielectrophoresis method. The SWNTs connected two different metal electrodes (titanium and gold), between which the difference in work function is relatively large. The CN-FETs showed a rectifying property and ambipolar behavior. We also investigated the surface potential of the working CN-FETs in vacuum by Kelvin probe Force Microscopy. The potential profiles along the SWNT channel obtained from the measurements with various bias voltages revealed the Schottky barrier model.

Spontaneous self-clustering of glycines on single walled carbon nanotubes and their specific bindings to alcohols

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High electron densities and proper Fermi energy levels of carbon nanotubes readily permit spontaneous charge transfers to specific organic and inorganic guest molecules, resulting in the formation of chemically grafted molecular layers or nanoclusters. Glycine, the simplest amino acid, has been spontaneously adsorbed on single walled carbon nanotubes (SWNTs) to form self-assembled nanoclusers. Self-clustering of glycine is believed to be initiated by specific interactions between carbon nanotubes and amine groups of glycines. Therefore, the size of nanocluster is linearly proportional to the concentration of glycine and the reaction time. Glycine is known to interact with alcohols strongly since it plays an important role in alcohol digestion in a stomach as well as in signal transduction in a brain.

Combining self-assembled glycine nanoclusters together with carbon nanotube field effect transistors (SWNT-FETs), selective bindings of alcohols have been monitored. Upon the exposure of isopropanol (IPA) to the glycine coated SWNT-FETs, the devices show unusual transport characteristics, i.e. they loose gate dependency, as confirmed by IDS-VGS characteristic curves. The devices are then completely recovered from anesthesia by natural evaporation in air or under pressurized Ar flow. The modulation of electrical properties of SWNT-FETs upon alcohol adsorption and desorption can be repeated multiple times without loosing the original transport characteristics. The simulation results about the mechanism of the modulation of gate dependency also will be introduced.

Flow rate detection by single SWCNT in the micro channel

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We describe a flow rate detecting ability of SWCNT nanoelectrode in microchannel. It will be a kind of nano flow sensors. We injected the DI water and 0.5M and 1M HCl solution into the microchannel with changing the flow rate. The increased flow rate of each solution induced the voltage. The induced voltages were increased gradually in high flow rate and high ion concentration fluid. Original data made the ratchet shape and showed that the relatively higher peak depends on the increasing liquid velocity.

The flow sensor using SWCNT bundle in glass tube of diameter such as the several cm had been reported. But we detected flow rates by the single SWCNT in the microchannel. The electric trend of both systems showed very similar results.

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Exciton Effects in Boron-Nitride Nanotubes: Theoretical Study

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Optical studies in carbon and boron-nitride (BN) nanotubes are being in progress intensively. The investigations are on the experimental side as well as on the theoretical side. In this talk, we will discuss exciton effects in single-wall BN nanotubes. Linear absorption spectra are calculated with changing the (n,m) geometries of the nanotubes. We consider the model used in [1]. Exciton effects are calculated using the CI technique [2]. The Coulomb interaction dependence of the band gap, the lowest exciton energy, and the binding energy of the exciton are discussed for the zigzag nanotubes. The optical gap of the (5,0) nanotube is about 6 eV at the onsite interaction U=2t with the hopping integral t=1.2 eV. The binding energy of the exciton is 0.50 eV for the same parameters. This energy agrees well with that of other theoretical investigations. We find that the energy gap and the binding energy are almost independent of the (n,m) geometries of the nanotubes. This novel property contrasts with that of the carbon nanotubes which show metallic and semiconducting properties depending on the geometries. Comparison with recent experiments will be discussed in the talk.

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Carbon nanotube as optical and THz nanoantenna

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An intriguing electromagnetic problem of nanoscience is the realization of nanoscale antennas for infrared and visible light. Such an antenna would allow a very desirable modality of communications between nanoelectronic devices and the macroscopic world. The idea of CNT nanoantennas is definitely attractive [1]. A theory of antenna effect in a finite-length isolated SWCNT is developed over a wide frequency range from terahertz to ultraviolet. The theory is based on a quantum-mechanical microscopic model of the conductivity and the rigorous formulation of electrodynamic boundary value problem for a finite-length CNT (the Leontivich-Levin equation for the induced surface current density). The polarizability scalar of an isolated finite-length CNT in the low-frequency regime is evaluated analytically and analyzed. The resonances of strongly retarded surface waves caused by the edge effects are revealed. The theory describes qualitatively recent measurements of constitutive parameters of CNT-based composites. The radiation pattern of a CNT antenna is calculated and some possibilities for pattern control are examined along with practical methods of exciting CNT nanoantennas. The analysis forms a basis for the design and development of CNT nanoantennas in different frequency ranges and to estimate the effective constitutive properties of CNT-based composites.

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Temperature dependence of photoluminescence and the role of dark excitons in SWCNTs

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We report experimental evidence for transfer between bright and dark exciton states in SWCNTs from a detailed study of the temperature dependence (1.5K to 250K) of the photoluminescence (PL) emission at both zero and high magnetic fields (19.5T). At zerofield PL emission is found to peak at temperatures between 20 and 100K, depending on the chiral indicies of the tube. At high temperatures the PL emission change is dominated by the temperature dependence of the radiative lifetime for a parabolic 1-D exciton ($T^{1/2}$), thus showing that dark excitons do not play a significant role in high temperature PL. At lower temperatures the emission falls due to an enhanced probability for excitons to populate the dark-exciton states. Analysis of the temperature dependence of the emission intensity suggest that the dark-light exciton splitting is strongly tube diameter dependent and is much smaller than has previously been suggested, with values in the range 1-5meV. This small splitting suggests that the majority of transfer to the dark exciton states takes place within the spin-singlet bands. When a high magnetic field is applied the PL is no longer suppressed at low temperatures, suggesting that the magnetic field acts to lower the probability of excitons populating the dark states.

Low temperature magneto-photoluminescence of SWCNTs

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We report a detailed study of the magneto photoluminescence (PL) of SWCNTs at low temperatures in fields perpendicular and parallel to the axis of the tubes using photoluminescence excitation (PLE) maps. We give findings on both PL emission intensity changes and band gap shifts. The PL intensities were found to be strongly enhanced by magnetic field at 4.2K, the magnitude of which was strongly diameter dependent with the largest enhancements (by factors of up to 2.5 in 19.5T) observed for tubes aligned perpendicular to the field. We attribute these enhancements to the lowering of the probability that excitons populate the dark states as we observe the opposite effect - a suppression of PL emission from tubes at zerofield. Red shifts of the band gap of tubes parallel to the applied field were observed at 4.2K and are consistent in magnitude with those predicted by the Aharanov-Bohm (A-B) effect. The use of PLE mapping also allows us to confirm the diameter^2 behaviour of these shifts. For tubes aligned perpendicular to the applied field we also observe distinct red shifts of the band gaps at 4.2K, which cannot be explained by the A-B effect.

Chirality dependence of the exciton effects in single-wall carbon nanotubes

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We have studied the excitation properties in single-wall carbon nanotubes by solving the Bethe-Salpeter equation [1,2] within the simple and extended tight-binding models [3]. The quasiparticle energies are treated within the conventional screened Hartree-Fock approximation [4]. The $2n+m$ =constant family behavior is found in the excitation energy, binding energy, wave function length, and the environment induced excitation energy shift. This family behavior is understood by the trigonal warping effect around the K point of graphite [5]. The screening effect from the electrons of carbon nanotubes is found to be essential in explaining the small energy shift by environment. The large family spread in the excitation energy Kataura plot is found to be mainly from the single-particle energy. Using the exciton wave functions, we will discuss exciton effects in resonance Raman spectroscopy intensities [6].

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Resonance window for Raman Scattering of Single Wall Carbon Nanotubes

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Resonance Raman intensity has recently been calculated by considering electron-phonon interaction [1]. In the previous calculation, resonance window parameter appeared in the energy denominator, igamma, was considered to be constant. However, when we see resonance Raman profile, the resonance window values (gamma hereafter) show strong chirality dependence. By calculating the life time of carriers [2], we calculated gamma value as a function of (n, m). When we compare the calculated results with experimental one, we found that while gamma values for semiconducting carbon nanotubes show good agreement, gamma values for metallic carbon nanotubes observed in the experiment are larger than the calculated ones. We expect an additional decaying process, e.g. interaction with plasmon, in metallic carbon nanotubes.

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Creation of mid-gap luminescent states in single-wall carbon nanotubes by weak UV illumination

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We have found that the electronic structures of semiconducting single-wall carbon nanotubes (s-SWNTs) can be substantially altered by a quite simple method [1]. Under relatively weak UV illumination (<4 mW/cm^2), their photoluminescence (PL) spectrum undergoes a dramatic change: the original PL peaks assigned to S_{11} transitions considerably decrease, while new and broader peaks emerge at the lower energy. This phenomenon occurs only for s-SWNTs that are well dispersed either in solution or in solid film using surfactants or polymers. The coincidence of the threshold in the action spectrum of this UV-induced change with the absorption edge of the dispersant demonstrates that the UV excitation of the dispersants triggers this phenomenal change. Hence the creation of these mid-gap luminescent states is attributed to chemical reaction between s-SWNTs and the UV-excited dispersant. This study clearly demonstrates that even mild UV illumination can strongly alter the electronic properties of dispersed SWNTs. The thus developed method may find applications in SWNT semiconductor technologies, especially for the design and control of their optoelectronic and electric functionalities.

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Light-harvesting function of carotenoids inside carbon nanotubes

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Single wall carbon nanotube (SWCNT) is an attractive platform for optoelectronic device applications. Development of a technique to harvest light energy in the spectral region where semiconducting SWCNTs have a low extinction coefficient will lift the limitation of their optoelectronic properties. Carotenoids do exhibit a light-harvesting function in photosynthesis. In this study β-carotene was encapsulated in SWCNT, and we found that encapsulated β-carotene can harvest light energy to SWCNT. The detailed structure of encapsulated β-carotene has been clarified by X-ray diffraction and polarization dependence of absorption spectra. Photoluminescence spectra revealed the energy transfer from the excited state of β-carotene to SWCNT. The observed excited energy transfer from encapsulated molecules to SWCNT will stimulate the development of dye-encapsulating SWCNTs as novel optoelectronic materials.

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Observation of Strong Third Harmonic Generation from Single-Walled Carbon Nanotubes

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Single-walled carbon nanotubes (SWCNT) with few nm diameters are the important new nano-scale functional materials due to their stable chemical structure, yet relatively strong interaction with irradiated optical field or applied electric field. To be realized as an actual device, the effective nonlinear optical response to intense laser light is needed to be studied for understanding the basic physics and electronic/optical functionalities. Using the intense femtosecond laser pulses in near infrared, we observed relatively strong third harmonic generation (THG) in visible region. Our THG signal were strong enough to be measured with a simple portable spectrometer without using a complicate gated lock-in amplifier technique as reported in literature. The SWCNT sample was prepared in bulk especially without using a substrate in order to completely remove the effect of the even stronger THG from the substrate. We expect the nonlinear optical characteristics of SWCNT would be one of the key elements in developing CNT based nano devices such as optical display, sensors, detectors, etc.

Optical Absorption Spectra in Carbon Nanotubes

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We have calculated the optical absorption spectra of carbon nanotubes within the density matrix formalism using the full tight-binding expression for the single-particle wave functions. This approach allows us to include many-particle interactions like excitonic effects and relaxation processes in a consistent way. First, we discuss the absorption coefficient for arbitrary nanotubes within the single-particle picture. For the special case of zig-zag nanotubes the absorption coefficient can be given analytically. We discuss the nanotube family behavior and the effects of trigonal warping on the transition energies and matrix elements. It can be shown that the widely-used approximation of constant matrix elements leads to a reduction of the optical absorption at small energies (approx. $E < 6$eV). The ratio between the absorption intensity of the first two transition energies changes with increasing chiral angle; it increases for -1 tubes, but decreases for +1 tubes. Zig-zag (n,0) nanotubes with n even have a characteristic optical peak at 5.4 eV that dominates in intensity over the other transitions. Within the tight-binding model these zig-zag nanotubes have a subband that is free of dispersion, which gives rise to the intense peak at 5.4 eV. Finally, we show how to extend our approach to include the Coulomb interaction (excitonic effects) and give some first results.

Mapping luminescence intensity from carbon nanotubes in the extended IR range

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A simple and efficient technique has been developed for measuring photoluminescence excitation (PLE) maps from carbon nanotubes (CNTs) in the extended IR range (900-2300 nm). It consists of preparing a CNT/surfactant/gelatin film and measuring PLE spectra using a tunable Ti-sapphire laser (695-1050 nm excitation range) and a FTIR spectrometer, equipped with an IR-enhanced InGaAs detector. The proposed sample preparation procedure allows to avoid undesirable IR absorption due to the solvent, yet preserving well-dispersed CNTs in an optically homogeneous film. This procedure has been applied to a wide range of commercial (HiPCO, CoMoCAT, Carbolex, Nanoledge, etc) and home-made single- and double-wall CNTs yielding chirality and diameters distributions. Note that those parameters are rather important both for synthesis and applications, but they are very difficult to obtain by existing methods. The reliability of the obtained results has been further supported by optical absorption and X-ray diffraction measurements. The advantages of the applied macroscopic techniques over the commonly used microscopic measurements (Raman, TEM), as well as the concomitant problems associated with deducing the CNT diameter and chirality distributions, will be discussed. In particular, strong dependence of PLE diameter distribution on the sample preparation will be demonstrated.

Cross-polarized absorption of single-walled carbon nanotubes by photoluminescence excitation spectroscopy

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Photoluminescence excitation (PLE) spectroscopy of single-walled carbon nanotubes (SWNTs) have been extensively studied for characterization of their unique electronic properties. In this report, we have studied polarized PLE spectra of various (n, m) nanotubes in surfactant suspension. Using a simple theory for PL anisotropy, we have obtained decomposed PL maps for parallel and perpendicular polarization from two PL maps measured by so-called L-format method [1]. Distinct absorption peaks corresponding to E12 and E21 transitions for perpendicular polarization were observed. Observed E12 and E21 energies compared to E11 and E22 were considerably blue-shifted than the single-particle expectation within tight-binding calculation of SWNT considering geometry optimization and curvature effect [2]. This qualitative discrepancy between measurement and single-particle calculation is attributed to smaller exciton binding energy for cross-polarized excitation.

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Optical switching of polymer functionalized carbon nanotube transistors

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Carbon nanotube transistors can emit or detect photons at wavelengths defined by the nanotube chirality. To extend their capabilities in optoelectronics, it is important to be able to tune these wavelengths independently of the nanotube structure. A way to achieve such a goal is to chemically functionalize the nanotube with molecules that bring their optical properties to the device. In the present study, we demonstrate that drastic photo-induced modifications of the electrical characteristics of self-assembled nanotube transistors functionalized by photoactive polymers can be achieved. We show that the polymer film acts as a wavelength dependent 'optical gate', which is significantly more efficient than a conventional electrostatic gate. The process impacts both the on- and the off-states of the transistor with a maximum change of conductance reaching four orders of magnitude between the dark and illuminated states. Depending on the applied biases and polymer characteristics the device can be optimized as a memory element or as a fast optical switch. The switching mechanism involves the creation and separation of photo-excited charges in the polymer, the spatial distribution and relaxation rates of which are studied, taking advantage of the very high charge sensitivity of nanotube transistors. The possible applications of these optically gated transistor will be discussed.

Photoluminescence of carbon nanotubes grown over trench

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The optical properties of single-walled carbon nanotubes (SWNTs) grown over trench are sensitive to environmental atmosphere [1, 2]. We have compared E_{11} and E_{22} of the SWNTs over trench with those of SDS-wrapped SWNTs reported by Weisman et al. [3] for 20 chiralities of semiconducting SWNTs with branch index 23-32. The energy difference depends on the chirality, in particular, on the chiral angle. This can be explained by the chiral angle dependence of effective mass. We have also investigated the time evolution of E_{11} and E_{22} after the growth of SWNTs, which showed step-like shifts after several days.

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Magnetic Brightening of Dark Excitons in Carbon Nanotubes

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To gain insight into the internal energy structure and radiative properties of excitons in single-walled carbon nanotubes, we have studied photoluminescence from individualized HiPco and CoMoCAT samples as a function of magnetic field (B) and temperature (T). In pulsed-field experiments (<60 T), we used film samples and varied T from 4.2 K to room temperature; photoluminescence intensity increased, or “brightened,“ with B and the amount of brightening decreased with T. In steady-field experiments (<45 T), we used micelle-suspended nanotubes at room temperature; photoluminescence peaks showed B-induced splitting with B-dependent relative intensities. These results are consistent with the existence of a dark state below the first bright state [1]. Magnetic flux removes K-K valley degeneracy, producing two equally-bright states at high B [2,3]. We calculate photoluminescence spectra through B-dependent effective masses, populations of finite-k states, and acoustic phonon scattering.

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Photo Luminescent of Double Wall carbon Nanotubes

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Photo luminescence of carbon nanotubes has been a powerful tool to investigate electronic structure and chirality assignment. This measurement has been applied to mainly SWNTs revealing that the electronic structures are greatly perturbed by the outer environment. For example, the emission of SWNTs shows a red shift when the dispersion surfactant is changed from SDS to cholate, which has been explained by enhancement of interaction between the SWNTs and the surfactant. In terms of this perturbation, DWNTs is one of the most interesting systems, inner layers of which are perfectly surrounded by their outer layers. The inner layer could be isolated from the environment or could be strongly modified by the outer layers. Furthermore, the inner layer of DWNTs is one of the fascinating candidates for nano electronic devices with perfectly surrounded FET channel by the outer gate layer. To investigate these problems and the electronic structures, we present here the photo emission spectra of the inner layer of DWNTs produced and purified by a high-temperature pulsed arc discharge with higher purity and narrow diameter distribution [1]. The results show that inner layer is strongly affected by the outer environment as if the outer layer did not exist.

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Photoluminescence Quenching in Peapods-Derived Double-Walled Carbon Nanotubes

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Photoluminescence (PL) behavior of peapods-derived double-walled carbon nanotubes (DWNTs) as the simplest form among multi-walled carbon nanotubes (MWNTs) is investigated. Even though the optical absorption and the resonant Raman spectra show the characteristic features of DWNTs, the PL signals originated form DWNTs are severely suppressed. This feature is resultant from effective interaction between the inner and the outer tubes that efficiently quenches the PL signals of the DWNTs.

Optical Studies of Carbon Nanotubes and Nanographites

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Resonance Raman and photoluminescence excitation (PLE) spectroscopies are used to study the optical properties of different types of carbon nanostructures such as single-wall and double-wall carbon nanotubes and nanographites. The Raman measurements were performed using a quasi-continuous set of excitation laser lines between 1.6 and 2.7eV. We will discuss the (n,m) dependence of the optical transitions and the influence of the dispersion and the different wrapping agents. We will also report PLE measurements in different samples of carbon nanotubes, where both direct and phonon-assisted optical transitions are observed. The results give new evidences that the optical transitions in nanotubes are associated with excitons and coupled exciton-phonons. We show that the excitonic effects are weaker for the E33 and E44 transitions, the energies being blue-shifted when compared to earlier predictions. We also analyze the intensity of the disorder-induced D band in nanographites, an important tool for defect characterization in graphitic materials, as a function of the nanographite in-plane crystallite size (La) and the laser excitation energy.

Photoluminescence imaging of suspended single-walled carbon nanotubes

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Single walled carbon nanotubes (SWNTs) suspended over trenches are imaged using their intrinsic near-infrared (NIR) photoluminescence (1.0 to 1.6 μm). Emission is observed from extended suspended lengths (~50 μm) with micron scale spatial resolution. The images are in addition spectrally resolved, combining nanometer scale spectral resolution with micron scale axial spatial resolution. SWNTs are classified based on the spatial uniformity of their emission intensity and emission wavelength. Chirality changes with preserving nanotube diameter are shown in two cases. Most SWNTs imaged on millisecond timescales show steady emission, but a few fluctuate and suffer a reduction of intensity. The internal quantum efficiency is estimated at 8%, which is dramatically higher than previous reports.

Photoluminescence from Double-Wall Carbon Nanotubes Synthesized by the Zeolite-CCVD Method

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Photoluminescence (PL) from purified double-wall carbon nanotubes (DWNTs) is reported, which have been synthesized by zeolite catalyst-supported chemical vapor deposition (Zeolite-CCVD). The PL contour mappings for various ratios (1-90 %) of double- versus single-wall carbon nanotubes by thermal oxidation have enabled us to identify the PL from inner tubes. PL from inner tubes of DWNTs was observed separately from that of SWNTs during the purification process.

Z-scan measurements of nonlinear optical properties of single wall carbon nanotubes

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Large non-linearity and high-speed response for incident light are highly required for optical switching devices. Recently, it has been proved that carbon nanotubes are a promising optical material due to their absorption ability in a very wide range of wavelength from the ultraviolet to the infrared. In this study, we have investigated the non-linear transmission and non-linear reflection of single wall carbon nanotubes by using the z-scan technique.

X ray photoelectron spectroscopy study of the decarboxylated SWNT derivatives

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Covalent functionalization is an important strategy to improve both solubility and processibility of single-wall carbon nanotubes (SWNT). In addition, it allows the unique properties of SWNTs to be coupled to those of other types of materials. The post-synthesis chemical processing could be also used to separate individual tubes according their diameter and chirality [1] by taking advantage of their differential reactivities. In chemically modified carbon nanotubes characterization, infrared spectroscopy is often used to determine the introduction of functional groups. However, since most of the chemical processing introduces around 5 wt% of functional groups on the SWNT surface, only the groups with strong IR activity will be detected in the IR spectra [2]. In this work, we present how X ray photoelectron spectroscopy (XPS) can been very useful in helping the characterization of functionalized SWNT samples [3].

We focus on the decarboxylation of SWNTs produced by arc discharge method, which were oxidized during a purification/cutting process using strongly oxidant agents, such as hydrogen peroxide and nitric and sulfuric acids. The decarboxylation was conducted in the presence of copper(I) oxide dissolved in a 50:50 solution of N-methylpyrrolidone and quinoline [4].

The SWNT-COOH and SWNT-CH derivatives were systematically characterized by X ray photoelectron spectroscopy (XPS) aided by FTIR and potenciometric titration studies. The TGA and Raman scattering analysis also provided supporting evidence for the assignment of the functional groups attached to the SWNT surfaces.

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Determination of carbon nanotubes concentration in solvent by using optical absorption spectroscopy

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In numerous applications of carbon nanotubes, dispersion in various solvents is an important step to enhance the performance of carbon nanotubes or host materials in composites, which usually involves ultrasonication and centrifuge steps. Information for nominal concentration of nanotubes at early stage is usually lost during the process, making the useful results ambiguous. In this paper we find a method of determining concentration of carbon nanotubes by using optical absorption spectroscopy. According to Beers law (A = log P0/P = a l c), the measured absorbance A is expressed in terms of extinction coefficient a, the light path length l, and the concentration of nanotubes c. The extinction coefficient was obtained by measuring the absorbance as a function of nanotube concentrations. The measured extinction coefficient of singlewalled nanotubes was in excellent agreement with theoretically predicted values. We have also tried to obtain the extinction coefficient for thin multiwalled carbon nanotubes. This work demonstrates that the concentration of un-known carbon nanotubes dispersed in aqueous solution can be easily determined by simply measuring the absorbance, once the extinction coefficient is determined.

Carbon nanotube mode-lockers for ultra-fast lasers

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Carbon nanotubes (CNTs) are efficient saturable absorbers, i.e. they are pass-high filters for light, becoming transparent for sufficiently high incident power [1,2]. This makes them ideal components for a wide range of photonic systems, such as all-optical switches, pulse compressors, noise regenerative filters, etc. Nanotubes can be processed into device by simple wet chemistry. Here we report a simple way to fabricate CNT-polymer films, combining polyvinyl alcohol or polycarbonate with CNT solutions. We show that these composites are promising passive mode-lockers [3]. Their absorption maximum can be easily tuned by using CNTs of different average diameter [3]. Saturable absorption is characterized by Z-scan. This confirms that these composites show the highest saturable absorption when the absorbance band of CNTs coincides with the Z-scan wavelength. Detuning from resonance leads to increase in non-saturable losses. We use these films to fabricate an ultra-fast (~600 fs) erbium doped fibre laser. We demonstrate wide spectral tunability of the output laser pulse (from 1560 to 1530 nm), by adding a dispersion control element in the cavity [3]. We report several hundred hours operation with no performance degradation. We also demonstrate passive mode-locking in ion-exchanged wave-guides and laser-written wave-guides [4]. This allows us to build compact ultrafast waveguide lasers [4].

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Prominent exciton effects on absorption of perpendicularly polarized light in carbon nanotubes

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Optical absorption spectra of carbon nanotubes are strongly dependent on the polarization of light. Analysis of inter-band transition revealed that for an electric field parallel to a tube axis, sharp peaks appear in optical absorption spectra due to van Hove singularity of joint density of states, while for perpendicular field, there is no peak because of a depolarization effect. On the other hand, it was theoretically predicted that exciton effects are extremely important because of the one-dimensional nature of the electronic states. Strong exciton effects were observed in experiments also. It is shown in this paper that a weaker but sharp exciton peak can be observed for perpendicularly polarized light in carbon nanotubes.

Exciton energy levels are calculated in an effective-mass approximation and the dynamical conductivity describing the optical absorption is calculated. It is revealed that a prominent peak due to an exciton appears in an absorption spectrum even when the depolarization effect is taken into account. However, the peak intensity is almost an order-of-magnitude smaller than that for parallel polarization. The peak position is shifted toward higher energy to be close or almost equal to the second lowest exciton peak for parallel polarization depending on the Coulomb interaction.

Quantization Conductance Study of Molecular Device

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Quantization Conductance Study of Molecular Device

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We were able to show the quantization conductance unit,2e^2/h, from the uncertainty principle and ascertain that it is the maximum conduction unit for a single electron. It is therefore not surprising to have conductivity at fractional quantization unit since the transmission probability would be reduced by many mechanisms such as Coulomb blockade, spin (Pauli) blockade, bond dissociation, impedance mismatch and oscillations.

Within the tight-binding model, we were able to derive the transmission and reflection coefficients for a 1d lattice wire embedded with a heterogeneous region. The resonance tunneling, impedance mismatch, and length dependence of oscillatory transmission were verified. The transmission at an electrical contact is modeled with two semi-infinite lattice wires. It is found to be greatly reduced by the disparity of the material properties. Similar equations were also derived from the Greens function method.

Molecular structures were studied with use of molecular orbitals (MO), valence bond (VB) model, Weibaum model, and configuration interaction (CI). An improved CI model by assigning two orbitals its own pair correlation function was able to get the best agreement with experiment at the least number of variational parameters. Taking helium atom as the example, the 1s trial wave function without the correlation effect gives the two electron ground state energy 77.5eV versus the 79.01eV of the experiment. With the correlation effect, the value is 78.63eV. This correlated configuration interaction (CCI) model with 1s, 2s orbitals and r12 and r12^2 terms gives 78.94eV, while extending to 3s and 4s orbitals gives 78.96eV with an error to the experimental by only 0.05eV. Similar calculation on hydrogen molecule gives 4.5eV bond energy versus the experimental 4.75eV. The code is being extended to include more terms to reach accuracy beyond 0.1eV, and is being applied to carbon nano tube study.

Effects of electron-phonon coupling on quantum conductance of a carbon nanotube junction

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While the electron-phonon (e-ph) scattering at low bias regimes is usually negligible in calculating quantum conductance of carbon nanotubes, resulting in a ballistic behavior1, it turns out to play an important role in the electronic transport of carbon nanotubes at higher bias voltages, leading to an inelastic current. In the present work, the microscopic e-ph coupling is computed for a nanotube junction2. The obtained couplings will be used in calculations of inelastic transport through nanotubes and investigation of the effect of external bias and temperature in transport.

Within tight binding formalism, a general method is developed to calculate the e-ph interaction from electronic band structure and phonon spectrum of the systems of interest. Here, the e-ph interaction is described as a coupling matrix determined by the product of the derivative of Hamiltonian with respect to atomic displacements and phonon eigenvectors.3 Phonon spectrum used in the calculations is derived from the dynamical matrix computed by finite difference method. Finally, the inelastic conductance is calculated taking into account the e-ph coupling.4

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Interplay between structure and magnetism in $Mo_{12}S_9I_9$ nanowires

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We investigate the equilibrium geometry and electronic structure of $Mo_{12}S_9I_9$ nanowires using *ab initio* Density Functional calculations [1]. The skeleton of these unusually stable nanowires consists of rigid, functionalized Mo octahedra, connected by flexible, bi-stable sulphur bridges. This structural flexibility translates into a capability to stretch up to about 20% at almost no energy cost. The nanowires are conducting and acquire a net magnetic moment in one of their structural isomers.

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Magnetic properties of Co nanorod inside multiwalled carbon nanotubes characterized by off-axis electron holography

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We have synthesized Co nanorods encapsulated inside multiwalled carbon nanotubes (MWCNTs) by microwave plasma enhanced chemical vapor deposition.

The transmission electron microscopy (TEM) bright-field images revealed that the Co was fully encapsulated inside MWCNTs. The face-centered cubic (FCC) structure of Co nanorods was confirmed by selected area diffraction pattern and often polycrystalline.

The magnetic properties of Co nanorods were carefully characterized using off-axis electron holography technique by a Philips CM200 TEM operating at 200 keV with an electrostatic biprism. An electrostatic potential of 130 V was applied to the biprism wire for hologram recording. The component of the magnetic induction was quantitatively determined to be 1.2±0.1 T based on an established cylindrical magnet model, and was independent of size of nanorods. This value is lower than the expected saturation magnetization of FCC bulk Co of 1.7 T. The X-ray microanalysis indicated that the oxidation of Co nanorod may degrade the magnetizing resonance. Moreover, the HR-TEM result revealed that Co (200) planes tend to be parallel to graphite (002) planes, therefore, the easy direction is not parallel to the actual magnetization direction.

Owing to the unique properties of the Co encapsulated MWCNTs, they have potential application for magnetic sensing.

Soft X-ray magnetic circular dichroism studies of metallofullerene nano-peapods

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Nano-peapods have attracted wide scientific attention owing to their unusual structural and electric properties, as well as commercial interests due to their potential applications in field effect transistors. In contrast to bulk-fullerene crystals, fullerene molecules encapsulated into hollow space of CNTs form linear chains in which each fullerene molecule has only two nearest neighbors (12 neighbors in a hexagonal or a face-centered cubic close pack arrangement of bulk-fullerene crystal). Further, intermolecular distances of encapsulated fullerene molecules are shorter than that of bulk crystal. Consequently, intermolecular interactions and dynamic behavior of the fullerene-pea are expected to be very different, and this would affect magnetic properties greatly. However, the investigation of magnetic properties of encapsulated metallofullerenes is very difficult due to ferromagnetic impurities such as Co and Ni particles, which are used as carbon nanotube synthesis catalyst. Here we report element specific magnetization of encapsulated endohedral metallofullerenes by using soft x-ray magnetic circular dichroism at SPring-8 BL25SU. A high brilliance synchrotron soft x-ray radiation source enables us to obtain MCD signals from very small amounts of samples (several micrograms).

Dynamic Magnetic Linear Dichroism in Carbon Nanotubes

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We have developed a technique to probe the dynamics of micelle-suspended single-walled carbon nanotubes (SWNT) in water through dynamic magnetic linear dichroism. Due to their anisotropic magnetic susceptibility SWNTs align with magnetic fields. Pulsed magnetic fields up to 58 T were utilized to induce absorption anisotropy, and the decay was used to determine the rotational relaxation time of the nanotubes. This new form of magnetic pump and optical probe spectroscopy was used to investigate nanotube length, degree of bundling, and suspension surfactant dependence. These results shed light on the Brownian motion of SWNT suspensions and deconvolution of alignment dynamics in previous investigations of the Aharonov-Bohm splitting in SWNT suspensions [1].

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Edge state and unconventional magnetism of nanographene/nanographite

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Nanographene, defined as nano-sized flat hexagon network having open edges, has edge-shape-dependent electronic structure, where, according to theoretical prediction, nonbonding pai-electron state (edge state) created around zigzag edges causes unconventional magnetism in nanographene or nanographite. We investigated the electronic structure of graphene edges in atomic resolution, and the magnetic features of activated carbon fibers (ACFs) which consist of disordered network of nanographite domains. UHV-STM/STS observations for zigzag edges with their edge carbon atoms hydrogen-terminated prove the presence of large local density of states populated in the edge region and a sharp density-of-states peak around the Fermi energy, in contrast to the absence of these features in the armchair edges. This importantly imparts experimental evidence of edge state as the origin of spin magnetism, which appears as unconventional magnetic features in nanographene or nanographite. Magnetic investigations demonstrate spin glass state of edge-state spins in the metal-insulator threshold in disordered network of nanographite domains. Host-guest interaction modifies the magnetic features of nanographite domains. Water adsorption in nanopores of ACFs shows a high-spin/low-spin magnetic switching phenomenon, in which a discontinuous reduction takes place in the magnetic moment at a threshold water vapor pressure when the nanopores are filled with water molecules.

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