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, strongly exceeding 500 at NT'06 in Nagano.

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. NT'06 took 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".

Locations of Previous Nanotube Conferences:

NT99

Michigan, USA

NT01

Potsdam, Germany

NT02

Boston College, USA

NT'03

Seoul, Korea

NT04

San Luis Potosi, Mexico

NT05

Göteborg, Sweden

NT06

Nagano, Japan

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CHARTA OF THE NANOTUBE 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

TIME	Sun 24	Mon 25	Tue 26	Wed 27	Thu 28	Fri 29	Sat 30
08:45 – 09:00		Announcements					DEPARTURE
09:00 - 09:45		P. AJAYAN Keynote 1	A. PÉNICAUD Keynote 2	F. BANHART Keynote 3	A. LOISEAU Keynote 4	M. FREITAG Keynote 5	
09:45 - 10:15	10:00 Registered	D. M. GULDI Invited 1	Y. ACHIBA Invited 2	M.I. ROMERO-ORTEGA Invited 3	K. KOSTARELOS Invited 6	E19 – J.-C. Coiffic E31 – K. Jensen E39 – P. Legagneux	
10:15 - 10:45		Introduction to Posters A	Introduction to Posters C	J-C. CHARLIER Invited 4	Introduction to Posters E		
10:45 - 11:15		Posters A with refreshments	Posters C with refreshments	Coffee-break	Posters E with refreshments	Coffee-break	
11:15 - 11:45				Y.-W. SON Invited 5		E54 – M. Steiner F01 – S. Berber F04 – R. Krupke	
11:45 - 12:30				F40 – A. H. Windle F50 – A. C. Ferrari			
12:30 - 14:00		Lunch	Lunch	Lunch	Lunch	Lunch	
14:00 - 15:00	TUTORIALS 14:00 A. H. Windle 15:00 M. S. Dresselhaus 16:00 D. Tomanek	Satellite report 1 – CCTN07 2 – MSIN07	B10 – M. Terrones B17 – T. Michel B31 – L. Novotny	14:00 GUIDED VISIT TO OURO PRETO	C31 – T. Pichler C37 – S. Giordani C62 – H. M. Cheng	P. JARILLO-HERRERO Invited 7	
15:00 - 15:30		Introduction to Posters B	Introduction to Posters D		Introduction to Posters F	F13 – Y.-S. Min D37 – D. A. Heller D46 – M. Zhang	
15:30 - 17:30		Posters B with refreshments	Posters D with refreshments		Posters F with refreshments	Conference Summary M. S. Dresselhaus 16:00 – 16:30 Concluding Remarks	
17:30 - 18:30		A07 - Y. Yao A23 - G. Eres A55 - S. Maruyama	C10 - G. Seifert C19 - B. Simard C28 - A.G. Souza Filho		D08 – Y. A. Kim D30 – R. G. Lacerda D35 – G. Scalia		
	19:00 Opening Ceremony and Welcome reception	19:00 Carnival show	Minas Baroque Concert		19:00 São João Party		

Tutorials

- Alan H. Windle: "Synthesis of nanotubes and related materials"
- Mildred S. Dresselhaus: "Why carbon materials are so special: from graphene to nanotubes"
- David Tomanek: "From understanding to utilizing the amazing properties of nanotubes"

Poster Chairs

- Posters A: Annick Loiseau, *ONERA-CNRS, France*
- Posters B: Riichiro Saito, *Tohoku University, Japan*
- Posters C: Esko Kauppinen, *Helsinki University of Technology, Finland*
- Posters D: Jean-Louis Sauvajol, *LCVN - University Montpellier II, France*
- Posters E: Eleanor Campbell, *Gothenburg University, Sweden*
- Posters F: Stephan Roche, *Commissariat à l'Energie Atomique, France*

KEYNOTE LECTURES

INVITED TALKS

CONTRIBUTIONS – Monday, June 25

POSTER SESSION B – Monday, June 25

POSTER SESSION C – Tuesday, June 26

POSTER SESSION D – Tuesday, June 26

POSTER SESSION E – Thrusday, June 28

POSTER SESSION F – Thrusday, June 28

KEYNOTE LECTURES

K01 - Engineering of Carbon Nanotube Based Structures

Pulickel M. Ajayan,

Rensselaer Polytechnic Institute

The talk will focus on the recent developments in our laboratory on the fabrication of carbon nanotube based architectures tailored for various applications. Various organized architectures of multiwalled, singlewalled carbon nanotubes and nanotube-nanowire structures can be fabricated using relatively simple synthetic approaches. The work in attaining control on the directed assembly of nanotubes on various platforms will be highlighted. Our efforts on the strategies of growth and manipulation of nanotube-based structures and in controllably fabricating hierarchically branched nanotube and nanotube-hybrid structures will be discussed. We have pursued several novel applications for these structures, for example, as nanostructured electrodes for sensors, electrical interconnects, unique filters for separation technologies, thermal management systems, multifunctional brushes, and polymer infiltrated thin film and bulk composites. A perspective of the field based on the work done in the author's laboratory will be presented here with with focus on future applications of this material.

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K02 - Mild dissolution of carbon nanotubes

Alain Pénicaud

University of Bordeaux

In order to take advantage in a macroscopic form, of carbon nanotubes extra-ordinary properties at the molecular level, a strong effort has been directed worldwide for quite some time at processing carbon nanotubes. One of the main problem to overcome, be it to obtain dispersions, films, composites, etc..., is to efficiently disperse carbon nanotubes. Two main routes have been followed, namely covalent functionnalization and non-covalent wrapping of nanotubes with surfactants, polymers, π-stacking molecules, etc.... aided with sonication at generally rather high power. Although highly efficient, there are a number of problems associated with theses methods, the main one being cutting or increasing of the defect density through fonctionnalization and / or sonication of the nanotubes.

We have recently developped a non damaging route to true thermodynamic solutions of single wall carbon nanotubes [1] that we describe as “mild dissolution”. This mild dissolution avoids any source of mechanical energy such as sonication; indeed, we discovered that alkali metal salts of carbon nanotubes are spontaneously soluble in polar organic solvents with no external energy needed. The solutions thus obtained, air sensitive, are made of undamaged and uncut carbon nanotubes allowing full benefit of the length-over-diameter ratio of carbon nanotubes. We will present a full description of the dissolution method and characterization of the solutions.

Discussion about exfoliation of carbon nanotubes bundles in these solutions will be presented as well as exploitation of these solutions.

[1] Spontaneous Dissolution of a Single Wall Carbon Nanotube Salt, A. Pénicaud, P. Poulin, A. Derré, E. Anglaret, P. Petit, J. Am. Chem. Soc., 2005, 127,8-9; Salting in nanotubes, Editor's choice, Science, 2004, 306, 2165.

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K03 - The processing of carbon nanotubes with energetic electron beams

Florian Banhart

University of Mainz

Carbon nanotubes exhibit unique properties when irradiated with energetic electrons. The high mobility of irradiation-induced defects such as interstitials and vacancies and the ability of the graphitic lattice to reconstruct after atom displacements enable us to create new and unique morphologies of nanotubes by applying electron beams. The controlled formation of point defects is the key to 'nanoengineering' of nanotubes or related graphitic structures. Irradiation experiments can be carried out in electron microscopes that permit in-situ observation of the transformations on an atomic scale.

Several alterations of the structure and morphology of carbon nanotubes were achieved. Examples are the merging of parallel or crossing single-wall tubes. Multi-wall tubes can be tailored under the electron beam by bending or collapsing the tubes. Bundles of single-wall tubes can be transformed into multi-wall tubes and vice-versa. Furthermore, carbon atoms can be injected into the inner hollows of tubes by applying an electron beam. Because of the high mobility of carbon atoms inside multi-wall tubes, the tubes can act as pipelines for atom transport. When the tubes are filled with transition metal rods, the irradiation-induced injection of carbon atoms into the metals leads to the growth of new nanotubes that can be observed in-situ at high resolution.

The removal of carbon atoms from the layers leads to a self-compression of carbon nanotubes. Interesting effects are observed when the tubes are filled with metallic nanocrystals. Under electron irradiation, the collapsing graphitic shells exert pressure onto the encapsulated crystals which are then subjected to elastic or plastic deformation. On the one hand, information about the compressive stress or pressure inside onions or tubes can be gained by observing the behaviour of the encapsulated crystals. On the other hand, such nanoencapsulates enable us to study, with high spatial resolution, deformation or phase transformations in individual nanocrystallites.

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K04 - Luminescence properties of Boron Nitride Nanotubes

Annick Loiseau [1], Perine Jaffrennou [2], Julien Barjon [3], Samuel Sonderreger [4], Jean-Sebastien Lauret [5], Jean-Daniel Ganière [4], Brigitte Attal-Trétout [6], François Ducastelle [2]

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Boron nitride nanotubes (BNNT) are, as their related bulk material, h-BN, wide band gap semiconductors and are expected to strongly emit in the UV range. Recent theoretical calculations show, that, as it has been experimentally demonstrated for h-BN, strong excitonic effects should occur in BNNT, with localized excitons of very large binding energy (quasi-Frenkel excitons).

Until recently, the lack of BNNT samples has prevented one to experimentally identify such effects. Thanks to the vaporization laser route to BN SWNT, developed at Onera [1], we have performed the very first absorption measurements on assemblies of single wall BNNT, which revealed the existence of three bands centred at 4.45, 5.5 and 6.15 eV [2].

In order to finely analyse the nature of these bands, we have undertaken two kinds of optical measurements on isolated BNNTs. First the dielectric response in low energy loss spectroscopy has been recorded in a STEM on individual SWNT. It provided the first measure of the optical gap found to be close to 5.8 eV [3].

The second approach consists in coupling cathodoluminescence spectroscopy and imaging of individual BNNT [4]. Spectra reveal that the luminescence is composed of two emission bands in 3 to 6.2 eV range. Both bands are also measured in h-BN single crystallites [5,6] but with a blue shift of 0.5 eV [5]. The first band is centered at 5.2 eV and is attributed to quasi-Frenkel excitons related to the optical gap at 5.7 eV. The second band is centered at 3.8 eV and has been shown to be due to impurities or defect centers. Finally time-resolved cathodoluminescence in the picosecond range confirms this interpretation.

[1] R. S. Lee et al, Phys. Rev. B Rapid Comm. 64, 121405 (2001).
[2] J. S. Lauret, et al Phys. Rev. Lett. 94, 037405 (2005).
[3] R. Arenal, et al, Phys. Rev. Lett. 95, 127601 (2005).
[4] P. Jaffrennou et al, submitted to Chem. Phys. Letters (2007).
[5] K. Watanabe et al, Nature Materials 3, 404 (2004).
[6] M. Silly et al, Phys. Rev B, PRB, 75, 085205 (2007).

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K05 - Carbon Nanotube Optoelectronics

Marcus Freitag

IBM Watson Research Center

Semiconducting carbon nanotubes incorporated between two electrical contacts and in close proximity to a third (gate) electrode can be switched on and off by applying voltages at the gate. Their small size, cylindrical shape, mechanical integrity, and high carrier mobility make them candidates for the ultimate transistor. Recent optical measurements have solved many open questions that are relevant for nanotube electronics: For example the exciton nature of optical transitions has been established. The giant exciton binding energies around 0.5eV have important implications for the electrical bandgap, which is usually inferred from the optical gap.

In many respects it is advantageous to combine electronics and optics and study the electro-optical properties of carbon nanotubes. This will be the focus of this talk. For example, by passing high currents in certain nanotube transistors, it is possible to impact-excite excitons and achieve higher exciton densities than what could be done optically. Preparing ambipolar nanotube transistors allows building a fascinating new type of light emitter with a mobile emission spot. Shining light onto nanotube transistors produces wavelength and polarization-sensitive nano light detectors, which facilitate spectroscopy on single nanotubes. Point defects emit light under unipolar currents and also separate photo-generated electron-hole pairs. The latter effect can be used to image them by scanning a laser spot across the device. This work was done in collaboration with James Tsang, Vasili Perebeinos, Jia Chen, and Phaedon Avouris.

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INVITED TALKS

I01 - Carbon Nanotube Nanoconjugates and Nanohybrids – Electron Donor Acceptor Interactions

Dirk M. Guldi

University of Erlangen

Carbon-based nanomaterials are currently under active investigations for producing innovative materials, composites, and electronic devices of greatly reduced size. Among the wide variety of carbon materials (i.e. fullerene, single and multi wall carbon nanotubes, carbon fibers, carbon nanoonions, and single wall carbon nanohorns), single wall carbon nanotubes (SWNT) and single wall carbon nanohorns (SWNH) are of particular interest.

The structure of SWNT is conceptualized by wrapping a one-atom-thick layer of a graphene sheet, that is, an interlinked hexagonal lattice of carbon atoms, into a seamless cylinder. The diameter of most SWNT is close to 1 nm, with a tube length that might be many thousands of times larger. Importantly, based on different arrangements, SWNT possess different electrical properties (i.e., semiconductor or metallic), which are the result of the electrons moving differently in the tube depending on the SWNT arrangement. SWNH, on the other hand, are typically constituted by tubes of about 2-5 nm of diameter and 30 to 50 nm long, which associate with each other to give rise to round-shaped aggregates of 100 nm of diameter. SWNH are easily produced in large-scale quantities (i.e., up to 50 g/h) with an extraordinary purity (>90%) and, most importantly, are free of metal residue, since they are produced in the absence of any metal catalysts. Their large surface areas (1006-1464 m^2g^{-1}) and inner nanospaces (0.47-1.05 mL/g) are of great importance, since they ensure a great affinity with organic electron donors and make them promising candidates for electrical and chemical solar energy conversion.

In this respect, I will highlight the opportunities that rest on carbon nanostructures – much beyond the well-studied fullerenes – within the context of electron transfer reactions in novel chemical and light driven systems. In particular, I will survey our approaches to design, characterize, and examine the potential for practical applications of super- and supramolecular association of carbon-based nanomaterials with electron donors towards stable donor-acceptor nanohybrids and nanoconjugates within the context of light induced charge separation and solar energy conversion. Important are the impact, the benefits and some of the promises that evolve from electron transfer reactions with carbon nanostructures on i) the stabilization of radical ion pair states, ii) multi electron catalytic reactions and iii) photoelectrochemical / photovoltaic solar energy conversion.

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I02 - Toward the production of SWNTs with a single chiral distribution

Yohji Achiba

Tokyo Metropolitan University

Controlling chiral distributiions of single wall carbon nanotubes (SWNTs) is definitely one of the most important issue for further development in science and technology of carbon nanotubes. In this paper, we will demonstrate the production of SWNTs with a very narrow diameter distributions and/or with almost a single chiral distribution. The method for the production of the SWNTs was a conventional laser vaporization-furnace apparatus, and Rh/Pd metal catalyst was used combined with several different foreign gas. By controlling several different experimental parameters such as gas pressure, gas flow rate and furnace temperature, it was found that the production of the semiconducting SWNT with (7,6) chiral index is very much enhanced in yield in comparison with the tubes with similar diameter distributions. It was also found that by further refining the condition, the sample consisting of almost a single chiral SWNTs with the (6,5) chiral index was produced. The purity of the chiral distribution of the samples was examined by Raman spectroscopy, luminescence measurements as well as optical absorption method. On the basis of the present experimental results, we will also present the growth model of SWNTs, particularly placing emphasis on how the furnace temperature and/or metal catalyst does work on the formation of SWNTs with a single chiral distribution.

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I03 - Carbon Nanotube Biology: Cell Growth and Neurointerfacing

Mario I. Romero-Ortega

Univ. Texas Southwestern Medical Ctr.

The extremely high thermal and electrical conductivity, tunable optical emissions and superior mechanical stiffness of carbon nanotubes has enable a variety of novel uses and the creation of new and more potent devices. Such unique characteristics also make nanocarbon an optimal tool for a plethora of biomedical applications such as: hypersensible electrochemical biosensing, controlled drug release, intracellular protein and/or gene delivery and tissue engineering. Here we report on the use of carbon nanotube sheets and yarns as viable substrates for long-term cell culture. This study provides support on the biocompatible nature of nanocarbon for several cell types, including fibroblasts and primary central and peripheral neurons, uncovering unique effects of this material in directing cell growth. Evidence will be presented on the use of CNT sheets as a more robust cell-electrode interface, and their particular application as enhanced neurointerface material for the neural control of advanced robotic prosthetics. This work adds support to the potential beneficial application of carbon nanotubes in biomedicine.

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I04 - Quantum Transport in Carbon Nanotubes

Jean-Christophe Charlier

University of Louvain

Their unusual electronic and structural physical properties promote carbon nanotubes as promising candidates for a wide range of nanoscience and nanotechnology applications. Not only can nanotubes be metallic, but they are mechanically very stable and strong, and their carrier mobility is equivalent to that of good metals, suggesting that they would make ideal interconnects in nanosized devices. Further, the intrinsic semiconducting character of other tubes, as controlled by their topology, allows us to build logic devices at the nanometer scale, as already demonstrated in many laboratories.

The tremendous importance of the transport properties of nanotubes, both from a fundamental and technological point of view, justifies wealth of work and theories developed to deal with 1D systems involving a confined electron gas. The purpose of the present talk is to define the electronic and transport properties of nanotubes in relation with their atomic structures. Since quantum effects are prominent in nanotube physics, the electronic quantum transport has been investigated using both the Landauer-Buttiker and the Kubo-Greenwood formalisms, allowing to extract generic properties such as quantum conductance, conduction mechanisms, mean-free-paths... Within both frameworks, the well-known ballistic properties of armchair metallic nanotubes have been reproduced. However, defects, doping and chemical functionalisation can alter this ideal situation. For example, even a small amount of boron or nitrogen dopants can drastically modify the electronic transport properties of the tube, which is certainly a key effect for future nanoelectronics. The chemical sensitivity of the electronic transport in carbon nanotubes under the physisorption of molecular species or covalent functionalisation is also an important issue as for example in sensing applications.

Like in most materials, the presence of defects in carbon nanotube has been demonstrated experimentally. These defects may take different forms : vacancy, bi-vacancy, “Stone-Wales” defect, 5/7 pair, atom in substitution, … and are known to modify the electronic properties of carbon nanotubes. It is crucial to understand the properties of these defects in order to conquer their detrimental effects, but also because controlled defect introduction may be used to tune nanotube properties in a desired direction. Consequently, the modifications induced by those defects in the electronic properties of the carbon hexagonal network have been investigated using first-principles calculations. Computed constant-current STM images of these defects have been calculated within a tight-binding approach in order to facilitate the interpretation of STM images of defected carbon nanostructures. At last, as these defects should also play a key role in the chemical reactivity of carbon nanotubes, the study of the modulation of the conductance due to specific molecules adsorbed at the defected nanotube surface will be presented.

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I05 - Electric field effects on spin transport in graphene nanoribbons and metallic carbon nanotubes

Young-Woo Son

Department of Physics, Konkuk University

Based on first-principles calculations, we investigate the effects of electric fields on the magnetic properties of graphene nanoribbons (GNRs) [1] and defective metallic single-wall carbon nanotubes (SWNTs) [2]. First, a half-metallicity is predicted in GNRs if the in-plane homogeneous electric fields are applied across the zigzag shaped edges of the systems [3]. Such asymmetric electronic structures for each spin originate from the fact that the spatially separated spin polarized states with opposite spin orientations in the semiconducting GNRs are shifted oppositely in energy by the applied fields. This closed the gap associated with one spin orientation and widens the other. Second, we show that vacancies or carbon adatoms in (10,10) SWNTs play a role of quasi-localized magnetic impurities and their relative energy levels with respect to the Fermi energy are changed by the applied transverse electric fields [2,4]. So, the resulting spin-polarized conductances in the systems are shown to be tunable. For some impurities, the orientation of the majority spin electrons in conducting channels at the Fermi energy can be switched to the opposite spin by an experimentally attainable electric field. Our results suggest that pure organic nanomagnets or perfect spin polarizations could be realized in carbon nanostructures and their spin transport properties are controllable by transverse electric fields.

[1] Y.-W. Son, M. L. Cohen, and S. G. Louie, *Phys. Rev. Lett.* **97**, 216803 (2006).
[2] Y.-W. Son, M. L. Cohen, and S. G. Louie, *submitted.*
[3] Y.-W. Son, M. L. Cohen, and S. G. Louie, *Nature*, **444**, 347 (2006).
[4] Y.-W. Son, J. Ihm, M. L. Cohen, S. G. Louie, and H. J. Choi, *Phys. Rev. Lett.* **95**, 216602 (2005).

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I06 - The emerging field of carbon nanotube pharmacology

Kostas Kostarelos

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University of London

The use of nanomaterials in medicine is growing at an unprecedented rate for a variety of therapeutic, diagnostic or combinatory applications. Carbon nanotubes possess properties that make them attractive materials for biomedical applications, however, their impact on the physiology of live organisms is still largely unexplored. What is becoming apparent today is that non-functionalised, purified carbon nanotubes pose some toxicological and adverse reaction risks following administration or implantation. On the other hand, we and others have elucidated through systematic investigation of functionalized carbon nanotubes that most such problems can be alleviated. This lecture will illustrate that water-soluble, individualised carbon nanotubes exhibit very interesting behaviour on interaction with biological matter in cell cultures (*in vitro*) and in tissues of living animals (*in vivo*) that allows their further development towards the clinic. Administration of carbon nanotubes for therapeutic or diagnostic applications requires determination of various fundamental *in vivo* pharmacological parameters such as blood circulation half-life, tissue biodistribution, excretion rates, which constitute the emerging field of carbon nanotube pharmacology.

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I07 - Superconducting junctions in carbon electronics

Pablo Jarillo-Herrero

Columbia University

In the past few years a novel class of carbon materials, namely carbon nanotubes and graphene, has enabled the realization of new types of Josephson junctions. In this talk I will review two recent experiments where we developed quantum supercurrent transistors based on carbon nanotubes and bipolar supercurrent transistors based on graphene. These studies clarify the role of size quantization and time reversal symmetry, respectively, in the induced superconducting properties of these materials.

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CONTRIBUTED ABSTRACTS

POSTER SESSION A

JUNE 25 (Monday)

A01 - CVD growth of carbon nanotube films with Ti-based catalysts

Leonid Grigorian, Robert Gump, Steve Colbern, Alex Moser, Sean Brahim, Daniel Niebauer

YTC America Inc.

Growth of CNT typically requires use of catalysts based on transition metal, such as Ni, Co, Fe. To the best of our knowledge, Ti was not shown previously to catalyze CNT growth on its own. In this work, we report CVD growth of CNT films on Si substrates using Ti-based catalysts free of other metals. We have optimized the CVD growth conditions and explored effect of addition of other metals such as Co, Fe, Mo and their combinations on the grown CNT films. Our CNT films were found to exhibit strong adhesion to Si substrates and may become a bridge to Si-compatible CNT electronics. Characterization with Raman spectroscopy, HRTEM, SEM, SAED, and other techniques, as well as potential applications are discussed.

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A02 - Simple Catalytic CNT Growth Method in Air

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In this work, arrays of carbon nanotubes have been grown normal to the surface of electrically conducting supports by the simplified method of catalytic CVD. Catalytic sites were formed due to surface break-up during oxidation of the support in laboratory air. The drop of liquid carbon source was deposited on the heated catalytic support to produce the carbon vapor atmosphere at the surface. The only conducting support was heated by electric current during the carbon nanotubes growth process. It allows easily to control and change the temperature during the process. Ethanol was used as a source of carbon by decomposition at high temperature near the surface of support. The process conditions were an open air laboratory atmosphere and no chamber or inert gas ambient was used. The nichrom wire (80% Ni, 20% Cr) was used as a catalyst and support. The process temperature was in the range of 1030 – 1070^{o}C. The produced straight carbon nanotubes, which diameter vary in the range of 50 to 80 nm and the length up to 0.1 mm. The length of hundred microns was obtained during the minutes from the ethanol source. The diameter and surface density of nanotubes produced is controlled by the method of catalyst preparation and by the process parameters. The sharp decrease and again increase in the process temperature by 400 ^{o}C, produce change in the nanotube diameter twofold on the same tube.

Observations by TEM proved the tubular structure of these nanotubes. Now the work is oriented towards the growth of dense layer of vertically aligned carbon nanotubes by CVD. Preparation of catalyst by wet chemistry methods and inert ambient is used.

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A03 - New aspects about the growth of metal filled carbon nanotubes on structured substrates and the tuning of their magnetic properties

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Nanostructured magnetic materials such as arrays of nanowires and filled nanotubes exhibit unique and tuneable magnetic properties e.g. the anomalous high coercivity, which make them favourable for applications in high density magnetic recording media.

We show effective CVD-routes for the defined growth of ensembles as well as individuals of metall-filled carbon nanotubes (Fe, Co, Ni) on structured silicon substrates and alumina substrates. The filled nanotubes were obtained due to continuous decomposition (thermic or plasma) of metal-containing precursors or hydrocarbons at 750-850°C. The nanotube dimensions can be controlled by the size of the catalyst on the substrate and with the reaction conditions. Further we report about a homogeneous embedding procedure of the CNT ensembles in a solid matrix. After the mechanical treatment the remaining nanotube stubs are analyzed with the magnetometer. In addition detailed investigations with transmission electron microscopy (TEM), atomic force microscopy (AFM) and Moessbauer spectroscopy give new insightes in the growth of filled carbon nanotubes.

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A04 - Carbon Nanotube Fabrication Using Functionalized Ferrocene Floating Catalyst Chemical Vapor Deposition Technique

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Floating Catalyst Chemical Vapor Deposition (FC-CVD) method was designed to fabricate carbon nanotube using benzene as a source of hydrocarbon, hydrogen gas as reacting gas flow rate ranging from 50 to 400 ml/min., temperature ranging from 700 to 900 ^{o}C and functionlized ferrocene as catalyst. This work will discuss the effect of reaction temperature, flow rate of hydrogen gas and type of catalyst on morphology and yield. Ferrocene derivative catalyst will be vaporized at 100-140 ^{o}C in the first hot area. This will reach second hot area 700-900 ^{o}C. Decomposed carbons will adsorb and diffuse to catalytic metal particles and synthesized as carbon nanotubes. Moreover, fine powder of MgO and NiO were located in the second hot area and carbon nanotube grows on its surface. Substrate catalyst of metal oxide position in second hot area is effecting on yield of carbon nanotube.

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A05 - Novel On-Chip Growth of Carbon Nanotubes using High Temperature Microheaters

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This paper reports the direct integration of Carbon Nanotubes (CNTs) on ultra thin fully CMOS gas sensors. This novel technique was used to grow CNTs locally on Silicon Nitride membranes and tungsten electrodes using high temperature low power micro heaters. It has been seen generally that the bulk heating of the device substrates for growth of CNTs can cause significant damage to the devices and its interconnects, but using this novel technique the Carbon Nanotubes are localised to the sensing region only and isolated from the region outside the membranes. The technique was optimised for thermal CVD using Fe catalysts and CNTs were analysed using SEM and electrical characterisation.

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A06 - CVD Growth of Single-Walled Carbon Nanotubes on Substrates

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Single-walled carbon nanotubes (SWNTs) are attracting enormous attention because of their unique properties, especially their electronic behavior depending on the diameter and chirality. In order to build various nanodevices based on SWNTs, growing SWNTs on surfaces is of special interest. Till now, chemical vapor deposition (CVD) is the only technique by which SWNTs can be grown on substrates in a well-controlled way. In this presentation, the various issues involved in the CVD process will be discussed, including the size control and patterning of catalyst particles, the interaction of SWNTs with substrate, and the alignment of the SWNTs. By carefully managing these parameters, SWNTs with desired size, location and orientation could be obtained. The using of non VIII-group metals as catalyst will be also discussed. Metallic copper, which is normally considered as a contaminant in the growth of SWNTs, was found to be an efficient catalyst to grow SWNTs under suitable conditions. It showed very high catalytic activity for the growth of both random SWNT networks and horizontally aligned SWNT arrays. Especially, high quality SWNT arrays were obtained when monodispersed copper nanoparticles were used. The weaker interaction between copper and silica surface plays an important role in the growth of high quality horizontally aligned SWNT arrays. This new synthesis process of SWNTs with a non-ferromagnetic catalyst brings more convenience to the study of magnetic properties of SWNTs and gives more insight in structure-controlled synthesis of SWNTs.

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A07 - Temperature Mediated Growth of Single-walled Carbon Nanotube Intramolecular Junctions

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Single-walled carbon nanotubes (SWNTs) possess superior electronic and physical properties that make them an ideal candidate for making the next generation electronic circuits that break the size limitation in the current silicon-based technology. The first critical step in making full SWNT electronic circuit is to make SWNT intramolecular junctions in a controlled manner. Unfortunately, although SWNT intramolecular junctions have been reported grown via several methods [1-3], they only grew inadvertently in most cases. Here we have developed an efficient method, i.e. temperature oscillated chemical vapor deposition, to grow SWNTs with controllable intramolecular junctions [4]. Under desired growth condition, a temperature oscillation either from high to low or from low to high may lead to the formation of flared or tapered structure of SWNTs. With this growth feature, we are able to provide the direct evidence to prove that higher temperatures favor the growth of thinner nanotubes and lower temperatures for thicker nanotubes for a given catalyst particle. Multi-oscillation of temperatures may generate SWNTs with multiply intramolecular junctions. Basically, by temperature oscillation, semiconductive nanotubes seem to favor the later growth of semiconductive ones, and metallic nanotubes like to junction with metallic. These findings provide a potential approach to grow SWNT intramolecular junctions at desired locations, sizes and orientations, which are important for making SWNT electronic circuits.

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A08 - Multi-walled Carbon Nanotubes Grown on Carbon Fiber Produced from Different Heat Treatment Temperature

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The influence on the morphology of multi-walled carbon nanotubes (MWCNT) is investigated using carbon fiber (CF) substrate obtained at different heat treatment temperature (HTT). CF samples were produced from polyacrylonitrile (PAN) precursor HTT of 1000, 1500 and 2000 ^{o}C at temperature steps of 330 K/h, under inert atmosphere with nitrogen flow of 1 $L.h^{-1}$. The samples were kept at the maximum temperature during 30 min and then cooled down to room temperature. To induce the MWCNT growth the samples were immersed in a $Fe(NO_3)_3.9H_2O$ ethanolic solution ("dip coating" technique) with concentrations of 37 mmol/l and 110 mmol/l, respectively . The MWCNT were produced using the CVD process in a microwave plasma chamber at 2.45 GHz. The nanoclusters formation was carried out during 5 min in N_2/H_2 plasma, at a substrate temperature around 760^{o}C. The MWCNT growth was performed by adding CH_4 carbon source to the gas mixture during 2, 5 and 10min depositions, at a substrate temperature of 780^{o}C. The reactor was kept at a pressure of 30 Torr during the whole process. Homogeneous and uniform MWCNT were observed covering even deep CF planes. Microstructural properties of PAN-based CF are strongly affected by HTT and influence the carbon nanotubes growth.

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A09 - Influence of growth parameters on the carbon nanostructures formation

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Multi-walled carbon nanotubes (MWCNTs) have been grown using catalytic thermal chemical vapor deposition (CVD), on a horizontal tubular quartz furnace at atmospheric pressure. The influence of different mixtures of gases (methane, acetylene, ammonium, hydrogen and nitrogen) on the MWCNTs growth process has been studied as well as the effect of the growth time (1-30 minutes) and process temperature (800-950 ^{o}C). Catalytic capability of different metals (Ni, Fe, Cu, Ni/Fe, Ni/Cu, etc.) has been compared. The effect of substrates has also been studied and differences in nanostructured carbon growth have been observed. For this study, two different substrates were used: (i) silicon oxide layers thermally grown over silicon wafers (SiO_2/Si substrate) and (ii) thin alumina films prepared by DC magnetron sputtering over silicon wafers (Al_2O_3/Si substrate). For characterization of the samples, high-resolution scanning and transmission electron microscopy (SEM and TEM, respectively), atomic force microscopy (AFM) and Raman spectroscopy were employed. AFM results showed the Al_2O_3 substrate roughness two orders of magnitude higher than that for SiO_2, whereas SEM inspection showed much higher density of CNTs growth for Ni deposited over Al_2O_3 compared with that for SiO_2. Mechanisms that may be responsible for this effect are discussed. Using different metals as catalysts, formation of different carbon nanostructures was observed. Based on the results obtained, the mechanisms of nanotubes/nanofibers nucleation and growth are analyzed. A new model explaining the nanotube nucleation as a specific instability occurring on the surface of a catalyst particle supersaturated with carbon is presented.

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A10 - Effect of Catalyst on Carbon Nanofiber and Nanotube Properties

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Carbon nanostructures take the interest of many researchers all over the world because of their interesting structural, electronic and mechanical properties. Chemical vapor deposition (CVD) method was chosen for synthesis the carbon nanostructures in this study, since controlling the metal catalyst properties allows controlling the properties of the CNF formed. Our goal in synthesizing carbon nanostructures was to correlate the morphology of the carbon nanostructure that is formed to the catalyst properties. In order to achieve such conclusion, a detailed research for the catalyst and carbon nanostructures has to be done; such as, the activity of the catalysts, surface and thermal properties as well as the morphological and structural characterization of cabon nanostructures. In this study, transition metal-organic acid based catalyst precursors were synthesized. The structural, surface and chemical properties, thermal stability of the catalysts and carbon nanostructures have been investigated using XRD, SEM-EDS, FTIR, BET, solid state 13C-NMR and TGA methods.

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A11 - The determining factors to grow defect-free Carbon Nanotubes

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To synthesize Carbon Nanotubes (CNTs) with predetermined properties a complete understanding of the growth mechanism is necessary. Common observations illustrate that the type of carbon nanostructure grown is significantly modified by each condition involved in the synthesis. However, the exact influence of each parameter and the details of the interplay between them remain largely unknown.

In this communication, we report on the decomposition of ethylene over Ni, Pt, and Pd nanoparticles deposited on SiO_2 substrates. The influence of temperature, pressure, gas flow ratios, and crystalline structure of the catalyst was systematically explored for each metal in a Chemical Vapour Deposition (CVD) chamber. Analyses were performed using a combination of high resolution microscopy, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and high resolution transmission electron microscopy (HRTEM).

Our results show a size-dependant reshaping of the nanoparticles due to self diffusion of metal atoms at the edges of the catalyst surface. Specifically, self-diffusivity is controlled by the initial quantity of carbon supplied to the nanoparticle during the nucleation stage. In addition, size and shape of the catalyst control carbon segregation, thus dictating the morphology of the grown nanostructure. We also show that there is an associated set of growth conditions to each nanoparticle size to grow a defect-free tube. Finally, the reasons why a carbon nanostructure shows different morphologies are widely discussed. Altogether, represents a step forward into the understanding of the growth mechanism and the synthesis of CNTs with controllable properties.

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A12 - Carbon nanotubes-Fe/Al_2O_3 nanocomposites: formation of CNTs from γ -$(Al_{1-x}Fe_x)_2O_3$ solid solution using methane as carbon source

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It is well-known that the metal particles that are active for the catalytic decomposition of hydrocarbon are exclusively those located at the surface of the matrix grains. Then, it is expected that the quantity of active particles can be increased using powders with high accessible specific surface area. Thus, with the aim to improve the quantity and the quality of the CNTs, experiments have been performed using γ-$[(Al_{1-x}Fe_x)_2O_3]$ powders with high specific surface area (~206 m^2/g). γ-alumina-based solid solutions were prepared by an alternative route, i.e., combustion of oxinates. The so-obtained solid solutions contain different amounts of Fe. The CNTs syntheses were performed by CCVD method using a mixture of H_2/CH_4 at 1000°C. Analysis of X-ray diffraction patterns of the obtained CNTs-nanocomposite products revealed the presence of α-Fe and cementite in addition to γ-alumina. In order to examine more specifically the various Fe phases present in the nanocomposite powders, Mössbauer spectroscopy analyses were performed at room temperature (RT) and at 15 K. In general, three components were found to be required to obtain adequate fits for the Mössbauer spectra (MS): (i) an outer sextet obviously due to α-Fe; (ii) an inner asymmetrical six-line pattern that is ascribed to Fe_3C; and (iii) a singlet due to γ-Fe probably alloying to carbon. For the sample with low iron content in the precursor ($x = 0.02$), clearly an additional, but very weak (~5 % of total absorption area) and rather ill-defined sextet appears in the MS. It is suggested that this additional sextet is due to an Fe-C component ($\delta \sim 0.11$ mm/s and $H_{hf} \sim 276$ kOe at RT). Additionally, a weak doublet (~ 6 % of the total area) with $\Delta E_Q \sim 0.66$ mm/s is present in the MS at RT. SEM images of the nanocomposites revealed the presence of long, flexible filaments which could be distributed as isolated nanotubes or in CNT bundles. An overview of the nanocomposite powder (TEM images) showed that, indeed, there are CNT bundles and isolated CNTs, in agreement with SEM observations. Furthermore, the presence of many metallic particles is observed besides rounded agglomerates which could consist of the matrix grain with metallic particles at the surface and carbon deposited. The presence of thicker, short filaments is observed as well. These filaments (about 15 nm in diameter) are attributed to fibers generated from large catalytic particles.

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A13 - Growth of vertically aligned carbon nanofibers above copper at 560°C using RF-PECVD: on the choice of a suitable metallic barrier.

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Growth trials of vertically field aligned carbon nanofibers (CNFs) are reported on copper (Cu) based substrates, using thin nickel (Ni) film as catalyst and an innovative radio-frequency (RF) plasma enhanced chemical vapor deposition (CVD) system. Due to CNF expected good electrical and mechanical properties combined with reduced dimensions, these experiments are the first steps to potentially address some applications in the field of microelectronics, such as, for instance, CNF-based nano electro-mechanical systems, electrically driven by Cu interconnects, or next generation interconnects, where more and more reduced vertical via openings above Cu lines could be filled with CNFs.The growth mode consists of an annealing treatment performed at 560°C leading to Ni nano-particles growth germs and a consecutive growth step achieved at the same temperature by igniting a RF glow discharge from a pure H_2 atmosphere. The process, in line with CNF in-situ growth on future electronic devices above potential silicon integrated circuits, ensures: (i) highly selective growth mode with no parasitic non catalytic carbon layer formation, responsible for electrical short-circuits, by resorting to a graphite sample holder as single carbon supply; (ii) high plasma stability, preventing electric arcing detrimental for the substrates. Concerning the CNF growth above a Cu layer, the intercalation of a suitable metallic barrier between the Ni film and the Cu layer is required, in order to avoid the Ni diffusion into Cu and in the same time ensure an electrical contact between the CNFs and the underlayers. TiN layers performed using two different deposition processes were investigated as a diffusion barrier material: a 50nm CVD-grown TiN layer and a 45nm TiN layer deposited by a physical vapor deposition technique. Scanning electron microscopy evidenced the growth inhibition from the Ni nano-particles for the CVD TiN, whereas the growth occurred for the PVD TiN. We will endeavor to understand these different outcomes by means of transmission electron microscopy and X-ray photoelectron spectroscopy analyses. Cu-Ni interplay phenomena will be underlined and the assumption of Ni particle poisoning by Cu above a critical concentration will be pointed out for this growth mode.

A promising and original material stack was finally developed to prevent the Cu-Ni interplay by using a highly thin metallic barrier, which could be easily integrated in future devices: a 10nm aluminium (Al) layer, deposited by e-beam evaporation between the Cu and the Ni layers allows the CNF growth. The key role played by Al is under investigation.

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A14 - Modelling gas-phase carbon nanotube synthesis on iron nanoparticles from carbon monoxide

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The underlying models of gas-phase CVD synthesis of carbon nanotubes are poorly understood. Only recently has progress been made in modelling early nanotube formation using molecular dynamics, which is very computationally expensive and cannot capture entire systems. In this work an operator splitting method has been used to couple a stochastic particle solver to the gas-phase chemistry equations, allowing these systems to be fully modelled.The model is compared to experimental data, in which a hot-wire generator (HWG) was used to produce nanoparticulate iron which was then mixed with a CO stream and fed to a CVD flow reactor where the nanotube growth took place [1].

The model includes a description of CNT and graphitic layer formation on particles, and rules for particle-particle interactions. CO disproportionation and hydrogenation were the only processes contributing to carbon addition to nanoparticles. A carbon atom can either diffuse into the particle or add to a graphitic layer or to a CNT. The rate of carbon dissociation at the surface is assumed to be the rate limiting step. Carbon is assumed to dissolve in a particle until a saturation condition is reached. Thereafter, carbon adds equally to a graphitic layer or CNT. The competition between carbon layer and CNT growth was used to dictate the time at which a CNT would form. Particles were modelled to deactivate, when the graphitic layer completely covered the particle surface. Nanoparticle diameter, CNT diameter and CNT length were chosen to characterise the simulations as all three were available from the experimental data. Parameter studies of carbon addition rate constant and fraction of carbon forming CNTs were performed, and demonstrated that CNT diameter was insensitive to these parameters. Comparison to experimental data showed that the model does not capture all aspects of the data well, however it did predict well CNT length, and should form a basis for future, more comprehensive models.

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A15 - Stress induced synchronous growth behavior of carbon nanotube forest

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Carbon nanotubes (CNTs) in CNT forests possess unique mechanical, electrical and thermal properties as macroscopic nanomaterials. During the synthesis of a CNT forest, a basic problem that remains is that the synchronous growth is still not understood and predictable. Until now, research on the CNT growth mechanism has been mainly on the atomic scale, and the vapor-liquid-solid (VLS) model has been developed. Recently, on the single CNT scale in the floating catalyst method, the active growth location of the forest was indicated as at the bottom of the forest, which was confirmed by catalyst labeling or multilayer growth. The CNT forest always shows luxuriant synchronous growth.

By experimental control of its multilayer growth with precursor stopping methods in the floating catalyst methods, the morphologies of the bottom, top and cross-sections at various heights of CNT forest were determined. Based on the VSL model and bottom up growth for single CNTs, a stress induced synchronous growth for CNT forest formation due to the interactions among the CNTs in the floating catalyst methods was proposed. The stress was developed gradually due to the formation of a weave structure on the surface in the initial two minutes and the presence of the active site at the bottom. The stress was confirmed by the G peak shift in the Raman spectra. The stress induced the CNT forest to grow synchronously. In agreement with most reports on CNT forest obtained by the floating catalyst method, two kinds of CNTs - with curve and straight morphologies - were found. We found the transitions for the curved CNTs from the randomly distributed structure to the order structures occurs in the length of 30-40 micrometers for CNTs. For long time growth, the curvature degrees of CNT forest were increasing gradually. The stress induced synchronous growth provides a way to understand the luxuriant forest growth based on the interactions of CNTs. Further work was needed to explain the synchronous growth behavior quantitatively. It may be possible to more precisely control CNT forest to have various morphologies in the future, which were full potential application in various applications, such as CNTs yarn formation, filter, display.

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A16 - Large Scale Growth of Aligned CNT Arrays on Spheres: Towards the Mass and Continuous Production

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The mass and continuous production of mm scale aligned carbon nanotube (CNT) arrays was successfully achieved in a lab-scale reactor by introducing large amounts of small spherical oxide particles as large-area growth substrates into floating catalysis chemical vapor deposition. The main differences and advantages of spheres were described as: first, the available growth surface that spheres provided was much larger, equaling to 10000 pieces of 2-inch wafer in our experiment, than conventional flat wafers; second, even the spheres after the CNT growth kept the perfect spherical morphology and thus excellent fluidity, allowing possible transport of as-grown product out and re-supply of new spheres for nonstop operation. The successful simultaneous large-area growth of CNT arrays on all spheres was attributed to the easy feedstock diffusion through stacked particles and the high strength of CNT arrays. Formation mechanism and potential large-scale application in composite material of these long and aligned CNTs are also discussed.

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A17 - Growth temperature-induced critical behavior of SiO_2 thickness for carbon nanotube synthesis on Si substrates by pyrolysis of iron phthalocyanine

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The synthesis of carbon nanotubes (CNTs) has been investigated in detail on native oxide and thermally grown SiO_2 layer with a distinct thickness on (111)-oriented Si substrates using iron phthalocyanine (FePc) by chemical vapor deposition (CVD). We have examined the effect of growth temperature on carbon nanotubes (CNTs) synthesis on thin SiO_2 diffusion barrier of Si substrates. Scanning electron microscopy (SEM) images indicate that CNTs can grow on 5.3-nm-thick SiO_2 layers at 1000°C, while not at 900 °C. No observable growth is induced on the SiO_2 with a thickness of less 5.3-nm irrespective of the synthesis temperature. A possible reason is proposed that explain the behavior. These findings confirm that a minimum (threshold) thickness of the underlying SiO_2 layer is required for efficient CNTs formation. Additionally, it is interesting to note that most active catalysts are observed to diffuse into the SiO_2 layers to a depth of around 100 nanometer when oxide layers with several hundred nanometer are utilized. This result could be of great use for optimizing CNT growth to be used in conjunction with Si technology.

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A18 - Synthesis and characterization of carbon nanotube grown by alcohol gas source in high vacuum

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Because of their unique electronic properties, carbon nanotubes (CNTs) have been expected for application as electronic device, such as field effect transistor (FET), electron emitters and wiring for LSI. However, growth mechanism of CNT has still not been evident, and control of CNT chirality has not been realized yet. For clarification of growth mechanism, CNT growth in a high vacuum is essential to realize *in-situ* observation, such as scanning electron microscopy (SEM). In this study, we attempted to grow CNTs using gas source technique in a high vacuum. SiO_2 (100 nm)/Si substrates were introduced into an ultra-high vacuum (UHV) chamber and Co catalyst of 1 nm was deposited on it by electron beam (EB) evaporation. To prevent oxidation of the catalyst, 1×10^{-3} Pa of H_2 gas was flowed during the increase of the substrate temperature. Then, ethanol gas was supplied onto the substrate surface to grow CNTs, through a stainless steel nozzle for 5 hours. The growth temperature was set between 350 and 900^{o}C, monitored by a pyrometer. The supply of ethanol gas was controlled by monitoring an ambient pressure, which was varied from 1×10^{-1} to 1×10^{-5} Pa. The grown CNTs were characterized by SEM observation and Raman spectroscopy (excitation at 514.5 and 632.8 nm). When CNTs were grown under 1×10^{-1} Pa, the density of CNTs reached its maximum at 700^{o}C and web-like CNTs were observed all over the surface. From the RBM peaks in the Raman measurements, the CNT diameters were estimated about 0.9 to 1.7nm, and the CNTs of 1.2 ~1.4 nm in diameter were dominant at this pressure. As the growth pressure decreased, the optimum growth temperature became lower, and the ratio of G band peak to Si peak (520 cm^{-1}) reached its maximum at 400^{o}C under 1×10^{-4} Pa. In addition, thinner CNTs (diameters were below 1.0 nm) were increased with the reduction of the pressure. The G/D ratio was about 12 for CNTs grown at 400^{o}C and 1×10^{-4} Pa. From these results, CNTs with a good crystalline can be grown even in a high vacuum by gas source technique. This technique can be applied to *in-situ* observation and also may be useful for low temperature growth of CNTs, which opens a new possibility for the fabrication of CNT based nanodevices, such as wiring for LSI.

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A19 - The Effect of Process Variables on the Characteristics of Carbon Nanotubes Obtained by Spray Pyrolysis

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This work reports the use of a novel and simple spray pyrolysis apparatus to multi-walled carbon nanotubes growth, starting from a ferrocene solution as precursor. Several experimental variables were studied, as the solvent (benzene or xilene), the growth temperature, the position of the aerosol generator and position in which the sample was formed. Samples were characterized using TEM, SEM, XRD and Raman spectroscopy and results showed a strong influence of these variables on the graphitization degree, homogeneity, diameter and alignment of the obtained carbon nanotubes. Vertically aligned MWNT array with high density were obtained in large areas (10 x 10 mm^2), with high yield (2.1 mg.cm^{-2}) and at a growth rate at 2.86 μm/min, by a suitable adjust of the experimental conditions.

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A20 - Catalyst particle engineering for carbon nanotube synthesis

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We present a flexible and versatile route to prepare individual nano-sized particles by an inert-gas condensation method using DC-sputtering at pressures in the mbar range. The route offers advantages in that the preparation of the catalyst particles is accomplished in a single step [1]. This allows a higher degree of purity to be achieved as compared to processes where the preparation of catalyst particles requires a series of chemical procedures (see, e.g. [2]). With the approach of separate catalyst preparation and CNT synthesis we are able to control the size and density and characterize the starting material which cannot be so readily achieved using more conventional CVD processes where the catalyst particles are formed in situ. Further, the detailed information on the catalyst particles prior to the CVD reaction itself combined with post reaction studies provide superior insight into the growth processes of CNT as a whole.

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A21 - The Viability of Growing Small Diameter Single-Walled Carbon Nanotubes by the Catalytic Method.

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We investigated the viability of forming very small diameter freestanding single walled carbon nanotubes (SWNTs) by the chemical vapor deposition (CVD) method [1,2]. Alumina aerogels impregnated with ironmolybdenum (Me= Fe:Mo= 1:0.2) catalyst nanoparticles were prepared by the sol-gel method with molar ratios Al_2O_3 : Me ranging from 4 to 2500 (BET surface area ca. ~400 m^2/g). Higher Al_2O_3: Me ratio is presumed to lead to smaller average diameter of the catalyst clusters [3]. We found that the decrease of catalyst particle size required for nucleation of small diameter tubes, results in a significant increase of the catalytic decomposition temperature of methane (by >150 ^oC), and the temperature required for nucleation and growth of nanotubes. On the other hand, high temperature endorses their agglomeration, as well as leads to deactivation of catalyst by interaction with the support material as revealed by magnetic and *in-situ* mass-spectrometer measurements, respectively. Raman spectroscopy (532 & 785 nm) and fluorimetry (658 & 783 nm) studies showed a wide range of SWCNT diameters (~0.7 to 1.32 nm), regardless of the initial particle size. The smallest tube found had a diameter of 0.669 nm and chirality (8,1). Our results suggest existence of a lower limit of the free standing SWCNT diameter which can be produced by the CVD method due to the peculiarities of very small catalyst particles, their evolution during nanotube growth and the required synthesis conditions.

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A22 - Measurement of catalyst lifetime favorable for SWCNTs growth: effect of composition and synthesis parameters

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Catalyst features are of central importance for the growth of carbon single-walled nanotubes (SWCNTs), with the lifetime being a key characteristic. The only approach described in the literature for estimation of the catalyst lifetime, is based on complicated measurement of nanotubes length evolution with time. Here, a special chemical vapor deposition set-up enhanced by an attached mass spectrometer, for in-situ parametrical studies, allows us to evaluate the catalyst activity during the growth of SWCNTs. Furthermore, to validate the period of catalytic activity and its relationship with nanotube growth, hydrocarbon gases with ^{12}C and ^{13}C isotopes are sequentially introduced at different stages of the growth. Analysis of the Raman spectra of the different samples thus obtained, allows us to adequately determine the lifetime of the catalyst. The dependence of the catalyst lifetime on its composition and synthesis parameters is also discussed.

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A23 - The Origin of Autocatalytic Kinetics in the Growth of Ultra Long Vertically Aligned Nanotube Arrays

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Kinetic studies of vertically aligned nanotube array (VANTA) growth using acetylene chemical vapor deposition reveal new reaction pathways for synthesis of carbon nanotubes. Real-time measurements of VANTA growth show characteristic features of autocatalytic kinetics in the form of autoacceleration at the onset of growth and an S-shaped time-dependent height curve. The autocatalytic behavior in VANTA growth is attributed to radical chain polymerization in pyrolysis of acetylene. The key factors that affect VANTA growth suggest that polymerization is a general reaction pathway in VANTA growth by pyrolysis of unsaturated hydrocarbons. In particular, we show that ferrocene–a prototype metallocene catalyst–plays an active role in sustaining the pyrolysis of acetylene resulting in growth of VANTA taller than 10 mm. The concept of polymerization for nanotube synthesis is significant because it offers the possibility of using molecular catalysts combined with stereospecific polymerization to address chirality control in large scale production.

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A24 - Investigation of incubation time for carbon nanotube growth by CH_4/H_2 plasma-enhanced chemical vapor deposition

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In this work, we focused on the incubation time (= time interval before starting CNT growth) and duration time of CNT growth with respect to the gas flow ratio in CH_4/H_2 plasma. Analyzing the incubation time of CNTs growth and the catalyst state is crucial for revealing the mechanisms of CNT growth. We observed the catalysts morphology before CNTs start to grow and CNTs using scanning electron microscopy and transmission electron microscopy. First, we investigated the effect of CH_4/H_2 gas flow ratio and process time on CNT growth [1]. At CH_4/H_2 = 30/0 sccm, CNT growth rate was fast (0.8 μm/min) but CNT growth was saturated for 30 min. At CH_4/H_2 = 27/3 sccm, CNT growth rate was decreased (0.3 μm/min), while CNTs continued to grow for 90 min. At CH_4/H_2 = 9/21 sccm, CNT growth stopped before the process time reached 10 min. These results clearly show that variations in $CH4/H_2$ gas flow ratio affect CNT growth. In this case, the growth rate and duration time of CNTs were changed. Possible explanation is that an addition of H_2 of an optimal amount realizes a longer duration time of CNTs by keeping the catalyst size small and active during incubation time and excess supply of hydrogen makes the duration time short. We consider that the CH_4/H_2 plasmas changed the morphology and chemical composition of catalysts during the incubation time. To confirm how the CH_4/H_2 gas flow ratio affects catalyst activity during incubation time, we varied the gas flow ratio during CNT growth: CNT firstly grew at CH_4/H_2 = 9/21 sccm for 10 min, and after then, we set the gas flow ratio at CH_4/H_2 = 27/3 sccm. This process did not promote any further CNT growth after CNT growth at CH_4/H_2 = 9/21 sccm for 10 min. This result also support an idea of CH_4/H_2 gas flow ratio affects the catalyst particles during incubation time. [1] A. Okita, et al., Carbon (2007) in press.

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A25 - Synthesis of Carbon Nanotubes on Lanthanide-series element by Thermal Chemical Vapor Deposition Method

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We studied the growth characteristics of carbon nanotubes (CNTs) which were directly grown from the lanthanide-series element prepared from cerium nitrate solution using spin coating method without any transition elements (catalyst; iron, nickel and cobalt).

As the first preparation step of forming cerium nitrate solution, we admixed cerium nitrate powder with water. Water has a good solubility for cerium nitrate at a room temperature. A cerium nitrate-hexahydrate, 0.5g, were dissolved in 50 mL of distilled water, 18 Megaohm-cm, (23.02 mM). The mixture, an aqueous solution containing 0.02 mol/L cerium nitrate, was stirred for 5 min. The cerium-nitrate solution was coated on molybdenum/glass-substrate by spin coating method. After spin coating and drying process, we confirmed the existence of cerium element by analysis the surface of the sample by Energy Dispersive Spectroscopy (EDS). And then, the substrate was loaded in vacuum chamber and annealed at 350-400°C in nitrogen ambient to decompose the nitrate compound. Decomposition conditions were investigated with thermal gravimetric analysis (TGA). In most drying-process cases, the surface oxidation of the substrate is a common occurrence because a cerium is an easily oxidizable element. For this reason of oxidation, we had to add reduction process by hydrogen gas for reducing the oxide form to metal state at 650-700 °C. And then, the substrate was transferred into the growth chamber and was consecutively heated around at 650 °C and sustained for 10 min in C_2H_2 and Ar ambient.

The substrate and as-grown CNTs were analyzed by the field emission scanning electron microscopy (FESEM, A0344, Philips) and the filed emission transmission electron microscope (FE-TEM, Tecnai F30).

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A26 - Utilization of commercial iron foam as catalyst to multi-walled carbon nanotubes growth

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This work reports the utilization of cheap commercial iron foam as catalyst to MWCNTs growth in a CCVD process. The catalyst is easily available in Brazilian supermarkets at coast of US$ 0.50 for each 60 grams, and it has almost metallic iron in its composition. The MWCNTs syntheses were carried out adding a small amount of catalyst (approximately 0.2 g) inside a quartz tube that was inserted in a tubular furnace. The system was heated under argon atmosphere and a gaseous carbon source was subsequently supplied. Several experimental variables were studied as kind of carbon precursor (benzene, xilene, toluene, ethanol), temperature of the furnace (700, 900 and 1100 ^{o}C) and position of the catalyst related to the furnace entrance. The black product obtained on the catalyst surface was isolated and characterized by XRD, Raman, TEM and SEM. Results indicate that large amount of MWCNT were obtained. Based on the experimental data, a mechanism growth to the carbon nanotubes was proposed.

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A27 - A DFT study of C atom diffusion in the process of nanofibers and nanotubes catalytic growth

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When considering the growth of carbon nanofibers or even nanotubes helped with catalytic nanoparticles, it has been, until very recently, assumed that (1) the reactant molecules containing the C atoms adsorb on the metallic nano-cluster surface, (2) the C atoms dissolve into the nanoparticle bulk, (3) they diffuse and (4) start to accumulate before a nucleation process starts, which gives birth to a graphene plan or a nanotube cap if the nanoparticle is small enough. In this model, the C diffusion is governed mostly by the concentration gradient between the metal-gas interface and the metal-graphene one.

However, recent theoretical studies, cf. Ref. [1], tend to suggest that the role of the metallic cluster surface is fundamental in the diffusion process. In their case, by not taking into account the fact the distance between the graphene sheet and the metallic surface can be very short [2], a surface diffusion appears to be the most favorable path. On the contrary, by setting the distance closer to the experimental one [3], our results favor sub-surface diffusion, in good agreement with a recent tight-binding calculations combined with Monte-Carlo simulations [4] and also a recent experimental study [5].

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A28 - The Interfacial Interaction Between Nanocatalysts and Various Oxide Substrates

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A clear understanding of the interaction between the catalyst and the substrate is essential for controlled growth of Single Walled Carbon Nanotubes (SWCNTs). We have investigated the interaction of transition metal (Fe, Ni, Co) catalyst particles with various substrates (SiO_2, Al_2O_3, MgO, ZrO_2) by studying the variation of the particle size and the particle density at varying temperatures. The substrate with dispersed particles was carefully studied by AFM, heated to a pre-determined temperature suitable for SWCNTs growth under flowing H_2/Ar or H_2/He gases, and cooled down to the room temperature. Then sample was again studied carefully using AFM. This was repeated for a series of temperatures with gradual increments until clear evidence for agglomeration (resulting larger particles and low density) was observed. The temperature at which the onset of agglomeration occurred was used to estimate the activation energy of the catalyst for the respective substrate. The experimentally estimated activation energies of the Fe particle for Al_2O_3, SiO_2, and ZrO_2 are 0.12, 0.10, and 0.09 eV respectively. To develop the interaction between catalyst clusters and substrate surfaces, we also performed density functional theory *ab initio* calculations. The theoretical results are corroborated reasonably well with the experimental values and reveal the influence of interfacial interaction on thermodynamic properties of clusters by comparison of “free” and “supported” clusters characteristics. Some discrepancy in the results for SiO_2 is also discussed.

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A29 - CNT growth from selectively electrodeposited catalyst nanoparticles

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In recent years carbon nanotubes (CNTs) have stimulated extensive research within the field of semiconductor device fabrication. In particular, CNT-based devices promise enhanced electronic properties including high current capacity, excellent thermal conductivity, and length independent resistance at the nanoscale. In the specific case of interconnect application for integrated circuit (IC) technology, CNTs could replace copper because they have lower resistivity and delay, lower dynamic power and better thermal behaviour in vias than copper.

Crucial factor to reach high quality growth and sufficient packing density is a suitable placement of catalyst species on the surface. Until now, physical vapor deposited (PVD) metal films and metal particle impregnated supports have been used for CNT growth. But they lack control over size, density and location. To address these challenges, we are investigating electrodeposition as an alternative technique for catalyst preparation, since it offers control over size, density and a high degree of selectivity, which is essential for IC integration. With this technique, monodispersed sub-nm to nm particles at a predefined location of patterned structures can be achieved. It also offers the possibility of preparing bicatalysts through the alloying of different metals. In this work, Ni and Co were compared using different electrolytes on a semiconductor surface and a metallike layer, (100) n-type silicon wafer and titanium nitride (TiN) respectively. The electrolyte composition and deposition parameters (potential, time) dependence were studied. The resulting nanoparticles were evaluated in terms of catalyst distribution and reactivity. Some of electrodeposited nanoparticles were very successful for CNT straight high density growth. Furthermore, nanoparticles were selectively electrodeposited at the bottom of 150 to 300 nm diameter via structures patterned in a SiO_2 layer resulting in the selective growth of CNTs within the vias. The nanoparticle sizes and densities were characterized by SEM, TXRF and the CNTs morphology by SEM, TEM and RAMAN spectroscopy.

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A30 - Effect of CO_2 addition on carbon nanotube growth by CVD using CH_4

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We report the effect of CO_2 addition on CNT growth by CVD using CH_4 gas. The CVD chamber is evacuated by a turbo-molecular pump followed by a rotary pump in order to eliminate the effect of H_2O and O_2 molecules. We used Mo(0:025)/Fe(0:05)/MgO(0:925) or Mo(0:025)/Ni(0:05)/MgO(0:925) as a catalyst, H_2 gas as a reductant and CH_4 gas as a feedstock [1]. CO_2 gas was introduced during the CNT growth at a temperature of 800°C and its concentration with respect to CH_4 was varied from 0.0037% (37 ppm) to 50%. The other experimental parameters are as follows: H_2 gas pressure = 100 Torr and flow rate = 100 sccm for reduction; CO_2/CH_4 gas pressure = 100 Torr and flow rate = 76 sccm for growth. The yield and the G/D ratio in the Raman spectra of CNTs grown in 10%- CO_2/CH_4 were slightly higher than those of CNTs grown in CH_4 only. However, scanning electron microscopy observation showed that CNTs were hardly grown when the CO_2 concentration was more than 10%. Single-walled CNTs (SWCNTs) grew when the CO_2 concentration was 37 ppm, and the yield for 60 min was 1.5 times higher than the 10-min growth. This suggests that SWCNT growth in a CO_2/CH_4 gas mixture was continued for 60 min. The CO_2 concentration of 37 ppm is smaller than the results by Nasibulin, et al, who confirmed the elongation of SWCNTs by introducing CO_2 with a concentration of 1000 ppm (0.1%) in CO disproportionation reaction [2]. The radial breathing modes (RBM) of the SWCNTs obtained by a 632.8 nm excitation shows that SWCNTs with a diameter range of 0.9 - 1.3 nm were grown and a few metallic SWCNTs were eliminated but most of semiconducting SWCNTs remained.

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A31 - Controlled *in-situ* pre-treatment to improve carbon nanotube growth by chemical vapor deposition

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Carbon nanotubes (CNTs) are touted as prospective candidates to overcome the scaling limit of conventional semiconductor technology due to their novel properties such as high conductivity, mechanical stability, thermal conductivity, and etc. Via interconnects (ICs) are expected to be one of the most important application of CNTs in the future integrated circuits. For CNTs to be integrated as via ICs in devices, on-chip growth of CNTs on catalyst film by chemical vapor deposition (CVD) is the most compatible growth technique currently available in the conventional semiconductor Fab. For via IC applications, maximizing the density of CNTs in the via holes is a prerequisite. In this report, we introduce an in-situ pre-treatment process composed of sequential gas treatments and plasma treatments at elevated temperature, to increase the density and to decrease diameters of grown CNTs. Using these pretreatments, the density of CNTs increases by an order of magnitude, whilst allowing reduction in the growth temperature to about 300^{o}C. These results and probable CNT growth mechanism will be discussed.

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A32 - Modeling size- and thermodynamic stability- effects on Fe-C and Fe-Mo-C nanocatalysts

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Catalytic Chemical Vapor deposition (CVD) method is widely used to produce carbon nanotubes. To improve our understanding of the CVD growth mechanism, we focus on the thermodynamics and the phase stability of catalyst Fe-C and Fe-Mo-C nanoparticles. Using a combination of ab initio methods and model thermodynamics [1,2], we investigate 1) the diffusion and solubility of carbon atoms in nanoparticles by calculating the distribution of carbon atoms inside the clusters, 2) the formation and stability of binary and ternary nano carbides 3) the effect of substrates on such structures, 4) the size-dependent interplay between iron rich phases and competing ordered carbide phases, and 5) the possible stabilization effects of C in alloys immiscible at the macro-scale and found to be active on CNT growth [3]. We address the implications of these results on NT growth, and give possible strategies to mitigate the problems. Research sponsored by Honda Research Institute Inc., USA.

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A33 - Synthesis of carbon nanotubes by spray pyrolysis of conventional and unconventional precursors

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There are only few reports about the synthesis of carbon nanotubes by spray pyrolysis method. Here we reported the synthesis of SWNTs by catalytic decomposition of conventional (ethanol) and unconventional precursors (turpentine oil and eucalyptus oil) on high-silica zeolite, impregnated with Fe/Co at 850^{o}C with reaction time 25 minutes at atmospheric pressure by simple spray pyrolysis method. Raman spectroscopy reveals that ethanol grown SWNTs are more pure and well graphitized than natural precursor s grown CNTs. It has been suggested in some other reports that oxygen atom in the carbon containing precursors increase the quality of the as-grown CNTs. But in our case no such improvement has been observed. The Id/Ig ratio for ethanol, turpentine oil and eucalyptus oil are 0.20, 0.26 and 0.31 respectively. Although eucalyptus oil contains one oxygen atom per molecule but Id/Ig ratio for eucalyptus oil is higher than turpentine oil (containing no oxygen atom per molecule). That means the oxygen atom in the carbon containing sources does not significantly improve the quality of the as-grown CNTs Not only single-walled but also single and double-walled CNTs have been synthesized on supported material by this simple and inexpensive technique. The as-prepared sample are well graphitized confirmed by SEM, TEM and Raman spectroscopy.

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A34 - Ion Implantation of Catalysts by Focused-Ion-Beam for Vertically Aligned Carbon Nanotube Growth

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Ion implantation is a very interesting method for catalyst preparation of carbon nanotube (CNT) growth for formation of FET channels and interconnects because the method can be applied in LSI process and catalysts can be implanted at desirable places such as the bottom of via holes. However, vertically aligned CNTs have not been achieved from catalysts prepared using ion implantation. For vertical alignment, dense catalytic particles must be formed on a substrate surface. In this study, we succeeded in growth of vertically aligned CNTs from Ni catalysts implanted using focused ion beam (FIB).

First, we separated Ni ions from Ni-P-Pt liquid metal ion source (LMIS) using a mass separator, and then Ni ions (Ni^+ or Ni^{2+}) were implanted into a 500 nm-thick SiO_2 layer on a Si substrate at an acceleration voltage of 30 kV with doses of 5.0×10^{16}-5.0×10^{17} ions/cm^2 using FIB. The implanted Ni was analyzed using EDX, SIMS and cross-sectional TEM measurements. After Ni implantation, the substrate was annealed at 450-700 °C in H_2 gas to form Ni particles. The substrates were introduced in a radical CVD apparatus [1] for CNT growth. CNTs were grown at 600 °C in a mixture of H_2 and CH_4 for 2h.

Interestingly, Ni particles were formed on the substrate surface after ion implantation without any treatment, probably caused by irradiation-induced diffusion of implanted Ni atoms. We investigated density and diameter distribution of Ni catalysts implanted with a dose of 5.0×10^{17} ions/cm^2 before and after the annealing at various temperatures. Over 600 °C annealing, the catalyst particles became larger and larger, resulting in a lower density. Although particles with a high density of 9.2×10^{11} /cm^2 were obtained after 460 °C annealing, vertically aligned CNTs were synthesized from catalysts annealed at 700°C. For the present CVD and substrate conditions, CNTs are preferably grown from large particles more than 10 nm. We can expect that optimization of the conditions would result in growth of much denser CNTs.

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A35 - Synthesis of Single-Wall Carbon Nanotubes in Micro-, or Meso-porous Materials by Catalyst-Supported Chemical Vapor Deposition

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The catalyst-supported chemical vapor deposition (CCVD) is one of the most promising methods to realize large-scale production of carbon nanotubes. Especially, CCVD using porous support materials possessing well regulated nano-space, such as microporous zeolites and mesoporous silicas, is an excellent candidate to realize selective synthesis of carbon nanotubes; these micro- or mesoporous materials provide us suitable ordered space to prepare regulated nano-sized metal particles. However, previously reported carbon nanotubes produced by CCVD using micro- or mesoporous materials have a large diameter distribution because of a large size distribution of metal nanoparticles which stems from nanoparticles deposited on outer surface of the support materials.

Here, we report the growth of single walled carbon nanotubes (SWNTs) by CCVD using size-controlled Fe, Co, Rh, Pd catalysts and their alloys particles supported into channels of the micro- and mesoporous materials. A solution of Fe, Co, Rh or Pd salts was used as a source of catalyst metals, which were mixed with a powder of Y-type zeolite [1] and FSM16 [2]. The metal salts except for an Fe salt, which are incorporated in micro- and mesoporous, were reduced by a high temperature H_2 reaction or UV irradiation in an H_2O/EtOH atmosphere, and Fe salts were pyrolytically decomposed at 1073 K. Prior to CCVD, the metal particles were treated at 573 K in air to enhance the catalytic activity [3]. CCVD experiments were carried out at 973-1173 K under an Ar gas flow for 30 min by using ethanol as carbon source. SWNTs so-obtained were characterized by TEM observations and Raman spectroscopy.

We will discuss the correlation between the diameter distribution of prepared SWNTs with pore sizes of the micro- and meso-porous materials and metal species of catalysts.

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A36 - Nanotube Epitaxy

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The organization of carbon nanotube arrays on surfaces is a critical prerequisite for their large-scale integration into nanocircuits. We have recently elaborated a series of substrate-directed mechanisms of carbon nanotube growth, which can be classified as different modes of ‘nanotube epitaxy’. These epitaxial modes of carbon nanotube growth include ‘lattice-directed epitaxy’ (by atomic rows), ‘ledge-directed epitaxy’ (by atomic steps) [1], and ‘graphoepitaxy’ (by nanofacets) [2]. Some of these epitaxial modes can be simultaneously combined with electric-field directed growth [3] for the orthogonal self-assembly of carbon nanotube crossbar architectures [4]. Nanotube epitaxy with different crystal surfaces yields unprecedented carbon nanotube array morphologies, including highly straight, kinked, wavy, crossbar, serpentine [5], and more.

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A37 - Synthesis of Carbon Nanotubes using Natural Gas as a Carbon Source

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The study of carbon nanotubes (CNTs) have been one of the hottest fields of research lately. However, the presence of CNTs due to the hydrothermal process in nature has been observed in graphitic mineral rocks (Y. Gogotsy. JMR., 2000). Also L.E. Murr (J. Nanosci. Nanotechnol., 2004) observed the presence of CNTs, and related fullerene crystals in exhaust streams from kitchen stove-top propane, natural gas (NG) burners, and liquid propane fueled vehicles, among others gas exhaust pipelines. In this sense, the use of NG as a natural source for the low cost, high-scale production is a new issue of study in the production of carbon nanotubes. Moreover, the NG contains up to 90 % of methane gas, with a presence of different kind of hydrocarbon-like impurities, which would provide difficulties on the formation of CNTs with high quality. Recently C. P. Bergmann (J. Mater. Sci. 2006) reported the formation of MWCNTs and SWCNTs using Fe/Mo/MgO catalysts by chemical vapour deposition (CVD) for temperatures higher than 900°C. In this work, we describe the production of single-wall carbon nanotubes using natural gas as carbon source, and ferrocene, acetates of metal transition as catalysts. Raman technique, and scanning electron microscopy were the mainly techniques used to characterized the products. SWCNTs were obtained in a temperature range between 700 and 900°C. A small reduction in the nanotubes diameter was observed as the deposition temperature increases. Presence of double-wall carbon nanotubes were also detected in some cases. A more detailed description of the nanotubes produced, and the growth mechanism will be also presented. Acknowledgements: This work was supported by Rede Nacional de Pesquisa em Nanotubos de Carbono (CNPQ Brazil).

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A38 - Construction of highly defined carbon nanotube architectures by atmospheric thermal CVD

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Recently, there has been considerable concentration on the development of CNT-based composites or nano-electro-mechanical-systems. However, it is still required to precisely grow CNT with designed structures and performances. We present systematic study of vertical growth of CNT arrays with well defined structures in a large scale. We employed atmospheric thermal CVD, which can independently control the process parameters, so that we can investigate the effect of various experimental parameters on the final CNT morphology and Raman spectra. We used acetylene or ethylene as a carbon feedstock and argon and hydrogen as carrier gases. Highly selective patterned CNT architectures were fabricated using electron beam lithography. Interesting effects concerning the influence of array pattern size on alignment will be presented, as will developments toward some practical applications.

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A39 - Controlled growth of SWNTs on various structured substrates for diameter and chirality control

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We present synthesis of SWNTs using various structured substrates to facilitate direct characterization of as grown tubes. For high controllability of the growth process, we used thermal CVD with methane and hydrogen gases. EB-patterned thin film catalyst and ferritin-derived nanoparticles were used as catalysts. Sizes of catalysts and grown SWNTs were estimated using AFM results. In addition to the plane substrates, multi-dimensional patterned substrates were fabricated to suspend SWNTs, which allow direct characterization of intrinsic properties of as grown SWNTs using TEM and Raman. We also grew SWNTs on silicon nitride membranes to investigate the size relationship between catalytic nanoparticle and resultant nanotube. Our results will be developed towards SWNTs' diameter and chirality control by optimizing the combination of controlled growth and characterization.

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A40 - Carbon Source and Byproduct Diffusion Limit in the CVD Growth of Aligned Carbon Nanotube Arrays

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In the root growth of vertically aligned carbon nanotube (CNT) arrays, where carbon source has to diffuse through the thick forest to contribute to the CNT formation, a new kind of diffusion limit arises and becomes a unique mechanism for the growth deceleration. In the present work, a simple approach was proposed to distinguish diffusion-controlled process from kinetic-controlled one. It was possible to evaluate the diffusion limit in different chemical vapor deposition (CVD) systems via the same non-dimensional factor. The results, which agreed well with experiments, suggested that mm scale SWNT arrays were usually suffering from strong feedstock diffusion limit while the growth of MWNT arrays were free of diffusion difficulties. For the 30 micron SWNT in alcohol CCVD, the result revealed that hundreds of ppm water was generated by the ethanol decomposition at the root of the array during the growth, which might be fatal for the catalyst lifetime.

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A41 - High density aligned CNT Arrays - A possible alternative to Cu interconnects

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The concept that Carbon nanotubes (CNTs) may be a future alternative to Cu interconnects in integrated circuit (IC) technology is one current pursuit of semiconductor device research. To out perform current Cu interconnects a number of key challenges must be met, on-chip, high density, size controlled, aligned CNT arrays are an essential requirement. We have successfully fabricated aligned high density CNT arrays using a combination of Plasma Enhanced (PE) and CCVD. During this investigation we have elucidated some critical CNT synthesis parameters to achieve high density whilst also maintaining alignment. In addition, the formation of an effective substrate-CNT contact is essential in characterizing the electrical properties of these CNT arrays. Consequently, our research efforts have focused on developing effective catalyst systems such as an Fe/Ti bilayer and Fe on TiN, and determining their influence on the type and morphology of the resultant CNTs. Such insights are essential if the full potential of CNTs as future interconnect materials are to be realized.

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A42 - Regeneration of catalyst particles in single-walled carbon nanotubes growth by CVD

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Single-walled carbon nanotubes (SWCNTs) are commonly synthesized by Catalytic Chemical Vapor Deposition (CCVD) using supported metal nanoparticles. A major issue in the CCVD elaboration of SWCNTs is the catalyst deactivation which limits the reaction yield and rate and prevents growing nanotubes of arbitrary length. Encapsulation of the particles by unreactive carbon is often considered as the main origin of catalyst deactivation. Catalyst-substrate interactions are also major causes of deactivation as highlighted by the growth of ultralong SWCNTs in the tip-growth mode [1].

Different oxidative treatments have been shown to improve or preserve the catalyst reactivity. The addition of water vapor dramatically reduces the catalyst deactivation and enables to grow densely-packed, millimeters-long SWCNTs with high growth rates (microns per second) for several minutes [2]. Zhang et al. [3] reported that the addition of oxygen during the growth promoted the growth of long and dense arrays of SWCNTs. Takagi et al. [4] reported that combining a pretreatment under air made a variety of metal nanoparticles (Au, Cu, Ag, ...) active for the growth of SWCNTs.

Here, we report on the regeneration of catalyst particles in SWCNTs growth from ethanol after successive oxygen treatments. To distinguish between the origins of catalyst deactivation, we combined Raman spectroscopy and high-resolution transmission electron microscopy (HRTEM) to study the catalyst activity and structure at the different regeneration steps. SWCNTs can be regrown after regeneration by oxygen, demonstrating that the particle encapsulation by carbonaceous species is one cause of deactivation. However, the catalyst activity generally decreases after several growth-regeneration cycles, which reveals a second and irreversible cause of deactivation. HRTEM studies showed that this deactivation was correlated with an important diffusion/reaction of the catalyst particles into/with the silicon oxide substrate from the very first growth, even at moderate temperatures. Interestingly, the catalyst deactivation by diffusion into the substrate was strongly dependent on the gas phase composition.

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A43 - Carbon nanotubes growth in 3D substrates

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Electrochemical deposition had been used to prepare Ni, Fe and Co nanoparticles with different nucleation and different particle diameters for multi-walled carbon nanotubes (MWCNT) growth. The main advantage of electrodeposition related to other methods more commonly used for catalyst deposition, such as dip-coating, spin coating or e-beam evaporator is the 3D character, which allows the MWCNT growth on the whole surface, such as in glassy carbon or carbon felt structures.

In this work we report the preparation of Ni catalyst films for growth of multiwalled carbon nanotubes. We have used an electrolytic solution of 0.01M $NiSO_4.6H_2O$ and 0.01M H_3BO_3 in water. The electrochemical deposition was carried out on a two-electrode cell with a DC power supply. Carbon felt and glassy carbon were used as substrates for MWCNT growth. The Ni electrodeposition system was mounted with the substrate as working electrode and platinum as counter electrode. A distance of 1cm and a current density of 2mA/cm^2 were established as standard.

The samples were washed by distilled water, dried at room temperature (22^{o}C), and then loaded into a microwave plasma chamber for MWCNTs deposition. The process consists in two steps: 1) nanoclusters formation, which was carried out during 5 min in N_2/H_2 plasma, at a substrate temperature around 760^{o}C; and 2) MWCNT formation, which was performed by adding CH_4 carbon source to the gas mixture during 2 min, at a substrate temperature of 780^{o}C. The reactor was kept at a pressure of 30 Torr during the whole process and the microwave power was 800 W. The results showed very good efficiency and homogeneity of MWCNT nucleation on the Ni nanoparticles, as verified by high resolution electron microscopy.

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A44 - Role of catalyst particles during CNT growth

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Mechanism of the single-walled carbon nanotube (CNT) formation is studied in the aerosol (catalyst floating) synthesis method. On the basis of *in situ* sampling experiments the role of catalyst particles is investigated. An essential role of CO_2 and H_2O vapor in the formation of single-walled CNTs is proposed. The detailed mechanism of graphene sheet transformation during the CNT growth is discussed.

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A45 - Growth of single-wall carbon nanotubes on substrates using Al/Fe and Fe thin films catalysts by CVD

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Single-wall wall carbon carbon nanotubes (SWCNTs) were grown on silicon substrates by thermal chemical vapour deposition (CVD). Iron (Fe) was chosen as the catalyst metal to promote CNT growth. Two different configurations were used to obtain a high yield of SWCNT. Firstly, Fe thin film (~1 nm) is deposited directly on the SiO_2/Si substrate. Secondly, the same Fe film is deposited on Al(10nm)/SiO_2/Si substrate.With this configuration we can analyze systematically the effect of the Al underlayer on the formation and yield of SWCNTs. Initially, the oxidized silicon substrates with both catalyst configurations were heated to 900^{o}C in argon atmosphere. The sample was maintained at 900 ^{o}C for 10 min with a flow mixture of methane, ethylene and hydrogen. By analyzing the results, we could observe that the growth performed using the Al/Fe catalyst generate a high yield of high quality single wall carbon nanotubes, while the CNT growth obtained by the Fe catalyst provided a low yield of a mixture of single wall and multiwall carbon nanotubes. In agreement with Lacerda (JAP 2004), the Al layer was transformed during the annealing into a nanoporous aluminum oxide layer. The Al underlayer plays an important role as a matrix for the adsorption of the Fe nanosized particles, avoiding the formation of large Fe clusters providing the suitable conditions for a high yield of SWCNT growth.

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A46 - Development of large scale production of single and double walled carbon nanotubes using fluidized bed reactor

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Great attention has been focused on Thermal Chemical Vapour Deposition (TCVD) due to its great potential for scale-up the synthesis of carbon nanotubes (CNTs) with powder catalysts. The main purpose of this work is to optimize the production of Fe-Mo/MgO Single Walled Carbon Nanotubes (SWNTs) and Double Walled Carbon Nanotubes (DWCNT) through TCVD. In order to that, the composition of the catalyst (Fe:Mo precursos ratio), the catalyst preparation route and synthesis conditions were evaluated (temperature, time and carbon source). Ethanol and Hexane were tested as carbon sources. Catalysts were produced through a Solution Combustion Synthesis technique, which allows a fast preparation of single or several oxides. The catalysts were tested in a convention horizontal CVD reactor and also in a large capacity fluidized bed CVD reactor. Iron and molybdenum oxides dispersed in magnesium oxide (MgO) matrix form an inexpensive CNT catalyst and the easily dissolution of the MgO in mild acids facilitates the purification process. In situ characterization by electrical conductivity of the catalysts were also used to evaluated the effect of several synthesis parameters. The diameter of the nanotubes were not significantly affected by the carbon source. Higher yields of SWCTs were obtained using hexane but also more deposition of amorphous carbon was observed. It was found that molybdenum addition in small amount (Fe:Mo;20) causes an increasing in the G/D ratio and yields SWCNTs, but higher amount causes an increase in the number of walls of CNTs and also the production of undesirable carbon nanostructures (nanofibers and carbon onions).

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A47 - Catalyst particle and CNT size and charge distribution in CO-ferrocene reactor

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We investigated the evolution of aerosol catalyst particle and carbon nanotube (CNT) sizes and charges during ferrocene vapour decomposition in an inert nitrogen and carbon monoxide atmospheres at different temperatures [1]. It was found the phenomenon of spontaneous charging of CNT bundles. On the basis of transmission electron microscopy observations and differential mobility analyser measurements mechanisms of catalyst particle and CNT charging is discussed.

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A48 - Synthesis and characterization of phosphorus and nitrogen doped multiwall carbon nanotubes

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Carbon Nanotubes have attracted great attention of the scientific community due to their unique electronic and mechanical properties. Inclusion of non-carbon atoms into the graphite network, also known as doping, leads to different electronic and chemical properties due to variations in their electronic structure. In this work, multi-wall carbon nanotubes arrays were synthesized using a solution of ferrocene and triphenyl-phosphine on benzylamine as carbon source in a spray pyrolysis experiment. Iron phosphide (Fe3P) nanoparticles acted as catalyst for MWCNT growth, leading to the formation of PN-doped Multiwall Carbon Nanotubes. Comprehensive characterization by SEM, HRTEM and STEM will be shown, as well as analytical information on the composition and stochiometry of the catalytic particles by EELS and EDX spectroscopy. Also, chemical stability is explored by means of thermogravimetric analysis in the presence of oxygen.

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A49 - Gas sensing devices based on aligned carbon nanotubes grown by plasma CVD and spray pyrolysis

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In this work, we report an investigation on the response of a simple two-terminal gas-sensor based on multiwalled nitrogen doped carbon nanotubes (MWNT) grown by plasma assisted chemical vapor deposition (PACVD) and spray-pyrolysis. Vertically aligned MWNT were grown by dc-PACVD using as precursor atmosphere a mixture of ammonia and acetylene. The catalysts were nickel nanoparticle grown from the annealing of a nickel film deposited onto the SiO_2/Si substrate. After the deposition, the films samples were treated by ammonia plasma before the plasma MWNT growth. Pure multi-walled CNTs and N-doped multi-walled CNTs were synthesized by the spray pyrolysis method. In our experiments, Ferrocene was dissolved in Toluene or Benzylamine. These two solutions were then pyrolyzed at around 800^oC in order to obtain two different types of tubes. The samples were characterized by transmission and scanning electron microscopy and Raman scattering. The detection is done by measuring changes in conductance response upon exposure to the gases. In this work, gasoline, carbon dioxide and ammonia were employed and the results show a slight dependence of the changes in the response within the nanotube growth method.

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A50 - Parametric study on the growth of carbon nanotubes and related nanostructures over palladium based catalysts

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The discovery of new catalysts and improved production methods remains as a current and growing field of carbon nanotube research. Only a few studies related to the formation of carbon nanostructures using Pd as catalyst have been reported. In this contribution we want to show an extensive study on experimental conditions in the CVD growth of carbon nanostructures using alumina-supported palladium as catalyst.

Palladium nanoparticles [1] supported on alumina were prepared by the Solvated Metal Atom Dispersion technique (SMAD). The decomposition of acetylene was carried out in a Chemical Vapor Deposition apparatus (CVD) composed of a horizontal tube furnace and a set gas flow lines [2]. The catalyst, Pd(1%)/γ-Al_2O_3, was placed in a quartz boat inside the tube reactor, heated up to 800 ^oC and annealed in a Ar/H_2 stream. Acetylene (40 ml/min) was then decomposed over the catalyst for 30 min. The above synthesis parameters are the optimum for the production of pure multiwall carbon nanotubes [3].

In this work we will present a parametric study of experimental conditions such as ramping rate, the influence of hydrogen pre-treatment, the use of methane as a carbon source and varying annealing times of catalyst. Depending of the experimental condition carbon nanotubes, nanofibers, encapsulated nanoparticles or microspheres were obtained. The effects of these conditions on the morphology of final carbon products were mainly analyzed by Transmission Electron Microscopy.

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A51 - Controlling the dimensions and cristallinity of multiwalled carbon nanotubes using low ethanol concentrations

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Since the discovery of carbon nanotubes, a lot of research has been carried out regarding their synthesis, leading to the development of different techniques of production. Among these methods, the chemical vapor deposition (CVD) method, based on the pyrolysis of hydrocarbons over metal catalysts, is widely used due to its practicality and low cost.

Common hydrocarbons used in this process are toluene, ethylene, xylene, methane, among others. So far, ethanol has been used in the synthesis of SWNTs [1]-[2] but its effect on the production of multiwalled carbon nanotubes (MWNTs) has never been studied. Important efforts have been directed to control nanotube dimensions and quality, previous works have been carried out to control the nanotube diameter by varying the catalyst quantities [3], and to improve purity of singlewalled carbon nanotubes (SWNTs) by adding small concentrations of water to the CVD ethylene solution [4].

In this work, we show a systematic study of the role of ethanol during the synthesis of MWNTs using the spray catalytic pyrolysis of toluene and ferrocene solutions. An extensive set of experiments, in which the amount of ferrocene and ethanol is varied, illustrates the effects of ethanol in the synthesis of MWNTs. For low concentrations of ethanol (0.5 - 2.5 % by wt.) the length and diameter of the tubes change depending on the quantity added to the solution; while the most crystalline tubes are synthetized when adding 1 % by wt. EtOH to the CVD solution. It is also important to point out that for higher concentrations of ethanol (5 - 7.5 % by wt.) the growth of nanotubes is inhibited, enhancing the production of iron carbides.

MWNTs carpets grown over quartz plates are studied by SEM, these images are used to analyze the statistical distribution of lengths and diameters of the produced samples. The soot material collected from the middle furnace section is analyzed with XRD, Raman spectroscopy and TGA. This powder is also used to test the dispersion of the produced MWNTs in isopropyl alcohol, being the easiest dispersed samples the ones with the lowest concentration of ethanol (0.5 - 1 % by wt.), suggesting the introduction of carboxylic groups on the nanotubes during synthesis. The present study reveals an easy way to tune the length and diameter of multiwalled carbon nanotubes and to improve the quality of the samples in a single step process without further treatments.

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A52 - Efficient growth of single-wall carbon nanotubes by arc discharge

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In this work we will present our efforts towards a large scale production of carbon nanotubes (CNTs) by arc discharge. Usually SWCNTs are grown by this method using Ni/Y as a catalyst in a He atmosphere. However, in spite of the great success of growing CNTs by this technique, the material obtained from arc discharge deposition contains a large quantity of spurious forms of carbon (~ 30%) and metal particles (30%) that do not participate directly on the CNT growth process. This means that the as-grow material has to go through a hard process of purification that sometimes can not be efficient enough to remove all the metal particles, especially carbides. In this sense, we have improved the growth efficient of our arc-discharge system. By using Co/Ni catalyst we were able to reduce by 30% the amount of metal catalyst. That is a significant reduction which provides an as-grown arc-discharge material with small amounts of metal particles enabling an easier purification process. Additionally, by tuning the growth conditions we were able to obtain up to ~ 4g of material per deposition providing an efficient route to grow large amounts of CNTs by arc discharge with low concentration of metal impurities.

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A53 - Production and Characterization of CN_x/C Coaxial Nanotube Junctions and Networks

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We describe a two-step process for the generation of coaxial nanotube heterocables consisting of nitrogen doped carbon nanotubes (MWNTs-CN_x) encapsulated inside carbon nanotubes (MWCNT). We refer to these structures as CN_x@CNT. The first step in the process involves the deposition of iron nanoparticles on MWNTs-CN_x using potassium hexacyanoferrate(III), $K_3[Fe(CN)_6]$ in an acidic medium. In the second step, toluene is pyrolyzed over these Fe coated tubes in a furnace.

The materials obtained by this procedure were after characterized by SEM, and new carbon structures junctions alike were found. A further HRTEM observation shown that the nanotubes forming these structures were different from their MWNTs-CN*x* precursors: they were composed of a core done of N-doped multiwalled carbon nanotubes wrapped by an outer shell of MWCNTs.

Coaxial nanotubes in this arrangement were found in some cases, while in the others bundles of MWNTs-CN*x* wrapped by a MWCNT were identified, just in a similar way to cables.

Thermogravimetric (TGA) analysis shown also two decomposition temperatures which ensure a composite structure achieved. To our knowledge, this is the first time that a similar structure to heterocables of the kind CN_x@CNT is reported.

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A54 – Predicting carbon nanotube growth parameters using continuum and atomistic approaches

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In catalyst-assisted chemical vapor deposition, carbon nanotubes are formed when a curved graphene island lifts off the surface of the catalyst particle on which it is growing. While this growth technique offers effective control over patterning and alignment, control over nanotube radius and chirality will remain elusive until one can better control the point at which lift-off occurs. In this contribution, we use continuum and atomistic approaches to model the lift-off process via the interplay between the excess energy required to grow a curved (and thus, necessarily defected) graphene island and the interaction energy between the growing island and the underlying catalyst. Lift-off of the growing island, and hence initiation of nanotube growth, is favored when the interactions with the catalyst can no longer offset the energy to grow a curved graphene island. The continuum model describes the critical island size for lift-off as a function of the size of the underlying catalyst. The atomistic approach is a hybrid technique implementing quantum and classical methods to develop Monte Carlo and Kinetic Monte Carlo models of island formation, growth, and lift-off.

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A55 - Growth mechanism of vertically aligned single-walled carbon nanotubes

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Following the first realization of VA-SWNTs [1] by alcohol catalytic CVD (ACCVD) method, various techniques are reported for the vertical aligned growth such as control of water, point-arc microwave plasma CVD, molecular-beam CVD, hot-filament control of atomic hydrogen, hydrogen/oxygen ratio control by oxygen-assisted CVD. Recently, it was revealed that VA-SWNTs by ACCVD method is composed of high-purity SWNTs with small bundles about 5 nanotubes through the cross-sectional TEM scan. The small-bundle morphology and nearly isolated electronic properties [2] of each nanotube is suited for various applications of VA-SWNTs. In this study, the growth mechanism of VA-SWNTs film is studied through the in-situ measurement of film thickness by laser absorbance [3]. The measured growth curves for various CVD temperature, ethanol pressure and ethanol flow rate in the alcohol CCVD technique are all described by a simple function with the exponential decay of growth rate, where initial growth rate and decay life time are parameters. The decay of growth rate was almost linearly proportional to the film thickness. This result implies that the catalyst metal is over-coated by carbon as the CVD reaction proceeds. Because the initial growth rate was almost proportional to ethanol pressure, the first order reaction can be assumed for the growth process. As the ethanol pressure increase, the decay time suddenly decreased. This phenomenon is explained by the excess rate of decomposition of ethanol beyond the possible over-all growth rate of the tangled film.

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A56 - Growth optimization of multiwalled carbon nanotubes forests over Mg-Fe thin films

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Vertically aligned carbon nanotubes present interesting applications, such as field-emission devices, composites, vacuum microwave amplifiers and optoeletronics. Multiwalled carbon nanotubes were growth with a low-cost thermal CVD apparatus using ethylene as carbon source at atmospheric pressure. Evaporated thin films of Mg and Fe over silicon wafers were used as catalyst. Several parameters as pre-reduction condition, synthesis atmosphere and substrate composition were investigated. Forests with height superior to 100 micrometres were produced in 20 min of synthesis. Uniform heights were achieved over substrate with several square centimetres.

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A57 - Effects of Plasma Ion Dose and Energy on the Nanotube Growth in the Electron Cyclotron Resonance Plasma

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Plasma-assisted carbon nanotube (CNT) growth is favorable because of its low temperature process, however, the role of ion energy and dose on the growth may not be clearly understood. Energetic ions with a proper density contribute to the migration of carbon atoms to assemble CNT structures, achieving the low temperature growing process. Also it may cause the damage on the bonding of CNTs and the deformation of the CNTs when ion dose and energy are larger than the critical values. Consequently the plasma ions play an important role in the CNT growth rate and structure of CNTs. In this study, CNT growth experiments were carried out in the electron cyclotron resonance (ECR) plasma source and the substrate temperate was fixed at 600. Process gas ratio (CH_4/H_2) was also fixed with ratio of 1:4 and the total pressure was about 1 Torr. Ion dose and energy in plasma were controlled with varying the ECR zone and bias voltage. And then plasma properties related with ion dose and energy were observed by a Langmiur probe. Resonated electrons in ECR zone have more energy than the other plasmas such as DC or any other RF plasmas, being employed to make high density plasma. Processes with high density plasma, namely, processes with high ion dose caused a rapid CNT growth rate due to the increase in number of ions participated in the growth process as well. However amorphous carbons instead of CNTs were observed when dose of ions exceeded a critical value. On the other hand, the substrate bias is more effective to control the incident ion energy on the target so that the dose and ion energy can be controlled separately. It was studied that the ion bombardment related with the ion energy on the substrate contributed to the size of catalyst particles and deformations of grown CNTs. After considering effects of the plasma ion dose and energy, it was investigated what the optimal ion dose and energy are for the maximum growth rate without the formation of amorphous carbons and severe deformations of CNTs.

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A58 - SabreTube: A Flexible, Low-Cost Desktop System for Chemical Vapor Deposition

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Growth of CNTs within laboratory-scale tube furnace has shown great promise in the production of CNTs. However, existing tube furnace designs limit the researcher's ability to fully separate critical reaction parameters such as temperature and flow profiles, particularly where the reactant mixture thermally decomposes before reaching the catalyst and/or growth substrate. Additionally, the use of heating elements external to the reactor zone necessitates the heating of a large thermal mass, precluding the ability to rapidly vary the reaction temperature. Conventional tube furnace designs also preclude mechanical and optical access to the reactor region and the growth sites, limiting the ability to observe and measure the reaction in situ.

We present our desktop CVD system, the "SabreTube", which features resistive heating of a suspended platform and thereby achieves heating and cooling rates of ~100 C/s [1] with non-contact measurement of temperature. Further, thermal pre-treatment of the reactant mixture is decoupled from heating of the substrate, as the gas is passed through a heated pipe where it is rapidly treated to 1000 C or above. By decoupling this thermal path, we achieve a 15-fold increase in CNT growth rate, while imaging the film thickness and topography in situ [2]. Modular fixturing of the SabreTube, using standard optomechanical parts, allows the user to reconfigure the setup and place sensors in close proximity to the reaction tube; for example, a commercial laser displacement sensor is placed above the suspended tube and measures film thickness in real time with micron precision.

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A59 - Tuning the diameter and areal density of aligned CNTs by engineered pre-treatment of the catalyst film

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Aligned architectures of carbon nanotubes (CNTs) are sought for applications such as microelectronic interconnects, heat sinks, and reinforced composites. These applications will require precise control of the diameter, wall structure, and areal density of CNTs on substrates. Further, CNT growth by CVD from thin films of metal catalyst offers potential for manufacturing scalability.

Here we demonstrate control of the diameter and areal density of vertically-aligned CNTs in a “forest”, simply by controlling the pre-treatment of an Al_2O_3-supported Fe catalyst film in atmospheric-pressure flows of H_2 and C_2H_4. Starting in each case with a 1 nm Fe film, we tune the diameters of CNTs by a factor of two, from 14 nm (6-8 walls) to 7 nm (2-4 walls); and we tune the areal densities by more than an order of magnitude, from 3×10^9 to 5×10^{10} CNTs/cm^2. Relationships between catalyst particle size, particle density, and initial growth rate are governed by the oxidation state of the catalyst and the reductive nature of the pre-treatment and growth atmospheres. Initial heating of the catalyst in an inert ambient followed by pre-treatment in C_2H_4 without added H_2 results in accelerated and very rapid growth when H_2 is later introduced, and we achieve a maximum forest growth rate of 400 microns per minute.

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A60 - GIGAS GROWTH of carbon nanotubes

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Camphor ($C_{10}H_{16}O$) is shown to have an amazing efficiency of producing carbon nanotubes (CNTs) by a technique greatly complying with the principles of *Green Chemistry*. Right from the first report of CNTs from camphor [1], Kumar and Ando remained involved with this environment-friendly precursor and established the conditions of growing single-wall & multiwall nanotubes (SWNTs & MWNTs) [2], and vertically aligned MWNTs [3] by a simple and inexpensive CVD technique. Recently, using a zeolite powder as the catalyst support, we succeeded in growing MWNTs at a temperature as low as 550°C, whereas SWNTs could be grown at relatively high temperature [4]. Using the same materials but different processing, we have discovered the experimental conditions to achieve an exceptionally high growth of MWNTs at 650°C at atmospheric pressure. In a common academic laboratory set-up, simple 30-min CVD of 12g camphor over Fe-Co-impregnated zeolite powder at 650°C yields 6g MWNTs of diameter 10 nm with an as-grown purity of 88%. Owing to the enormous CNT growth, the zeolite bed inflates by 1000 wt% and 5000 vol%. Camphor-to-CNT production efficiency is 50% and source carbon-to-CNT conversion efficiency is 61%. These figures are incomparably higher than that of any CNT precursor by any method. Hence we call it *gigas growth*. It may be debatable whether the key of *gigas growth* lies in the source material -- camphor, or in the optimization of 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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[3] M. Kumar, Y. Ando, Chemical Physics Letters 374 (2003) 521-526.
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A61 - In situ optical characterisation of PECVD nanotube and nanofibre growth

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Dc plasma-enhanced CVD growth of nanotubes and nanofibres is studied as a function of plasma power (3-40 W). The dependence of the nanotube/nanofibre morphology for growth on thin iron films and lithographically prepared individual nickel dots is investigated. In both cases, large differences in the morphology of the carbon nanostructures are observed as the plasma power is changed. In situ optical emission spectroscopy is used to obtain insight into the important parameters affecting the growth [1]. For Fe catalysed growth there is a crossover from aligned multiwalled nanotube growth at low plasma power (< 20 W) to individual carbon nanofibres at higher power. This can be related to the relative amount of hydrogen atoms in the plasma.

In addition we report the results of in situ laser reflectivity measurements used to monitor the growth of multiwalled carbon nanotube films grown by dc PECVD from an iron catalyst film. The initial growth rate is high (as much as 10 µm per minute) and then drops off rapidly to reach a steady level (2 µm per minute) for times beyond 1 minute. We show that a limiting factor for growing thick films of MWNT using PECVD can be the formation of a thin amorphous carbon layer at the top of the growing nanotubes. In situ reflectivity measurements provide a convenient technique for detecting the onset of the growth of this layer.

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A62 - Laser direct writing carbon nanotube arrays on transparent substrates

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The authors report the synthesis of multiwalled carbon nanotubes on transparent substrates by utilizing a diode laser to locally heat the catalysts to high temperature instead of a huge chemical vapor deposition furnace. Wellaligned bamboo-shaped multiwalled carbon nanotubes can be synthesized on glass substrate covered with a carbon black layer. If the carbon black was substituted by the commercial graphite inner coating, randomly oriented but high quality multiwalled carbon nanotubes were obtained with excellent field emission performance. This laser direct writing approach enables the direct position-controlled synthesis of carbon nanotubes on low melting point transparent substrates, which facilitate the fabrication of carbon nanotube field emitters for flat panel displays without limitations on the geometry size and temperature requirement of the substrate.

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A63 - CNT production by use of high temperature thermal plasma

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SINTEF has designed and built a high temperature plasma reactor for the production of CNT (Carbon nanotubes) on a pilot scale, the PPM-reactor. The method and reactor is patented. This method is believed to be efficient for production of straight CNT at a high production rate and with a low density of defects.

In the PPM-reactor the vertical distance between the cathode and the hollow anode can be varied 0 – 25 cm in the present setup, typically 10 cm. The arc burning between these electrodes is rotated by the externally applied magnetic field controlled by magnet coils. Rotation of the arc provides a voluminous thermal plasma. Carbon feedstock, plasma gas, as well as catalysts can be introduced through lances at the top of the reactor. The anode is provided with holes allowing recirculation of the plasma gas, giving carbon particles or gaseous carbon compounds a second chance to pass through the plasma region, and thus give a more complete evaporation or dissociation of the carbon containing feedstock. On the way out of the reactor the gas passes a cooler and a filter.

Experiments have been carried out typically at a pressure of 0.6 bara using He as plasma gas and with methane CH_4 as carbon feedstock. The arc current have been varied 300-900 A, and the power 65-155 kW. In most of these experiments the temperature on the reactor walls was around 2000 ^{o}C. In the voluminous thermal plasma region the temperature is estimated to be around 5000-20000 ^{o}C. At once methane is introduced into the reactor it cracks to carbon and hydrogen. The carbon containing gas recirculates in the reactor and the carbon condenses on the “cold” anode walls as multiple wall nanotubes (MWNT) in variable amounts, depending on the process conditions. These are scraped off the anode inside. Carbon collected in the filter has a high concentration of CNT, with typically average diameter in the range 12-16 nm. When catalyst is added, single wall nanotubes (SWNT) are also produced.

The CNT produced are straight with an apparently low density of defects. Several of the desired attractive properties gained by using CNT are dependant on CNT quality and CNT structures in possess of a low density of defects on an atomic level are in demand. The developed technique and equipment for CNT production are promising, and the work to develop the process further will continue.

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A64 - Selective area growth of carbon nanotube on SiC(000-1) using Ti mask pattern

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It has been reported that zigzag type of Carbon Nanotubes (CNTs) selectively grow up after annealing 6HSiC(000-1) substrate in a vacuum [1]. In this growth technique, carbon nanocaps are formed on the SiC surface at first [2], then CNTs gradually grow into SiC substrate during annealing. Therefore, CNT position can be controlled using mask patterning technique. However, in this CNT growth, the growth temperature is too high (>1300 ^{o}C) to apply conventional mask materials, such as SiO_2 or SiN, so it has been difficult to realize selective area growth of CNTs. To avoid this problem, we have been applying Ti, high melting point metal, for a mask material [3]. In this study, we carried out selective area growth of CNT using Ti mask by optimizing the mask and growth conditions.

After fabrication of Ti mask pattern (100 nm in thickness) with equal line/space (20 mm period) on 6HSiC(000-1) substrates by a conventional lift-off technique, the substrates were annealed at 1500 ^{o}C for 30 min in a vacuum electric furnace. Then, the samples were characterized by scanning electron miscroscopy (SEM), X-ray photoelectron spectroscopy (XPS), micro-Raman spectroscopy and transmission electron microscopy (TEM).

SEM observation showed that Ti mask pattern was maintained even after annealing, although the surface roughness of the mask was rather increased. XPS spectra also showed that most of Ti mask remained on the substrate surface after annealing. These showed that Ti mask can withstand annealing up to 1500 ^{o}C within 30 min. After annealing, G band appeared on the open area among the Ti mask by the Raman measurement and the growth of CNTs of 50 nm in length was confirmed by TEM observation. In addition, no decomposition of SiC was observed in the underlayer of Ti mask from TEM images, indicating that Ti mask can suppress CNT growth. These results show that Ti mask is useful to realize selective-area growth of CNTs.

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A65 - Synthesis of Carbon Nanotubes by Laser ablation

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We report the synthesis of Carbon Nanotubes by laser ablation of a graphite target, in a 1300K oven. In our experiment, we have synthesized carbon nanotubes by ablating a graphitic target that contains few percent of Ni and Co particles. We ablate the target with a 200 us Nd:YAG laser pulse, focused at the target surface. The first part of the laser pulse induces the vaporization of the target, generating carbon atoms, clusters and very small particles of graphite, together with the metal vapor. The second part of the pulse is absorbed by the generated plume increasing the amount of carbon atoms by dissociating the graphite particles and carbon clusters.

As the plasma jet expands and travels inside the oven, it condenses and carbon nanotubes are synthesized by a self assembly process. After traveling about 50cm inside the oven, the carbon nanotubes condensates at the refrigerated Si collector, and at other cold parts of the system.

Raman spectroscopy showed that a very large fraction of this deposit consists of semiconductor, single wall carbon nanotubes, with diameter of about 1.35 nm.

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A66 - A novel apprpach towards purity control of arc generated carbon nanotubes

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An attempt is made to understand the focusing electric field induced changes in the composition of arc-generated cathode-deposit, often called as the storehouse of carbon nanotubes (CNTs). Using mass-measurement, Raman spectroscopy and transmission electron microscopy, we show that relative purity and quantity of carbon nanotubes within the cathode deposit is tunable by controlling the focusing electric field. It is inferred that such a modified reactor at the optimized conditions achieves bulk-productivity of highly pure CNTs extirpating the process inherited loss of feedstock material that diffuses out of the plasma zone and deposits on the reactor chamber wall in the form of amorphous carbon and/ fullerenes. We observe that a focusing voltage of 400V for the used electrodes configuration creates an environment conducive to optimized purity and yield of the as-synthesized nanotubes. We conclude that guding the positively charged carbon precursors towards the cathode with the help of an appropriate external electric field, a stuation can be arrived, at which both the purity and yield of as synthesized CNTs are maximized.

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CONTRIBUTED ABSTRACTS

POSTER SESSION B

JUNE 25 (Monday)

B01 - High Catalytic Activity of Multi-Walled Carbon Nanotubes Incorporated in Layer-by-layer films

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Carbon nanotubes incorporated in polymeric matrices have been widely exploited in nanostructured films to exploit their unique electrical and electrochemical properties. A limitation to be overcome in this approach, though, is that the film preparation requires surface treatment of the nanotubes that may have their electrochemical and electrical properties affected. In this context, the layer-by-layer (LbL) technique has been an ideal choice to prepare films with architecture-controlled multilayers. The main advantage is the synergy between composite components due to the intimate contact within the multilayers. In this study we describe the fabrication and electrochemical characterization of LbL films combining layers of nickel tetrasulfonated metallophthalocyanine (NiTsPc) and polyamidoamine-PAMAM-incorporating multi-walled carbon nanotubes (PAMAM-NT). The assembly of the PAMAM/NiTsPc and PAMAM-NT/NiTsPc LbL films was monitored via UV-vis spectroscopy and with atomic force microscopy (AFM) images. Infrared spectroscopy pointed to a strong interaction between - NH^{3+} terminal groups from PAMAM and -SO_3- from NiTsPc. Cyclic voltammograms showed a well-defined electroactivity (redox pair at 0.84 V and 0.87 V), reversibility, charge-transfer controlled process, high stability and a high sensitivity and electrocatalytic activity toward dopamine (DA), ranging from 1.0×10^{-5} mol L^{-1} to 4.0×10^{-5} mol L^{-1}, for both LbL films. Furthermore, the presence of carbon nanotubes (PAMAM-NT/NiTsPc film) caused a significant change in DA detection, in comparison to PAMAM/NiTsPc films, as the oxidation potential for DA was reduced from 0.72 V to 0.65 V. In other words, the composite carbon nanotube-NiTsPc immobilized in multilayers enhanced the catalytic activity for DA.

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B02 - A Versatile Plasma Tool for the Synthesis of Carbon Nanotubes and Few-Layer Graphene Sheets

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Microwave plasma-enhanced chemical vapor deposition (PECVD) is a versatile tool for the synthesis of carbon nanotubes (CNTs) and few-layer graphene sheets. Nickel particles, deposited on silicon oxide substrates, catalyze the growth of CNTs according to the tip growth mechanism. When the catalyst gets saturated by abundant carbon, the growth of CNTs stops and the remaining carbon radicals are inserted at the sidewalls and tips of the CNTs, forming graphene sheets, implying the catalyst condition induces a switch from growth of CNTs to growth of graphene. The graphene sheets are stacked together forming thin graphite flakes, only a few atomic layers thick but up to several micrometers wide. The important role of the catalyst in determining the geometry of the as grown carbon nanostructures, either tubular CNTs or plain graphene sheets, during experiments with identical process parameters, is demonstrated by the synthesis of few-layer graphene sheets on various substrates without the presence of a metallic catalyst. The formation of freestanding few-layer graphene sheets is monitored by in situ optical emission spectroscopy and related to an extensive analysis study by Raman spectroscopy, electron microscopy, x-ray diffraction and x-ray photoelectron spectroscopy. Individual few-layer graphene sheets were ultrasonically dispersed in ethanol and imaged with scanning tunneling microscopy. Field emission experiments of few-layer graphene sheets grown directly on titanium substrates show low turn-on voltages which are promising results for potential applications.

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B03 - Imogolite Nanotubes

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The aluminosilicate mineral imogolite is composed of nanotubes, naturally occurring in soils of volcanic origin with a stoichiometry of $(HO)_3A_{l2}O_3SiOH$. The main feature of these tubes is their monodispersiveness, which makes them unique compared to all other presently known types of nanotubes and attractive for the design of nanomaterials with well-defined physicochemical properties. Internal and external hydroxy groups offer interesting applications as proton conductors or catalysts.

We calculated structure, stability, electronic and mechanical properties of imogolite nanotubes using the density-functional based tight-binding method (DFTB). Zigzag (8,0)...(25,0) and armchair (5,5)...(14,14) imogolite tubes with diameters ranging from 14 to 40 Å have been studied. The highest stability of all studied imogolite tubes has (12,0) chirality, in contrast to conventional nanotubes the stability decreases for larger radii. This is in full agreement with experimental data, as shown by comparison with the simulated XRD spectrum. The Young's moduli of imogolite nanotubes are about 240 GPa, similar to those of other inorganic nanotubes (MoS_2, GaS, chrysotile). An analysis of the electronic densities of states shows that all imogolite tubes, independent on their chirality and size, are insulators with a band gap of ~ 10 eV.

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B04 - Efficient Formation of Carbon Nanowalls Using Helicon Wave Plasmas

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The efficient formation of carbon nanowalls is investigated using helicon-wave plasmas [1,2]. The highest growth speed (250 ~ 300 nm/min) of the carbon nanowalls is realized owing to distinct qualities of the heliconwave plasmas, such as a high density and high degree of disassociation even in the range of low gas-pressure. Furthermore, the correlation between the formation of the carbon nanowalls and the ion flux irradiated to a growth substrate is clarified through the experiment in the plasma production region, and as a result of the ion-flux control, the carbon nanowalls are successfully formed at the lowest substrate temperature of about 400 ^{o}C. On the other hand, effects of ion-energy and -flux on the growth of the carbon nanowalls are studied with the precisely controlled helicon-wave plasmas in the plasma diffusion region. A clear threshold of ion-energy for the growth of the carbon nanowalls is found to exist around 80 eV. Interestingly, an obvious formation transition from the carbon nanowalls to carbon nanotubes is also observed with an increase in the energy of ions coming into the substrate.

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[2] G. Sato, T. Morio, T. Kato, and R. Hatakeyama: Jpn. J. Appl. Phys. 45 (2006) 5210.

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B05 - Optically Active Single-Walled Carbon Nanotubes

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The optical, electrical and mechanical properties of single-walled carbon nanotubes (SWNTs) are largely determined by their structures, and the bulk availability of uniform materials is vital for extending their technological applications. Since they were first prepared, much effort has been directed toward selective synthesis and separation of SWNTs with specific structures such as diameter, length and chirality. Little attention, however, has been paid to another important feature, namely the optical isomers that arise from the spiral alignment (either left- or right-handed) of the hexagonal carbon rings along the nanotube axis in chiral SWNTs. Although their optical properties have been predicted theoretically, optical activity originating solely from carbon nanotubes has not been reported so far.

Here, we report, for the first time, the preparation of optically active SWNTs that show a pair of opposite and symmetrical CD spectra, which is intrinsic to the SWNTs. In this process, ‘chiral nano-tweezers’ comprising meta-phenylene-bridged zinc(II) diporphyrins are used to extract and enrich nanotubes of a single mirror image form for each chiral index. In the extraction, the ‘chiral nano-tweezers’ recognize the helical (left- and righthanded) structures of SWNTs to form complex with either one of the helicities preferentially and dissolve it into liquid phase. A remarkable advantage of the present method is the easy and complete removal of the tweezers from the complexes, enabling recovery of pristine SWNTs free from the dispersing material. Other methods that use molecules such as DNA or other surfactants tend to have difficulties in this removal phase.

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B06 - Growth of Novel Architectures with Aligned Nanotubes using Controlled Micro-patterning of Si Substrates by Electrochemical Methods

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The fabrication and characterization of different micro-morphologies of aligned multi-walled nitrogen doped carbon nanotubes is described. These micro-morphologies grown on self-assembled micro-islands, pre-patterned on porous silicon substrates using electrochemical etching. This etching method results in the formation of different types of uniform ring-shaped SiOx micro-patterns on the PS substrates, which are formed by the action of hydrogen bubbles on the PS during the electrochemical process. After thermolyzing benzylamine/toluene/ferrocene solutions at 800°C in an Argon atmosphere over these etched substrates, we obtained different microstructures resembling: flowers, volcanoes, cactuses and cakes; all consisting of aligned carbon nanotubes grown on the PS substrate. We obtained different nanotube arrays using specific etching conditions of the PS substrates. Based on our observations, we propose a possible growth scenario for these fascinating nanotube architectures.

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B07 - Synthesis of carbon "nano" filaments using CuNi as a catalyst. Influence of the support on their morphology and characteristics

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Since their discovery in the last century, 1D carbon nanomaterials have received great interest because of their high aspect ratio and their unique physicochemical properties. Their synthesis via catalyzed chemical vapor deposition is more and more studied and it has been settled that the nature of the nanofilament is closely linked to the metal catalyst. Both nanotubes and nanofibers thank to their peculiar morphologies and characteristics possess various applications (such as nanomaterials for reinforcement, catalysts or supports for catalysis and nanoreactor).

Here, we report the influence of a Cu-Ni catalyst on the morphology and characteristics of the as-synthesized carbon nanofibers. The different carbon nanofilaments were synthesized using a well-known CVD technique, by decomposition of ethane on a Cu-Ni catalyst supported on graphite felt, Yttrium Stabilized Zirconia (YSZ) plate or Si wafer. The Cu and Ni phases were deposited on the support using an incipient wetness impregnation method. After calcination and reduction of the catalyst, the synthesis was performed at 700°C in a mixture of ethane and hydrogen. Yields, morphologies and intrinsic characteristics of the as-synthesized carbon nanofilaments have been investigated using TEM, SEM, BET, and TPO. The synthesized carbon nanofilaments diameter ranged from 10 nm to up to 1 µm, with specific surface area up to 400 m^2/g, which is one of the highest specific surface area for 1D materials with diameter up to micro meter.

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B08 - Pyrolysis of thiophene and nickelocene as a Y-junctions synthesis method: temperature gradients, thiophene amount and nickel effect.

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Since CNTs Y-junctions were theoretically proposed [1], there have been reported different synthesis methods to produce them, motivated by their potential electronic properties as nanodevices. Nevertheless, each method yield totally different structure of the Y-junctions obtained. Outstanding, due to their reported higher yield of such nanostructures, are the pyrolysis of methane over cobalt supported on magnesium oxide [2] and the pyrolysis of nickelocene along with thiophene [3].

The present work has taken the pyrolysis of nickelocene with thiophene method [3] and systematically analysed the different type of products obtained along the different temperature conditions included at different zones of the experimental device. We have also modified the amount of thiophene in the reaction, obtaining drastic changes in the morphology of the products obtained. Even more, we explored the difference of using ferrocene instead of nickelocene in the experiment.

Along with the different type of nanostructures obtained at different temperature regions, it is remarkable the obtention of five different types of covalent Y-junctions when different experimental conditions are applied (amount of thiophene or type of catalyst), from Y-junctions with arms of micrometers in diameter, Y-junctions of cone-stacked carbon cylinders to perfect multi-walled CNTs Y-junctions.

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B09 - SWCNT interference devices: Synthesis and electronic properties of Y-junction rings and heterojunctions

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Molecular nanostructures such as single wall carbon nanotubes (SWCNT) are a promise candidate for prospective nano-scale electronic devices. A variety of geometrical shapes, like junctions, quantum dots and crossing objects are needed for a successful incorporation into the devices. Recently we reported on the realization of double-slit interferometers made purely of single walled carbon nanotubes [1]. We state the first time observation of such a ring-like structure naturally connected to nanotube leads using transmission electron microscopy. An in situ investigation of a merging process of the asymmetric ring into a symmetric one is presented, employing electron beam irradiation at high-temperatures of 800°C.

The electronic properties of the systems are studied using Monte Carlo simulations and environment dependent tight binding calculations adopting real-space Greens function formalisms. We address the possibility of formation and dispersion of standing waves inside the ring and define the associated wave numbers. We compare these results with the properties of heterojunctions, a similar 1-D structure. In both systems, we are able to define a quantum dot behaviour with subsequent quadratic dispersion of the standing waves. The dispersion properties are remarkably independent of the junction area atomic geometry and are basically identical for both systems. This raises the possibility of using both systems as nanoscale tuneable electronic switching devices.

However, we observe only in the Y-junction ring region localized density of states peaks near the Fermi level, which are identified as interference effects of the ring like interferometer. Moreover, we could distinguish the aperture of conductance channels by defect induced tunnelling and the usual transport reduction as well as suppression due to quantum interference processes of counter-propagating electron waves.

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B10 - In-situ growth of single- and multi-walled carbon nanotubes under high resolution transmission electron microscopy

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The growth of carbon nanotubes with desired chiralities and diameters is the most important challenge in nanotube science. We report the formation of carbon nanotubes in an entirely condensed phase process which allows us, for the first time, to monitor the nucleation of a nanotube on the spherical surface of a metal particle. When multi-wall carbon nanotubes containing metal particle cores are electron irradiated, carbon from graphitic shells surrounding the metal particles is ingested into the body of the particle and subsequently emerges as single- or multi-wall nanotubes inside the host nanotubes. These observations at atomic resolution in an electron microscope show conclusively nanotube formation involving bulk diffusion of carbon through the body of catalytic particles.

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B11 - In vitro Photo-Dynamic Therapy study of a new C_{60}/polyvinylpyrrolidone photosensitizer against Leishmania sp

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Due to their unique photo-physical and photochemical properties [1], the fullerenes are excellent candidates for photosensitizers in Photo-Dynamic Therapy (PDT). However, because of their low solubility in water, the fullerenes must be modified for this purpose. Several methods for obtaining fullerene derivatives that are soluble in water have being intensively investigated, mainly because their vast range of potential biomedical applications [2]. One of the simplest method to obtain aqueous solutions with fullerenes is by non-covalent binding with polymers like the polyvinylpyrrolidone (PVP) [3]. In this work we studied the photodynamic lethality of a fullerene (C_{60}), solubilized in water with PVP and under UVA illumination, in cultures of Leishmania sp., the microorganism responsible for the cutaneous and visceral tropical disease known as leishmaniosis. The fullerenes used in this study were synthetized by the arc discharge technique and soxhlet extracted from the soot [3]. The complex fullerene/PVP was obtained after a modification of the method reported in [4]. To evaluate the anti-leishmanial activity of fullerene, 10^6 promastigotes of different Leishmania species were cultivated in 24 wells plates in Schneider medium supplemented with calf serum. After 24h of growth, a fullerene/PVP solution was added to cultures in different concentrations. The cultures were then exposed to UV light (366 nm) for 10 min. and incubated for additional 24hs or 48hs, when parasites were quantified to determinate the percentage of growth inhibition. Preliminary results demonstrated that the fullerene/PVP solution is highly active against all the Leishmania species tested, which are etiological agents of cutaneous leishmaniasis. Although further studies are required, these results suggest that Fullerene may be a simple and low cost alternative treatment for this illness.

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B12 - “Single-beam pumped” Coherent anti-Stokes Raman Scattering

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Giant optical fields locally generated in nanoscale metal structures through the local excitation of surface plasmons underlie a variety of nonlinear optical processes. Metallic particles of 5-100 nm size as well as metallic film with a roughness type structure in the range of 10-100 nm are convenient supports to confine the electromagnetic energy in subwavelength-sized regions. Using silver and gold, reproducible enhancements of the Raman signal of the order of 10^2 - 10^4 on various polymeric and semiconducting materials including carbon nanotubes, have been demonstrated.
An abnormal anti-Stokes Raman emission, reminiscent of Coherent anti-Stokes Raman Scattering (CARS), is accurately observed on nanometric thin film on different materials such as copper phthalocyanine, poly(bithiophene), carbon nanotubes, etc. Restricting our attention to the single-walled and double -walled carbon nanotubes, we demonstrate that under a tight-focusing of the excitation light, a CARS emission, resulting from a wave mixing process between the incident laser light (ωl) and Stokes Raman light (ωs) generated by a Surface Enhanced Raman Scattering (SERS) mechanism, is produced. The results which corroborate the CARS emission are the following: i) a square relation between the CARS signal intensity and the film thickness; ii) a square relationship between the CARS signal intensity and the exciting laser intensity; iii) a dependence of the CARS intensity on the numerical aperture (NA) of the microscope objective used for the detection of the anti-Stokes emission; iv) a polarization ratio in the anti-Stokes side always greater in comparison with that measured for a spontaneous Stokes Raman emission.
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B13 - Kohn anomalies and non-adiabaticities in doped carbon nanotubes

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The high-frequency Raman-active phonon modes of metallic single-walled carbon nanotubes (SWNTs) are thought to be characterized by Kohn anomalies (KAs), which are expected to be modified by the doping-induced tuning of the Fermi energy level ε_F, obtained through the intercalation of SWNTs with alkali atoms or by the application of a gate potential.We present a Density-Functional Theory (DFT) study of the phonon properties of a (9,9) metallic SWNT as a function of electronic doping. For such study, we use, as in standard DFT calculations of vibrational properties, the Born-Oppenheimer (BO) approximation. We also develop an analytical model capable of reproducing and interpreting our DFT results. Both DFT calculations and this model predict, for increasing doping levels, a series of EPC-induced KAs in the vibrational mode parallel to the tube axis at the Γ point of the Brillouin zone, usually indicated in Raman spectroscopy as the G^- peak. Such KAs would arise each time a new conduction band is populated. However, we show that they are an artifact of the BO approximation. The inclusion of non-adiabatic (NA) effects dramatically affects the results, predicting KAs at Γ only when ε_F is close to a band crossing E_X. For each band crossing a double KA occurs for ε_F = E_X *hbar\omega2*, where ~! is the phonon energy. In particular, for a 1.2 *nm* metallic nanotube, we predict a KA to occur in the so-called G^- peak at a doping level of about N_{el}/C=\pm 0.0015 atom (ε_F ~0:1 *eV*). Furthermore, we predict that the Raman linewidth of the G^- peak significantly decreases for ε_F |geq \hbar\omega/2.

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B14 - Optical properties and Resonant Raman response of SWNTs : Non-Orthogonal Tight Binding Model and isolated identified tubes.

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The optical properties and the electronic structures of SWNTs have been studied by different techniques in the last years: Resonant Raman Spectroscopy, Photoluminescence, Scanning Tunnelling Spectroscopy. It is now well understood that the excitonic effects play a major role in the interpretation of the experimental data. However, a precise description of the excitonic (and other correlation) effects is still under investigation. In this communication, we compare our Non Orthogonal Tight Binding simulations for the electronic transitions energies to the available experimental data. In particular, we focus on the Resonant Raman Scattering obtained on SWNT identified by Electron Diffraction .We show that the first and second transition for semiconducting tube can be explain if an 1/R excitonic binding energy is considered. But the third and fourth transitions are interpreted in absence of excitonic contributions.

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B15 - Deformed Single-Walled Carbon Nanotubes and Resonance Raman Spectroscopy

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Strain plays an important role in tuning material properties. In single-walled carbon nanotubes (SWNTs), it can act as an important factor for modulating the band structure and properties. The electronic band structures of carbon nanotubes can be modulated under these different strains. Theoretical calculations show that the effects of strains, including uniaxial strain and torsional strain, on electronic structures are related to q = (n-m) mod 3. Resonant Raman spectroscopy (RRS) have been used to measure the electronic band structures of SWNTs. We present herein a systematically investigation of resonant Raman spectroscopy of individual strained ultra-long single-walled carbon nanotubes (SWNTs). When a SWNT is manipulated by atomic force microscopy (AFM) tip, the torsional and uniaxial strain can be introduced into SWNT. These two kinds of strain exhibit different effects on Raman spectra of SWNTs. The torsional strain can make frequency of radial breath mode (RBM) upshift while uniaxial strain has no effect on that. The uniaxial strain causes some G modes downshift and others remain no shift which is different from previous results. The electronic transition energy Eii variation along SWNTs by torsional strain follows a family pattern based on q = (n-m) mod 3: for semiconducting SWNTs, E33S increases for q = +1, E33S decreases and E22S increases for q = -1, and for metallic SWNTs, E11M always increases.

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B16 - The in situ Raman spectroelectrochemistry of carbon nanostructures using isotope engineering

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The isotope engineering is a frequently applied method. In the present study we combined the isotope engineering with in situ Raman spectroelectrochemistry to study carbon nanostructures. The materials under study have been the C_{60} fullerene peapods and double walled carbon nanotubes (DWCNTs) containing highly 13C enriched C_{60} and inner tubes. Raman spectroscopy is a convenient spectroscopic method for carbon nanotubes due to a strong resonance enhancement. The radial breathing mode (RBM) of carbon nanotubes is significantly dependent on the tube diameter and thus the DWCNTs exhibit distinct RBM bands for inner and outer tubes, respectively. On the other hand the TG, D and G’ modes exhibit only weak diameter dependence. Thus it is not possible to distinguish the bands of inner tubes and outer tubes in DWCNTs from each other. Nevertheless these modes can be “deconvoluted” using spectroelectrochemistry. This strategy is based on the fact that the position and intensity of the TG, D and G’ modes change with the applied electrochemical potential in a different way for the outer and inner tubes. This is because the inner tubes are influenced only by the electrostatic potential of the outer tubes. On the other hand, the outer tubes behave similarly to SWCNTs, i.e. the double layer charging of DWCNTs causes the corresponding spectroelectrochemical feedback of the outer tube only. Therefore at high electrode potentials applied the frequency shifts of the TG, D and G’ differ significantly for inner and outer tubes and they can be clearly distinguished.

This study applies C_{60} fullerene peapods and DWCNTs containing highly 13C enriched C_{60} and inner tubes, respectively. The Raman spectroscopy and in-situ Raman spectroelectrochemistry has been employed in order to follow the influence of 13C enrichment on vibrational pattern of these carbon nanostructures. The Raman response of $13C_{60}$ after encapsulation in fullerene peapods differs from that of isotope-natural species, $NatC_{60}$. The Raman $A_g(2)$ mode of encapsulated $13C_{60}$ is upshifted compared to that in $NatC_{60}$ peapods with the same filling factor. The chemical doping of $13C_{60}$ peapods with K-vapor leads to the downshift of $A_g(2)$ mode similarly as in case of $NatC_{60}$ peapods. The $13C_{60}$ peapods were successfully transformed into DWCNTs, which confirms high filling of SWCNT with $13C_{60}$. The DWCNTs exhibited distinctly downshifted TG and D Raman modes for inner tubes, which confirms that only inner tubes were enriched by 13C. The Raman spectroelectrochemistry of $NatC_{60}$ exhibits strong anodic enhancement, while this enhancement is weak for $13C_{60}$ peapods. On the other hand, the electrochemical charging of the inner-tube labeled double walled carbon nanotubes 13Ci-DWCNTs followed the behavior of ordinary NatCi-DWCNTs as indicated by in situ Raman spectroscopy. In addition we follow the spectroelectrochemical behavior of the TG mode of inner tubes in 13Ci-DWCNTs from the start of the doping, which was not possible for NatCi-DWCNTs.

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B17 - Raman spectroscopy of well-identified individual semiconducting single-walled carbon nanotubes

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Raman spectra are measured on freestanding single-walled carbon nanotubes identified by electron diffraction . The radial breathing mode frequency vs diameter relationship is derived for tube in the 1.4-3 nm diameter range without any modelization of nanotube electronic or mechanical properties [1]. The role of the environmental conditions on the radial breathing mode frequency is discussed. The dependence of the frequency of the tangential modes (LO and TO) with the diameter of semiconducting tubes is found and compared with the predictions of different models [2]. The comparison between incident excitation energies, for which an intense Raman signal was observed, and the calculated transition energies allowed us to determine the values of the optical transition energies ES33 and ES44 for SWNTs in the 1.4-2.4 nm diameter range [2]. These latter results question the origin of the correction, usually considered as related to the electron-electron correlation and exciton binding energy. For semiconducting tubes, our experimental findings suggest that the exciton binding is very small or missing for the higher transitions ES33 and ES44, contrary to the lower transitions ES11 and ES22 [3].

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B18 - Raman studies of individual and isolated metallic single-walled carbon nanotubes

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In this communication, Raman spectroscopy experiments performed on individual metallic single-walled nanotubes are presented. In a first part, we discuss results obtained by combining electron diffraction and Raman experiments on freestanding SWNTs [1]. Among these results, we focus on the profile of the G-modes of index identified metallic SWNTs.We also discuss the EM11 transition energy derived from Raman experiments [2], and compare our data with others available in the literature. In a second part, we report Raman spectra obtained on isolated SWNTs lying on a substrate and connected by metal electrodes. This experimental configuration allows investigating the same SWNT by AFM, transport measurements and Raman spectroscopy. Preliminary results concerning the Raman active phonon frequencies and line shape of such SWNTs are presented. The Raman signal of an individual SWNT, unambiguously identified as metallic from its I(V) features, is reported [3]. The comparison of both set of results question the Raman response of the G-modes of isolated SWNTs with respect to the tube environment.

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B19 - D Band Intensity Calculation for Graphene and SWNTs

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The D band Raman peak in graphene and single wall carbon nanotubes (SWNTs) has been widely used to characterize the studied samples regarding the presence of structural defects.[1] It has been shown lately that the D band intensity depends both on the crystallite sizes and on the laser excitation energy. To better understand the role of the defect on the D band intensity within the double resonance Raman scattering, it is necessary to calculate the elastic scattering amplitude between electronic states of different eigenvectors. The elastic scattering amplitude can be calculated using the T-matrix formalism. The T-matrix is usually obtained in an approximated way in terms of the eigenfunctions of the unperturbed system. However, the knowledge of the eigenfunctions of the perturbed system allows for a full calculation of the T-matrix, which is independent of any approximation. Recently, the D band intensity dependence on excitation energy and crystallite size was calculated in the Born approximation and considering nearest-neighbors only for armchair edged graphene ribbons.[2] Although this approximative approach can give insight to the overall properties of the D band Raman peak, a more detailed analysis is necessary in order to well characterize the graphene and SWNT samples with respect to their crystallinity. In this work we perform a full calculation of the T matrix in terms of the overlap between the eigenvectors of the full Hamiltonian and that of the unperturbed system. The real part of the self energy is obtained in terms of the eigenenergies of the perturbed system while the imaginary part is calculated self-consistently. The elastic scattering amplitude is then calculated for different systems such as graphene ribbons, graphene flakes, and small size nanotubes. In the case of the graphene flake the hamiltonian of a L_x *times* L_y graphene system is diagonalized without any periodic boundary conditions. In the case of graphene ribbons and SWNTs, the periodic boundary condition is assumed in one of the directions. The crystallite size is varied by changing L_x or L_y. The D band intensity dependence on crystallite size and laser excitation energy is compared to recent experimental results in nanographite[3] and small length carbon nanotubes[4].

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B20 - DFT phonon dispersion of SWCNTs

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Accurate knowledge of the phonon dispersion of single walled carbon nanotubes (SWCNTs) is crucial for the correct interpretation of their Raman spectra. Calculations on the density functional theory (DFT) level are sparse in the literature, and is mostly restricted to achiral tubes. The reason for that is the large number of carbon atoms in the unit cell of chiral tubes. We have carried out first principles DFT calculations for the phonon dispersions of many SWCNTs, achiral and chiral as well.We have made use of the helical symmetry of the tubes, thus decreasing the computational demands significantly. Special care was taken in the case of the RBM and other Gamma point modes, as well as the D and D* bands. Also, the appearing of Kohn-anomaly has been investigated on the DFTlevel, without applying perturbation theory.

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B21 - Raman Effect by Length Control of the Single Wall Carbon Nanotube

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Since excitonic effects are important in the optical properties of the single wall carbon nanotubes (SWNTs), we should consider an exciton picture to study Raman scattering.We have developed an exciton model by solving the Bethe-Salpeter equation in the SWNTs within tight binding model [1]. Unlike single particle picture, the excitonphoton matrix elements [2], as important factor to calculate the Raman intensity, strongly depend on the diameter but no tube type and chiral angle dependence. Especially, the exciton-photon matrix element has larger value for long SWNT, because the exciton wave function coefficient depends on tube length related to number of wave number k. For the first resonance Raman scattering such like RBM and G-band, the Raman intensity in the range of tube length more than 100 nm does not hardly depend on tube length due to length normalization. However, for very short SWNT, i.e. 20 nm, the Raman intensity considerably becomes weaker relative to tube length more than 100 nm. The reason is that the exciton wave function coefficient to be included in exciton-phonon matrix term quickly decreases with reducing tube length rather than tube length normalization in the Raman intensity formula. We will also compare our calculated results with experiment [3] for double resonance Raman scattering.

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B22 - Exciton properties for Raman spectra of single wall carbon nanotubes

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The first-order and the second-order Raman intensities as a function of (n,m) are given theoretically with using the exciton wavefunctions, which are compared with single nanotube spectroscopy [1]. The exciton wavefunction is calculated by solving the Bethe-Salpeter equation within the extended tight binding method [2]. The excitonphoton and exciton-phonon interaction can be calculated by taking an average of electron-photon and electronphonon interactiones over the k region of the exciton wavefunction [3]. The Eii optical transition [4], metallicity [5], type, chirality, and environment effect [6] to Raman intensity of RBM, G, and G'-band will be discussed with use of the exciton wavefunctions.
Many body correction will be modified by those effect which is systematically understood by effective mass of an electronand a hole in the energy subbands, curvature effect and trigonal warping effect. Especially for smaller nanotubes and zigzag nanotubes with medius diameters, we found that a simple rule of cutting line does not work well. We will discuss how to observe this phenomena by experiment.

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B23 - *In-situ* Raman measurements of suspended individual single-walled carbon nanotubes under strain

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We present a technique for *In-situ* Raman measurements of suspended individual single wall carbon nanotube (SWNT) under strain. The measurements were carried out using a combined micro-Raman/AFM system. Micro mechanical Si cantilever structure was fabricated to apply a strain force to the suspended SWNT by AFM tip manipulation. We observed a strong decrease in the radial breathing mode intensity and for strain greater than ca. 3% there is a clear up-shift in the G-mode frequencies accompanied by an increase in intensity of a broad peak at a position associated with the D-mode. For lower strain, the G-mode peaks (A_1, E_1 and E_2) do not change in position but change in relative intensity.

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B24 - Effects of boron doping on the optical transition energies and diameter distribution of single-wall carbon nanotubes

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In this work we use resonance Raman spectroscopy with sixty-six excitation energies between 1.61 eV and 2.71 eV to study boron-doped single walled carbon nanotubes (SWNTs) made by pulsed laser vaporization technique. The samples were prepared with different quantities of boron on the graphite targets, i.e., non doped sample, 1.5 at.% and 3.0 at.% in mass. Our study shows significant changes in the profile of the radial breathing mode band of the boron doped samples (B-SWNTs) compared to pristine SWNTs. The change of diameter distribution with doping is quantitatively studied, showing smaller tubes with the increasing of doping. A blueshift of the E*ii* resonance energies of the doped nanotubes is observed and analyzed.

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B25 - Strain and friction induced by van der Waals interaction in individual single-walled carbon nanotubes

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Axial strain is introduced into individual single wall carbon nanotubes (SWNTs) suspended from a trenchcontaining Si/SiO_2 substrate by employing the van der Waals interaction between the SWNT and the substrate. Resonance Raman spectroscopy is used to characterize the strain, and up to 3% axial strain is observed. It is also found that a significant friction between the SWNT and the substrate, on the order of 10pN/nm, governs the localization and propagation of the strain in the SWNTs sitting on the substrate. This method can be applied to introducing strain into materials sitting on a substrate, such as a graphene sheet.

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B26 - The effect of Cerium addition to catalysts in the diameter distribution of single-wall carbon nanotubes

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Controlling the growth of carbon nanotubes has been a great expectation in tailoring their structural and electronic properties. Raman spectra of single-wall carbon nanotubes, SWNTs, prepared by the arc discharge technique using different compound catalysts were obtained. Two pairs of samples were selected differing in the catalysts by the addition of cerium to one of the compounds. The pairs were: MnNiCo mixture, $Ce(MnNiCo)_5$ alloy, and FeNiCo powder mixture, $Ce(FeNiCo)_5$ alloy. The radial breathing modes region of the spectrum, excited with the 514.5 nm laser line, differs appreciably for the two samples of each pair. The differences consist of a remarkable narrowing of the Raman profile, peaking preferentially at higher wave numbers when Ce-contained catalysts were employed. The same effect was observed for both pairs. For $Ce(MnNiCo)_5$/SWNTs 10 lines are needed to fit the radial breathing modes feature while for MnNiCo/ SWNTs just 6 lines are sufficient. Analysis of the radial breathing modes features using Kataura-type plots [1] allowed identifying the most of these lines as E_{33} optical transition energies from semiconducting SWNTs. The data indicates that some tubes are present in both samples but with different population. The peaks appearing at higher wave number are the same for both samples but at lower wave numbers a surplus of lines is obtained for MnNiCo/ SWNTs. The differences are greater for the pair FeNiCo/SWNTs, $Ce(FeNiCo)_5$/SWNTs, for which not only the lowest wave number lines of the first are lacking in the second sample spectrum, but also two additional lines appear at the opposite side. An increase of intensity of the lines was also observed for the highest wave numbers. The results may be interpreted as a narrowing of the diameter distribution around the lowest diameters by addition of cerium to the three-metallic catalyst, for the sub-set probed with the 2.41 eV resonance.

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B27 - Third and Fourth Optical Transitions in Semiconducting Carbon Nanotubes

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We have studied the optical transition energies of single-wall carbon nanotubes over broad diameter (0.7 to 2.3 nm) and energy (1.26 to 2.71 eV) ranges, using their radial breathing mode Raman spectra. We establish the diameter and chiral angle dependence of the poorly studied third and fourth optical transitions in semiconducting tubes. Comparative analysis between the higher lying transitions and the first and second transitions show two different diameter scalings. Quantum mechanical calculations explain the result showing strongly bound excitons in the first and second transitions and a delocalized electron wave function in the third transition.

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B28 - Debundling Effects on the Tangential Raman Modes of Carbon Nanotubes

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We have used resonant Raman spectroscopy to study the effects of debundling on the tangential Raman modes of carbon nanotubes. Most of the methods of producing carbon nanotubes yield thick bundles of tubes having distinct chiralities, the tubes in the bundle being held by the van der Waals interactions. These interactions are known to have a strong influence on both their vibrational and electronic properties, and thus a method for separate these bundles is made necessary for the study of the properties of isolated carbon nanotubes. We have measured the Raman spectra of different samples having different diameter distributions, both in bundles and dispersed in water with two different surfactants (SDS and cholate). We observed that the ratio between the intensities of the G+ and G-components of the G-band of semiconducting carbon nanotubes is higher for the dispersed nanotubes than for the bundled ones, the G- intensity being very sensitive to the degree of debundling achieved with the dispersion process. This result challenges the well accepted idea that these two components are associated with the intrinsic vibration (transverse or longitudinal) of a single nanotube. The results presented in this work suggest that the intensity of the G- component may be somewhat related to the intertube interaction when the tubes are in bundles. In the case of metallic carbon nanotubes, the characteristic BWF feature was observed even for the most dispersed sample, contradicting the assumption that it is related to bundling effects. The intensity of the BWF was found to dependent significantly on the surfactant used in the dispersion, indicating that this feature is actually sensitive to charge transfer effects.

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B29 - Raman intensity analysis of the Radial Breathing Mode in a Single Wall Carbon Nanotube sample with diameters ranging from 0.7nm to 3.0nm

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In this work, we measure the Raman spectra of a SWNT sample in the energy range from 1.26 eV to 2.71 eV. Using the RBM spectra we assign (n,m) indices to 84 different SWNTs with diameters ranging from 0.7nm to 3.0nm. We analyze the intensities of the features associated with each carbon nanotube present in the sample in regard to its diameter, chirality and the observed optical transition, as well as the kind of nanotube (metallic, semiconductor type I or type II). Finally, we show an empirical equation dependent on (n,m) and the optical transition that fits the experimental intensity data.

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B30 - Experimental determination of non-adiabatic and anharmonic effects in the Raman spectra of nanotubes.

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Raman spectroscopy is a powerful non-destructive technique for the characterization of carbon materials, and is widely used for the study of carbon. The shape and position of the G-band in metallic single walled carbon nanotubes (SWNT) strongly depends on the effects of the electron-phonon coupling (EPC). Indeed, the EPC (i) is responsible for the onset of Kohn anomalies, which affects the position of the G-band, (ii) determines the phonon life-time and the Raman peaks line-width, and finally (iii) limits the ballistic transport in carbon nanotubes [1-3].

Here we show that the effects of the EPC in SWNTs cannot be correctly described by lattice dynamics theories based on the adiabatic Born-Oppenheimer approximation. In fact, even if in almost all cases the lattice dynamics of metals is well described within the adiabatic Born-Oppenheimer framework, the coupling between ionic and electronic degrees of freedom cannot be excluded a priori in materials where the electronic gap is of the same order or smaller than the phonons energy [4]. In particular, we show that the temperature dependence of the G-band in SWNTs can be explained only by including contributions that account for the dynamic, time dependent nature of phonons [4,5].

The inclusion of the so-called dynamic effects results in an excellent agreement between theory and experiments, consistent with the assignment of the Raman G+ and G- peaks of metallic SWNTs to TO (circumferential) and LO (axial) modes, the opposite of semiconducting SWNTs [2]. Finally, by comparing the experimental measurements with the theoretical computation of the dynamic effects, it is possible to experimentally evaluate the anharmonic contribution to the phonon frequency temperature dependence [6]. This parallels what observed in doped and undoped graphene at room temperature and as a function of temperature [6].

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B31 - Nanotube and Graphene Defects Studied with Local Raman Spectroscopy

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Defects and dopants in graphene and carbon nanotubes are of high technological interest because they allow materials to be locally engineered, similar to semiconductor integrated circuits. Using near-field Raman spectroscopy we show that defects in single-walled carbon nanotubes lead to localization of the photoluminescence signal and of the disorder-induced Raman D band. We are able to resolve individual tube-tube junctions with a spatial resolution of 20nm and determine that the phonon transition region is on the order of 40-100nm.

A model system for understanding the role of defects in nanotubes is the graphene edge. We used confocal Raman spectroscopy in combination with atomic force microscopy to determine the spatial localization of the disorder-induced D band near the graphene edge as well as the transition lengths for the G and G’ bands. These measurements provide an estimate for the electron mean-free path and the electron-phonon scattering length.

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B32 - Dependence of the G’-band intensity in Raman spectra on the metallicity of single wall carbon nanotubes

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We report a peculiar behavior of the G’-band intensity in Raman spectroscopy that shows a strong dependence on the metallicity of single wall carbon nanotubes (SWCNTs). The G’-band intensity is enhanced in metallic SWCNTs, whereas the peak intensity is significantly reduced in semiconducting SWCNTs. This phenomenon is further confirmed by our samples with abundant semiconducting SWCNTs that are selectively separated SWCNTs by several methods such as nitronium ions and hydrogen peroxide. This metallicity dependence is explained in terms of electron-phonon interaction calculated by the extended tight-binding calculations. The calculated results show that G’-band intensity for metallic SWCNT is relatively stronger than that for semiconducting E22 resonance with the laser energies ELaser: 2.41 eV, 1.96 eV, and 1.58 eV.

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B33 - Determination of the concentration of a SWCNT-suspension

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SWCNTs possess outstanding properties which can lead to innovative products with extraordinary or improved properties and functionalities. For realisation and commercialisation of such SWCNT-based products process chains for fabrication with industrial potential are necessary.Within these process chains it is important to monitor and control specific parameters of the used materials to ensure a high quality fabrication and to optimise the processes. One of these parameters is the SWCNT-concentration of the processed suspensions. SWCNT concentration control requires concentration determination.

This can be done very precisely using FT-Raman spectroscopy. In our presentation we report on calibration of a Raman spectrometer to perform such measurements. Using different internal standards and different methods for determination of the intensity of characteristic peaks in the Raman spectrum, a set of calibration curves is calculated. Furthermore a ranking of the calibration curves is presented and the error for concentration determination of SWCNT-suspensions is quantified.

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B34 - High pressure study of C_{70} peapods: probing the stability of nanotubes from inside

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The Raman signature of fullerene and nanotubes in carbon nanotubes peapods have well differentiated features. We have used this fact to explore the high pressure properties of peapods and nanotubes. We consider that our results allow to establish unambigously the relation between pressure induced modifications in carbon nanotubes and characteristic Raman signatures. These results are particularly important in view of the confrontation of experimental results and theoretical calculations. For that we have investigated the high pressure behaviour of bundled 1.35 ± 0.1 nm diameter single wall carbon nanotubes filled with C_{70} fullerenes using Raman spectroscopy and compared the obtained results with the behaviour of the empty closed C-SWNT. The fullerene C_{70} molecules appear to be an excellent probe to determine the onset of nanotube and fullerene interactions. In fact, contrarily to C_{60} peapods, we have not observed any sign of fullerene polymerization. This allows for a proper monitoring of the only fullerene-nanotube interaction. This fact is well explained by the zig-zag alignement needed for polymerization in C_{70}. We have then exploited this to show that: i) the onset of the widening of the nanotube Raman radial breathing modes signal is a signature of the onset of the modification of the nanotube cross section. ii) this transition is followed at higher pressures by the collapse of the tubes which is associated with a frequency drop in the nanotube Raman tangential modes. The two transitions are observed at 2.5 ± 0.5 and 11 ± 2 GPa respectively for the C_{70} peapods and 2.0 ± 0.5 and 14 ± 1 GPa for the empty tubes. In the case of peapods they are concomitant respectively with a change in the pressure evolution of the fullerene modes (cross section-change) and with the disappearance of most of the fullerene modes (collapse).

The differences in transition pressures between both systems are discussed on the base of structural differences with respect to high pressure application. Our results are also discussed in view of previous high pressure investigations.

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B35 - Carbon nanotube fiber microelectrodes and actuators

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Because of their high specific area, high electrical conductivity and good chemical stability carbon nanotubes [1] (CNT) have gained considerable attention in recent years. In particular, the ability to promote electron – transfer reactions make them particularly attractive for a wide range of sensing applications [2]. Here, in a first part we report on the preparation and promising electrochemical behaviour of CNT fiber [3] microelectrodes. By combining the advantages of CNT with those of fiber electrodes, this type of microelectrode differs from CNT modified or CNT containing composite electrodes, because it's made of only CNT without any other component like additives or binders. Performances of these electrodes have been characterized with respect to the electrocatalytic oxidation of analytes via deshydrogenase mediated reactions. They have been tested by modifying the surface of the CNT electrodes [4], leading finally to a miniaturized biosensor with promising properties. In particular we show that CNT fiber microelectrodes can be superior to conventional carbon fiber microelectrodes that are already used and commercialized for bio-sensing applications.

In a second part of this presentation, we investigate the electromechanical properties of CNT fibers. Besides their significant mechanical strength, CNT can directly convert electrical energy into mechanical energy due to the combination of quantum and double layer electrostatic effects under physiological conditions and low voltage. This feature makes them highly attractive for a number of electromechanical applications. Since 1999[5], only few studies have been reported. Only macroscopic assemblies and sheets of CNT were only concerned. We present here characterizations of electrochemical CNT fiber actuators. We show that the stress generated by CNT fibers upon electrical stimulation is greater than that of previous CNT actuators made with CNT sheets. We believe that the enhancement of the electrochemical properties is due to the alignment of the CNT inside the fibers. Several kinds of further optimizations will be discussed.

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B36 - Electricals Properties of Carbon Nanotubes by EFM

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The understanding of the electronic behavior of charged carbon nanotubes is of a crucial importance in electronic applications such as field-effect transistors or CNT-based nanoelectromechanical devices. Electrostatic properties of single-walled carbon nanotubes have been investigated by charge injection and electric force microscopy - EFM experiments. Tests have been performed using doped silicon substrates covered with a 100 nm thermally grown insulating SiO_2 layer. The samples consist of single-wall carbon nanotubes (functionalized and nonfunctionalized), multi-wall carbon nanotubes and fullerenes. Electric force microscopy appears as a tool to map and study the spatial distribution of electric field and charges at the nanometer scale, but up to now only few studies have applied this technique to carbon nanotubes. Charge injection is achieved by touching a given nanotube with the EFM tip biased with respect to the silicon substrate. The resulting transfer of charges along the nanotubes is then characterized by EFM, in which electric force gradients acting on the tip shift the EFM cantilever frequency of oscillation. Charge injection and EFM experiments were performed at room temperature under a controlled atmosphere. The influence of the tip-sample contact time, types of tips, ambient humidity, scanning speed and tip bias was analyzed. In a second step, this technique is employed for charging different nanotubes and analyzing their respective Raman spectra.

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B37 - Effect of catalyst on the state of nitrogen incorporated into CNx nanotubes

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Multiwall CN*x* nanotubes have been synthesized by chemical vapor deposition (CVD) method using acetonitrile contained carbon and nitrogen atoms. Two kinds of catalyst source have been probed: (1) bimaleates of Ni, Co, and Fe and their mutual solid solutions and (2) ferrocene. Bimaleate powder has been put into heating zone of the reactor, decomposed with formation of metal nanoparticles, and then, acetonitrile vapor was introduced. In the second case, ferrocene has been dissolved in acetonitrile and the mixture was injected into reactor volume. Decomposition of acetonitrile over pre-formed metal nanoparticles produced random nanotubes, while the aerosol-assisted CVD method yielded arrays of the aligned nanotubes. Electronic state of nitrogen in CN*x* nanotubes was examined by means of X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS) near the K-edge of nitrogen. XPS data revealed a presence of pyridinic and three-coordinated nitrogen in the random CN*x* nanotubes and dependence of ratio of these forms on catalyst composition. The largest proportion of pyridinic nitrogen was achieved when catalyst contained equal quantities of Ni and Co. The aligned CN*x* nanotubes were found to contain molecular nitrogen additionally. Angle-resolved XAS spectra detected orientation of N_2 molecules along tube axis.

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B38 - Modelling of Nanotube Based Actuators and Experimental Validation

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Actuators that convert electrical energy into mechanical energy find applications in different fields of engineering. There is a need for improved actuators generating high forces at low voltages. In order to introduce such devices into light weight structures it is desirable to use low density bulk material.

Carbon nanotubes have the potential to generate high forces at very low voltages. The density of the bulk material is just 1.3 g/cm^3, which makes them well suitable for lightweight applications. Moreover, active strains of up to 1% can be achieved - due to the CNTs dimensional changes on charge injection. The effect has been shown in different experimental studies up to now.

In the present study a new aproach to model the actuating behavior based on irreversible thermodynamics is developed. The model contains only few mechanical and electrical degrees of freedom. The overall static and dynamic behavior of the actuator system can be described by the model. A large variety of experiments was carried out to extract the parameters. It could be shown, that one set of parameters describes the behavior in static conditions as well as in different dynamic and transient dynamic processes. This modell will be a milestone on the way towards the application of such actuators, since it is possible to derive rules for the optimisation of such systems directly from a theory based model.

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B39 - Molar Absorbance Coefficients of Carbon Nanotubes in π-plasmon Region

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Realizing carbon nanotubes (CNT) as an individual "molecules" is the key process for studying optical properties and chemical reactivity of CNT, which also leads to a systematic evaluation of CNT. In this study, we have succeeded in determining the number density of CNT in dispersion and the molar absorbance coefficient with a new spray technique followed by AFM observations. Single-walled carbon nanotubes (SWNT) of purified HiPco were dispersed in 1 wt% aqueous sodium dodecyl sulfate (SDS) surfactant by ultrasonication and were centrifuged at 197,000 *g* for 1 hour. The resultant dispersion was characterized by absorption spectroscopy (JASCO V-570) and photoluminescence (SHIMADZU NIR-PL). The solutions were sprayed onto SiO_2 substrates by the spray method we developed without any perturbation. The samples were observed by AFM (Veeco Digital Instruments Nanoscope IV). The number density of SWNT in the dispersion sample should be proportional to the absorbance at 280 nm (π-plasmon). The molarity of CNT dispersion can be estimated by this method, so that we have succeeded in calculating the molar absorbance coefficient of SWNT. The molar absorbance coefficient and its coefficient per a carbon atom of SWNT are estimated to be 1.86×10^7 [L mol^{-1} cm^{-1}] and 8.78×10^{-22} [L nc^{-1} cm^{-1}], respectively. These coefficients enable us to treat SWNT as individual "molecules". This also can provide a fair comparison of the molar coefficient of SWNT with that of other π-conjugate compounds such as benzene and C_{60} molecules. The obtained molar coefficient of CNT is only 100 times larger than that of C_{60}, even though the number of carbon atoms in a CNT is 1000 times as large as that of C_{60}. Therefore the coefficient per carbon atom is 10 times as small as that of C_{60}.

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B40 - Electric Field Induced Deformations of Carbon Nanotubes

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Carbon Nanotubes (CNTs) can be used as key elements in nanoelectromechanical systems (NEMS) such as nanorelays, nanoswitches, nanotweezers and feedback device which are designed for memory, sensing or actuation uses.[1] Their electric field induced deformation is a key character for these promising applications, as well as for their fabrication, separation and electromanipulation. How carbon nanotubes behave in an external electric field? What will be the influence of field intensity and direction on the tube deformation? What are the tube geometry effects on it? What are the defect effects? To answer these questions, we have computed the deformations of semiconducting[2] and metallic[3] CNTs induced by uniform electrostatic fields, by minimizing total potential energy calculated using a monopole-dipole-interaction model combined with an empirical many-body potential (AIREBO). The effects of field strength, field direction tube geometries and defects on the electrostatic deformation are investigated for both single- and double-walled CNTs. The electrostrictive deformation of single-walled CNTs is found to be proportional to the square of field strength. These results could apply to recently designed devices based on cantilevered carbon nanotubes. Moreover, we wish that they could help to design some new nanoelectromechanical devices.

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B41 - Fabrication of hybrid sensor using microcantilever combined with SWNT devices

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In recent years, highly sensitive and selective detection of biomolecules (e.g. virus, bacteria, DNA and proteins) by MEMS/NEMS (Micro-/Nano Electro-Mechanical-System) structures have attracted extensive attention for its importance in clinical diagnostics. Many of the cantilever based sensors use optical techniques to measure deflection coming from the binding of biomolecules. Recently, Shekhawat et al. showed that CMOS transistor combined cantilever can be used as a sensitive biosensor, where deflection of cantilever can be transduced as na electrical conductance from the transistor. We fabricated single-walled carbon nanotube (SWNT) devices on microcantilever to interpret the deflection of cantilever by measuring the electrical conductance from SWNT device. Preliminary measurement shows that the deflection of microcantilever can be scaled with the electrical conductance of SWNT device. Detailed mechanisms of the signal transduction and possible applications for biosensors will be discussed.

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B42 - Structural properties of intercalated carbon nanotubes studied by X-ray absorption spectrocopy

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SingleWalled Carbon Nanotubes (SWNT) have been shown to be amphoteric in character. The local structure of intercalated SWNT is probed by X-ray absorption spectroscopy (EXAFS). These carbon nanostructures are doped with either alkali metals (such as rubidium atoms) or halogen compounds (such as iodine atoms). In the first case, we show that the environment around the Rb atom is getting more and more ordered with the doping time. At the saturation stage, Rb ions are facing an hexagon. The interstitial site (between three tubes) is ruled out by our results. Rb atoms are localized either outside the bundles or within the tubes.

The intercalation compound Ix-SWCNT is obtained by immersing the SWCNT powder in molten iodine at 140°C for several days. EXAFS investigation performed at ESRF provides new information on the local structure of iodine.We found out that the first carbon shell around iodine contains 2.2 atoms, a number which is in agreement with the inner volume filling and which excludes definitively the triangular sites as the mainly occupied site. In addition, unlike previous works, our EXAFS results suggest that iodine species are actually disordered I5- chains (two adjacent I2 molecules surrounding a central I- ion).

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B43 - The Federal University of Minas Gerais Center of Microscopy

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Electron microscopy and Raman spectroscopy are nowadays the two basic main techniques used in nanotubes and nanoparticles characterization. Recently the Federal University of Minas Gerais started a process of improving high-end research infrastructure in the state of Minas Gerais creating a Center of Microscopy. Discussions to create a Materials and Molecules Characterization Center are underway.

The Federal University of Minas Gerais is one of the largest and most respected in Brasil. Around 35.000 regular students are spread over 20 Academic Units, which host about 48 undergraduate courses and 61 “stricto sensu“ graduate courses. Also about 20.000 students attend yearly around 500 not regular courses, from computer science to languages, open to the general community. Strong scientific research groups are also spread over different areas and subjects.

The Center of Microscopy was created to meet an increasing demand, in between others, from strong research groups at biology, chemistry, engineering, pharmacy and physics departments involved in research of nanoscale materials. The chemistry and physics departments work heavily on nanotubes and nanoparticle synthesis with na increasing interface on the application of those materials with several biology, engineering, pharmacy researcgroups.

A 1060m^2 complete new building with special environmental characteristics required for high resolution electron microscopy was inaugurated at the end of last year. The building comprises rooms to host the lower resolution microscopes that already existed throughout the Engineering School, the Institute of Biological Sciences and the Institutes of Geosciences and Exact Sciences and also six special rooms for higher resolution microscopes. Also several sample preparation and data treatment laboratories and administrative rooms are available. A TecnaiG2-20 and TecnaiG2-spirit transmission electron microscopes and one Quanta 200-FEG-scanning electron microscope, from FEI are being installed and tested. A Focused Ion Beam microscope has recently been acquired and will be installed at the end of the year. Sample preparation laboratories for several areas are also in process of being installed. Finally we expect to submit the acquisition of sub-angstron microscopes and high resolution analytical microscopes soon.

The availability of this ensemble of microscopes and advanced analysis programs in a multi-user facility is generating cross-talk between researchers with strengths in different areas. Such interactions are allowing us to better investigate the interfaces between physics, materials science and biology in emerging areas such as bioengineering.

We will present this new facility, which will be fully available to the whole scientific, state and private enterprise communities shortly.

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B44 - Preparation and Electrochemicacharacterization of Multi-Walled Carbon Nanotube Electrodes

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Carbon paste electrodes have been widely used in electrochemistry and electroanalysis because their low background current, high surface activity, wide potential window and chemical inertness. The use of carbon nanotubes as active material in carbon paste electrodes has been reported during the last few years, showing good performance when compared with similar electrodes built from graphite or glassy carbon. This work reports the construction of carbon paste electrodes using iron and iron oxide-filled multiwalled carbon nanotube (MWCNTs), mixed with mineral oil (Nujol). The MWCNTs were prepared trough the ferrocene pyrolysis1. The electrochemical behavior of electrodes prepared with different MWCNT/Nujol proportions was studied in a solution of potassium ferricyanide using cyclic voltammetry, and compared with that of paste electrodes prepared with commercial graphite and glassy carbon. The results showed high redox peak currents, well defined quasi-reversible voltammograms for redox of iron couple, good stability upon continuous cycling potentials and analysis of the current as a function of the scan rate resulted in a linear i_p *vs.* $v^{1/2}$ relationship.

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B45 - Closing Rates of Holes in Single-Wall Carbon Nanohorns

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A previous report showed that holes in single-wall carbon nanohorns (SWNHs) can be closed by heat treatments of 1200*o*C in Ar, which were evidenced by the N_2 adsorption measurement [1]. Experimental results and theoretical calculations indicated that only the holes at the tips of nanohorns can be closed but not those in the sidewalls. In this study, we investigated the effect of heating temperatures (600 ~ 1200 ^{o}C) on hole closing. To open the holes, SWNHs were oxidized in flowing air by slow combustion method [2] with target temperatures, (Tox) of 400, 450, 500, or 550 ^{o}C (NHox). For closing the holes, NHox was heat-treated (HT) at 600, 800, 1000, or 1200 ^{o}C in Ar for 3 h. The hole closing was examined by measuring xylene-adsorption quantity (Q) using thermogravimetric equipment. The Q value decreased with the HT temperature, which exhibited the numbers of closed holes increased with the HT temperature. When Tox was higher than 500 ^{o}C, the hole closing mainly occurred at HT 1200 ^{o}C. To analyze the hole closing rate, we heat-treated NHox (Tox of 300, 350, 400, 450 or 500 ^{o}C) at 1200 ^{o}C for different periods. As a result, we found that the holes show the tendency of closing with HT duration period. However, we also noticed that the closed holes were once again opened during HT, which will be explained in the presentation.

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B46 - Study on the growth of vertically aligned carbo nanotubes by Mössbauer Spectroscopy

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Nanostructured materials are the focus of great interest in science and technology. In particular, carbon nanotube (CNT) is one of the most studied materials and the achievement of controlled growth is essential for technological applications. Plasma enhanced chemical vapor deposition (PECVD) method can be a powerful tool for nanodevices fabrication in association with optical and electron bean lithography. Additionally, it is also well known that metallic magnetic nanoparticles (Ni, Fe, Co) are widely used for CNT growth. Thus, a better understanding of the final encapsulated catalyst within the CNT is fundamental not only to have insights on growth mechanism but also for possible new applications. In this work we produced vertically aligned multiwall CNT's growth by PECVD method using a thin layer of ^{57}Fe as catalyst. Mössbauer technique was performed to probe the final phase of the Fe metal particle. This technique was used due its sensibility making possible to get unique information about the different Fe phases that exists after growth. This knowledge can provide important indications about growth mechanisms of CNTs using PECVD. SiO_2 film of 60 nm was deposited by sputtering over a Si substrate. After that, a ^{57}Fe film of 7nm was deposited by Molecular Beam Epitaxy (MBE). The growth temperature was about 700^{o}C in the presence of ammonia to prevent amorphous carbon formation and acetylene. A DC voltage of - 600 V was applied to generate the plasma. Micrographs of the sample were obtained using a Scanning Electron Microscopy (SEM). Mössbauer Spectroscopy showed the presence of two Fe phases: iron carbide (Fe_3C - Cementite) and a metallic iron phase with diluted carbon (Austenite). It was interesting not to find pure iron phase (Ferrite) or iron oxide. Based on these data we will propose a growth model of CNTs using PECVD method and iron as catalyst.

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B47 - Electronic structure of MgO-coated carbon nanotube by X-ray-absorption spectroscopy*

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In this study, the MgO-caoted carbon nanotubes-fabricated by thermal chemical vapor deposition process-was carried out to study the electronic structures by x-ray absorption near edge structure (XANES). The intensities of both π*- and σ*-band C 1s K-edge XANES feature [1] are found to be significantly reduced in MgO-coated CNTs, and the intensity of two peak between π*-and σ*-band C K-edge XANES feature [2] are enhanced and shifted several eV. Results indicate that the influence of different transition and electronic structure for CNTs is attributed by MgO coating.

Keywords: Carbon nanotube, Electronic structure, X-ray-absorption spectroscopy

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B48 - DEVELOPMENT OF CARBON NANOTUBES ELECTRODES FOR ELECTROCHEMICAL APPLICATIONS

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Carbon nanotubes (CNTs), due to their nanometer size and unique properties, such as high specific surface area, good electrical conductivity and high stability, have been the object of great interest for many applications like batteries, flat panel displays, chemical sensors, fuel cells among others. Our work consists in developing electrodes using carbon nanotubes with different architectures to study its electrochemical properties for future applications in fuel cells. Different methods were used to build the CNT electrodes. One of them was fabricated by growing directly on inox-steel and silicon substrates vertically aligned carbon nanotubes by DC-PECVD. Another approach was to prepare a CNT paste electrode using mineral oil as binder. By using a spray technique different CNT´s solutions were sprayed on different substrates (glass, silicon, inox-steel). The electrodes were electrochemically characterized by linear sweep voltammetry. Good electrochemical response in aqueous ferrocyanide system suggests that carbon nanotubes have promising potential to be used as an electrode for fuel cell applications.

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B49 - Nanoscale optical characterization of single carbon nanotubes

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Near-field photoluminescence (PL) and Raman spectroscopy were used to study the electronic and vibrational properties of semiconducting single-walled carbon nanotubes (SWCNTs). We present both PL and Raman scattering of SWCNTs obtained simultaneously with nanoscale resolution down to 10 nm. The technique we used is based on the local field enhancement effect at a laser-illuminated metal tip [1]. High-resolution images reveal that Raman scattering and PL vary not only from nanotube to nanotube, but also within the same nanotube. We observed localization of PL and variations of emission energies along nanotubes on a length scale of about 30 nm [2]. We attribute such variations to fluctuations of the dielectric function of the surrounding media. In addition, we investigated the dependence of the signal enhancement on the tip-sample distance. Simultaneous detection of Raman scattering and PL allows us to distinguish different contributions and to extract the effect of PL quenching. This technique is ideally suited to study hybrid nanoscale systems such as DNA-wrapped SWCNTs and QD-SWCNTs. We report on our first result on these systems.

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B50 - Electro-optical properties of polymers and carbon nanotubes for application in devices

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In this work we perform studies on electrical and optical properties of conjugated copolymers, carbon nanotubes and ionic conductor polymers (polymer electrolytes) with the purpose of developing electro-optic devices. The chosen materials consist of conjugated copolymers (semiconductors), their correspondent oligomers (thiophene-phenylene) and single-Walled carbon nanotubes (SWNT), synthesized by arc voltaic technique. After purification, the SWNT sample reached 90% of purity degree, measured by thermogravimetry. For improvement of the SWNT solubility in organic solvents, the tube ropes were opened by previously dispersing the purified SWNT in aqueous solution containing surfactant (SDS-sodium dodecyl sulfate) and re-precipitating in acetone. The employed electrolytes were composed by dissolving $LiClO_4$ salt in poly(ethylene) – block – poly (ethylene oxide) (PE-POE, Mw=900 daltons) at concentrations of 0, 1, 5, 7,5, 10 and 15% w/w. According to our previous studies, the carbon nanotubes absorb in the ultraviolet region and emit in the visible region of the spectra, the same is true for conjugated polymers. Based on impedance studies and thermal and structural analyses of electrolytes, we conclude that the concentration of 10% w/w optimizes the electric and structural correlated properties. Supported by these results we consider two types of electro-optic devices: the first one would be an electrochemical cell of light emission (LEC), formed by an electrolyte and a conjugated material blended; and the second one is a photovoltaic cell, formed by the composite conjugated material and carbon nanotube.

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B51 - Initial Friction Coefficient Studies On PDMS with MWCNT

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Poly(dimethyl siloxane) (PDMS) and derivatives are from a class of hybrid organic/inorganic polymers. This class is called silicone, it been extensively studied and commercialized. They are water repellent, heat stable, highly chemical resistant, and are electrically insulating. Due to these special properties, they are finding diverse industries applications as cosmetics, drug delivery, fabric care and paints and inks [1]. Because they can be operated at high and low temperature, they are also commonly used as oils, rubbers, hydraulic fluids, electrical insulation and moisture proofing agents. Multi Wall Carbon Nanotubes (MWCNT) has been attracted great attention because of their unique properties such as high mechanical strength and light weight, good heat conductance, and large surface area. A large number of papers have been reported that the nanoparticles addition on lubricant is effective in reducing wear and friction. The friction and wear decrease is dependent on nanoparticles characteristics, such as size, shape, and concentration [2]. In this paper we presented friction coefficient results of pure PDMS and PMDS with different concentrations of MWCNT. The MWCNT were dispersed in the PMDS by using ultrasonic bath. The tests were performed using a CETR ball-on-plat tribometer. The nanotubes were synthesized by plasma microwave in $H_2/N_2/CH_4$ environments, on titanium substrates covered by nickel particles as catalyst.

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B52 - Effect of synthesis conditions of N-doped multiwalled carbon nanotubes (CNx) on X-Ray Diffraction Patterns

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In these work, a series of Nitrogen-doped multiwalled carbon nanotubes (CNx) synthesized under different conditions by CVD process, were analyzed in terms of crystallinity using powder X-Ray diffraction. Results obtained suggest an inverse relation between d-spacing for signal of the (002) plane of graphite and synthesis temperature. This behavior has been verified for CNx obtained from different precursors (i.e. Fe-catalyst and Nhydrocarbon source) ratios. It also seems that when synthesis is performed with increasing amounts of Fe-catalyst, smaller d-pacing in G(002) peak is detected. XRD patterns for CNx samples synthesized around 700°C and for those synthesized around 900°C exhibit a poorly-defined graphite peak. SEM observations for these samples reveal reduced amounts of CNx and an important presence of amorphous carbon.On the contrary, nanotubes samples obtained between 800-850°C, present sharper graphite peaks indicating more crystalline character. Iron carbide “cementite” phase (Fe_3C), which is present in all cases, becomes considerable in samples produced at low temperatures (700-750°C). Thermogravimetric (TGA) analyses were also conducted with the aim of complete phase identification. Results exhibit a reduction in thermal stability as synthesis temperature decreases.

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B53 - The internal structure of vertically aligned single-walled carbon nanotube films

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In this study, we investigated the internal structure of ‘as-grown’ vertically aligned single-walled carbon nanotube (VA-SWNT) films by cross-sectional transmission electron microscopy (TEM). The VA-SWNTs were produced by the alcohol catalytic CVD method [1, 2], and transferred onto a TEM grid using a hot water technique [3]. The resulting freestanding VA-SWNT film was observed along the alignment direction, revealing cross-sections of the interior of the film. Cross-sections at various depths into the film were obtained by changing the focal plane. Due to the alignment of the SWNTs, many bundle cross-sections were observable, revealing the film consists of very small bundles, typically containing 3-10 SWNTs per bundle [4].

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B54 - Composition, structure and heat capacity of a double-walled carbon nanotube commercial sample

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Double-walled carbon nanotube (DWNT) samples were characterized by transmission electron microscopy (TEM), thermogravimetry (TG) and Raman Spectroscopy. The DWNT average outer and inner tube diameters were ~3 nm and ~ 2 nm respectively. The main thermooxidation characterized by TG occurs at 474°C with the loss of 90 wt% of the sample and a residue of 3.6 wt% of metal oxide was determined in triplicate. Thermooxidation of the DWNTs was also investigated by high resolution thermogravimetry, which allowed the determination of the amount of amorphous and graphitic carbonaceous material in the sample. A fraction of 5 wt% of the material was stable in air up to 800 °C and TEM images revealed the presence of a large content of nanotubes in this fraction. The heat capacity of the DWNT sample was determined in the range of temperature between -50 and 290 °C. The values of Cp for the DWNTs were compared to the Cp values of a SWNT sample of average diameter close to the inner layer of the DWNT

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B55 - Solid State Double Layer Capacitor Prepared with Polymer Electrolyte and Carbon Nanotube/Carbon Black Based Electrode Composite

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Multi-walled carbon nanotube (MWNT) and carbon black (CB) with high surface area (1500 m^2/g) were used as a mixture of carbonaceous materials to prepare an electrode composite in a polymer matrix. Solid double layer micrometric capacitors were assembled by using a thermoplastic polyurethane (TPU) and $LiClO_4$ as polymer electrolyte films and TPU/MWNT-CB/$LiClO_4$ electrode films. Electrolyte and electrode films in various concentrations were studied by differential scanning calorimetry, microscopy and impedance spectroscopy. The double layer capacitors were investigated by impedance spectroscopy, cyclic voltametry and cronocoulometry. The device with 4 wt% MWNT and 8 wt% CB was designed with final thickness of approximately 100 μm and delivered a capacitance of 5 F/g with a cyclability of more than 1000 cycles at room temperature.

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B56 - Elucidating and mapping morphological variations in CNT films by small-angle X-ray scattering

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The thickness of dense aligned films of carbon nanotubes (CNTs) grown from thermal CVD can reach several millimeters [1], suggesting manufacturing feasibility for prospective applications including thermal and electrical interface layers and reinforced composite materials. Traditionally, characterization of the orientation and CNT diameter within these films has been performed using scanning and transmission electron microscopy (SEM and TEM). However, the requirement of removing CNTs from the substrate and the restricted field of view in TEM make it challenging to elucidate spatial variations in film morphology. Furthermore it is difficult to obtain quantitative measurements of orientation using SEM. Here, we demonstrate how small-angle X-ray scattering (SAXS) can provide locally averaged, non-destructive, quantitative measurements of these parameters [2]. By obtaining SAXS data from different regions of a film, we elucidate and map the native variation of morphological properties in asgrown films and in films which are deformed and/or densified by direct mechanical or capillary-induced action [3]. Our investigations demonstrate that typical CNT films exhibit maximal alignment in the center region, that CNT diameter decreases slightly as film growth proceeds and may correspond to evolution of the substrate-bound catalyst particles, and that scattering in the low-q regime can be correlated to the spatial density of CNTs within a film.

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B57 - Annealing effects on the electrical properties of carbon nanotubes

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In order to better understand the properties of composites it is important to know the specific behaviour of each component of the composite. Therefore, self standing papers of carbon nanotubes were submitted to different thermal treatments in inert atmosphere in the range of 675C-1425C for one hour. Electrical conductivity measurements and Raman spectroscopy were used to characterize these samples.

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B58 - Carbon Nanotube interactions with Biological Systems

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We compared the toxicological effects between pure carbon multi-walled nanotubes (MWNTs) and N-doped multi-walled carbon (CN_x) nanotubes. For this matter, we used two different approaches. In the first one, different doses of nanotubes were administered in various ways to mice: nasal, oral, intratracheal and intra-peritoneal. In the second one, a comparative cell viability study of *Entamoeba histolytica* in the presence of the two different types of carbon nanotubes was performed; HM1:IMSS trophozoites were incubated in vitro with MWNTs and CN_x MWNTs, at different doses (from 0.1 to 100 $\mu g/10^5$ cells). We have found that when MWNTs were injected into the mice's trachea, the mice could die by dyspnea depending on the MWNTs doses. However, CN_x nanotubes never caused the death of any mice. We always found that CN_x nanotubes were far more tolerated by the mice when compared to MWNTs. Extremely high concentrations of CN_x nanotubes administrated directly into the mice's trachea only induced granulomatous inflammatory responses. Importantly, all other routes of administration did not induce signs of distress or tissue changes on any treated mice. On the other hand, it was demonstrated that CN_x MWNTs are innocuous to the proliferation of the trophozoites, whereas MWNTs became lethal. Moreover, CN_x MWNTs were actively phagocyted by trophozoites with no evidence of cellular damage or distress, in contrast to MWNTs that induced cellular lysis. These results encourage further studies testing CN_x nanotubes in biological systems to define their potential for drug delivery and cell targeting. We conclude that CN_x nanotubes are less harmful than MWNTs or SWNTs and might be more advantageous for bioapplications.

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B59 - Tilt Effects in Electron Diffraction Analysis of SWCNTs

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Electron diffraction technique has proven to be a direct, fast and trustful method for (n,m) determination of single-walled carbon nanotubes (SWCNT)[1]. An important issue in electron diffraction analysis of nanotube is that the tilt of the tube with respect to the incident electron beam in a transmission electron microscope (TEM) has a serious influence on the accuracy of the determination[1,2]. Unfortunately, the tilt angle of the nanotube is usually unknown, and is practically hard to quantify. In this contribution, we evaluate the tilt effects on structural analysis of SWCNTs by various electron diffraction techniques. An experimental procedure is proposed for confident evaluation of the tilt angle of the nanotube with respect to the electron beam.

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B60 - Neutron activation study of gold-decorated single-wall carbon nanotubes

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The study of carbon nanostructures (CN) encloses several areas of knowledge like chemistry, physics and materials science. Among the CN applications, those within the biological and health sciences are, by far, the most investigated due to the greater potential. Recent proof-of-concept works indicate that CN can be used, for example, as DNA and protein biosensors, drugs carriers, and scaffolds for tissue growing. However, very few studies focused their tissue biodistribution, absorption and clearance rates [1, 2]. Such studies are of extreme importance for the developing real CN-based biomedical applications. The motivation of this work is therefore to understand the biodistribution in mice and rats, of a novel single-wall CN decorated with gold nanoparticles. The first step of this work comprised a novel route for the preparation of these nanotubes. First, they were synthetized by arc discharge technique of doped graphite electrodes, purificated burning the amorphous carbon and removing the metals with hydrochloric acid, and funcionalizated with carboxyl groups (-COOH) by nitric acid reflux. Finally they were decorated with gold reducing choroauric acid ($HAuCl_4$) with nitric acid, UV and hydrazine (N_2H_4) routes. The former process already reported in the literature [3] and the later is a novel route of decoration SWNT with nanoparticles of gold developed in the Laboratory of Nanomateriais of the Department of Physics of the UFMG. Atomic Force Microscope (AFM) images confirmed the decoration. Gold-decorated CN samples were then neutron irradiated at the TRIGA MARK 1 IPR-R1 Reactor of the CDTN facility, and the 197Au isotope was transmuted in 198Au, which decayed in 198Hg emitting a characteristic gamma of 411KeV. Through the gamma spectrometry it was possible to quantify the amount gold present in the nanotubes and show that these gold-decorated CN can be used later as probes for the biodistribution of the nanotubes in tissues, organs and fluids of mice and rats.

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CONTRIBUTED ABSTRACTS

POSTER SESSION C

JUNE 26 (Tuesday)

C01 - Targeted Removal of Bioavailable Metal as a Nanotube Detoxification Strategy

Robert H Hurt, Daniel Morris, Xinyuan Liu, Lin Guo, David Murray, Agnes Kane

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The carbon nanotube community has a window of opportunity to understand and manage nanotube health risks before manufacturing becomes truly widespread. Ultrafine transition metal particles pose documented health risks upon inhalation, but their contribution to nanotube toxicity has been unclear due to their apparent encapsulation by carbon shells. The degree of encapsulation is a key toxicity variable because the major biomolecular pathways of metal toxicity involve soluble ions, which must first be “mobilized” from metal nanoparticles, or made “bioavailable“ by reactive dissolution processes that require fluid access.

Recently we developed quantitative assays for the bioavailability of Ni, Fe, and Y in carbon nanotubes, and applied them to study the effects of nanotube source, physiological fluid properties, and common nanomaterial stresses (sonication, oxidation) on metal bioavailability. We found that from 0.5% to 10% of the total metal is typically bioavailable, and the corresponding release can lead to toxicologically significant metal concentrations in either extracellular or intracellular spaces.

Here we explore the potential for reducing nanotube health risks by selectively removing the small fraction of the total metal that is found to be bioavailable. This talk presents results of nanotube treatment with non-oxidizing acids and chelating agents, and examines the effects of pH, time, wash protocol, and re-deposition of metal on nanotube outer surfaces by ion exchange. By targeting the bioavailable rather than the total metal, it is possible to identify simple purification protocols that may reduce nanotube health risks without causing tube damage.

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C02 - Debundling of Single Walls Carbon Nanotubes in Peptide-based Dispersions

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In the last few years carbon nanotubes have attracted a great deal of attention because of various interesting properties correlating their characteristic chemical properties with their small dimensions, high anisotropy and tube-like structures. The utilization of carbon nanotubes in various applications has although been hampered by the fact that they are difficult to solubilise and tend to aggregate into large bundles extremely difficult to separate. In the present work an amphiphilic -helical peptide (NANO-1) has been used to disperse single-walled carbon nanotubes (SWNTs) in water. Large scale debundling of single-walled nanotubes has been demonstrated by dilution of the nanotubes/peptide dispersions. Atomic force microscopy (AFM) shows a decrease of the mean bundle diameter with decreasing concentration. Infrared photoluminescence spectroscopy has been used to confirm the AFM results, showing evident increase pf the detected intensity with decreasing concentration; hence indicating effective debundling. Number and mass fractions of individual nanotubes also increase with decreasing concentration. Detailed analysis of both miscroscopical and spectroscopical data suggests the presence of an equilibrium bundle number density. The dilution process has also been compared with the effects of ultracentrifugation, showing the dilution method to be a viable and effective alternative.

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C03 - Gas-phase experiments with carbon nanotubes

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We present experimental results regarding the realization of beams of single-wall carbon nanotubes (SWNT's) under high vacuum conditions. The free flying tubes are adsorbed on a substrate and characterized both by Raman spectroscopy and transmission electron microscopy (Thanks to the workgroups of Prof. Kuzmany and Prof. Karnthaler (both University of Vienna)).

We discuss the application of such a nanotube beam and we propose a gas-phase sorting scheme to separate metallic from semiconducting SWNT's in a three grating deflectometer. The idea of the sorting setup is demonstrated with fullerenes in a near field matter wave interferometer and we describe how an optimized version of this experiment, operating in the classical Moiré mode, may be successful in achieving a partial enrichment of more than 60% for the metallic nanotubes.

We argue that a clean nanotube beam will have many advantages for the preparation of single tube and bulk devices and we discuss ideas how to achieve orientation alignment for free-flying nanotubes, which may be an important prerequisite for the structured and oriented deposition of isolated carbon nanotubes.

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C04 - Design of a Dispersant for Carbon Nanotubes in Organic Solvent

Seong Jae Choi [1], Seon-Mi Yoon [1], Hyeon-Jin Shin [1], Jae-Young Choi [1], Ki Kang Kim [2], Kay Hyeok An[2], Young Hee Lee [2], Jin-Hyon Lee [3], Ungyu Paik [3]

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The effect of dispersant structures to dispersing singlewalled carbon nanotubes (SWCNTs) was investigated. The 3-hexylthiophene was used as a starting material to design a dispersant for dispersion of SWCNTs in organic solvent by varying number of head groups (thiophene), regio-regularity of head groups, and head to tail ratios (hexyl group). The SWCNT solutions were characterized with UV-Vis-NIR spectroscopy and transmission electron microscopy. An increase in the number of head groups made SWCNTs highly dispersed and a regio-regular structure of head groups, rather than a regio-random structure, and played an important role in dispersing SWCNTs. Furthermore, Raman spectroscopy and X-ray photoelectron spectroscopy showed that sulfur atoms in the head group of thiophene enhanced interactions between thiophenes and the SWCNT walls. Our analysis demonstrated that the designed thiophene (H12,RR) could provide the well-dispersed SWCNTs solution with long-term dispersion stability even under an extremely low dispersant concentration for dispersion of SWCNTs (weight ratio of CNTs/dispersant = 1, dispersant concentration = 0.1 g/L).

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C05 - Highly stable dispersions of SWNTs in some organic solvents

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Stable dispersions of purified single-walled nanotubes (HiPCO) have been demonstrated in six common solvents at the initial concentration of 1 mg/ml without the need for any other dispersants. While some large nanotube aggregates form, these can be removed by mild centrifugation. By measurement of the absorbance before and after centrifugation as a function of concentration, the concentration of the dispersed nanotube phase could be estimated. After centrifugation, the dispersions are stable against sedimentation for at least several weeks. These stable dispersions were characterized by atomic force microscopy (AFM), UV-vis-NIR and near-infrared photoluminescence (IRPL) spectroscopy. The bundle diameter distributions of SWNTs dispersed in each solvent were measured by AFM. From this, we could calculate the mean bundle diameter which was typically in the range of 5-10nm and the fraction of individual nanotubes, typically les than 20%. However on dilution of all samples by a factor of ~10, in all cases the mean bundle diameter fell dramatically to as low as <2nm, while the fraction of individual nanotubes increased to >50% in a number of cases. The latter measurement could be confirmed by measurements of the nanotube IRPL before and after dilution. In addition, in some solvents IRPL peaks for certain nanotube types increased more on dilution compared to other nanotube types. These experiments can be used to rank solvents for nanotubes in terms of both dispersibility and ability to exfoliate.

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C06 - Debundling and Cutting of Single-Wall Carbon Nanotubes Solubilized in Aqueous Solution during Cup-Horn Ultrasonication

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Tokyo University of Science

The process of debundling of single-walled nanotubes (SWCNTs) is based on powerful cavitation effect and subsequent substitution of powerful nanotube-nanotube Van der Waals forces by surfactant micelles or polymer wrapping. The colloidal aqueous dispersions of strongly hydrophobic SWCNTs are usually obtained by powerful ultrasonication. At present, two types of ultrasonicators are commercially available: horn (or tip) and cup-horn ultrasonicators. A horn ultrasonicator is inserted directly to a vessel, and the ultrasonication power is transferred at high local intensity to samples. A cup-horn ultrasonication gives rather the small input power to the samples because the input power is transferred through a water bath but it will assure a relatively homogeneous sound intensity in the sample volume.

In order to understand the debundling and the cutting of carbon nanotubes in aqueous Sodium Dodecyl Sulfate (SDS) solutions, we investigated the effect of ultrasonication on SWCNTs by using a commercial cup-horn type ultrasonicator (Nanoruptor, TOSHO DENKI Co. Ltd., 350W, 20 kHz) working in on-off cycles (60 seconds on and 30 seconds off). The cup-horn ultrasonication experiments were conducted for sealed sample vials inserted in the temperature controlled water bath (4 ^{o}C). The samples' pH and temperature were monitored during ultrasonication. All ultrasonicated samples were investigated by absorption, dynamic light scattering, and Raman spectroscopy.

The pH of the nanotubes dispersed solution decreases strongly with the ultrasonication time following an exponential law. The reason for the pH decrease is thought to be the generation of HNO_3 and HNO_2 through a couple of reactions induced by powerful cavitation. In order to avoid pH effects, all spectroscopic measurements were conducted after buffering the samples toward the neutral pH with a mixed buffer solution of standard potassium phosphate monobasic buffer solution and sodium phosphate dibasic buffer solution (pH 6.86) at 4:1 ratios. Results of dynamic light scattering, and Raman spectroscopic measurements revealed that the debundling and the cutting of single-walled nanotubes were occurred with the increase of the sonication time. The cup-horn sonication did not give so large damages to SWCNTs in spite of the long time sonication. The characteristic differences between the horn type sonication and the cup-horn ultrasonication will be discussed.

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C07 - Purification and opening of carbon nanotubes using steam

Gerard Tobias, Lidong Shao, Christoph G. Salzmann, Yoon Huh, Malcolm L. H. Green

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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 steam 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.

[1] G. Tobias, L. Shao, C.G. Salzmann, Y. Huh, M.L. H. Green. J. Phys. Chem. B 110, 22318 (2006).

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C08 - Study of the dispersion process of carbon nanotubes in aqueous solution by using UV-vis spectroscopy

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The current bottleneck to carbon nanotubes (CNT) application in composite materials field consists in the difficulty of dispersing them in solvents. As a result of strong van der Waals interactions, as produced CNTs are tightly bundled in ropes of several tubes, rendering the carbon-powder insoluble in aqueous and organic liquids, and thus unprocessable [1].

The insolubility of CNTs has prompted research efforts focused on nanotube functionalization combined with dissolution in organic solvents and water. Functionalization by acid attack allows the dispersion of CNTs in various organic solvents, but introduces a significant number of defects in raw material, damaging CNTs' properties [2]. Moreover, the interest in applications that require water-soluble CNTs is growing and many attention is being directed to the study of surfactant aqueous solutions, in which surfactants can successfully suspend carbon nanotubes. In a typical dispersion procedure, after the surfactant has been adsorbed on the nanotube surface, ultrasonication helps surfactants debundling and exfoliating nanotubes, providing a mechanical energy able to overcome van derWaals interactions in CNT bundles. The electrostatic repulsion between surfactant polar heads that remain in solution allows the colloidal stability.

In this study the dispersibility of HiPco single walled carbon nanotubes (SWNT) in water has been evaluated by using UV-vis spectroscopy analysis. All kinds of CNTs are active in UV-vis region and exhibit characteristic bands depending on diameters and chiral vectors. Therefore, it is possible to detect individual CNTs via spectroscopic technique: there is a relationship between individually suspended CNTs in solution and the intensity of absorption spectrum at a determined wavelength [3]. This characteristic allows a dispersion analysis based on the study of the modification of CNTs spectral features with different parameters, such as solution sonication time, surfactant nature and concentration: an increase of exfoliated CNTs in the solution results in an increase of the absorbance value [4].

In this study, aqueous solutions of SWNTs have been prepared by using three types of surfactants, anionic, cationic and nonionic, in order to evaluate their dispersion abilities and to optimize dispersion process in terms of sonication time and surfactant concentration. Solutions at different surfactant concentrations have been analyzed after various sonication periods, enabling the classification of dispersion ability of these surfactants depending on surfactant chemistry, such as molecular formula, critical micelles concentration and polarity. A microscopical characterization by using Atomic Force Microscopy has been conducted in order to evaluate SWNTs dispersion and surfactant organization around nanotubes structures.

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[4] Grossiord N., Regev O., Loos J., Meuldijk J., Koning C.E. - Analytical Chemistry 2005; 77:5135-5139

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C09 - Separation of single-walled carbon nanotubes using a microfluidic chip

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Using dielectrophoresis in a micro-fluidic channel, we developed the separation technique collecting both of Metallic-SWNTs (M-SWNTs) and Semiconducing-SWNTs (S-SWNTs). Combination of an H-filter and electrodes which generating the non-uniform electric field was used to extraction of two types of SWNTs concurrently and continuously. The SWNTs suspension and the buffer solution in the H-filter device flowed along with their own path without mixing each other due to laminar flow. By applying non-uniform electric field, M-SWNTs were driven into the buffer solution by the strong dielectrophoretic force, while S-SWNTs followed the stream of SWNTs suspension due to the weak dielectrophoretic force. The successful separation of SWNTs was demonstrated based on the optical absorption and the resonant Raman spectroscopy.

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C10 - Carbon nanotubes wrapped by DNA molecules

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Complexes of carbon nanotubes (CNTs) and nucleic acids allow to fully exploit the potential of the CNTs in nanoelectronic devices, both by a size-specific matching of the two components and by the possibility to anchor also non-polar CNTs on the polar substrates such as oxides. The wrapping CNTs by the nucleic acid molecules allow also a transfer of CNTs into water solutions and a performance for their radii and lengths separation.

In the present work for the first time the stability and electronic properties of the associates of the single-walled carbon nanotubes wrapped by homopolymeric single-stranded DNA molecules (CNT@DNA) are studied using a dispersion corrected modification of quantum mechanical density-functional tight-binding method (DFTB). A phenomenological model of the CNT@DNA formation energy depending on the nanotube radii is developed, which shows that the decoration of a CNT by a few DNA chains leads to a high water solubility of CNT@DNA. Pyrimidine-based DNAs are found to be more effective to wrap the CNTs than other DNAs. The densities-ofstates of the CNT@DNA complexes are close to the superposition of those of the "free" components with some additional states below Fermi level. The band gap in a hybrid CNT@DNA system is determined by the competition between the Fermi levels of the "free" DNA and CNT. In a few specific cases (complexes of polyC-DNA and a chiral metallic CNT) a considerable charge transfer from the DNA to the CNT was observed, combined with an additional gain in the CNT@DNA formation energy. Experimental results were found to be in good agreement with the calculations. DNA molecules arequite effective in dispersing CNT bundles into single-walled nanotubes in aqueous solution. Experiments done with different oligonucleotides showed that poly-T DNA (pyrimidine-based oligonucleotide) was giving more efficient suspension than its counterparts. Interestingly, RNAs were also giving sufficiently good suspension. AFM images showed that about 20% surface coverage was sufficient for suspension and full surface coverage was not observed. The dispersed CNT solutions were stable for more than one year, thus proving that the interactive forces are very stable in time. It was observed that functional field-effect transistors can be build from DNA-suspended CNTs, thus showing that the inherent characteristics of semiconductig CNTs were preserved in the hybrid structures (CNT@DNA). In agreement with the results from the calculations only very little covalent interaction does exist between CNTs and DNA.

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C11 - Dipersion of carbon nanotubes into copolymers matrix

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The dispersion of carbon nanotubes into different polymeric matrix is considered decisive for eliminating the interaction between the nanotubes (bundling effects) and lead to composites with improved optical and mechanical properties. The use of polymers and copolymers for dispersing carbon nanotubes has been efficiently demonstrated. In this work we report the encapsulation of carbon nanotubes into polymeric systems that are alternative for the traditional SDS and P123, and they are known as good systems for drug delivery. We used individual copolymers as F127, F127, E116B52E116, E60B60E60, F87, F88, E50P50, on the concentration of 1%w/w the 1:1 proportion, obtained through anionic copolymerization. The obtained solutions are analyzed by resonance Raman spectroscopy which shows G band linewidths typical of individually dispersed nanotubes.

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C12 - Dielectrophoresis of well-dispersed single-walled carbon nanotubes

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The use of alternating current dielectrophoresis (a.c.-DEP) for the precise placement of nanoparticles on the predefined circuit structures is widely reported. In this research, we are aiming to fabricate an individual singlewalled carbon nanotube (SWNT) between pre-patterned electrodes by a.c.-DEP. Potential future applications of this work are a separation of metallic SWNTs and controlled fabrication of two-dimensional planar nanotube circuit structures such as an SWNT field effect transistor. For an electrolyte of DEP, SWNTs wrapped by several surfactants are prepared. Control of the dielectrophoretic force on the individual SWNT is shown to facilitate the fine dispersion of the SWNTs. This allows the dispersed SWNTs to be examined by UV-vis-NIR spectroscopy. After a.c.-DEP, between gold electrodes the SWNT is first rinsed to remove the surfactants from SWNTs and then observed by scanning electron microscopy. The electric properties of assembled carbon nanotubes are characterised by Raman spectroscopy with different wavelengths.

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C13 - Simple purification process for CVD SWCNT-DWCNT without use of acid reagents.

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A purification process based on centrifugation was applied to SWCNT/DWCNT produced by CVD process. The as produced carbon nanotubes, the catalyst and the catalyst support were dispersed in water by ultrasonic sonication and a surfactant. The centrifugation process allows the effective separation of the encapsulated metal particles, carbon shells and catalyst particles. No acid treatment was employed in any part of the process, which minimizes de damage to the carbon nanotubes and the emission of hazardous effluents. The purification process greatly improved the electrical and optical properties of the produced material.

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C14 - Removal of metal catalyst from carbon nanotube samples

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The purification of single-walled carbon nanotube (SWNT) samples without damaging their tubular structure is a challenging problem. The amount of impurities present in the SWNT sample depends on the synthesis method used (CVD, arc-discharge, laser ablation), but mainly consists on amorphous carbon, graphitic particles and metal catalysts. The removal of the latter is typically done by an acid wash. However, these metal catalysts are often coated by graphitic shells which prevent them to be attacked by the acid.

Here we report on a novel method to eliminate the graphitic shells coating the catalyst without altering the carbon nanotube structure, as suggested by Raman spectroscopy. By HRTEM studies we provide direct evidence of the removal of the graphitic layers around the metal. Moreover, thermogravimetric analyses (TGA) confirm the elimination of the metal catalyst from the SWNT samples.

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C15 - Effects of H_2O_2 oxidation on the surfactant-assisted dispersion of carbon nanotubes

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Hydrogen peroxide has been widely employed as an oxidant agent in purification routes of carbon nanotubes. Although several oxygen-containing functional groups can be added to the ends and surfaces of nanotubes, recent studies have showed that hydroxyl (-OH) groups are preferentially formed. In this work, we studied the effects of hydroxyl groups introduced by H_2O_2 oxidation on the solubility and surfactant-assisted aqueous dispersion process of carbon nanotubes. Multi- and single-wall carbon nanotubes were oxidized by refluxing in 30 vol % of H_2O_2 in H_2O under different experimental conditions. Fourier transform infrared spectroscopy (FT-IR), X ray photoelectron spectroscopy (XPS) and acid-base potentiometric titration analyses were carried out to characterize the changes in the chemical environment on the carbon nanotube surface after H_2O_2 treatments. The surfactantassisted dispersions of oxidized nanotubes were characterized by optical absorption and Raman spectroscopies and atomic force microscopy (AFM). The oxidized nanotubes showed improved solubility in polar solvents, such as water, ethanol, nitrophenol and dimethylformamide. The ability of surfactants to suspend the modified nanotubes is dependent of the extension of the chemical modification.

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C16 - Influence of Structural and Dielectric Anisotropy on the Dielectrophoresis of Single-Walled Carbon Nanotubes

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We report on a carbon nanotube network composed of aligned metallic and randomly oriented semiconducting single walled carbon nanotubes. The material is formed by using a novel radio-frequency dielectrophoresis setup, which generates very large dielectrophoretic force fields and efficiently suppresses electrothermal motion and thus allows for dielectrophoretic assembling of nanotube films up to 100 nm thickness. Polarization dependent absorption measurements provide experimental evidence for the electronic type specific alignment behavior.

The experimental results cannot be explained in the framework of the model of nanotube dielectrophoresis, which has been used so far and is based on a scalar dependence of the polarizability of the external field, neglecting the strong structural and dielectric anisotropy of carbon nanotubes. Within an advanced model that also incorporates contributions from the polarizability orthogonal to the nanotube axis, we predict a strikingly different alignment behavior of metallic and semiconducting nanotubes under the influence of an electric field. Also, due to the orthogonal polarizability a deposition of semiconducting nanotubes for frequencies above the crossover frequencies defined before is expected for very large electric fields.

Our polarization dependent measurements of the optical absorption on films of dielectrophoretically deposited carbon nanotubes give clear evidence for the high degree of alignment of the metallic nanotubes and a random orientation of the semiconducting nanotubes, as predicted. Additionally, we illustrate the decisive influence of the orthogonal polarizability onto the dielectric force acting on semiconducting nanotubes by means of finite element simulations and show that semiconducting nanotubes deposit under very large fields due to their transversal polarizability even for high field frequencies.

M. Pimenta and L. M. Malard are greatly acknowledged for performing Raman measurements on the nanotube networks. The results nicely agree with the absorption spectroscopy data.

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C17 - Separation Techniques for Single-Walled Carbon Nanotubes

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Separation techniques for single walled carbon nanotubes (SWCNTs) have become an important research field within the last few years, mainly for the reason that the synthesis of carbon nanotubes does not allow to grow nanotubes with 100% purity, well defined length, diameter and chirality. Hope exists that by controlling the catalyst and growth conditions (n,m)-specific growth could be achieved in the future. Until then separation techniques are inevitable whenever application or fundamental research require nanotubes with well defined properties.

A successful separation depends on the intrinsic capability of the chosen technique, but also on many other parameters. For example the separation efficiency strongly depends on the degree of individualization and up to date no technique exists which individualizes SWCNT samples by 100%. Besides that no integral measurement is available today to quantitatively determine the bundle content in a nanotube dispersion. Only AFM allows distinguishing unambiguously a single nanotube from a nanotube bundle. For that purpose dispersions are spin casted onto a surface and height profiles are measured on a large number of tubes or bundles to determine the fraction of bundles. Since this is a rather time consuming procedure many researchers rely solely on the detection of fluorescence or sharp absorption peaks as indicators for individually dispersed tubes and thereby do not determine the residual bundle content.

Individualizing SWCNTs often needs several processing steps (purification, sonication, acid treating, functionalizing) and during every step the properties of the tubes might be altered which often influences the results of the chosen separation techniques or even inhibits separation. Also because different researchers use tubes from different source (Laser ablation, Arc discharge, CVD) made by a different synthesis method the SWCNTs require a different treatment. In any dispersing step sonication is always required to overcome van der Waals forces between the walls of neighbouring tubes. Unfortunately sonication introduces defects and causes rupture of the tubes.

My contribution aims at giving an overview over separation techniques we are currently using for SWNTs and the characteristics of separated nanotube material. I will discuss (i) how one can achieve separation due to different electronic properties (metallic, semiconducting), length, diameter and chirality via size exclusion chromatography, electrophoresis, dielectrophoresis and density gradient centrifugation, (ii) how those separation methods work for different SWNT materials (HiPco, Laser ablation, CoMoCat) and (iii) how different pre-treatments and surfactants influence the separation efficiency.

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C18 - Purification of Carbon Nanotubes Obtained by Chemical Vapor Deposition using Ethylene and Fe-Mo/MgO and Fe-Mo/Al_2O_3 Catalysts

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The methods of carbon nanotubes synthesis in large escale produce samples that are not pure. Residual growth catalyst, amorphous carbon and ceramic matrices are the most common impurities, being the real composition of the final samples dependent on the synthesis and purification routes. Several purification protocols are found popular in the literature, but studies that better characterize the impurities and enable to understand their limited chemical reactivity to common purification methods are missing. In this work, we report a carefully study on purification of carbon nanotubes which were synthesized in our laboratory by CVD using ethylene as carbon source and Fe and Fe-Mo supported in MgO and Al_2O_3 as catalysts. The samples were purified by refluxing in 6M aqueous HCl for 24 hours. The catalyst and nanotubes were characterized using X-ray diffraction (XRD), thermal analysis, Mossbauer spectroscopy, scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). Mossbauer spectroscopy and XRD identified the complete elimination of MgO and Al_2O_3 supports and $Fe_{(1-x)}O_x$ phases after acid treatment. However, impurities containing carbide phases of Fe and Mo are still remained. Although the EDS analysis determined the completely removal of Mg and Al in nanotubes after the purification process, traces of Mg- and Al- containing phases were detect by DRX and Mossbauer spectroscopy, suggesting that these phases remaining encapsulated inside the carbon nanotubes.

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C19 - Chemistry: The solution for making high performance SWNT-based materials

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Single-walled carbon nanotubes (SWNT) exhibit the best mechanical, thermal and electrical properties of any known material. Combined with their very high aspect ratios that can reach well over 1000, SWNT is the dreamed material for the fabrication of composites with ultimate performance. Unfortunately, despite the wide availability of SWNT and despite of many attempts, all SWNT-based composites reported to date showed rather poor performance, often worse than those of the pure matrices. The main reasons for this are 1) highly variable purity and quality of the SWNT samples used, 2) poor dispersion/exfoliation and, 3) poor interface compatibility with the matrix. The second and third reasons are related to the intrinsic strong van der Waals interactions among the SWNT which lead to the formation of large bundles and to the intrinsic chemical stability of SWNT which makes binding to matrices rather di_cult. It is now widely accepted that chemistry is central to the development of high performance materials based on SWNT. Chemistry can solve the problems associated with bundles and the lack of binding with the matrices. In the past 5 years, side-walled covalent functionalization on neutral SWNT has received considerable attention. Strategies to anchor all the practical functionalities have been developed. One draw back is that completion of the reaction at the single tube level requires substantial amount of time because the SWNT are inherently un-reactive and importantly they are bundled. Reaction completion takes several hours, even days. Recently, Penicaud et al., showed that SWNT can be readily ex-foliated in standard solvents by reduction with alkali metal though electron transfer mediated by alkali-naphthalene-THF complexes. As the SWNT get charged negatively, they ex-foliate as a result of electrostatic repulsion. This is an important practical advance because it readily allows chemistry at the single tube, thus saving considerable amount of time. As chemical processing is the major cost associated with the integration of SWNT in advanced materials, any reduction in processing cost makes industrial utilization of SWNT more plausible. In addition, reduced tubes acquire higher nucleophilic character thus allowing new chemistry. Here, we explore such chemistry and demonstrate that reduced SWNT reacts with a variety of electrophilic reagents or radical donor/acceptors. In particular, we have developed a patent pending rapid functionalization procedure that takes only minutes rather than hours to effect side-walled functionalization. We have integrated these functionalized SWNT into thermoset resins of various grades and obtained significant improvements in mechanical properties. Each of these subjects will be discussed and supported with data. This presentation will emphasize that the quality of SWNT and chemistry are central into the development of high performance SWNT-based materials.

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C20 - Biocompatibility studies of chemically modified carbon nanotubes

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The interaction of chemically modified carbon nanotubes with the immune system proteins is a topic that is important for assessing the biocompatibility and potential toxicity of carbon nanotubes. The complement system is considered as the chief recognition and effector component of innate immunity; it is involved in inflammation and the adaptive immune response. The complement system can be activated via three different pathways termed the classical, alternative and lectin pathways. Here we report decreased activation of the human serum complement system and decreased human plasma absorption after chemical modification of Multi- walled carbon nanotubes (MWNTs). Four different types of chemically-modified samples were tested for complement activation via the classical and the alternative complement pathways using haemolytic assays. Covalent functionalisation of MWNTs altered the level of activation of the complement system via both the classical and the alternative pathways. Binding of human plasma and serum proteins to chemically modified carbon nanotubes was highly selective. Fibrinogen and High Density Lipoprotein were the major binding species.

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C21 - Transversal electron field effects on functionalized carbon nanotubes

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Carbon nanotubes have been exhaustively investigated in the last 15 years due to their promising physical and chemical properties, what make them main candidates to a new array on technology and science development for the XXI century. Since their discovery, lot of attention has been attracted on the possibility of modify such properties in order to make them even more versatile. This have been done mainly by chemical attachment of molecules and chemical groups on the surface, such as NO_2, O_2, $CONH_2$ and COOH. However, physical agents may also alter the electronic structure of carbon nanotubes. Both, experiments and computational simulations, show that vacancies and Stone-Wales defects are able to deeply modify the electronic structure of such materials, leading to completely new devices. The presence of structural defects on the nanotube surface induces alterations in the intrinsic electronic structure of the nanotubes by modifying the orbital geometries and electronic population. Such effects can be enhanced by adding a new element - a transverse external electric field. The external electric field leads to a subsequent rearrangement of the orbital and the respective electrons, leading to a further functionalization. In the this work, density functional calculations are presented on pristine and functionalized carbon nanotubes by a COOH group under transversal external electric fields. We observe that the applied external electric field induces relevant modifications on the structural and electronic properties, leading to new compounds in a chemical point of view. The influences of the strength and orientation of the electron field are investigated and the resulting structures are shown and discussed.

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C22 - Adsorption of Benzonitrile on Pristine and Fe-doped Carbon Nanotubes

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Carbon nanotube bundles have become promising materials for adsorption of toxic compounds aiming its large specific surface area. In this work, we have investigated the interaction of benzonitrile molecule C_7H_5N with the (8,0) and (5,5) pristine SWNTs using ab initio methods. Firstly, we studied the molecule in several configurations on the perfect nanotube surface in order to find the most stable configuration whose the higher binding energy was calculated as 0.3 eV. We also have analyzed the effect of introducing a vacancy on the tube in the interaction with the benzonitrile molecule. Since benzonitrile is suitable for forming complex with transitions metals, we introduced an Fe atom between the tube surface and the benzonitrile molecule aiming to improve the molecule adsorption. The charge transfer and electronic band structure of the modified systems are discussed.

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C23 - Trihalomethanes adsorption on carbon nanotubes

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Carbon nanotubes are good candidates for several potential applications such as sorbent materials for toxic chemicals. The possibility of trihalomethanes (THMs) adsorption on carbon nanotubes bundles was recently pointed out in the literature. THMs like $CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$ and $CHBr_3$ are sub-products in water treatment processes and its managing is very important for environmental related applications. In this work we investigate the interaction between THMs ($CHCl_3$ in particular) and carbon nanotubes using ab initio Density Functional Theory based calculations and resonant Raman spectroscopy. Theoretically, we study the interaction of $CHCl_3$ with the pristine (5, 5) and (8, 0), vacant and carboxylated nanotubes. Modifications on the electronic structure in different geometric configurations are discussed in order to evaluate the tube-THM stability aiming to understand the adsorption process. Experimentally, we performed the interaction of carbon nanotubes in aqueous solution of $CHCl_3$ at different concentrations. The samples were analyzed by Resonant Raman Spectroscopy (RRS). The calculations suggested a weak interaction which agrees with Raman spectroscopy data.

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C24 - Self-Assembly of Nanocrystals and Quantum Dots at the Surface of Functionalized Boron Nitride Nanotubes

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Carbon Nanotubes (CNTs) and Boron Nitride Nanotubes (BNNTs) have generated considerable interest due to their remarkable intrinsic properties and their use in a range of technological applications. A key feature which has enabled many of the developments concerning carbon nanotubes (CNTs) has been the ability for the surface of the nanotubes to be chemically modified or functionalized. In particular the surface functionalization of these materials has been used as a means by which their assembly may be controlled in solution and at substrates. The controlled assembly of such materials is seen as a fundamental step towards utilization of their novel intrinsic properties for a range of electronic, catalytic, sensing and materials science applications. While there have been significant developments concerning CNTs, there has been comparatively little progress concerning boron nitride nanotubes (BNNTs) and their integration with nanoscale materials. Several reports in recent years have described the surface modification of BNNTs as a means by which BNNTs may be solubilized, their electronic properties modified, and also to template the immobilization of materials from solution. Although these reports describe the utilization of BNNTs to integrate with materials such as polymers and bio-molecules, the density of functional groups which facilitate such interactions at the surface of the BNNTs is believed to be low in comparison with the modification of CNTs or the surface modification of conventional condensed phase materials such as nanoparticles or nanorods. In this context, the modification of BNNTs which results in the generation of high densities of functional groups at the surface of BNNTs is believed to have much potential for the utilization of these materials as nanoscale templates and for the integration with host materials to form composites.

Boron nitride nanotubes (BNNTs) have been functionalized for the first time by the generation of amine groups at their surface following an ammonia plasma irradiation treatment. The amine-functionalized BNNTs were covalently modified by the coupling of a series of organic molecules terminated with functional groups. The modification of the BNNTs was characterized using FT-IR, NMR, XPS, EELS, EDS. Functionalized BNNTs were used to template the assembly of nanoparticles and quantum dots in solution. The resulting assemblies were characterized by TEM, SEM, and EELS. This approach constitutes a basis for the preparation of highly functionalized BNNTs and for their utilization as nanoscale templates for the assembly and integration with other nanoscale materials.

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C25 - Fluorination specificity of double-wall carbon nanotubes

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We compared reactivity of double- and single-wall carbon nanotubes relative to fluorination. Fluorination of samples has been performed using a mixture of BrF_3 and Br_2 at room temperature. Transmission electron microscopy showed retention of tubular structures under these conditions. Composition of samples obtained from analysis of X-ray photoelectron data was found to depend on number of tube shells and tube length. Raman and X-ray absorption spectroscopy revealed fluorination of the outer tubes in double-wall structures. Fluorination of double-wall nanotubes resolved the features of optical absorption spectrum allowing the observation of the configuration of the inner shells. The fluorinated double-wall carbon nanotubes has been annealed in vacuum at the fixed temperatures and X-ray photoelectron spectroscopy showed almost no fluorine in the sample heated to 300 ^{o}C.

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C26 - Improved Biodistribution and Toxicity Profiles of Functionalised Carbon Nanotubes

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Carbon nanotube (CNT) development for biomedical applications is in the nascent stages, however is thought to lead to novel types of diagnostic, therapeutic and regenerative nanomedicines. The construction of CNT-based delivery systems able to traffick intracellularly and deliver drug molecules including nucleic acids requires engineering such nanotube features as the efficiency in delivering the therapeutic molecules at the target sites and cellular compartments, and optimization of their pharmacological and toxicological profile, by maintaining therapeutic efficacy. In this communication we will be discussing the critical *in vivo* parameters, namely the toxicological and pharmacological profiles of CNT. Therapeutically-relevant doses of serum protein-coated purified CNT (pCNT) and functionalised CNT (*f*-CNT) were administered intravenously in rodent species. Striking differences were found between the liver and lung tissues of animals injected with nanotubes. Pcnt exhibited significant accumulation in both tissues 24 h post-administration. *f* -CNT circulated in systemic blood circulation for 5 min, accumulated in the renal cortex and rapidly trespassed the glomerular filtering system excreted in urine in the absence of any tissue accumulation or damage. The biocompatibility and biodistribution of CNT appears to be dramatically dependent on the surface functionalisation of these nanostructures, making *f* -CNT viable material for a variety of biomedical applications.

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C27 - A Structure-Reactivity Relationship for Single Walled Carbon Nanotubes Reacting with 4-Hydroxybenzene Diazonium Salt

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The goal of this work is to obtain the relationship between the electronic band structures of individual single walled carbon nanotubes (SWNT) and their reactivities with 4-hydroxybenzene diazonium salt as a model electron acceptor. This necessitated the deconvolution of the UV-vis-nIR absorption spectra of SWNT, recorded after the reactions. Our deconvolution algorithm simplifies this non-trivial problem by grouping nanotubes with similar transition energies and assigning weights to their spectral contributions, which were approximated by Voigt lineshapes. Linewidths for the metallic and semiconducting regions were obtained from the absorption spectra of DNA-wrapped SWNT fractionated by ion-exchange chromatography. Rate equations based on an adsorptionreaction scheme have been used to model the surface coverage plots that were obtained after the deconvolution of the reaction spectra. The rate constants of representative nanotubes were related to their band structures through the use of Marcus theory and Gerischer-Marcus theory, both of which concern electron transfer reactions.

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C28 - Electronic properties of exohedrally doped double wall carbon nanotubes

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The electronic properties of exohedrally doped DWNTs with acceptor molecules are investigated through ab initio calculations and resonant Raman scattering.We find that the charge localization on the inner and outer tubes is different and strongly depends on the configuration of the co-axial arrangement of semiconducting and metallic tubes. It is predicted that the metallic tubule is very sensitive to doping effects even when it is enclosed inside a semiconducting shell. Conversely, when the outer shell is metallic, the external electrostatic field is screened by the metallic tube and the inner semiconducting tube is only weakly affected by the chemical doping. Our results indicate that it is possible to modify the transport properties of the outer shell while preserving the optical properties of inner tube, thereby creating systems with non-uniform doping characters. The theoretical findings are supported by resonant Raman scattering data on DWNTs exohedrally doped with acceptor (Br_2 and H_2SO_4) species. The Raman studies confirm univocally the theoretical conclusions and point out a general trend independent on the electronegativity of the doping species.

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C29 - Heck reaction on the single-walled carbon nanotube surface

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Few materials have attracted the fancy of many scientists around the world as Carbon Nanotubes (CNs) since their discovery due to their unique mechanical, electronic and optical properties [1], which make them excellent candidates for optoelectronic applications [2]. Nevertheless, over the past few years, researchers have begun to focus their interest on the chemical properties of CNs and how these properties can be modulated through functionalization. Covalent chemical functionalization promises extensive diversity in nanotube modification, allowing the coupling of various molecular structures to the nanotube surface [3] and we have described some new reactions on the CN surface [4].

Here, we describe by the first time the Heck reaction to synthesize novel single-walled carbon nanotube (SWNT) derivatives starting from p-iodophenyl-functionalized SWNT [5].This material reacts with a variety of acrylates affording cross-coupled SWNT products. Reaction products were characterized by several techniques.

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C30 - Chemical Modification of CNT/PEG Based Novel Bio-Nanosensor by Plasma-Activation Method

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In order to chemically modify single-walled carbon nanotubes (SWNTs), plasma ion irradiation (plasma activation) is demonstrated on a bio-nanosensor based on poly[ethylene glycol] (PEG)-grafted SWNTs (PEGSWNTs). According to X-ray photoelectron spectroscopy (XPS) analysis, peaks which correspond to COOH radicals are observed. In addition, evaluation of the bio-nanosensor for characteristic response to beef serum albumin (BSA) and anti-BSA is revealed an increase in impedance due to an antigen-antibody reaction when anti-BSA is injected. In these results, it was found that this bio-nanosensor reacts with a quick response time (60 s).

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C31 - Catalytic reaction inside a metallocene filled single wall carbon nanotube nanoreactor

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We present a novel route to explore chemistry within the one dimensional confinement inside a metallocene filled single wall carbon nanotube (SWCNT) [1]. A thermally activated chemical reaction inside this nanoreactor allows producing double wall carbon nanotubes (DWCNT) with a defined doping. The evolution of intermediate reaction products and the formation of differently functionalized inner tubes were traced by photoemission and TEM. A detailed study of the Raman pattern of the inner tubes was utilized to elucidate different growth mechanisms (i.e. catalytic or non-catalytic and with or without predefined caps) of inner nanotubes inside a DWCNT synthesized from different precursors. In addition, the application of different metallocene precursors and different reaction times allows to accurately tune the doping level and magnetic properties of the filled SWCNT and DWCNT. Given the large amount of organometallic precursors, this process paves the way to engineer purpose built nanoscale devices for spintronics and nanoelectronics and to study the chemistry inside functionalized SWCNT.

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C32 - The Synthesis of SWNT based One-Dimensional (1D) Nanoscale Heterojunctions

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In this presentation we describe the results on the formation of heterojunctions between single-wall carbon nanotubes (SWNTs) and one-dimensional (1D) gold nanorods (AuNRs) assembled directly on surfaces. Au NRs are grown directly and selectively on surface-attached SWNTs by depositing hexanethiolate-terminated Au monolayer protected clusters (MPCs) on the SWCNTs and growing Au MPCs into NRs by seed-mediated growth, involving reduction of AuCL4- onto Au MPCs in the presence of cetyltrimethylammonium bromide (CTAB). UV-vis, AFM, and SEM show highly selective growth of Au on SWNTs only. Different combinations of junctions are possible, including AuNRs connecting two or more SWNTs or several AuNRs attached to one SWNT. We also observe Surface-Enhanced Raman Scattering (SERS) of SWNTs in these structures. Several NRs and SWNTs integrated into a connected assembly were studied.We also synthesized branched SWNT-GaAs nanowire heterostructures using pulsed laser vaporization where Au nanorods attached to the SWNTs serve as the catalyst particles. These heterostructures consisting of metallic SWNTs can be useful as interconnects for assembly of nanostructure networks.

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C33 - Impact of Functionalized Carbon Nanomaterials on the Immunocompetent Cells

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The biomedical applications of carbon nanotubes (CNT), particularly in the delivery of therapeutic molecules, are intensifying [A. Bianco, et al. Chem. Commun. 2005, 571]. This is certainly related to the capacity of this type of material to penetrate into the cells. The demonstration of CNT cell uptake has opened the way to their exploration as novel carrier systems for different types of biomolecules, including peptides, proteins, nucleic acids and small drugs [W. Wu, et al. Angew. Chem., Int. Ed. 2005, 44, 6358]. This allows envisaging the development of new vaccine formulations or targeted therapies. In this context, it is necessary to carefully evaluate the impact of CNT at the cellular, tissue and organ level. In this poster, we will present the interaction between functionalized carbon nanotubes and the cell responsible of the control of the immune system. Cell membrane binding and internalization mechanisms will be described. In addition, we will present data concerning the impact of CNT on viability and functionality of these primary immune cells [H. Dumortier, et al. Nano Lett. 2006, 6, 1522]

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C34 - Bromine-doped Single-Walled Carbon Nanotubes via HBr Solution Based Protocols

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The charge transfer in bromine–doped carbon nanotubes has been amply discussed, motivated mainly by the possibility of sorting the nanotube molecules by type. The adsorption of both atomic and molecular bromine species has showed to be preferential on metallic nanotubes compared to semiconductor tubes [1]. However, most of the investigations relies on the interaction between elemental bromine liquid and the carbon-based materials. Br_2 molecules can intercalate into graphite layers forming C_8Br [2] or accumulate on carbon nanotubes as carbon–Br_2 complex [3]. Only recently, the modification of single-walled carbon nanotubes induced by a HBr solution at room temperature has been considered [4]. The method allows the interaction with Br atoms and bromine derivatives present in the solution and may lead to structural changes without cutting of the nanotubes, preserving the high aspect ratio of these systems. In this work, we explore the reaction between purified SWNT and HBr solution in different chemical environments, by using active solvents or oxidizing species for *"in situ"* generation of bromine species. The use of milder and more selective reagents eliminates the need to handle the highly toxic and corrosive elemental bromine and may lead to a better control on the bromination reactions and the further chemical treatments that can be easily performed from halogenated SWNTs. All SWNT-Br derivatives have been characterized by thermogravimetry (TG), fourier transform infrared spectroscopy (FTIR), X ray photoelectron spectroscopy (XPS), energy dispersive X ray spectroscopy (EDS), scanning electron microscopy (SEM) and Raman scattering. The generated Br species and their interaction with SWNT are discussed.

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C35 – Ab initio study of substitutionally Ni-doped single-wall carbon nanotubes: structural and electronic properties.

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SWNT's are unique prototype materials for modeling one-dimensional systems[1]. They are remarkable nanomaterials that can present either semiconducting or metallic behavior depending on their geometry[2]. In this work we report the structural and electronic properties of substitutionally Ni-doped, either metallic (5,5) or semiconductor (8,0), single-wall carbon nanotube (SWNT) by using spin-polarized total-energy *ab initio* calculations. We find two stable geometries for these systems with Ni atom in an outward or inward local distortion relative to the tube surface. These structures agree with the previous experimental results by Ushiro et al. using extended x-ray absorption fine structure (EXAFS) and x-ray absorption near edge structure (XANES) techniques [Phys. Rev. B 73, 144103 (2006)]. The outward configurations are always more stable that the inward ones. We explore also the change on the electronic properties after Ni doped SWNT's. The, initially metallic, (5,5) SWNT becomes semiconducting, with an energy gap of 0.33 eV for the outward geometry and 0.14 eV for the inward one. For the (8,0) SWNT a reduction of the gap is observed from 0.80 eV to 0.39 eV for the outward geometry and 0.37 eV for the inward one. A zero spin polarization is obtained for all the systems which may be understood as a consequence of the strong hybridization between the neighboring carbon atoms and the metal states [2].

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C36 - Selenium functionalized carbon nanotubes

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The modified carbon nanotubes systems are very promising for applications because these hybrid structures have improved chemical properties relative to pristine counterparts. In this work we report an study of Se functionalized carbon nanotubes. In particular, the combination of Se and nanotubes is interesting because it can be further exploited to convert the Se in other functional materials such as ZnSe and CdSe decorating the carbon nanotubes. The hybrid samples were prepared employing anionic SWCNT species, formed by treatment of this with organolithium compounds. Afterwards, it was performed the treatment of anionic species with elemental selenium, followed by oxidation, leading to Se and carbon nanotubes hybrid systems. The samples were analyzed using resonant Raman spectroscopy. It was observed a surpression of the radial breathing mode and the appearance of very sharp mode at 237 cm^{-1} which was attributed to Se-Se stretching mode. The suppression of the RBM along with the observation of Se-Se stretching is interpreted as being the Se dimmers/chains welding the carbon nanotubes.

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C37 - Functionalisation of Carbon Nanotubes

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CNTs display a range of unique properties and, as a result, a variety of applications of these architectures can be envisioned in both the physical and life sciences. However, pristine, isolated CNT are rarely available in sufficient quantities, which presents a major problem. Due to their great flexibility and high surface energy, they tend to aggregate into bundles and superstructures of bundles with still a higher degree of entanglement (ropes, mats). The solubilisation of CNTs can be achieved following two major pathways: 1) covalent functionalization, 2) non-covalent supramolecular modifications. Covalent functionalization of CNTs has been shown to be an efficient method for increasing their solubility and processability, and they include i) esterification or amidation of oxidized nanotubes, ii) side-wall covalent attachment of functional groups. Here, we present the latest developments realized in our group on covalent functionalization of carbon nanotube derivatives.

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C38 - Covalent functionalization of single wall carbon nanotubes using organic dye molecules

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Increasing interest is being focused on the rational functionalization of both single and multiwall carbon nanotubes to fabricate functional nanostructures with novel properties. In this work we investigated methodologies for the covalent functionalization of single wall carbon nanotubes (SWNTs) with organic dye molecules. Three different dyes were employed: phenosafranin (3,7-diamino-5-phenylphenazinium chloride), Nile blue (5-amino- 9-(diethylamino) benzo(a) phenoxazin-7-ium sulfate) and azure C (3-amino-7-methylaminophenothiazin-5-ium chloride). The interest in these dyes resides in the fact that such molecules can act as photosensitizers in energy and electron transfer reactions.

Chemical modification of carbon nanotubes was made by reaction of oxidized SWNT and the amine functionalities of the organic molecules. SWNTs were oxidized in aqueous H_2SO_4:HNO_3 (3:1) 30 % solution under magnetic stirring for 6 h at ambient temperature (ca. 25 ^{o}C), to produce SWNTs terminated with COOH groups. After this reaction, nanotubes were separated by centrifugation and washed with deionized water until neutral pH. For the synthesis of the composites, 0.01 g of oxidated SWNT was added to 50 mL of a 2.10^{-4} mol.L^{-1} dye solution in acetonitrile in the presence of 2.10^{-3} mol.L^{-1} dicyclohexylcarbodiimide, as a condensation agent. The system was kept in under stirring in the dark for 24 h. Dye-modified nanotubes were then separated by centrifugation and washed with deionized water and ethanol.

Hybrid SWNT-dye nanocomposites were characterized using spectroscopic techniques. Changes in characteristic Raman vibrational features of the dyes suggest covalent modification of nanotubes with the organic molecules. Specifically, the vibrational modes assigned to the NH_2 moieties of the dyes are seen to disappear in the SWNTdye nanocomposites, corroborating the bond formation between amine groups in the dyes and carboxyl groups in the oxidated nanotubes. In addition, changes in fluorescent emission spectrum of the organic molecules bonded to carbon nanotubes revealed an electronic interaction between both moieties in the nanocomposites. In the case of phenosafranin, a significant redshift of the dye fluorescent emission upon chemical interaction with the nanotube was observed. Such bathocromic effect can be assigned to a decrease in the HOMO-LUMO gap due to electron transfer process in the composite.

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C39 - B-doped Single Wall Nanotubes synthesized by HV-CVD of liquid feedstocks

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It is well known that one method of tailoring the electronic properties of single wall carbon nanotubes could be the chemical modification through incorporation of heteroatoms within the tube walls. Experimental studies on the synthesis of boron (B) doped carbon nanotubes (CNTs) have been successfully carried out with methods such as substitution reactions, arc discharge and laser ablation. However, a chemical vapor deposition (CVD) approach has still a number of interdependent parameters to overcome to make possible such synthesis. In this work, we report the feasibility to synthesize B-doped SWNTs of high quality produced from a pure liquid B/C containing feedstock by high vacuum CVD. From Raman and TEM we observe a very low defect concentration concomitant with small nanotube bundles containing 5-8 tubes with a narrow diameter distribution. The actual Boron content was probed by XPS and does not exceed 4%.

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C40 - Sidewall Covalent Functionalization of Fluorinated Single Wall Carbon Nanotubes Using with Urea and Related Structures for Radiation and Composite Applications

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Sidewall covalent functionalization of carbon nanotubes is necessary to achieve smaller bundles, link to other functional moieties, and aid in better dispersion in composites. In the present study, we present a one step functionalization using fluorinated single wall carbon nanotubes (F-SWNTs) as precursors, which were then further derivatized using urea, guanidine and thiourea. These bi-functionalized nanotubes were characterized by Raman spectroscopy, Fourier Transform infrared (FTIR), thermo gravimetric analysis (TGA), scanning electron microscopy (SEM), x-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM) and atomic force microscopy (AFM). Compared to fluorinated tubes, Urea-F-SWNTs among the three derivatives have shown the highest stability in DMF and the sidewalls are densely functionalized as evidenced by TEM. Guanidine-F-SWNT had the least amount of residual fluorine on the sidewall as determined by XPS. Along with the development of Urea-F-SWNT, we also present Alkylated-Fluorinated-SWNT (A-F-SWNT) which had been previously developed by our group, in a radiation study with 40 MeV Protons. These functionalized nanotubes all had shown some interesting shifts in Raman spectra, and these will be shown. The derivatives have potential in creating an interface between the nanotubes and polymers resulting in strong composites and some preliminary composite work, such as DSC, Tensile test, and TGA will also be shown. The three urea derivatives are quick and simple to synthesize and this method can be easily upscaled for applications such as creating an integrated polymer network for stronger composites, coatings, and biomedical applications.

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C41 - Raman spectroscopy study of single-walled carbon nanotubes treated with sulfuric acid

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In this work we have studied the effect of sulfuric acid (H_2SO_4) treatment on the single-walled carbon nanotubes (SWNTs) produced by the HiPCO process. The effect of the exposure of the nanotubes to H_2SO_4 was investigated. We observed changes in the Raman bands associated to radial and tangential vibration modes for treated samples compared with the pristine counterpart. The changes in the electronic structure and vibrational properties were observed through an up shift of the G band frequencies and loss of the Breit-Wigner-Fano tail in the spectra of metallic tubes which is attributed to a charge transfer from the nanotube π states to the sulfuric acid. The average diameter of the SWNTs used in this work is similar to the inner tubes of DWNTs.We discuss the effect of H_2SO_4 intercalation on the SWNTs in comparison with DWNTs in order to establish doping differences between these two systems.

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C42 - Non-covalent interaction of benzonitrile with single-walled carbon nanotubes

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In this work we studied the interaction of a Lewis base (benzonitrile) and SWNT (Carbolex, Inc.). As-received and purified carbon nanotubes (5 mg) were added to 5 mL and 50 mL of pure benzonitrile. The resulting suspensions and solids samples were characterized by TEM, SEM, EDS, Raman, ATR-FTIR, UV-Vis and photoluminescence. The suspensions obtained with as-received SWNT (hereafter SUS-AS-SWNT), in all cases, showed light orange/gray color and were stable over long periods of time. On the other hand, the suspensions obtained with purified SWNT were colorless. This observation suggests that benzonitrile can interact more strongly with amorphous carbon and carbon nanoparticles than with carbon nanotubes. TEM images of SUS-AS-SWNT indicated the presence only of amorphous carbon and carbon nanoparticles in the suspension. In addition, UV-Vis spectra of SUS-AS-SWNT showed an absorption band at 450 nm and the photoluminescence spectra showed a red-shift of 30 nm in the emission band if compared to pure benzonitrile. However, no significant shifts were observed in the radial mode, disorder induced D-band and the tangential mode G-band in Raman spectra of SWNT when these nanoparticles (as-received and purified) were submitted to interaction with benzonitrile. This result tells us that the benzonitrile-SWNT interaction is very weak. Then, probably, the benzonitrile did not interact with nanotubes through free electron pair of nitrile groups but through of a π-orbital interaction between the benzonitrile aromatic rings and C-ring of the SWNT. This interpretation is also in agreement with our results of the ATRFTIR spectra of the solid samples in which showed that nitrile band was only slight change (from 2228 cm^{-1} to 2226 cm^{-1}) after the interaction. In conclusion our results suggested that the interaction of benzonitrile with carbon nanotubes was weak probably involving a π-orbital interaction between the benzonitrile aromatic rings and C-ring of the SWNT. However, the benzonitrile interacts strongly with carbon nanoparticles and amorphous carbon suggesting that this step could be useful for purification methods.

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C43 - Titanate nanotubes: chemical composition, structure, properties and cytotoxicity

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From the structural point view carbon nanotubes could be originate from graphite layers (graphene). Considering this approach a lot of effort has been devoted to prepare nanotubes from other layered materials. The first studied inorganic nanotubes were WS_2, MoS_2, BN and NbS_2. The preparation of these nanotubes from layered materials leads to the thought that is possible to prepare nanotubes from all materials whose bulk counterpart is a layered compound. Nowadays, a considerable list of inorganic nanotubes is known and it is increasing at an amazing rate. Among the inorganic nanotubes, titanium oxide nanotubes are very attractive because these nanostructures are promising for applications as photocatalysts, UV absorbers, dye-sensitizing solar cells, self-cleaning devices, and catalyst supports. In this work we discuss the chemical composition, structure, properties and cytotoxicity of titanium oxide nanotubes obtained by hydrothermal treatment of TiO_2 and NaOH in different conditions of time and temperature. Based on ion exchange reactions and the thermal decomposition of titanium oxide nanotubes we propose a new composition for the as-prepared nanotubes as being $Na_2Ti_3O_7.nH_2O$ (titanate). Our results also suggest that nanotube walls have structure similar to those of the layer of the bulk $Na_2Ti_3O_7$. Depending on how the washing process is performed on the nanotubes (water or acid solutions) the Na^+ content can be modified via the exchange reaction of Na^+ by H^+. Thus, a general chemical formula was also proposed: $Na_{2-x}H_xTi_3O_7.nH_2O$ ($0 \leq x \leq 2$), x being dependent on the washing process. In addition, we evaluated the use of titanate nanotubes as catalyst in heterogeneous photocatalysis for degradation of textile dyes (reactive blue 19). The efficiency of color removal as function of time was measured by absorption spectroscopy. We observed that titanate nanotubes were more efficient than anatase TiO_2 in the color removal. Experiments to evaluate the cytotoxicity of the titanate nanotubes were carried out using cultured hamster V79 fibroblasts and the results were discussed. Two endpoints were measured in V79 cells: 3-(4,5-dimethylthiazole-2-yl)-2,5-biphenyl tetrazolium bromide (MTT) reduction and neutral red uptake (NRU). In conclusion, our results suggested that titanium oxide nanotubes obtained by hydrothermal treatment of TiO_2 and NaOH have structure similar to those observed in the layered bulk $Na_2Ti_3O_7$ titanate and composition equal to $Na_{2-x}H_xTi_3O_7.nH_2O$. If nanotubes are washing with acid solution, the Na^+ can be exchanged by H^+. The nanotubes can be used as a catalyst in heterogeneous photocatalysis and showed low cytotoxicity.

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C44 - Functionalization of carbon nanotubes for biological applications

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In this work, we propose two methods of CNT functionalization aiming biological applications. The first is a one-step, soft method for the dispersion of CNTs in water by using ammonium hydroxide (NH_4OH). The second one is a method for functionalization with lalanine, which is a first step to achieve the binding of peptides to CNTs. The starting material was purified (95%) single wall carbon nanotubes (SWNT), prepared by conventional arc discharge technique in our laboratory. The one-step procedure for the NH_4OH functionalization is very simple: the purified CNT powder is dispersed in a NH4OH solution in an ultra-sound bath for 2-3 minutes. After that, the solution is dried. The functionalized SWNT powder can be dissolved again in water, and form a solution that is stable for more than six months without significant material precipitation. The method for the functionalization with l-alanine is more complex. In short, it consists of a reflux in nitric acid solution, in order to attach carboxyl groups to the CNTs, followed by a reflux in dimethylformamide and l-alanine. The materials at different stages were characterized by several techniques including atomic force microscopy (AFM), Raman spectroscopy, infrared spectroscopy (IR), and thermogravimetric analysis. Finally, although for both cases the precise mechanisms of functional group attachment to the SWNT walls are not completely understood, it is clear that that presence of such groups at the nanotube walls inhibits their re-bundling and thus permits their relatively large dissolution in water.

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C45 - Iron Nanoparticles Casted inside Carbon Nanotube Channel : Microstructure and Magnetic Properties

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Carbon nanotubes have received an increasing scientific and industrial interest because of their unique physicochemical properties. It was expected that the tubular morphology and the high aspect ratio of these carbon nanotubes could induce peculiar properties of materials trapped inside their channel. In the wake of their discovery, several attempts have been focused on the introduction of foreign elements inside their empty tubule with a hope of generating new composite materials with unusual properties. Magnetic nanoparticles have potential applications in various areas such as magnetic recording, magnetic data storage devices, and magnetic resonance imaging, etc. However, until now the selective filling of the carbon nanotube channel with magnetic nanoparticles by a simple method still remains a challenge, especially on the control of the nanoparticle location with respect to the nanotube surface. The most interesting range of magnetic nanoparticle for the applications cited above is centered between 20 to 80 nm with a large emphasize on the range of 40 nm which could find a specific application as magnetic composite in magnetic resonance imaging system. The attractiveness of the Fe_3O_4 nanoparticles/CNT system in the enhancement of the magnetic resonance imaging system has been reported recently by Miyawaki et al. [1]. Carbon nanotubes loaded with magnetic particles could find also attractive applications as nanodevices for drug delivery in a precise locations in the body using an externally applied magnetic field for targeting and heating.

Here, we report the exclusive filling of carbon nanotubes channel by iron oxide and/or metal nanoparticles (10-40 nm) by modification of their surface properties. Commercial multi-walled carbon nanotubes from Applied Science Pyrograf were pretreated by acidic functionalization followed by a heat treatment at high temperature (800°C) under inert gas in order to remove the oxygenate functional groups. These pretreated nanotubes were then selectively infiltrated by different solutions of iron salts through an incipient wetness impregnation method. Such magnetic nanomaterials could find applications in the field of high density data storage or in the magnetic resonance imaging [2,3]. The relative simplicity of the filling method allows one to prepare magnetic filled commercial carbon nanotubes with low cost and an easily scale-up.

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C46 - Optical characterization of carbon nanotubes functionalized with diazonium groups

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Carbon nanotube samples functionalized with diazonium groups were studied by resonant Raman, photoluminescence and optical absorption spectroscopies. Samples with different degrees of functionalization were used in the experiments. The interaction of functional groups with the nanotube causes modifications in the electronic and phonon structure, whose understanding is important for the development of nanotube-based sensors. Suppression of the optical absorption and photoluminescence spectra as well as of the radial breathing mode spectra has been observed when the nanotubes are hardly functionalized. The effects of the functional groups on the electronic and phonon structures were addressed by a resonant Raman investigation using several different laser excitation energies. A dependence of the optical excitation energies on the nanotube functionalization is reported. A shift in the optical transition energies as well as a broadening in the resonance Raman profiles are observed for the functionalized samples, caused by the charge transfer between the nanotube and the functional group. Comparison between Raman and optical absorption results reveals a dependence of the functionalization with the nanotube diameter. An excitation energy dependence of the ratio between the dispersive D-band and G-band intensities, a metric commonly used to benchmark functionalization in these systems, is reported, allowing an estimation of the amount of functionalization by a comparison between the ratios measured at different wavelengths. The influence of the chemical modifications in some two-phonons Raman modes is also presented.

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C47 - Covalent functionalization of single walled carbon nanotubes with N- and S-containing groups

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Classical protocols used in Organic Chemistry has been successfully applied in this work for the derivatization of carboxylic groups to rend N-alkyl and S-alkyl SWNT derivatives.We started from the well known activation of the acid-terminated purified SWNT with thionyl chloride to generate acyl chloride groups, which further reacted to form amide and thioester. The derivatization was still extended to amine and thioether formation. The use of reactants with long alkyl chains lead to improved solubilization of the derivatives in organic solvents. FTIR, XPS and acid-base potentiometric titration analyses were carried out to characterize quali and quantitatively the changes in the chemical environment on the SWNT surface in each step of the functionalization route. The purity and structural quality of the SWNT samples were evaluated by TG, SEM and Raman spectroscopy. Besides anchoring nanoparticles, quantum dots, catalytic sites and biological entities, N- and S-containing groups SWNT derivatives could be also explored in chirality-based bulk separation of carbon nanoutbes.

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C48 - Direct synthesis of nitrogen-doped carbon nanotubes, Changes in morphology and characteristics

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Since decades carbon nanotubes have been studied for their unique properties in many fields, and this should grant them a key role in forthcoming industrial applications in various domains. For some fields, like catalysis or drug delivery, the functionnalisation of the carbon nanotube surface with chemical groups is needed. Recently, Ismagilov et al. [1] have demonstrated that adding nitrogen during the MWNT synthesis allow to replace some carbon atoms by nitrogen ones. The presence of these nitrogen atoms leads to a better dispersion of the metal particles deposited by an incipient wetness impregnation through novel metal/support interactions. The improvement of the metal dispersion can be explained by the presence of a free electron pair from the nitrogen atoms that enhance the affinity between the metal and the support. In the same time, Terrones et al. [2] have shown that Ndoped CNTs are far much more tolerated by mice than usual CNTs which pointed out the benefit effect of nitrogen doping. Here, we report the direct CVD synthesis of N-doped carbon nanotubes by decomposition of C_2H_6 on a catalyst in presence of NH_3 gas. The yield, morphology and composition of the as-synthesized carbon nanotubes were extensively investigated.

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C49 - Effects of Oxidation by Hydrogen Peroxide and Nitric Acid on the Structures of Multiwalled Carbon Nanotubes

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The oxidation process has had a great importance for carbon nanotubes applications, since it is necessary for their purification and functionalization. However, in functionalization process the oxidation causes chemical and structural changes on carbon nanotubes, which modify their properties. For this reason is important to know the relationship between different kinds of oxidation and the alterations caused on carbon nanotubes in order to can choose the oxidation method more appropriated for each application. Thus, in this work was carried out a study about the effects of two oxidation methods on morphologies and chemical structure of multiwalled carbon nanotubes (MWCNT). The first oxidation method occurred by reaction of MWCNT with hydrogen peroxide (H_2O_2) 33 wt%, in periods of 1, 2, 3, 4 and 5 days. The second method used nitric acid (HNO_3) 3 $molL^{-1}$ and the reaction was maintained under reflux for 12 hours. The effects of oxidation methods on MWCNT morphology and thermal stability were evaluated by Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM), and by thermogravimetric analysis (TGA), respectively. The functional groups formed in surface of carbon nanotubes were identified by Fourier transform infrared spectroscopy (FTIR). The results showed a reduction in the diameter and length of the carbon nanotubes in both methods, however, this reduction was more intense for HNO_3 oxidation. Although the both oxidation methods result in the formation of several functional groups on MWCNT surfaces, such as carboxylic (-COOH), carbonyl (-C=O), and hydroxy (-OH) groups, it was observed that hydroxyl groups were preferentially formed during the oxidation with hydrogen peroxide.

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C50 - Theoretical studies of alanine functionalized carbon nanotubes

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Carbon nanotubes (CNTs) are materials of high functional versatility, among their diverse functions, the biological and medical ones are quite interesting. In this sense, carbon nanotubes can be used as biosensors, drug deliver agents, scaffold for cellular growth, etc. However, for the development of such technologies, the CNTs must be functionalized, leading to hybrids materials. In this work we present the results of theoretical investigation, by Density Functional Theory, of the single wall carbon nanotubes (SWNTs) funcionalization by alanine molecules.

Alanine ($C_9H_{11}NO_3$) is an amino acid produced in vivo and is a component of proteins presents in alive organisms. Alanine is also produced artificially, for industrial use or scientific research, being synthetized from propanoic acid, Gabriel synthesis or Strecker synthesis. This work consists in the investigation of several possible alanine attachments to the CNTs, considering both chemical and physical adsorption, directly on CNTs external surface or indirectly, through carboxylic acid, in both cases, different functionalization sites are tested. At last, the new hybrid material electronic properties are studied.

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C51 - Theoretical study of polyynes encapsulated in carbon nanotubes

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Carbon nanotubes can encapsulate molecular species into their one-dimensional cavity, such as fullerenes, water molecules, organic compounds, etc. The existence of a new hybrid material, $C_{10}H_2$@SWNTs (single walls carbon nanotubes encapsulating $C_{10}H_2$ molecules, namely pollynes) was already reported (1). Polyynes ($C_{2n}H_2$, n 2) are linear carbon-rich molecules. They constitute a linear array of even sp-carbon atoms with alternating single and triple bonds and two capping hydrogen atoms at both ends. In this work we present an ab initio Density Functional Theory study concerning $C_{2n}H_2$@SWNTs (with n from 6 to 10). At first, the electronic, structural and vibrational properties of isolated polyynes and metallic and semiconductor nanotubes were calculated. Then, the same properties were calculated for polyynes encapsulated inside the nanotubes. Several physical quantities as such, geometry variations, electronic charge transfers, formation energies, electronic band structures and vibrational spectra are then obtained. Our results lead to interesting insights concerning the present subject and in particular the vibrational spectra we have calculated can be helpful for a better understanding of Raman spectroscopy data.

1- D. Nishide et al, Chem. Phys. Lett. 428 (2006) 356.

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C52 - Silanol radicals interacting with carbon nanotubes

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Carbon nanotubes (CNT) dispersed into a matrix is a very promising system for high performance composites, whose properties are dependent on the linkage between carbon nanotubes and the matrix. It has been demonstrated that variations in the silane precursors and in the CNT content leads to composites materials with a range of capacitance, electron-transfer rates, and potential to control the selectivity of some molecules. In this work, we report an ab initio study based on density functional calculations of several silanols radicals interacting with single-wall carbon nanotubes. We found that the adsorption of the silanol radical in geminal form behaves similar to the adsorption of COOH and OH groups, where the modifications of the band structures of the SWNTs are caused by sp^3 hybridization of the C atom that makes a bond with the silanol radical. This sp^3 hybridization results in impurity levels across the Fermi energy that can be used/manipulated to control the electronic properties of CNTs, what is interesting for possible applications as electronic devices.

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C53 - ZnO Nanoparticles on Single-walled Carbon Nanotubes

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ZnO nanoparticles were grown on single-walled carbon nanotubes (SWNTs) by atomic layer deposition using diethylzinc (DEZ) and water. We discuss that, because of chemical inertness of nanotubes to DEZ and water molecules, such nanoparticles are not likely to grow on the wall of clean and perfect nanotubes. Rather, the growth of ZnO nanoparticles should be attributed to imperfection of nanotubes, such as defects and carbonaceous impurities. Lifetime of field emission from SWNTs with the ZnO nanoparticles is 2.5 times longer than that from the as-grown nanotubes. It is thought that the protection of the defects or impurities by ZnO nanoparticles mainly contributed to the improvement of the field emission lifetime from SWNTs.

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C54 - Variable charge density in doped single wall carbon nanotubes

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Control over the electronic band structure, e.g., ability to tune the Fermi level, is very important for various potential applications of SWNTs. The SWNT band structure can be modified by doping with various molecular and atomic species such as halogens, alkali metals, metal halides, oxides, etc. In this work, we demonstrate experimentally that distribution of dopant-transferred charge among doped nanotubes may be significantly uneven and offer a procedure to separate doped SWNTs into fractions with homogeneous charge density. Implications of variable charge density for band structure and electronic properties of doped SWNTs are discussed.

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C55 - QM and MM simulations of the growth process and the material properties of inorganic nanotubes and nanotube composites

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Nanotubes and similar nanostructures composed of materials other than carbon represent an interesting field of research with many opportunities yet to come. We present our recent research results on the application of our numerical methods to simulate and proliferate understanding of the growth processes of inorganic nanotubes, of the synthesis of nanotube/matrix composites and of the characteristic material properties.

Here, we focus on on the mechanical properties of BN nanotube/Si-B-N ceramics composites, on the synthesis of BN nanotube/Si-O composites and on the template growth of amorphous silicon oxide nanotubes.

To treat reaction mechanisms realistically and avoid finite size effects and to reach thermodynamical limits, we apply our developed quantum mechanical parallel software package ESPACK and our molecular mechanical parallel software packages TREMOLO.

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C56 - Stability and electronic properties of vacancies and antisites in BC_2N nanotubes

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The equilibrium geometry, energetic and eletronic properties of antisites and vacancies in BC_2N nanotubes are studied by spin density functional calculations using generalized gradient approximation (GGA) to the exchangecorrelation functional. We investigate these defects in both the zigzag (4,0) and the armchair (3,3) nanotubes, which have 6.54 and 8.34 Å in diameter, respectivelly. We find that boron and nitrogen occupying nonequivalent carbon sites (*BCII* and *NCI*) in both tubes have lowest formation energies, showing that they are energetically favorable to form under B-rich and N-rich growth conditions. They also exhibit acceptor and donor properties, suggesting the formation of defect-induced *p*-type and *n*-type BC_2N nanotubes. In addition, carbon at boron and nitrogen sites (*CB* and *CN*) also exhibit *p*-type and *n*-type properties, respectively, as well as low formation energies. However, *BCI* , *NCII* , *BN* and *NB* have higher formation energies, rising deep levels in the band gap. Vacancies are less favorable defects with high formation energies as compared to the most stable antisites. Once a vacancy is formed, a strong reconstruction occurs, resulting in an undercoordinated atom which typically gives rise to deep levels in the band gap, changing the eletronic properties of the nanotube. Our results suggest that with suitable growth conditions, it would be possible to synthesize BC_2N nanotubes with intrinsic donor and acceptor character by inducing selective antisites defects.

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C57 - Comparative Structural Study of Titanium Oxide Nanotubes Obtained by Chemical Treatments

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Titanium oxide is a well known multifunctional material for its attractive physical, chemical, and optical properties. In the past few years, there have been several reports on the formation of titanium oxide nanotubes (TiO_2-NT) using different methods. One of them, the hydrothermal treatment (HT) shows the formation of trititanate oxide nanotubes; however our measurements using HR-TEM, and high resolution XRD performed in the Brazilian Light Synchrotron Laboratories corroborate that, and showed the presence of few quantity of TiO_2 amorphous phase as well. The electron microscope image of the products after the HT shows a tubular structure with a presence among 3-5 layers in the multi-wall tube, with an interlayer distance in the range of 0.88-0.68 nm, and diameter of approximately 8 nm.

The reflux method (RM) was a second method chosen by our group to obtain titanium oxide nanotubes, which show the presence of lepidocrocite titanium phase mainly. Indeed the nanotubes method showed an interlamellar distance of 0.78 nm, and the presence of 1-3 layers rolled up. Raman spectra of the RM method showed a presence of vibrational modes associate to the E_g, and B_{1g} of the anatase, however the Raman spectra of the HT show different kind of signal.

The first attempts of titanium oxide-carbon nanotubes heterostructure were measured by Raman, where a presence of vibrational modes of the trititanate oxide was detected. So this work presents a detailed description, and discussion of the different phases present in both methods using XRD, and HR-TEM, and Raman techniques.

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C58 - Comparative Study of Nanorods, Nanotubes, and NanoUrchin of Vanadium Oxide

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The first report on inorganic nanotubes in 1992 [1] has been largely unnoticed due to the overwhelming volume of research into carbonaceous nanostructures during last decade. Metal oxide nanostructures are now receiving a revived interest for their potential application in battery technologies, intercalation chemistry, and for their ability to be readily functionalized both structurally, and photonically. Since the initial report of vanadium oxide nanotubes [2] using a self-assembly approach followed by hydrothermal treatment, a plethora of inorganic oxide nanostructures with varied properties have been discovered. The valence of the vanadium in the nanotubes, however, is not uniquely (5+); valences of (4+) with a percentage V^{5+}/V^{4+}ratio of 55%/45% have been observed, and recent studies evidence vanadium oxide nanotubes with trivalent vanadium (3+) specie [3]. This improves the versatility of this material for structural applications. Thus, the use of various surfactants together with defined hydrothermal treatment conditions can produce variations in the V^{5+}/V^{4+}ratio. As a result, the formation of inorganic vanadate nanostructures with markedly different structures can be achieved [4-6]. This work presents a structural description, relation, and discussion of various nanostructures like tubes, rods, and urchin, and their relation to the V^{5+}/V^{4+}ratio.

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C59 - Synthesis of TiO_2 Nanotubes and applications

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Nanotubular materials have been intensively studied since the discovery of carbon nanotubes. Noncarbon nanotubes, in special titanium dioxide (TiO_2) nanotubes, gained special interest for their relatively easy synthesis and their several applications in photocatalysis, hydrogen sensing, storage and separation, and biological applications.

In the present work, we report the synthesis of a TiO_2 nanotube film grown by anodic oxidation of a pure Ti sheet (99,99% pure) in electrolytes of aqueous HF (0.5%wt) and NH4F (0.5%wt in glycerol) at room temperature. The optimum voltage was found to be 20 V. The sheet was exposed for 20 minutes in the HF electrolyte and for 13 hours in the NH_4F electrolyte. A graphite electrode was used as the inert cathode.

By Scanning Electron Microscopy (SEM) we can confirm that the nanotubes are well aligned in the direction of the electric field between the electrodes in a dense and self-assembled matrix. One end of the tubes was always open while the other end, which is in contact with the titanium sheet, was always closed. After anodization in the HF electrolyte, the nanotubes present medium inner diameter of 80 nm and are about 500 nm long whereas with NH_4F electrolyte, the nanotubes were found to have medium inner diameter of 35 nm and are in average 2 μm long.

The two electrolytes have different growth dynamics. For the HF electrolyte, the nanotubes appear to grow close together, sharing their walls, and in the NH_4F electrolyte we can observe isolated tubes. The fact that the topology of the tubes depends on the electrolyte is interesting, since we can study different properties of TiO_2 nanotubes, such as gas sensing with HF-prepared tubes and the conductivity of a single tube with the material prepared with NH_4F.

We present a preliminary study of the application of the film synthesized with the HF electrolyte in a hydrogen sensor at atmospheric pressure. The film was annealed at 500°C for 6 hours in O_2 rich atmosphere and Pd contact pads were evaporated to be used as the electrodes. The sensibility appears to be dependent on the temperature and several temperature-dependent measurements were made and will be presented.

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C60 - Alanine adsorption on carbon nanotubes: vibrational spectroscopy and molecular dynamics

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The modification of the surface of carbon nanotubes (CNTs) is a key aspect prior to their use in any biologyrelatedapplication can be envisaged. CNTs functionalization may be achieved through different processes as adsorption, electrostatic interaction, covalent and non-covalent bonding of different molecules. Chemical treatments may render them more hydrophilic, improving their water solubility and transforming completely their biocompatibility profile. Efficient solubility of CNTs has been demonstrated by using covalent and non-covalent adsorption of surfactants, polymers, and biomolecules. In this work, we demonstrate l-alanine adsorption on single wall carbon nanotubes (SWNTs) through non-covalent bonding, which confers high water solubility opening new possibilities for biological applications. A vibrational spectroscopic study of the l-alanine functionalized nanotubes was performed using the Ar-ion laser green line (514.5 nm) as excitation. The spectra of pristine and l-alanine functionalized tubes are seen to differ particularly in the D-band region: a single band is observed for the pristine tube against two bands in the case of the l-alanine-adsorbed tube. As this is the typical region for disorder of the carbon network, the additional band may be interpreted as disorder effects due to the presence of the amino acid. The results are compared with Fourier transform infrared spectroscopy data. Molecular dynamics simulations were performed, and the results suggest a non-covalent interaction between the l-alanine and the SWNT.

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C61 - Large area growth of aligned sub-30 nm individual ZnO nanowires

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Single-ion nanolithography is presented as a novel and faster alternative to e-beam and FIB lithographs for patterning large areas with catalytic metal islands to grow semiconductor nanowires. An array of vertically aligned ZnO nanowires of 25 nm diameters was grown selectively using single-ion nanolithography and physical vapor deposition. The Zn nanowires are grown in a tube furnace by evaporation of a ZnO:graphite mixture onto sapphire substrates patterned with Au catalyst. The substrate patterning was performed using random ion beam irradiation with Au ions at 20 MeV with a fluence range from 10^9 to 10^{10} cm^{-1}. A thin PMMA film of 50 nm was spin coated on the sapphire substrates and then subjected to the ion irradiation. Each ion interacts individually with the PMMA film forming a cylindrical path of latent chemical damage, which is then developed using MBIK:IPA solution. The density of wires is controlled independently of the wire diameter by the irradiation fluence and the lithography exposure is performed over cm2 areas in a single step of ~2 s. The ZnO arrays are single crystals as verified by x-ray diffraction and high resolution transmission electron microscopy.

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C62 - Controlled synthesis of quasi-one dimensional boron nitride nanostructures

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A floating catalyst chemical vapor deposition (FCCVD) method is developed for the synthesis of quasi-one dimensional (1-D) boron nitride (BN) nanostructures. By carefully tuning the experimental parameters such as growth temperature, floating catalyst concentration, and boron precursor, high quality 1-D BN nanostructures including nanotubes, nanobamboos, and nanowires were produced selectively. The microstructures of the obtained 1-D BN nanomaterials were characterized; and it was found that the nanostructures are composed of hexagonal BN phase with (002) planes stacking in different manners. A growth mechanism of the BN nanostructures was proposed based on the analysis of their structural characteristics and growth conditions.

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C63 - Carbon nanotubes as sacrificial templates for rutile nanotubes

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Titanium dioxide (TiO_2) is among the most important oxide based materials with applications in photochemical, catalytic and electrochemical technologies. Of the two important phases of TiO_2, anatase is kinetically favoured over rutile, which is thermodynamically stable. There is strong evidence that rutile would be favoured over other types of titania in terms: e.g. of selectivity and improved kinetics in photochemical reactions [1]. There have been some attempts to produce anatase and tri-titanate nanotubes [2-3]; hitherto there are no reports on the successful synthesis of titania nanotubes with rutile phase. Here we report the first pure rutile nanotubes produced by a modified sol-gel route using sacrificial carbon nanotubes as templates, with subsequent heat treatment to convert the templated anatase to rutile [4]. The applied characterisation tools include SEM, (HR)TEM, XRD, FTIR/Raman spectroscopy and thermal analysis (TGA/DSC).

We used tetrabutyloxytitanate (TBOT) as titanium precursor, ethanol/benzylalcohol as solvents and water as gelator. The carbon nanotubes were prepared by chemical vapour deposition (CVD) using ferrocene as catalyst precursor and toluene as feedstock. After coating with amorphous titania and crystallisation at 400 °C the carbonaceous template was thermally removed to leave pure anatase nanotubes (diameters between 70 and 350 nm, dcrys ~18 nm). Alternatively, the anatase coating was heated in nitrogen at elevated temperatures to induce phase transformation to rutile with subsequent removal of the template to produce pure rutile nanotubes (diameters between 50 and 400 nm, dcrys~20 nm).

A key aspect of this method is that the carbon nanotubes support the structure during the reconstructive phase transformation, preventing break up due to the transformation stresses involved as well as crystal growth, thus leading to high surface area rutile materials. A further advantage of this method is that the templates can be used to control the internal diameter of the rutile nanotubes, while synthesis conditions control the wall thickness. The initial thickness of the titania coating furthermore determines the final morphology of the rutile tubes. Thick coatings lead to rough tubes (dcrys~50 nm, SS~10 m^2/g), while thin coatings result in smooth tubes (dcrys~10 nm, SS~80 m^2/g).

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CONTRIBUTED ABSTRACTS

POSTER SESSION D

JUNE 26 (Tuesday)

D01 - Synthesis and Thermophysical Properties of Vertically Aligned SWNT-PMMA

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SWNT-composites have not been fully exploited and may offer exciting opportunities for new composites because of unique properties of SWNTs. We present the simple experimental method of synthesizing uniformlydistributed and vertically-aligned SWNTs (VA-SWNTs) -polymethyl methacrylate (PMMA) composite. This simple synthesis may be applied with other polymers. VA-SWNTs were grown on quartz substrates using the alcohol catalytic CVD process. VA-SWNT-PMMA film was synthesized by polymerizing PMMA-sonicated toluene in which aligned SWNTs were immersed. Conventional SWNT-PMMA films were processed using polymerizing monomer MMA in which SWNTs were infiltrated.

The weight fraction of SWNT-composites was estimated to be 0.5%. The kinetics of oxidative thermal degradation of PMMA from composites were delayed by SWNTs. The thermal degradation of composites having different degrees of nanotube dispersion was also compared. PMMA and poorly aligned SWNT-PMMA showed the lower thermal stability than PMMA from VA-SWNT-PMMA because well dispersed SWNTs into PMMA have larger surface areas. Thermal conductivities of PMMA and VA-SWNT-PMMA samples coated with Au were measured by photothermal radiometry. The estimated thermal conductivity of the pure PMMA sample fitted well with simulation results. However, the photothermal behavior of the SWNT-PMMA sample is quite unique suggesting that the anisotropy of thermal conductivity due to aligned SWNTs in PMMA.

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D02 - Computational Study of the Percolation Threshold in a Polymer-Nanotube Composite with a long range interaction

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Nanocomposites produced by doping of conjugated polymers with carbon nanotubes (CNTs) can have many applications in electronic devices. They can be applied, for instance, as electromagnetic shielding/absorbing or as electrostatic dissipative layer to prevent interference with and from other devices. The introduction of cabon nanotubes in the polymer increases the electrical conductivity of the resulting composite but also increases signi- ficanly its weight, reducing the surface quality and manufacturability of the material. To avoid those problems it is important to use carbon nanotubes with very high length-to-diameter aspect ratio which decreases the critical concentration of CNTs required to a significant increase of the conductivity (percolation threshold). In this work we study the percolation threshold in conjugated polymer/CNTs composites assumig the presence of a dipole-like interaction between the CNTs imersed in the polymeric matrix. Such interactions were observed in composites of polymers and fullerene. Modelling the carbon nanotubes as one dimension sticks, the energy of interaction between two CNTs was calculated analytically. We then perform numerical simulations using a two dimensional system of many sticks with the orientation distributed according to the cumulative distribution function derived from the interaction energy. For weak potentials the alignment degree of the CNTs tends to be random but we found that a preferential orientation of the CNTs is obtained as the interaction between the sticks becomes stronger. This effect enhances the system anisotropy which increases the percolation threshold compared to a system where the sticks orientation is random.

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D03 - Application of carbon nanotube-metallic nanoparticle composites for fuel cells

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The operation and main components of fuel cells are considered from point of view of the carbon nanostructured materials application. One of the main properties of the carbon nanomaterials, which attracts the developers of fuel cells, is their high effective surface. At the same time, these materials are characterized by the high mechanical strength, electrical conductivity and chemical resistance that is the necessary condition in order to be used in fuel cells. One of the possible applications of carbon nanotubes in fuel cells is the use as the support for catalytic nanoparticles for the electrodes of fuel cells. In this report the approach is presented in accordance with which the carbon nanotubes are grown directly on pressed pellets of the nickel powder. Such pellets simultaneously serve as the gas diffusion layer and current collector. Carbon nanotubes were grown at temperature of 420-4500 C in helium atmosphere by chemical vapor deposition (CVD) method. The commercially available granular polyethylene was employed as the precursor. As the substrate the above mentioned pellets were used. The morphology and content of the carbon nanotubes received were investigated by transmission electron microscopy (TEM) and x-ray diffraction . It was found that nanoparticles of nickel are formed on the tips of carbon nanotubes in the process of growth with dimensions that match the diameter of nanotubes. As the result the composites containing of carbon nanotubes and nanoparticles of nickel (CNT/Ni) are formed. Electrocatalytic properties of composites obtained were investigated by linear sweep voltammetry in aqueous and alcohol solutions of alkaline, and in aqueous solution of sulfuric acid respectively: 0.1 M KOH, 0.1 M KOH + 0.01 M C_2H_5OH, 0.1 M KOH + 0.02 M C_2H_5OH, 0.1 M H_2SO_4. The application of carbon-nickel nanocomposites for the technology of fuel cells is discussed.

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D04 - Electrical percolation in Polymer - Nanotube/Nanodisks composites: The effect of the geometry of the filler particles and the solvent choice.

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Solution processed composites, based on polyvinylalcohol have been fabricated with either multiwall-nanotubes or carbon-nanodisks as fillers, for a range of volume-fractions using three solvents; water, NMP and DMSO. Electrical tests were made for each composite, demonstrating that the electrical properties depend not only on the geometry of the fillers but also on the solvent used. A low percolation-threshold of 10^{-3} was observed for the DMSO and NMP-based composites while a maximum conductivity of ~1S/m was attained for the NMP-based composites. The water based composites displayed percolation thresholds of 0.4vol% for nanotubes compared to 2.1vol% for the nanodisks. For these composites the nanotube threshold is broadly in line with theory, the disk value is not as low as expected. The effects seen in the polymer-nanotube composites are attributed to the formation of solvent dependent polymer coatings around the fillers, which act as tunnelling-barriers thus limiting the conductivity.

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D05 - Effect of single-walled carbon nanotube purity on the thermal conductivity of carbon nanotube-based composites

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Raw (AP) and purified single-walled carbon nanotubes (SWNTs) were utilized for the preparation of SWNTepoxy composites.[1] Purified functionalized SWNTs provide a significantly greater enhancement of the thermal conductivity, whereas AP-SWNTs allow the best electrical properties because of their ability to form efficient percolating network. A series of SWNT samples of varying purity but identical chemical functionality were prepared to delineate the effect of SWNT purity on the thermal conductivity of SWNT-epoxy composites. We found that purified SWNTs provide ~5 times greater enhancement of the thermal conductivity than the impure SWNT fraction demonstrating the significance of SWNTs quality for thermal management.

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D06 - Physisorption of DNA and RNA Nucleobases on Carbon Nanotubes in the Low- and High-Curvature Limit: A First-Principles Quantum Mechanical Study

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We report the results of our first-principles investigation on the interaction of the nucleobases adenine (A), cytosine (C), guanine (G), thymine (T), and uracil (U) with both graphene and with a (5,0) zigzag carbon nanotube (CNT). Graphene is used in our study as a model system for the low-curvature limit of CNTs with very large diameter, while the (5,0) tube with a diameter of merely 0.392 nm is representing the high-curvature limit. In the present study, we employed density functional theory (DFT) within the local density approximation (LDA) and for comparison also Hartree-Fock plus second-order Moller-Plesset perturbation theory (HF+MP2). We find that LDA is suitable to determine the equilibrium geometry in this van der Waals bound system. However, compared to HF+MP2, the binding energy may be underestimated by 40-60%. Our results show that the nucleobases can exhibit significantly different interaction strengths when physisorbed either on graphene or on the surface of a (5,0) CNT. The calculated binding energies of the nucleobases follow the hierarchy: G > A > T > C > U. The stabilizing factor in the interaction is clearly dominated by the molecular polarizability of the nucleobases which gives rise to a weakly attractive dispersion force. Regarding the equilibrium geometry, we find that the high curvature of the (5,0) CNT allows the base molecules to bind at a smaller vertical distance from the surface than it is the case for graphene. The present study is part of a larger project which aims towards a first-principles understanding of how the base sequence of DNA affects its interaction with CNTs, as observed experimentally.

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D07 - Surface composition of carbon nanotubes-Fe-alumina nanocomposite powders: an integral low-energy electron Mössbauer spectroscopy (ILEEMS) study

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The surface state of CNTs-Fe/Fe_3C-Al_2O_3 nanocomposite powders was studied by transmission Mössbauer spectroscopy (TMS) and by integral low-energy electron Mössbauer spectroscopy (ILEEMS). Several samples, prepared by reduction of the α-$Al_{1.8}Fe_{0.2}O_3$ precursor in a H_2/CH_4 atmosphere applying the same heating and cooling rate and changing only the maximum temperature (800 - 1070 °C), were investigated. The TMS spectra are superpositions of four components: (i) an outer sextet with hyperfine parameters characteristic of ferromagnetic α-Fe, (ii) an inner sextet that could be attributed to ferromagnetic Fe_3C, (iii) an Fe^{3+} doublet due to iron species present in the α-alumina structure, and (iv) a singlet that corresponds to a non-magnetic iron phase that may be alloyed with carbon (γ-Fe-C). On the other hand, the ILEEMS spectra of samples reduced at 800, 850 and 910 °C do not show any contribution of α-Fe and Fe_3C components. Only the presence of the Fe^{3+} doublet and the (γ-Fe-C) central line is observed in these spectra. The contribution of the γ-Fe-C is the same for transmission and emission spectra. The absence of α-Fe and Fe_3C components in the emission spectra is fully accounted for by an increased spectral area (i.e., contribution to the total spectrum) of the Fe^{3+} component. The ILEEMS spectra of samples reduced at 990 and 1070 °C show all four iron phases with slight changes in the relative areas as compared to the transmission spectra. The nature of the iron species (Fe^{3+}, Fe_3C, α-Fe, γ-Fe-C) is correlated to their location in the composite material. At low reduction temperatures (800, 850 and 910 °C), Fe^{3+} ions located on the inner grains are reduced giving rise to cementite and α-Fe particles, which consequently are located on the inner grain boundaries within the matrix, thus explaining why Fe_3C and α-Fe do not shown up in the ILEEMS spectra. On the other hand, at higher temperatures (990 and 1070 °C) surface and bulk of the nanocomposite powders have similar compositions as far as the various Fe phases is concerned. It is further found that for all applied final temperatures the γ-Fe-C particles are present on the surface of the matrix grains in the same proportion as in the bulk.

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D08 - Enhanced thermal conductivity of carbon fiber/phenolic resin composites by the introduction of carbon nanotubes

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The development of light-weight and non-metallic composites, exhibiting high thermal conductivity and a low coefficient of thermal expansion, have been critically needed for achieving an effective heat conduction that could be used in numerous industrial processes. We report a significant enhancement in the thermal conductivity of a conventional carbon fiber/phenolic resin composite system by introducing highly crystalline multi-walled carbon nanotubes [1]. We demonstrate that 7 wt% of carbon nanotubes dispersed homogeneously in a phenolic resin acted as an effective thermal bridge between adjacent carbon fibers and resulted in an enhancement of the thermal conductivity (e.g. from 250 to 393 W/m-K). These results indicate that highly crystalline carbon nanotubes can be used as a multifunctional filler to enhance simultaneously the mechanical and thermal properties of the carbon fiber/phenolic resin composites.

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D09 - Characteristics of Plasma Modified Multi-Walled Carbon Nanotubes Derivatives and Their Composites with Polyolefins

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Covalent sidewall functionalization of multi-walled carbon nanotubes (MWNTs) has been accomplished by reaction of fluorinated MWNTs (F-MWNTs) obtained by CF_4 plasma treatment with aliphatic amines. X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FTIR) spectroscopy results provide evidence of functional groups attached to the surfaces of MWNTs. Subsequently, the modified MWNTs were mixed with polyolefins by melt blend at different concentration of modified MWNTs. The composites show significant increase in electrical conductivity in comparison with pristine MWNTs/ polyolefins composites. The characteristics and properties of the composites will be presented.

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D10 - Decoration of carbon nanotubes with gold nanoparticles and polythiophene

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Since their discovery, carbon nanotubes (CNTs) have attracted extensive attention owing to their exciting potential applications in sensors, molecular devices, nanocomposites or advanced materials with new electronic and optical properties. Many efforts have been made on the surface modification of CNTs mainly to enhance their solubility and processability. In particular, the deposition of metal nanoparticles (NPs) on the CNTs surface yields novel and fascinating materials with tunable electrical, magnetic and optical properties arising from the nanoscale coupling. Methods developed to decorate nanotubes with NPs typically involve harsh oxidative pretreatment and/or modification with surfactants, making them less useful for potential applications. This work reports the preparation and characterization of a novel material formed by gold nanoparticles homogeneously deposited on the surface of multi-walled carbon nanotubes and recovered by a thin layer of polythiophene. The material was prepared with no previous CNTs surface functionalization, based on an in situ thiophene polymerization and gold nanoparticles synthesis in a CNT containing media. Characterization of the resulted materials was carried out by XRD, Raman Spectroscopy and TEM. XRD data shows peaks related with fcc metallic gold. Raman spectra of the material show the characteristic polythiophene bands. The TEM images show NTCs with the external surface covered with a thin polymer layer and homogeneously dispersed gold NPs, with diameter varying from 3 to 10 nm.

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D11 - Fiber composites reinforced by aligned carbon nanotubes

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While CNT-polymer composites are widely used as conductive plastics, mixing and dispersion-based techniques typically prevent incorporation of CNTs at concentrations beyond a few wt% and make it difficult to align CNTs within matrix materials. These hindrances have prevented CNT-based composites from achieving signifi- cant enhancements in mechanical properties, which are vital for structural applications. We present a platform for large-scale integration of aligned CNTs into existing advanced aligned and woven fiber composites, where locally high weight fractions of aligned CNTs significantly enhance mechanical and multifunctional characteristics, by reinforcing matrix-dominated interfaces between adjacent fibers and fiber layers (plies).

Rapid wetting of long aligned carbon nanotube (CNT) forests [1] with off-the-shelf (no solvent added) commercial thermoset polymers is demonstrated experimentally and a technique for creating vertically aligned CNT composite microstructures of various shapes is presented [1]. Direct characterization of the mechanical properties of the nanocomposites structures reveals a 220% increase of the Young´s modulus at 2% volume loading [3], supporting the feasibility of using these CNT forests in large-scale hybrid advanced composite architectures reinforced with aligned CNTs. A hybrid composite architecture consisting of aligned carbon nanotubes (CNTs), woven ceramic fiber cloth, and a thermoset epoxy, is described, fabricated, and tested [4]. Fabrication begins with growth of aligned CNTs on the surface of fibers in a ceramic fiber cloth using a thermal chemical vapor deposition process and a liquid-based catalyst, and nano-engineered laminates are constructed using conventional hand layup techniques. The strength of the interlaminar reinforcement is investigated experimentally, and initial results give 70% higher shear strength, 160% higher interlaminar toughness, and 107 increase in electrical conductivity compared to an unreinforced laminate. Ongoing work focuses on extending this model architecture to carbon fiber based advanced composites.

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D12 - Exploring potential applications of conductive Titania/Multi-walled carbon nanotube nanocomposites

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Multi-walled carbon nanotubes from Nanocyl S.A. have been added to a Titania-based sol in different concentrations and a stable dispersion was achieved by using a microfluidizer processor. Films from this sol were produced by spin-coating onto borofloat substrate. Different parameters as the photocurrent, contact angle, electrical and optical properties have been measured. When subbmited to CO_2 laser beam, the electrical properties of the coating have been changed. Based on the results obtained, we discuss the possible applications of the nanocomposites.

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D13 - Preparation of Homogeneously Dispersed Multi-walled Carbon Nanotube/Sulfonated Polyaniline Composites and Their Electrical Properties

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Sulfonated polyaniline (SPAN), ramification of polyaniline (PANI), is a water-soluble conducting polymer and has potential applications in electronic devices. However, its conductivity is much lower than that of PANI in many cases. In this paper, multi-walled carbon nanotubes (MWNTs) were used to improve the conductivity of SPAN. Firstly, MWNTs were wrapped with SPAN by in situ polymerization of aniline followed by sulfonation with chlorosulfonic acid in an inert solvent and by hydrolysis in water. Subsequently, well-dispersed MWNT/SPAN composite film was prepared by mixing SPAN-wrapped MWNTs with pristine SPAN in water solution and then evaporating the water. The structure and electrical properties of the MWNT/SPAN composite film were investigated in detail. It was found that the composite fabricated via this route exhibits low electrical conductivity due to the uniform dispersion of MWNTs in the composites. □-□ interaction between the MWNTs and SPAN were found to play an important role in the better interfacial bonding between them and homogeneous dispersion of MWNTs within the SPAN.

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D14 - Preparation and Properties of Carbon Nanotube-Reinforced Hydroxyapatite Composites

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Hydroxyapatite (HA) has been used for more than 25 years in surgery to replace bone. While HA promotes bone growth along its surface, its mechanical properties are insufficient for major load-bearing medical devices [1]. Carbon nanotubes (CNTs), due to their high strength and stiffness combined with their nanoscale topology [2], have the potential to reinforce HA without significantly reducing its bioactivity [3]. We have therefore studied the production, microstructure and mechanical properties of HA-CNT composites for major load-bearing orthopaedic devices. We have focused on methods to achieve a good dispersion of nanotubes in the HA matrix, choosing sintering parameters and an atmosphere that will yield a high-density material with minimal burnout of the CNTs, and correlating the process conditions to the resultant microstructure and properties. HA was synthesised by a wet chemical method using $Ca(OH)_2$ and H_3PO_4. Multiwalled CNTs were grown by chemical vapour deposition, with some of the nanotubes then being surface treated by chemical oxidation to improve their dispersion and interaction with the HA matrix. The composites were made by either mechanically mixing the two materials or by *in-situ* formation of HA in the presence of CNTs. The resulting HA-CNT powders were pressed and sintered at temperatures up to 1200^oC. The raw materials, composite microstructure, and HA-CNT interface were investigated using SEM, TEM, XRD, FTIR, TGA, and BET surface area. Additionally, the mechanical properties of the composites have been evaluated by diametral compression tests. The effects of nanotube type (pristine vs. oxidised), loading, and sintering parameters have been investigated. It was found that oxidising the CNTs greatly improved their dispersion, and thus the overall homogeneity of the composite. TGA studies showed wet Ar to be the best sintering atmosphere to retain both the CNTs and the hydroxyl groups of the HA. However, density and BET measurements showed CNTs hold the structure of the composite open during pressureless sintering, preventing full densification of the material. Some improvement was found in the mechanical properties of the composites when compared to pure HA. A detailed study of mechanical properties is currently underway.

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D15 - Conducting composites based on multi-wall carbon nanotubes and polystyrene-polybutadiene-polystyrene block copolymers

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Polymeric nanocomposites based on carbon nanotubes (CNT) are of increasing academic and technological interest due their ability to combine the remarkable properties of CNT (i.e. extremely high electrical and thermal conductivity, low density, high tensile strength, Young's modulus, etc.) with the versatility, processability and mechanical properties of polymers. Because nanocomposites are multiphase systems, their properties can be tailored by the modification of their components'ratio, allowing the customization of these materials to suit the desired applications. The employment of elastomers in the fabrication of electroconductive materials allows the production of flexible materials with outstanding mechanical and electrical properties. These materials can be applied in electrostatic charge dissipation (ESD), electromagnetic interference (EMI) shielding, artificial muscles, electromechanical actuators, touch control switches, shape-memory polymers (SMP), etc. In this work, nanocomposites of multi-wall carbon nanotubes (MWCNT) and polystyrene-polybutadienepolystyrene (SBS) block copolymer were investigated. The samples were prepared by solution casting method, mixing a solution of the polymer matrix in toluene with a sonicated dispersion of MWCNT in xylene. The dynamic mechanical properties and DC conductivity of the films were also evaluated.

In general, the mechanical strength of the composites was increased after the addition of the MWCNT. It was observed that MWCNT interact with both phases, but their interaction is stronger with the polystyrene blocks, probably due the presence of the aromatic rings. The polymeric dispersant agent employed acts as a plasticizer to the polystyrene blocks, increasing their flexibility, although it decreases the stiffness of the composites. Therefore, there is a competition between the effects of these two components. The DC conductivity was drastically increased even at low loadings of MWCNT. A value of ~10^{-4} S/cm has been obtained for the sample containing 1wt.% of MWCNT, and the percolation threshold achieved for these systems lies in the range of 0.25wt.% - 0.50wt.%. These results imply that these materials have great potential as charge dissipaters in electronic equipment and EMI shielding.

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D16 - Electrical and Optical Properties of Carbon Nanotubes/Polymer Nanocomposites

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We have measured the optical and electrical properties of nanocomposites thin films made of poly-3-hexilthiophene (P3HT) and multi-walled carbon nanotubes (MWNT) filled with iron/iron-oxide, as well as the performance of photovoltaic devices built with such films.We found that the conversion efficiency of the devices presented a maximum for a certain MWNT concentration and that the electrical behavior is mainly dependent on the charge transport properties of the MWNT. To compare, we used poly[2-methoxi-5-(2'-ethilhexiloxi)-1,4-phenilenevinelene (MEH PPV) and amount of carbon nanotubes as active layer in a photovoltaic device. The percentage of nanotubes witch the efficiency is higher is different compared with P3HT devices. By varying the nanotubes concentration we develop a model based on drift-diffusion with space-charge effects to understand the electrical results. We found different behaviors associated to different microscopic mechanisms: a drastic increase for the injection current due to drain channels provided by the nanotubes, a percolation transition at a critical concentration, and a fractal-like structure for transport after the percolation threshold. Also we present a novel porous bilayer structure that has been constructed to improve the photocurrent where the carbon nanotubes are perpendicular to the substrate and to the polymer, the second layer.

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D17 - New Methods for Preparing Transparent, Electrically Conductive Films of Carbon Nanotubes

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Transparent electrically conductive films are a critical component of most modern display technologies, including liquid crystal, electroluminescent, and touch-sensitive screens. Currently, indium tin oxide (ITO) is the transparent conductor of choice due to its low sheet resistance and excellent optical clarity (~10 ohms/square at 90-95% transmittance). However, achieving these properties requires expensive and cumbersome vacuum deposition techniques, which are not practical for preparing very large quantities of material for lower end applications such as transparent anti-static packaging materials. Furthermore, ITO films are brittle and easily damaged by bending or folding the substrate. This presentation will introduce new techniques for preparing transparent conductors from carbon nanotubes. In one approach, MWNT are dispersed in a poly(methyl methacrylate) (PMMA) matrix. The use of a low volatility solvent enabled long spin times (up to 42 min) without significant evaporation, leading to thin films that are optically transparent. However, with these long spin times, the phenomenon of shear-induced aggregation becomes an important issue, especially in regards to how the resulting microstructure affects the conductivity of the film. Alternatively, the nanotubes may be grown continuously using a CVD process, and following synthesis, they are immediately transferred to a polymer substrate at a rate of ~10 meters/minute, allowing us in our current capacity to prepare kilometers of material per day. The very low areal concentration of nanotubes facilitates good optical transmittance (~95%), while the ability to collapse the material into a 2D network leads to low sheet resistance values (1-3 kiloOhms/square). These properties approach those of colloidal dispersions of ITO, which are easily deposited but require a high temperature (typically 600 ^{o}C) to reach comparable specifications. Furthermore, the mechanical properties of the CNT-polymer composite films that we prepare are dominated by the substrate, so that the conductive layer is not susceptible to cracking or delamination when the material is bent or folded.

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D18 - Benzyl Alcohol and the TiO_2-CNT Interface

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Recently, we reported the synthesis of pure rutile nanotubes produced by a modified sol-gel route using sacri- ficial carbon nanotubes as templates, with subsequent heat treatment to convert the templated anatase to rutile [D. Eder, I.A. Kinloch, A.H. Windle, Chem. Commun. 13, 1448-1450 (2006)]. A key aspect of this method is that the carbon nanotubes support the structure during the reconstructive phase transformation, preventing break up due to the transformation stresses involved as well as crystal growth, thus leading to high surface area rutile materials.

Here we describe the role of benzyl alcohol (BA) as a surfactant and complexing agent in the coating process with carbon nanotubes as well as its influence on the crystallisation of TiO_2 and the phase transformation from anatase to rutile. We used tetrabutyloxytitanate (TBOT) as titanium precursor, ethanol as solvent, and water as gelator. The carbon nanotubes were prepared by chemical vapour deposition (CVD) using ferrocene as catalyst precursor and toluene as feedstock. The applied characterisation tools include SEM, (HR)TEM, XRD, FTIR/Raman spectroscopy and thermal analysis (TGA/DSC).

Thermal analysis and FTIR spectroscopy suggest that the formation of a Ti-O-Ti network is significantly decreased with increasing benzyl alcohol content, enabling the titania sol to form an interaction with the carbon nanotubes with the aid of the aryl group of benzyl alcohol. The coating of carbon nanotubes with amorphous titania was most uniform and homogeneous at a BA:Ti ratio of 4-5. Benzyl alcohol also prevents grain growth and retains the phase transformation from anatase to rutile, as observed after heat treatment in argon at 600 °C. Again, the optimum BA:Ti ratio was found to be 4-5, at which the crystal sizes of both anatase and rutile were considerably decreased (from 30/45 nm at BA:Ti = 0 to 8/15 nm at BA:Ti = 5, for anatase and rutile crystals resp.), while still enabling a nearly complete phase transformation (R:A > 85%). At higher concentrations, the phase transformation is strongly impeded (e.g. R:A < 35% at BA:Ti = 40) without further effect on the crystal sizes.

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D19 - Strong AMWNT/PVA Composite Film by Vacuum Filtration

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Well-aligned multi-walled carbon nanotube(AMWNT) with length up to 2mm have been successfully prepared by floating CVD method. After mixed-acid treatment, filtration and compaction, AMWNT films can be easily made. But the interaction between CNTs was relatively weak. It is known that there is strong interaction between CNT and PVA. Thus PVA can be used to bind CNTs together and fill the interstices to strengthen the AMWNT films. In order to intensify the osmosis and diffusion of PVA in the AMWNT film and obtain even distribution of PVA in the AWMNT films, vacuum filtration of PVA solution was adapted. Strong AMWNT/PVA composite films have been prepared. After preparation, the films were characterized by FT-IR, Raman, SEM and the measurements of electrical conductivity and mechanical properties.

During the preparation of AMWNTfilms, different temperatures of mixed-acid treatment had been investigated from 90°C to 130°C. 110°C was adapted because carboxy group was introduced to obtain monodisperse AMWNT, and the mass loss was not high. The tensile strength is up to 7.5 MPa and the tensile modulus is 785 MPa. The volume resistivity is only 1.0×10^{-2} Ωcm. When preparing the composite films, the filtration time varied from 30min to 24hr. It was found 10 hour is optimal. There could be enough amount of PVA diffusing uniformly to the AMWCNT films. With too much PVA concentrating on the surface, the electrical conductivity and mechanical properties would be influenced. After 10 hour filtration, the combined properties of the composite films were enhanced significantly. The tensile strength was 12 times higher than that of AMWNT films, is up to 96.1 MPa.The tensile modulus was almost 8 times that of AMWNT films, reaching 6.23 GPa.Meanwhile, the order of magnitude of volume resistance of AMWNT /PVA composite films was the same with that of AMWCNT films, remaining 10^{-2} Ωcm.

SEM image shows that CNTs are pulled out before abruption in the fracture surface of AMWNT films. In AMWNT/PVA composite films, the interstices are filled and PVA distributes uniformly both on the surface and the inner, and CNTs are wrapped by PVA firmly. The modified Halpin-Tsai equation was adapted to calculate the tensile modulus of the composite films. And the experimental value was one order lower in magnitude than the calculated value. It meant that there was still space for enhancement of the mechanical properties of the composite films.

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D20 - Mixed Ionic-Electronic Transport in Zirconia/Carbon Nanotube Composites

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Composites materials in which carbon nanotubes (CNT) are added to a matrix to improve its mechanical, electrical or thermal properties have been widely investigated, especially polymer/CNT composites. The addition of CNT to ceramic materials has been also examined, mainly in attempts to improve their fracture toughness. More recently studies on the electrical properties of ceramic/CNT composites have been reported. In this work, we investigate the electrical properties of zirconia/CNT composites. Composites with CNT concentration from 0 to 10 wt.% were prepared by the liquid mixture (in ethanol) of commercial yttria-stabilized zirconia (YSZ) and purified single-walled carbon nanotubes (SWNT), produced by the arc-discharge technique. The resulting composite powders were pressed and sintered in inert (or reducing) atmosphere at 1400 ^{o}C. The resulting pellets were characterized by scanning electron microscopy, Raman spectroscopy, and impedance spectroscopy in a wide temperature (T) range ($20<T<800$ ^{o}C). The electrical properties of the YSZ/SWNT composites present interesting features. At room temperature the dependence of the conductivity on the SWNT concentration follows a typical insulating/conducting (YSZ/SWNT) percolative behavior. Whereas at high T the ionic transport along the YSZ phase starts to dominate. In summary, CNT/YSZ composite can be envisioned as potential components of electrochemical devices due to their mixed ionic-electronic transport properties.

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D21 - High-concentration carbon nanotube composites with spontaneous macroscopic-scale uniaxial tube alignment

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We recently demonstrated [1] that carbon nanotubes (CNTs) can be aligned and at the same time well dispersed in lyotropic liquid crystals based on the standard surfactant sodium dodecyl sulfate (SDS). The maximum CNT concentration was however moderate (0.01 wt.-%). By instead using sodium dodecyl benzene sulfonate (SDBS) for dispersing the nanotubes, and the cationic surfactant cetyl trimethyl ammonium bromide (CTAB) for forming the liquid crystal phase, we now succeeded in increasing the CNT concentration by a factor 20, without losing the nanotube alignment. Our new composite, containing 0.2 wt.-% HiPco single-wall CNTs, now has so high CNT concentration and alignment quality that the sample acts as a linear polarizer: the anisotropic nanotube properties are transferred to the macroscopic world by the LC.

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D22 - Composite of Carbon Nanotube/carbon felt functionalised with Ferrocene di-carboxylic acid

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The efficiency of electrodes for microbatteries and microcapacitors are important for their superior performance. The performance of a microcapacitor electrode can be improved by applying new materials or combining components with unique properties into electrode materials. Individual carbon nanotubes exhibit extraordinary mechanical, thermal and electrical properties. Composite materials, using carbon nanotubes, are expected to show similar superior properties. This study reports synthesis of carbon nanotubes/carbon felt (CNT/felt) composite by chemical vapor deposition and its functionalisation with ferrocene di-carboxylic acid (FDCA) aiming capacitor application. Carbon nanotubes were grown on each fiber of carbon felt substrates using methanol decomposition at 650°C and CoMn as catalyst. Characterization of the CNT/felt was carried out using scanning electronic microscopy, FTIR and cyclic voltammetry. It was found CNT covers the felt with surface of each single fiber having an uniform coating deposit as cotton-like. TEM reveals that the CNTs of the composite electrode have predominatly structure that can be recognized as cup-stacked. The functionalisation of CNTs with FDCA (Ferrocene di-carboxylic acid) was performed as follows: first an -OH group in the carboxy molecule was exchanged by a –Cl termination using $AlCl_3$ in dichloromethane and irradiated in a 280Wmicrowave oven during 20 s. The extraction of the Lewis acid was performed by hydrolisis and the product was washed in water and then with acetone, filtered and dried. This formed the molecular composite electrode. Microcapacitors using this electrode were tested in a conventional three-electrode electrochemical cell with a Li counter- and a reference-electrode. The non-aqueous electrolyte was a 1 M LiPF6 in dimethyl carbonate-DMC and ethylene carbonate-EC (Selectipur-1:1 w/w). The capacitance was checked by multiple CVs (from from 10 to 200 mV/s) in the potential range from -0.4 V to 0.8 V. The voltammograms consisted in the usual CV characteristics by the CNT-felt composite with an added voltammetric peak located around 0.35 V, consistent with the ferrocene redox potential. The peak current grew linearly with the scan rate, indicating that the organic redox couple was firmly attached to the carbon felt/CNT composite. A second voltammetric peak, showing a diffusional behavior, appeared at the slowest scan rates, suggesting the trapping of some redox species inside the cup-stack CNT structure. The charge/discharge cycles were continuosly repeated showing that the new hybrid material has a durable electrochemical behaviour. The microcapacitors tested so far showed an integral capacitance of the order of 10 F.g-1 in 2.6mA.cm^2 of the composite electrode.

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D23 - Pt:Ru carbon nanotubes/carbon felt for direct methanol fuel cells

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In this work we have investigated binder-free composite electrodes based on cup-stacked and bamboo-like carbon nanotubes and carbon felt for direct methanol fuel cells. Pt:Ru particles with an average particle size of the electrocatalysts of 3.5 ± 0.8 nm were supported on cup-stacked-type carbon nanotubes. Scanning electron microscopy results revealed that Pt-Ru particles were well dispersed on the carbon felt support. The electrocatalytic properties of the Pt-Ru/fiber catalysts toward methanol oxidation revealed that the catalytic activity of the electrodes is better to 5% Pt-Ru/carbon nanotube/carbon felt composite than 10% of Pt-Ru (weight proportion between Pt-Ru and carbon nanotube/carbon felt). The results shown that the studied composite has potential to be used in direct methanol fuel cells.

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D24 - SUPERCAPACITORS OF CNTs/Carbon felt

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Supercapacitors made of CNTs are now well-known electrochemical devices. In this presentation we shall examine the capacitance of CNTs of different shapes and loadings on top of carbon-felt substrates. Several drops of the catalytic mixture were added in controlled amount over C-felt substrates, and after a drying process was fired at 650 ^{o}C for 10 min in nitrogen atmosphere saturated with an methanol or acetone (for the growth of cup-stack and multiwall structures, respectively). Residual traces of the catalytic mixture were removed in concentrated HCl during 10 min at room T, and washed in distilled water. SEM pictures have shown that CNTs were obtained with different morphology and that the HCl treatment is effective in removing the excess of metallic particles used as catalizator of the CNT growth. In order to perform the electrochemical characterizations, the carbon-felt/CNT composites were attached to a Au wire in a standard three-electrode cell, using a Pt gauze as counter-, and a hydrogen reference-electrode. Sulphuric acid (1 M), deaireted by nitrogen bubbling, was used as the cell electrolyte. The electrode capacity was evaluated mainly by CV, although other techniques (i.e. chronopotentiometry and impedance spectroscopy) have been used as well. The CV results indicate that highest capacitances have been obtained with cup-stack CNT-felt composites, where a CNT loading of 41% in weight (with respect to the total composite mass) is present. The current density to charge this capacitor is up to 7 A/g of total composite weight with capacitance of 14 F/g. The multiwall structures, on the contrary, showed only 1/10th of this capacitance and charging currents less than 1 A/g.

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D25 - New technique for production of transparent and conductive networks using carbon nanotubes

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A new method for deposition of transparent carbon nanotubes networks (CNTNs) was developed. This method allows the deposition of functionalized or surfactant stabilized carbon nanotubes dispersed in water. The nanotubes films can be applied over complex geometries, on non-conductive rigid or flexible substrates and over large areas in a continuous way. The carbon nanotubes films are made by electrophoretic deposition (EPD) using a thin film layer of a conductive metal as Aluminium or Titanium. The carbon nanotubes films can be easily patterned using this technique.

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D26 - Novel technique for selecting Carbon Nanotubes

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In this work we present a novel, simple, inexpensive and fast technique that allows characterizing samples of carbon nanotubes (CNTs) and their ability to form electrically conductive percolating networks. This technique is based on measuring the electrical conductivity of the tested material suspended in electrically insulating liquid. The concentration dependence of conductivity shows a percolation behaviour similar to that observed in electrical composites with an insulating matrix. The value of the critical percolation concentration is strongly determined by the aspect ratio of the particles forming the network through a dynamic percolation.We characterized several single- and multi-wall carbon nanotubes materials by the newly proposed method and received a good correlation with the results obtained by methods commonly used for CNTs characterization (Raman spectroscopy, transmission electron microscopy and electrical conductivity of self standing papers). This method can yield important information for CNTs producers and for the selection of electrically conducting structures for composites applications.

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D27 - Improvement of ceramic matrix composites with boron oxide modified CNTs

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Carbon nanotubes (CNTs) offer scope for the development of fundamentally new composite materials with several applications in different areas. However, less than 4% of the reports on CNT composites are concerned on CNTs ceramic matrices composites (CMC). Great part of this lack is mainly due to the poor interaction between CNTs and the ceramic matrix achieved and to the difficulty of densification of the final composites. The main focus in this work was to improve the interaction between the ceramic matrices and CNTs. It is already known that boron and carbon could react substitutionally and form stable covalent bonds. A study of the modification of CNTs using boron oxide to achieve a better interaction between filler and matrix will be presented. Several compositions of inorganic glasses and boron oxide modified CNTs were studied. Scanning electron microscopy, Raman spectroscopy, EELS and XPS were used to evaluate the compatibility. Boron oxide modified CNTs CMC demonstrated not only improvement on the electrical properties, but also a better thermal stability. Some potential applications were envisioned for the next generation of CMC boron oxide modified CNTs.

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D28 - Comparison of transparent carbon nanotubes networks prepared through different post-growth Techniques

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Ultra-thin, transparent, optically homogeneous, electrically conducting films of pure carbon nanotubes (CNTs) give rises for broad applications for electrical coupling in photonic devices. In the present work we studied and compared different post-growth techniques for the production of these networks: dip-coating, filtration method and spray-coating using SWCNTs produced by HiPCo method.We also studied how the opto-electrical properties of the networks changed using different CNTs prepared through CVD method: SWCNTs, DWCNTs and MWCNTs. These materials were characterized by transmission electron microscopy, Raman spectra and conductivity in liquid. Morphology and roughness of the prepared networks were also evaluated using scanning electron microscopy and atomic force microscopy. A study of the electrical properties versus transparency will be presented and correlated to the morphology of the nanotubes and their networks.

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D29 - Single Walled Carbon Nanotubes Silica composites through an Inorganic Sol-gel route

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One promising approach for the preparation of the organosilica hybrid materials is sol-gel process; which normally consists of two steps: hydrolysis of alkoxysilane and then polycondensation of the hydrolysis products. Nevertheless, there still remain some drawbacks of the conventional sol-gel process such as using expensive alkoxysilane precursors that demands extreme pH conditions for gelification. In the present work, we present a convenient and economic sol-gel route for the preparation of carbon nanotubes composite materials using silicic acid, which is extracted from water glass, an abundant and more affordable silica precursor. For the first time, it is reported the successful incorporation of single walled carbon nanotubes (SWCNTs) into a silica matrix prepared through an inorganic sol-gel method. In this sol-gel route the network former (silicic acid) is water soluble and do not interfere in the dispersion of the nanotubes. Therefore, it allows the use of water dispersion of nanotubes assisted with amphilic surfactants, instead of chemical functionalization that could damage the structure of CNTs and is time demanding.

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D30 - Carbon nanotube biocomposite for tissue engineering

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Recent advances on bone tissue engineering led us to search new materials that are biocompatible, with different active bio functions and characteristics which are similar to real growth tissues. Recently, it has been demonstrated that new composites with improved mechanical and electrical properties can be created by the introduction of small amounts of carbon nanotubes (CNT) into other matrizes (like polymers). Based on this characteristic we will present a biomaterial composed by a mixture of collagen and carbon nanotubes. This biocomposite is a scaffold that can have important implications in a wide range of biotechnology areas with potential to substitute biological structures, to allow a more effective tissue regeneration, restitution and physical properties.

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D31 - Synthesis of gold nanoparticle decorated carbon nanotube hybrids

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Carbon nanotubes are extremely resistant to tension, are highly flexible and can exhibit semiconducting, metallic or even superconducting properties. In short, they are the ideal building blocks for molecular nanoelectronics and very strong materials. On the other hand, noble metal nanostructures, particularly gold nanoparticles, are the focus of many researchers because of their special optical properties, unusual electronic properties including conductivity by activated electron hopping, remarkably high catalytic activity and so forth. The hybrid nanostructures combining the two kinds of materials, nanotubes and nanoparticles, might improve the performances or extend the applications. In this line we present results of the synthesis of gold nanoparticle decorated multi-wall carbon nanotube hybrids (AuNPs@MWCNTs).
MWCNTs were synthesized by decomposition of acetylene over Pd/-Al_2O_3 catalyst [1, 2], in a Chemical Vapor Deposition (CVD) system. Raw nanotubes were purified by alkali and acid treatments to eliminate alumina and catalytic particles.
The AuNPs@MWCNTs nanohybrids were prepared by two methodologies: the Solvated Metal Atom Dispersion technique (SMAD) and the assembly with bifunctional molecules. In the SMAD procedure bulk Gold and organic solvents like 2-propanol or acetone were evaporated and later condensated into a frozen matrix at liquid nitrogen temperature. After warming this matrix to room temperature, a colloid with very small and highly reactive gold clusters is obtained. These clusters react, in the same reactor, with carbon nanotubes, forming anchored gold nucleus. Unlike SMAD method, the assembly with bifunctional molecules consists in an ex-situ attachment of AuNPs with CNTs once AuNPs have been stabilized. We found that in SMAD method the AuNPs were strongly anchored to CNT walls as compared to the bifunctional assembly. Nanohybrids prepared by SMAD method were very stable to heat treatment up to 400 ^{o}C since a thin layer of graphitic carbon is encapsulating gold nanoparticles. On the other hand, thermal treatment in nanohybrids prepared by bifunctional assembly induces AuNPs sintering. We will discuss the results mainly as function of TEM, FTIR and TGA characterizations.

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D32 - Vertically-aligned multi-walled carbon nanotube - polymer electrolyte composites: morphological and electrochemical investigation

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Composite films composed of vertically aligned multi-walled carbon nanotube (VAMWNT) impregnated with a polymer electrolyte (PE) were investigated as electrodes for electrochemical devices. The VAMWNT were formed on stainless steel substrates by plasma enhanced chemical vapor deposition. Scanning electron microscopy (SEM) showed that the VAMWNT form uniform arrays with height of ~1 μm. The polymer electrolyte (PE) was based on thermoplastic polyurethane, copolyether and $LiClO_4$. SEM images indicated that the polymer electrolyte impregnated homogenously the nanotubes and no excess of polymer is located in the composite surface. A test electrochemical cell was produced by assembling two composite films having a layer of pure polymer electrolyte as separator. Cyclic voltammetry was applied to study the electrochemical stability of the VAMWNTPE/ PE/VAMWNT-PE cell and impedance spectroscopy was performed to access the conductivity behavior of the electrode and electrolyte separately. These studies were performed between 25°C and 95°C. The cell presented a large window of electrochemical stability (~ 5V). Impedance diagrams show in the low frequency range a straight line at 45°C which may be related to a doping effect of the polymer electrolyte on the carbon nanotube.

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D33 - Bulk and surface conductivity of poly(3-hexylthiophene)/MWNT composites prepared with different methodologies

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Multi-walled carbon nanotubes (MWNT) with ~10 nm thickness and 1 μm length were dispersed in chloroform successfully. Poly(3-hexylthiophene)-P3HT/MWNT composites have been prepared in chloroform and precipitated in methanol. The bulk conductivity of these films showed percolation at 0.1 wt% of nanofiller as characterized by impedance spectroscopy measurements. The self-assembly of P3HT on the surface of MWNT was observed by transmission electron microscopy and corroborated by infra-red spectroscopy which showed increase of polymer conjugation length with the addition of nanotubes. The limitation of the bulk conductivity after percolation (at 4 wt% MWNT) to 10^{-2} S/m is assigned to the resistance of the polymer layer in the internanotube connection1. Thin films of P3HT/MWNT were also prepared by using different solvents to produce a conjugated polymer arrangement of fibrils and favor electronic conductivity. Surface conductivity has been measured by four points probe and indicated that by applying potentials beyond a characteristic value the surface arrangement allowed high levels of electronic transport. Cyclic voltametry of thin films showed the electrochemical behavior typical of the P3HT system.

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D34 - Adhesion, proliferation and viability of human osteoblast-like MG 63 cells on carbon nanotube-polysulfone composites

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Recently, nanostructured artificial materials offer enormous promise for the repair of damaged or lost tissues and organs. Most of the components of the natural tissues are in nano-dimensions, thus the nanometer scale features (i.e. those from 1 to 100 nm) can control the cell behavior, such as its adhesion, morphology, migration, proliferation and differentiation both in vitro and in vivo [1]. Carbon nanotubes are perspective for various advanced biomedical technologies, including improved tracking of cells, sensing microenvironments or delivery of transfection agents [2]. However, relative little is known on their influence on cell-substrate adhesion and their potential use in tissue engineering.Therefore, in this study, we investigated the potential use of carbon nanotubes for construction of carbonpolymer composites applicable in bone tissue engineering. In our experiments, seven different samples were studied: (1) polysulfone (PSU) + 0.5 wt% of single-walled nanohorns (SWNH), (2) PSU + 1 wt% SWNH, (3) PSU + 2 wt% SWNH, (4) PSU + 0.5 wt% multi-walled nanotubes (MWNT), (5) PSU + 1 wt% MWNT, (6) PSU + 2 wt% MWNT. As control materials, pure PSU and standard polystyrene cell culture dishes were used.

The materials in a form of foils were sterilized in H_2O_2-plasma (Sterrad 120, ASP, Johnson & Johnson), inserted into 24-well-multidishes (TPP, well diameter of 15 mm) and seeded with human osteoblast-like cells of the line MG 63 (European Collection of Cell Cultures, Salisbury, UK). Each well contained 5 000 cells and 2 ml of Dulbecco-modified Eagle´s Minimum Essential Medium supplemented with 10% of fetal calf serum. On day 1 and 3 after seeding, the cells were fixed with 70% ethanol, stained with propidium iodide and counted on digital pictures taken under microscope Olympus IX 50. On day 5 after seeding, i.e. when the cells were confluent or 264 even overlapping, the cells were trypsinized and counted in ViCell Analyser (Beckman Coulter). For evaluation of cell viability, the cells were stained with LIVE/DEAD-Viability/Cytotoxicity Kit (Invitrogen).

On day 1 after seeding, the number of MG 63 cells initially adhering to all tested composites ranged from 1668 ± 268 to 2591 ± 430 cells/cm2 and was similar to the values found on the pure PSU as well as control polystyrene culture dish. The viability of cells ranged between 89% and 99% in all tested materials including the control polystyrene dish. The lowest viability (89.0 ± 2.5 %) was detected on the composite containing PSU with 1 wt% of SWNH and the highest viability on pure PSU (99.0 ± 0.9 %).

On day 3 after seeding, the viability of cells on the composites has not changed or even slightly increased from the 1st day after seeding. However, the cell population density was significantly lower on composites containing 0.5 wt% of MWNT (4386 ± 1216 cells/cm2), 2 wt% of MWNT (5077 ± 742 cells/cm2) and 2 wt% of SWNT (5405 ± 910 cells/cm2) in comparison with control polystyrene dish (11300 ± 2569 cells/cm2). On the first two composites, also the incorporation of bromodeoxyuridine (BrdU) into the newly synthesized DNA (detected in 3-day-old cells by Cell Proliferation ELISA BrdU Colorimetric kit, Roche Ltd., Prague, CR) was significantly lower than in cells on the control polystyrene. The absorbances obtained on the composites containing 0.5 wt% and 2 wt% of MWNT reached only 77.3% ± 1.8 and 60.3 ± 6.3% of the control value obtained on polystyrene, respectively. A relatively low absorbance was also obtained on the PSU with 1 wt% of SWNT (66.0 ± 2.1% of the control value). Both cell numbers and BrdU incorporation in cells grown on the remaining composites were similar to the values obtained on the control polystyrene.

On day 5 after seeding, the population densities of cells on all tested composites as well as the pure PSU were detected to be significantly lower than on the control polystyrene culture dish. The lowest number of cells was found on the composite containing 1 wt% of MWNT (43 029 ± 9746 cells/cm2 compared to 108421 ± 7801 cells/cm2 on polystyrene, $p \leq 0.001$, Student‘s test for unpaired data). Nevertheless, the viability of cells on all tested materials still reached high values more than 91%. On composites with 1 wt% and 2 wt% of MWNT, the viability was 99.8 ± 0.2% and 99.9 ± 0.1%, respectively, which was significantly higher than on the control polystyrene (95.6 ± 1.7%).

The lower proliferation activity of cells on polymer-nanotube composites could be explained by a relatively large cell spreading area. This area was significantly larger in cells cultivated on composites containing multiwalled nanotubes than on control polystyrene or composites containing single-walled nanohorns. The largest cell adhesion area was detected on the PSU containing 2 wt% of MWNT (1774 ± 94 um2 compared to 1402 ± 113 um2 on the control polystyrene), i.e., on one of the samples with the lowest cell numbers and lowest BrdU incorporation. It is known that the proliferation activity is the highest at the intermediate adhesion strength. If the cell-material contact area is very large, the cells could skip the proliferation and enter the differentiation program [3].The relatively large cell spreading area on polymer-nanotube composites was accompanied by well developed filamentous beta-actin cytoskeleton. It can be concluded that both SWNT- and MWNT-containing polysulfone are suitable carriers for colonization with bone cells and thus applicable for bone tissue engineering. Composites with MWNT seem to be more appropriate in situations where the good initial cell adhesion, spreading and formation of rich actin cytoskeleton is desirable.

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D35 - Carbon nanotubes aligned by liquid crystals and liquid crystals doped with carbon nanotubes: functional materials for functional composites

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When carbon nanotubes are mixed with liquid crystals - fluids with a degree of orientational order – composites with new and unexpected properties arise. We have shown that single-wall carbon nanotubes align along the same direction as the host liquid crystal molecules. As a uniform, unidirectional alignment of the liquid crystal can easily be achieved over areas as large as centimetres, the large scale alignment can be transferred to the nanotubes as well. Moreover, by applying an electric field the orientation of liquid crystal molecules can be changed at will. We have proven that SWCNTs in this way can be reoriented following the movements of the molecules of the host phase. Thus, liquid crystals appear to be an attractive tool for manipulating CNTs. On the other hand, there are recent reports on the effect of CNT doping on the electro-optic properties of liquid crystals in displays. In our work we show, however, that the concentration of the CNTs plays a fundamental role for determining if the effects of nanotube doping will be beneficial or adverse. The electric field-driven reorientation of the liquid crystal molecules (switching) occurs above a threshold voltage. At high CNT concentration this threshold increases by the presence of nanotubes but for very low concentration the opposite effect seems to occur.

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D36 - Tailoring Gas Sensing Properties of Carbon Nanotubes

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Owing to their unique mechanical, chemical and electronic properties, carbon nanotubes (CNTs) have been widely pursued as building blocks for effective ultrasensitive chemical and biological sensors. Nanotube sensors offer significant advantages over other conventional sensor materials such as higher sensitivity, lower operating temperature, and faster response times. In spite of these outstanding sensor attributes, several key issues remain to be resolved, such as inhomogeneity (mixture of metallic and semiconducting nanotubes) of CNT samples, as well as selectivity, reversibility, and reproducibility of sensing. These will ultimately determine the usefulness of CNT-based devices in practical sensing applications. In this work, we report on the fabrication and performance of novel metal-CNT hybrids as gas sensors. The sensing mechanism primarily involves charge transfer between electron donating/electron withdrawing gas molecules and CNTs, resulting in changes in the CNT impedance. Our strategy is based on tuning the selectivity of CNTs by modifying electronic density of states of CNT through forming metal-CNT hybrid materials. Such materials have been found to be capable of detecting NO_2 down to sub-ppb levels at room temperature. The feasibility of this approach for gas sensing will be discussed with respect to (1) diameter and chirality distribution of the starting CNT materials, (2) metal-CNT hybrid materials, and (3) the selectivity towards gaseous species being detected. The characteristic impedimetric behavior of different metal-CNT hybrid sensors in response to various gases will be evaluated along with appropriate equivalent circuit modeling and analysis.

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D37 - Optical Detection of DNA-Drug Interactions in Live Cells Using Single-Walled Carbon Nanotubes

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The intrinsic near-infrared emission of single-walled carbon nanotubes (SWNT) exhibits an environmental sensitivity which has been employed for optical detection of important analytes. We used this property to develop DNA-nanotube complexes which serve as sensitive molecular beacons for the activity of alkylating compounds in biological media. Complexes of oligonucleotides and SWNT exhibit a red-shift in emission energy of up to 30 meV upon binding to alkylating agents. Nanotube photoluminescence undergoes spectral changes upon DNA-drug interaction via a solvatochromic shift mechanism. Nanotube-DNA complexes are colloidally stable and fluoresce from within live cells and tissues. Nanotubes are absorbed by mammalian cells via endocytosis without exhibiting cytotoxic effects. Within single 3T3 cells, the complexes detect DNA damage and transmit real-time chemotherapeutic drug activity information via nearinfrared photoluminescence changes. The complexes will be employed to investigate drug degradation and multidrug resistance in cancer therapy, as well as DNA damage via endogenous pathways.

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D38 - Appling of carbon nanotube for miniaturized NO_2 gas sensor development by electrical impedance analysis

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This study presents an impedance analysis method with carbon nanotube (CNT) application for NO_2 gas sensor development. We used an interdigitated electrode (IDE) coated with CNT material as a signal transducer. With the absorption of different levels of nitrogen dioxide (NO_2) in CNT layer, the conductance of electrodes was parameter as the index for monitoring and quantifying of NO_2. When NO_2 molecules exposed to the test chamber at 25 °C, the conductance response was increased proportionally with the concentration of NO_2, and the detection limit by our developed system was ppm-level approximately. It also was found that sensor using a single-wall CNT coated had higher sensitivity than a sensor coated with multi-wall CNT. In addition to gas sensitivity, response time and reproducibility of the electrical response resulted to be dependant from the preparation conditions of CNT and IDE gap size. In our study, the MWNT based gas sensor showed fast dynamic of the electrical response and high reproducibility of the electrical properties. This system also provided the advantages of real time monitoring, automatic detection and mini-scale design for on-line gas detection.

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D39 - Mechanisms for the Cellular Internalization of Functionalised Carbon Nanotubes

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The development of nanomaterials for biomedical and biotechnological applications is an area of research that holds great promise and intense interest. Carbon nanotubes (CNT) are thought to lead to novel types of nanomedicines. In our laboratories, CNT were made compatible to physiological environments after functionalisation by the 1,3-dipolar cycloaddition reaction. This has allowed their exploration as a platform to construct delivery systems for drugs and nucleic acids in vitro and in vivo.

The interaction between cells and CNT is a critical issue that will determine any future biological application of such structures. In this communication we present the great potential offered by water-soluble functionalised CNT (*f*-CNT) as new vectors for delivery of plasmid DNA to cells and organs. Moreover, we will show that various types of *f* -CNT exhibited a capacity to be uptaken by mammalian and prokaryotic cells and can intracellularly traffick through different cellular barriers. The mechanisms by which *f* -CNT are able to cross cell membranes and deliver their cargo will also be discussed. Energy-independent mechanisms are explained based on the cylindrical shape and high aspect ratio of *f* -CNT that can allow their penetration through the plasma membrane, similar to a 'nanosyringe'.

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D40 - Functionalization of Carbon Nanotubes With Biological Membranes

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Our group has previously shown that acid-treated multiwall carbon nanotubes (MWNTs) can be coated with a bilayer of phospholipids that mimics a biological cell membrane. Following fusion of vesicles (liposomes) with fluorescent lipids on the surface of MWNTs, atomic force microscopy reveals a smooth coating with occasional transitions to a second bilayer and the coated nanotubes can be observed with fluorescence microscopy.

We have now used different carbon nanotubes, phospholipids, and vesicle preparation methods to investigate the mechanism of lipid coating. Bilayer formation depends on the nanotube diameter and the vesicle size; nanotubes greater than 40 nm in diameter can be consistently coated when the vesicles are smaller than 100 nm. Bilayer coating of MWNTs by vesicle fusion works with charged and uncharged liquid-state phospholipids but not with gel-state lipids. By including charged lipids in the vesicles the number of bilayers that wrap the nanotube can be modulated. Surprisingly, the lipid bilayers remain attached to the MWNTs after removal of water from the MWNT dispersion, and these membrane-functionalized nanotubes can be stored for several months at room temperature.

Purified membrane proteins are routinely incorporated in vesicles of synthetic lipids for biophysical characterization. We prepared such proteoliposomes with a fluorescently labeled transmembrane peptide, and demonstrated that vesicle fusion on the MWNTs leads to the formation of lipid bilayers containing this membrane peptide. Significantly, this is the first example of carbon nanotube functionalization with a membrane protein segment. Functionalization with larger membrane proteins could enable carbon nanotube biosensing with the G-protein coupled receptors that are targeted by pharmacological drugs.

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D41 - Lipid-Modulated Assembly of Carbon Nanotubes in Millimeter-Scale Structures

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Biomolecule-functionalized carbon nanotubes (CNTs) combine the molecular recognition properties of biomaterials with the electrical properties of nanoscale solid state transducers, and this hybrid material could enable bioelectronic devices with novel functionalities such as biosensing of pharmacological drugs. Unfortunately, selfassembly of CNTs into extended networks - a requirement for integration with conventional electrical circuitry - presents a technological hurdle, especially in the aqueous environment in which biomolecules function.

In this study, we investigated the CNT structures that are formed by the evaporation of dilute aqueous suspensions of iron-filled multi-walled CNTs (Fe-filled MWNTs) that are coated with double-chain surfactants (lipids). Unlike single-chain surfactants such as the detergent sodium dodecyl sulfate, lipids are biocompatible molecules; lipid bilayers mimic biological cell membranes and can accommodate pharmacologically relevant membrane receptor proteins. Controlled evaporation of droplets of lipid-coated Fe-filled MWNT suspensions in a magnetic field yielded symmetric fractals and linear assemblies of end-to-end oriented nanotubes. These CNT networks were only formed in the presence of lipids and with magnetized Fe-filled MWNTs, indicating that radial flow forces in the evaporating droplet, inter-tube van der Waals and electrostatic interactions, and magnetic forces all play a role in the self-assembly of the extended networks. Significantly, the linear patterns of Fe-filled MWNTs were up to a millimeter long. Such large assemblies of end-to-end oriented lipid-coated CNTs are promising components for electronic biosensors.

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D42 - Development of a Novel Taste Sensor Based on a Carbon Nanotube-Polymer Composite Material

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With the aim of developing applications for these new nano-devices in the field of biomedical engineering, we are investigating the development of bio-nanosensors based on nanocarbon materials with novel functions, such as fullerene and carbon nanotubes. Here, we report the basic characteristics of a taste sensor based on a composite material made from single walled carbon nanotubes (SWNTs) and polyethylene glycol (PEG). The fabricated sensor-chip uses a back-gate type FET with a source-drain electrode. The PEG-grafted SWNTs (PEG-SWNTs) network is dropped between the source and drain electrodes in the sensor chip. PEG-SWNTs are synthesized by heat treatment of toluene solution containing Azo-PEG (macro-azo initiators) with stirring. In the case of saltiness and umami, a clear differences between the same kinds were not observed. In the case of sourness, impedance in the solution decreases rapidly when citric acid is used, since its acid-ionization constant (ka) is about half that of acetic acid. In addition, the response times for acetic acid and citric acid (t = 35 and 15 s, respectively) show a numeric relationship with ka . When sucrose (sweetness) is used, the impedance of PEG-SWNTs becomes predominant because sucrose does not ionize, although it diffuses immediately due to its high solubility in water. On the other hand, when saccharin sodium, which is a salt, is used, an great impedance change due to ionization appears. The results for bitterness are particularly interesting; a significant difference in response time of materials is observed. This is thought to be due not only to the difference in the solubilities of the solutions (which results in ionization), but also to the effects of adsorption to PEG-SWNTs. Moreover, the sensor is able to distinguish most of the experimental taste materials with a short response time (~60 s).

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D43 - Enhanced microwave heating effect using carbon nanotubes

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There is a great demand from the electronics and packaging industries for light-weight, easily formable electromagnetic shielding materials. Such demand also exists within the polymer processing industry for highly efficient energy absorption from microwave fields, to reduce the loading of absorbing filler required. The effectiveness of multi-walled carbon nanotubes (MWCNTs) in fulfilling this role has been studied by measurement of the temperature rise of dispersions of MWCNTs in silicone oil. MWCNTs were grown by CVD method from a toluene feedstock with ferrocene catalyst. Iron catalyst remaining on the surface of the tubes and within the tubes was removed in one of two ways; treatment with concentrated acids, or a high temperature anneal in an inert atmosphere. Untreated, acid treated and heat treated tubes were dispersed in silicone oil by shear mixing, and the absorbing power compared with carbon black (CB). Testing was carried out in a resonant chamber with a magnetron source operating at 2.45 GHz, with the temperature being measured in situ.With all fillers, the absorbing power increases with increasing loading of filler, with CB showing an absorbing power of 4.26 W at a loading of 0.03% by weight (c.f. 2.88 W for pure silicone oil). In contrast, untreated MWCNTs showed an absorbing power of 54.8 W at the same loading, with heat treated tubes showing 92.1 W. Tubes that had undergone an acid treatment however showed an absorbing power of only 6.9 W. The high efficiency of untreated and heat treated tubes is likely to be a result of the low percolation threshold (due to the high aspect ratio) compared with CB. The surface modification resulting from the acid treatment is also thought to inhibit network formation. The absorbing power of the samples has also been compared to their conductivity.

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D44 - Sputtering of Single-Walled Carbon Nanotubes Controlled by Ion Irradiation Energy Flux

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Carbon nanotubes (CNTs) can be sputtered by the ion irradiation which sputtering contributes to deformation. The deformation increases linearly with increasing energy and dose of irradiated ions. When the ion transferred energy is greater than the bonding energy of carbon atoms, carbon atoms may be taken away from the lattice of CNTs. Consequently the total energy transferred from the incident ions to CNTs can be considered with the energy flux, Φ_E which is consisted of the ion irradiation energy, and dose, as $\Phi_E = E_iD_i$. Here $E\ i$ can be controlled with the sheath potential on the target CNTs, from 20 to 150 eV. D_i is determined by the Bohm velocity of ion $u\ B$, the plasma density at the sheath edge n and the ion irradiation time t , so that $D_i = nu_Bt$. The ion energy flux may be varied with bias potential on the substrate, plasma density and irradiation time. Even though the Bohm velocity varies with the plasma temperature, the temperature is not changed significantly in this plasma source, being considered a constant 4 eV. Experiment is carried out with the single-walled carbon nanotubes (SWNTs) bundle because the defects are easily observed. The intensity ratio of D to G band of Raman spectra (I_D / I_G) increases linearly with the ion energy flux. It implies the defects on the CNTs are linearly proportion to the accumulated energy on CNTs. Irradiation ion energy and ion dose play a different role in the deformation of CNTs. For a fixed ion energy flux, the I_D / I_G have a larger value in the low dose and high energy compared to that of high dose and low energy. Energetic ion collision is more effective to sputter atom out of the CNT lattice. More results and analyses will be presented.

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D45 - High Energy (> keV) Ion Irradiation on Single-Walled Carbon Nanotubes

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Deformation of carbon nanotubes (CNTs) has been considered under the low 150 eV of ion irradiation energy [1], revealing the sputter-etching and tip opening of CNTs. Especially the etching length of MWNTs increases linearly with the irradiation ion energy in the low irradiation energy. The dose of irradiated ions may contribute to the milling process on the top of CNTs, resulting in the tip-opened MWNTs. For the high irradiation energy up to few keV, the deformation of CNTs may proceed through the penetration and welding of nanotubes which was expected theoretically [2]. In this study, the irradiation ion energy varied in the range of keV. Argon ion was chosen due to its heavy mass and the chemical reaction free with carbon. Using the ion beam accelerator, the ion irradiations were carried out to the single-walled carbon nanotubes (SWNTs) bundled sheet on the substrate. Scanning electron microscope observation of the few keV ion irradiated SWNTs bundles reveals the serious structural deformations. Welding of SWNTs in the bundle and further the cross linkage of bundles were observed, resulting in the cone and fence types of structural deformation widely over the SWNTs sheet. Raman spectra show that the G^- peak, corresponding to the circumferential vibration mode of SWNT character, is disappeared and D band intensity increases. It implies that the energetic ion up to keV may penetrate into the SWNT bundle and chop the SWNT bundle. Also the accumulated energy on CNTs may contribute to welding of CNTs so that the deformed CNTs sheet may lose the SWNT property. More results and analyses will be presented.

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D46 - Single Wall Carbon Nanohorns Carrying Photosensitizing Drugs for Photodynamic Therapy

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We present that single-wall carbon nanohorn (SWNH) could be a drug carrier for the photodynamic therapy. The photosensitizing drug of zinc phthalocyanine (ZnPc) was loaded on SWNHs by immersing the hole-openend SWNHs in ZnPc-saturated solutions. The loaded quantity was about 40 percent. After the loading, SWNHs were chemically modified with a protein, bovine serum albumin (BSA), to enhance their solubility in aqueous solution. The obtained conjugates of ZnPc-SWNH-BSA with their size distribution in a range of 100-150 nm were dispersed almost individually in phosphate buffered saline. In-vitro studies showed that ZnPc-SWNH-BSA was taken inside rat cancer cells. After the uptake of ZnPc-SWNH-BSA by the cells, the light was irradiated for 5 minutes, and then most of the cells were killed. This suggests that ZnPc-SWNH-BSA is potentially useful in the photodynamic therapy.

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D47 - Wall-Controlled and Pattern Growth of CNTs for X-Ray Electron Sources

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In order to utilize carbon nanotubes(CNTs)as field-emission (FE) x-ray sources (XRS), we synthesized the CNTs on a stainless plate with a 5 mm diameter and Si wafer. Catalytic Fe nano-particles size was controlled in order to control the wall number of the carbon nanotubes. The size and distribution of the Fe nano-particles varied according to the growth conditions, heat exposure time and the thickness of the catalytic metal layer, resulting in a change in the wall number of the grown CNTs. The performance characteristics of the compact FE-XRS system are shown to be promising for non-invasive imaging in biomedical research and industrial inspection. A compact XRS was constructed in a triode configuration using the CNTs as its cold electron source, showing good potential in high resolution x-ray radiography. Some industrial groups are planning to develop non-thermionic XRS, for which the use of a FES is indispensable. The present work may pave the way to the next generation of x-ray technology.

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D48 - Processing and Property Investigation of Singleand Multi-walled Carbon Nanotube Buckypapers for Composite Application

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The great challenge to take advantage of the exceptional mechanical, thermophysical and electrical properties of carbon nanotubes in high performance composites is to get 1) a homogeneous dispersion of tubes throughout the matrix without destroying their integrity; and, 2) a good carbon nanotube-matrix interfacial interaction. The second factor is specially critical for reaching better mechanical properties. Several chemical processings and different preparation procedures have been extensively proposed, but improvements in mainly mechanical behavior and thermal conductivity are still limited. Due to the nanoscale dimension and intensive van derWaals interactions of the nanotubes, composites made by directly mixing the tubes with polymer matrix have poor tube dispersion and low tube loading. An interesting approach that might soon enable the manufacturing of stronger composites in large scale has been the development of thin membranes, called buckypapers, to form networks of carbon nanotube ropes. Since SWNT and MWNT can form dense networks, a high thermal conductivity is also expected. In this work, we prepared a series of buckypapers of SWNT and MWNT using different water-based surfactants, such as sodium dodecyl sulphate, sodium dodecylbenzene sulphonate, sodium cholate, Triton X-100 and carboxymethylcellulose. Thin membranes up to 50 microns thick were prepared by multiple steps of tube dispersion and suspension filtration and systematically characterized by AFM, SEM, EDS, FTIR and Raman spectroscopy. The effects of surfactant type, dispersion degree, tube concentration in suspension, presence of contaminant and surfactant-tube interaction has been evaluated. Electrical conductivity was also measured.

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D49 - Carbon Nanotubes: an efficient tool for siRNA delivery into mammalian primary cell culture and immortalized cells

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A new and powerful strategy for gene silencing is RNA interference (RNAi), which depends on an efficient intracellular delivery of small double stranded RNAs. Mammalian primary cells are often desired for such experiments due to the similarity to their in vivo counterparts than immortalized cells. This type of cells tends to be more difficult to transfect, which has limited their use for siRNA experiments. Therefore, the siRNA delivery is a critical step for its potential application. Several authors observed that Carbon Nanotubes (CNT) could penetrate into mammalian cells and further transport various cargos, including peptides, proteins, nucleic acids and siRNA (Kam et al, 2005).

The aim of this work was to verify if CNT could be an alternative for efficient siRNAs delivery into hard-totransfect cells, such as cardiomyocytes and Dorsal Root Ganglion (DRG) primary culture. We also investigated the siRNA delivery into SkHep-1 cells, an immortalized cell line. In this study we showed, by immunofluorescence images, that cutted SWCNT can efficiently delivery siRNA into immortalized cell line and also in mammalian primary cell culture, resulting in InsP3R (type I and II) silencing. These results suggest that CNT can be a useful tool for siRNA delivery into several cell types.

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D50 - Microwave-promoted Hydrogenation and C-C Coupling with Palladium Supported on Multi-walled Carbon Nanotubes

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The unique physicochemical properties of carbon nanotubes (CNTs) have stimulated an increasingly research for possible applications in different areas of engineering, fuel cells, and catalysis. CNTs have exceptional strength and stiffness along with high thermal and electrical conductivity. Various beneficial applications, such as field emission displays, nano-scale electronic devices, composite polymers, artificial muscles and hydrogen storage have recently been discovered. These unique properties and their low density have attracted much attention for the preparation of metal loaded nano-particles of controlled size and shapes. In addition, the large surface areas and good conductivity make CNTs ideal supporting materials for the transport and vectorisation of microwaves [1]. Here we report the first use of CNTs-Pd(0) loaded nano-particles assisted by microwave irradiation for: (i) the catalytic hydrogenation of dihydrocinnamic esters, a common structural framework in numerous compounds of biological interest, and (ii) the C-C cross-coupling (Sonogashira reaction) between alkynyl-derivatives and halogeno substrates under eco-friendly experimental conditions.

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D51 - ELCAT project: Electrocatalytic Gas-Phase Conversion of CO_2 in Catalysts confined in Carbon Nanotubes

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In the presence of an adequate electrocatalyst, carbon dioxide can be reduced to useful hydrocarbons (Fischer- Tropsch-like products, C_1-C_{10} hydrocarbons and alcohols). The reaction can take place at room temperature and atmospheric pressure with an appreciable hydrocarbon yield. Tessonnier et al. [1] have already pointed out the interest for using carbon nanotubes as confined reactor to protect air-sensitive materials. Apparently, the morphology of carbon nanotubes seem to have an important influence on the reaction taking place inside their tubule because of the confinement effect and to their high aspect ratio. Here, we report the first results of the use of the confinement effect of the nanotubes to promote unconventional catalytic reactions such as the electrocatalytic gas-phase conversion of CO_2 into FT-like products.

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D52 - Helical organization of short DNA single-strands upon carbon nanotube wrapping

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It has been demonstrated that certain short single and double strands of synthetic DNA can bind to carbon nanotube surface through π-stacking, resulting in a very stable helical wrapping around the tube. This strong interaction makes the DNA/CNT hybrids very promising candidates for a new generation of nanoelectronic devices and nanoscale sensors and for biomedical applications. Moreover, DNA wrapping renders CNTs dispersable in water and allows their separation by type [1]. Carbon nanotube/DNA complexes have been use, e.g. in as a sensor in living cells by monitoring the shifts in the near-infrared emission spectra of SWNTs and to build self-assembled carbon nanotube field effect transistors. All these applications require a fully understanding of DNA-nanotube interaction mechanism which is still lacking. We have carried a systematic study on the interaction of DNA with the carbon nanotube surfaces. In this work we present our findings on the self-organization of poly d(GT) *n* (with n= 10, 30 and 45) and homopolymers of poly dA, poly dC and poly dT (with 20 bases) around single-wall carbon nanotubes (SWNTs). From our circular dichroim (CD) results, we demonstrate for the first time that purified SWNTs growth by HiPco and laser ablation techniques induce the transition of GT-DNA oligonucleotides upon dispersion from the right-handed B-form to the left-handed Z form, without any addition of divalent cations or other chemical species. For homopolymeric single-stranded DNA molecules, the CD results also indicate marked changes on the helical organization. In the particular case of poly dA (pH=8.0), our result suggest that SWNTs act as a π-stacking anchor, providing an improvement of the right-handed helical structure of the molecule. We further demonstrate that the conformation assumed by the GT-DNA sequences is dependent on the chemical groups attached to the SWNT surfaces and the ionic strength. FT-IR, UV-Vis-NIR absorption and AFM results strongly suggest that carboxilic groups drive the poly d(GT) 10 strand to assembly onto the carbon nanotube side-walls without wrap around them. For SWNTCOOH/ d(GT)10 solutions the B-Z transition was only observed after the addition of $HgCl_2$. We discuss the results in terms of the changes of the first hydration layer around the macromolecule.

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D53 - Y junctions: the Full detail Branching Mechanism when S is present

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Assemblying nanostructures into ordered micro-networks remains a challenge in modern nanotechnology. 2D and 3D Ordered Networks based on Carbon nanotubes (ON-CNTs) have been proposed, showing intriguing mechanical and electronic properties of the assembled arrays [1]. In order to achieve the challenging task of an experimental network, a first step is to study in full detail the obtention of a node (multi-terminal junction of CNTs). CNTs multi-terminal junctions (>2 terminals) were first theoretically proposed as a “Y” junction [2], which has obtained special interest motivated by its potential electronic properties as nanodevices [3]. Since then experimental advances in their synthesis have been reported; outstanding, due to the higher yield of such nanostructures, the CVD process: by pyrolysis of methane over cobalt supported on magnesium oxide [4] or by pyrolysis of nickelocene along with thiophene [5]. Unfortunately, little is known regarding the Branching Mechanism that produces such nanostructures, basic knowledge that is necessary to improve the efficiency and control of their synthesis. The present work reproduces the synthesis results reported with thiophene and nickelocene [5] in order to perform an exhaustive high resolution characterization of the nanostructures, to understand and elucidate the Branching Mechanism that produces such Y junctions during the synthesis. The experimental evidence obtained by SEM, STEM, HRTEM and High Resolution EDX measurements together with full DFT calculations allowed to understand in full detail the Branching Mechanism, from the Driving Force that originates the opening of a branch until the structural detail of the final junction at the graphene layers level. The exhaustive High Resolution characterization revealed that the structure of the junctions obtained from pyrolysis of nickelocene and thiophene [5] correspond to Y junctions of cone-stacked carbon cylinders.

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D54 - Single wall carbon nanotubes adsorbed with oligonucleotides disrupts appressorium formation in the fungus Uromyces appendiculatus

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We describe the adsorption of oligonucleotide sequences to the surface of a single wall carbon nanotube by non-covalent interaction, the introduction of the oligonucleotide nanotube complex inside a fungal cell, and the disruption of a physiological event of the cell due to the oligonucleotide. Moreover, we show by Infrared spectroscopy and Atomic Force microscopy that the oligonucleotide are deposited around the nanotube in a ordered fashion. Infrared analyses also show that the nanotubes are able to cross the cell wall and cell membrane barrier and accumulate inside U. appendiculatus cells. Fungal cells are not phagocitic therefore, the presence of carbon nanotubes inside the cell is probably a passive phenomenon. The oligonucleotide sequence used is a portion of the Inf24 gene in an antisense configuration. The oligonucleotide sequence in sense has no effect in the cell physiology as describe previously (Barja et al., 1998). The treatment of U. appendiculatus cells with nanotube+antisense Inf24 sequence results in inhibition of cell differentiation (appressorium formation). The sense +nanotubes, natotubes alone or oligonucleotides (sense or antisense) sequences by itself did not inhibit appressorium formation. The procedure can be used in the future for gene silencing in gene therapy protocols, the study of gene function on cells and the development of new disease control protocols. The standard procedure for gene disruption in U. appendiculatus is the microinjection of antisense sequences. However, this method is laborious and cumbersome. We believe that oligonucleotide adsorbed nanotubes are a far more efficient and will replace microinjection in the future as the method of choice.

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CONTRIBUTED ABSTRACTS

POSTER SESSION E

JUNE 28 (Thursday)

E01 - Non-auxetic to Auxetic Transition in Carbon Nanotube Sheets

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We report Poisson's ratios measurements of carbon nanotubes (CNTs) sheets. The sheets were formed from suspensions employing ultra-sonication to disperse the CNTs into a surfactant solution of Triton X-100 in water. The single-walled nanotubes (SWNTs) used in this study were made by the HiPco process while the multi-walled nanotubes (MWNTs) were grown using a CVD growth method employing iron catalyst and a feedstock of acetylene diluted in helium. Carbon nanotube sheets comprised of SWNTs, MWNTs, and six intermediate mixtures of the two types of nanotubes were formed using identical filtration and drying processes. We observed a negative in-plane Poisson's ratio (a property of auxetic materials) of about 0.20 for 100% MWNTs sheets and a transition to positive values when SWNTs are mixed in MWNTs sheets. The measured thickness-direction Poisson's ratios were 0.75 and 0.33 for as-produced MWNT and SWNT sheets, respectively. As often observed experimentally for quite different materials, the negative Poisson's ratio for the MWNT sheet appears to enable a relatively giant Poisson's ratio for the orthogonal direction. A simple model is presented for the complex structure of the CNTs sheets. The model captures basis features of the CNTs sheets by mimicking the fiber arrangements through the presence of levers and void spaces as the ones observed in the random in-plane real network sheet. The nanotube fibers are represented by struts connected by rigid junctions. Two elastic mechanisms were considered: the stretching mode, associated to the elongation of the struts, and the hinging mode, due to the movements at the junctions due to angle changes. The analytically derived Poisson's ratios from this strut/junction array qualitatively reproduce the non-auxetic to auxetic transition.

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E02 - Energy barrier for extinction of buckling in carbon nanotubes

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We have investigated the process disappearing a buckling of carbon nanotubes using the current-induced thermal energy. The fullerene-encapsulated single wall nanotubes were used, which enables us to estimate an energy barrier of the process from the well-known coalescence reactions. The nanotubes were aligned and protruded from the edge of a Pt-coated Si substrate to prepare a nanotube cartridge. The nanotube cartridge and a Pt-coated Si tip were set on manipulation stages installed in a transmission electron microscope (TEM) with an acceleration voltage of 90 kV. The Si tip was manipulated to contact to a free end of a nanotube in the cartridge and push it until a buckling was formed. A voltage was applied to flow current through the buckled nanotube.

The change of the nanotube with fullerenes was observed as a function of the current. The coalescence of fullerenes started first at 3 micro-A (for 3-nm diameter of the initial stage of the nanotube) (a) and proceeded to form a tube structure with increasing the current to 21 micro-A (b), the coalescence of the grown tubes with the original nanotube started (c) and was completed at 25 micro-A (d), the buckling disappeared at 23 micro-A (the voltage was same as in (d)) (e), and then the sublimation proceeded to reduce the diameter (f) and finally the nanotube was broken (g). In (f) the current continuously decreased to 15 micro-A just before the breaking even the voltage was increased.

This sequential change of the structure is due to the increase of the temperature. From the previous works; coalescence of fullerenes at ~1500?K within 24 h [1], coalescence of tubes at ~1800?K within 2 h [2] and sublimation of nanotubes at 2500?K within 1 min [3], their barriers can be roughly estimated using E=kTln (vt) where $v \sim 10^{12}$ Hz and k is the Boltzman constant. Those are ~5 eV, ~5.7 eV and ~6.9 eV, respectively. The order of these values is consistent with the experimental results and suggests that the barrier of the extinction of buckling is between 6 eV and 7 eV.

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E03 - Simultaneous Dielectrophoretic Separation and Assembly of Single-Walled Carbon Nanotubes on Multi-Gap Nanoelectrodes and Their Thermal Sensing Properties

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The unique physical and chemical properties of carbon nanotubes have attracted wide interests. Single-walled carbon nanotube (SWNT) arrays devices were indicated to potentially serve as novel thermal sensors with low power consumption. By using the specifically designed multigap nanoelectrodes, we demonstrated an effective approach for the simultaneous dielectrophoretic separation and assembly of metallic and semiconducting singlewalled carbon nanotubes (SWNTs). An approximate metallic-semiconducting-metallic multiarray structure was created by an inward-propagative sequential assembly of SWNTs under ac electric field. Such kinds of SWNT multiarray structures exhibited ultra-low-power consumption and excellent thermal sensing performances with the sensitivity being dependent on the number of gaps: the more gaps, the higher sensitivity. The effective separation of metallic and semiconducting tubes in different gaps is believed to be responsible for the improved sensitivity to temperature.

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E04 - Thermal Stability of Peapod-derived Double Walled Carbon Nanotubes

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Recently much attention was paid on double-walled carbon nanotubes (DWNT) because it is proved that they exhibit different physicochemical properties compared to single walled carbon nanotubes and multi-walled carbon nanotubes, due to their coaxial morphology. Up to now, there are three ways of preparing DWNTs: catalytic chemical vapor deposition, thermal treatment of nano-peapod, and arc method [1-3]. The structural and thermal stabilities of DWNTs strongly depend on their synthetic methods. Therefore, it is important to evaluate thermal stabilities of both CCVD-derived and peapod-derived DWNTs comparatively. In this study, we investigated structural and thermal stabilities of both DWNT samples in detail by using Raman spectroscopy, thermal gravity analysis, scanning field emission microscopy and transmission electron microscopy.

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E05 - Carbon and Inorganic Nanotubes under radial compression

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Theoretical investigations on the mechanical properties of nanotubes are important for their understanding and for the development and improvement of nanocomposites and nanodevices. This is especially important as there is still a large gap between practical applications, which partially resulted in products, and the understanding of the properties which make these nanoparticles unique.
In the present work we investigate the behaviour of various organic and inorganic nanotubes (carbon, BN and MoS_2) with different chiralities under uniradial compression. We employ a hybrid method using molecular mechanics (MM) and quantum mechanics. Two grips, parallel to the tube axis, provide the pressure acting through a Lennard-Jones potential. The tubes are described using approximate density-functional theory with dispersion correction (DC-DFTB). The results show the different response of the nanotubes to the mechanical load, a decrease of their mechanical resistance was observed in the sequence C!BN!MoS2. The final structures of the squeezed carbon and BN nanotubes depend on the chirality: for armchair tubes the graphite-like and for zigzag tubes haeckilte-like monolayers were obtained, whereas MoS2 nanotubes decompose, independent on their chiralities, into two MoS_2 nanostripes.

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E06 - Effect of the thermal treatment on the oxidative resistance of CNTs

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The use of CNTs in various fields such as electronic, optoelectronic, reinforcement materials or catalyst support have received a huge scientific interest because of their outstanding physico-chemical properties. New developments on the low cost synthesis of these carbon nanomaterials by catalytical route allow the significant reduction of the cost and render these materials more accessible. However, the remaining problem is the oxidative resistance of these nanomaterials. Most of their foreseen applications require them to resist to high temperature in aggressive atmosphere conditions. Our present study reports the CVD synthesis of CNTs using a mixture of C_2H_6 and H_2 on iron supported on -Al_2O_3 as catalyst. The reproducibility of the synthesis (in terms of yield, morphology and thermal resistivity) and the influence of the most common treatments - acidic treatment, low medium and high thermal treatments under inert gas - on their oxidative resistance in air have been investigated. Simultaneously, the amount of non carbonaceous impurities (catalyst and support) has also been quantified after each treatment. The present work reveals that the oxidative resistance of crude CNTs can be improved by more than 200 °C with a significant decrease of non carbonaceous impurities after high thermal treatment under inert gas.

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E07 - Evaporation of Various Metals on Vertically-Aligned Single-Walled Carbon Nanotubes and Bonding Their Metal Surfaces to Bulk Metals

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For prospective electronics and thermal applications of Vertically-Aligned Single-Walled Carbon Nanotube (VASWNT) films, electronic contact resistance and thermal boundary resistance between metal and the VASWNT film is extremely important.

Aiming at obtaining low resistive contact, metal evaporation of different metals (Au, Ti, Al and Pd) onto VASWNT films was studied. Observations through Scanning Electron Microscopy (SEM) showed a clear metaldependence of the deposition layer structure on the VASWNT film, reflecting the wettability and cohesive energy of each metal. These characteristics also influence the structures of the metal penetrated through the top surface into the VASWNT film, where metal forms particles inside the VASWNT film except for Ti, which wets the SWNT bundles. Furthermore, annealing of the Au-deposited VASWNT film was performed at different temperatures. As a result, the annealing was found to be effective to flatten the metal surface and to reduce the amount of penetrated metal particles. We also observed that, under certain conditions, the annealing results in peculiar morphology: rupture of the VASWNT films by the deposited metal.

In addition, we have attempted to bond the Au-deposited VASWNT film to bulk metal. This was done by connecting the Au-deposition layer to a metal block with a bonding material in between and annealing the whole system in argon gas. A systematic study was carried out for different bulk materials (brass and copper), bonding materials (gold foil and silver wax), and annealing temperatures (600-850°C). The results show that the sufficiently firm connection can be achieved at around 750°C for most of the tested combinations of bulk and bonding materials. The bonding technique opens up the possibility for various electronics and thermal device application of the VASWNT film.

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E08 - Alkali Metal Doping of Carbon Nanotubes in the Low-Concentration Regime: Non-Homogeneous Deformations and Defect States

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Alkali metal doping of single-wall carbon nanotubes (SWNT) is a topic of strong interest recently. From analogies with graphite intercalated compounds, where it is generally assumed that each alkali metal atom donates one electron to an extended conduction band state of the SWNT, it is expected that extra electrons produce homogeneous lattice expansion and therefore downshifts of phonon frequencies. Chen et al. [1] performed Raman scattering studies of K-doped isolated SWNTs that showed a non-monotonic frequency shift of the high-frequency tangential (G) band. In this work, we explore the low-concentration regime of donor impurities in SWNTs. Our calculations are based in pseudopotential scheme and density functional theory within the local-density approximation (LDA), using the SIESTA code. We find that charge-induced deformations are non-homegenous and depend on the nanotube chirality.We also find that extra electrons are localized around the impurity, giving rise to defect states.

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E09 - A critical view on pressure induced phase transformations in carbon nanotubes as studied by Raman spectroscopy

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Recent results on the high pressure Raman scattering of bundled or individualized carbon nanotubes are presented. Theoretical results and experiments agree on the existence of pressure induced phase transitions based on the evolution of the nanotube cross sections. In particular ovalization has been predicted as taking place at pressures range from 1 to 3 GPa for 1.4 nm diameter tubes. Based on our recent results on the high pressure studies of individualized nanotubes [1] and on bundles of nanotubes and peapods [2] as well as the existing literature, we address a critical overview of the pressure effects on single wall carbon nanotubes. Two main aspects are discussed: i) the effect of the pressure transmitting medium [1,3] and ii) the evolution of resonant conditions with pressure.

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E10 - Structural stabilization of carbon nanostructures through nitrogen and boron doping

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Since their discovery in 1991, the outstanding mechanical and electronic properties of carbon nanotubes have been shown by many research groups. It has been theoretically predicted that carbon nanotubes properties depend of their diameter and chirality. Depending on the nanotube growing technique, the carbon branched structures and topological defects can be observed through the nanotube structure. These topological defects can be formed due the inclusion of five-, seven-, or eight-membered rings in the hexagonal network of carbon bonds. In this work it was analyzed the role played by the inclusion of nitrogen and boron atoms in the structural stabilization of defective regions of junctions and bends. Geometry optimizations were carried out through quantum chemistry calculations based on Hartree-Fock (AM1 and PM3 semiempirical methods) and Density Functional (B3LYP functional) theories. Results of theoretical studies on nitrogen substituted carbon nanojunctions showed that the nitrogen is best accommodated in pentagonal sites, resulting in a structural stabilization of defective regions [1-3]. Preliminary results on B-N pair substitution in carbon bonds network showed that there is a preferential distribution of the B-N pair in the defective regions. This also will result in a structural stabilization of $B_xN_yC_z$ nanostructures.

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E11 - Carbon Nanotubes as gas sensors: a first-principles Study

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One promising application of carbon nanotubes is the fabrication of chemistry sensors for gas detection. Recently [1] it was experimentally shown that the effect of the interaction between distinct gases and the nanotube on the system capacitance is specific and may be used to build a capacitive sensor device. In this work we have applied first-principles calculations based on the Density Functional Theory (DFT) in order to analyze the interaction of carbon nanotubes with distinct molecules (benzene and oxygen, for instance) and determine the effect of the interaction on the nanotube capacitance. For each molecule we first determine the equilibrium geometry close to the nanotube wall, then we do calculations in distinct charge states to obtain the capacitance. Our results show that there is a definite relationship between the change of the density of states (DOS) close to the Fermi level upon interaction of the nanotube with the oxygen molecule and the change of the capacitance, which means that the quantum contribution to the capacitance may be used to sense oxygen molecules. As for the benzene, the effect on the capacitance is null, as well as the change in the DOS close to the Fermi level. We employ the SIESTA [2] implementation of the DFT formalism, which makes use of pseudopotentials and a basis set composed of pseudo atomic orbitals of finite range.

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E12 - Objective Molecular Dynamics

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We present a generalization of periodic molecular dynamics that we term *objective molecular dynamics*. It is a method of doing molecular dynamics for a restricted set of atoms, nonperiodically mapping the time-dependent displacements of this small set of atoms onto the full, typically infinite structure, such that the full structure satisfies exactly the full, unconstrained set of equations of molecular dynamics subject to certain group-invariant initial conditions. The method is applicable to a wide variety of interesting molecular structures including the tails, capsids and other parts of many viruses, carbon nanotubes, many of the common proteins, C_{60} and many other nanostructures now being synthesized, especially via the process of self-assembly. Overall, the strength of the proposed symmetry-based approach is that (i) it heavily reduces the computational effort through a drastic reduction in the number of atoms to be accounted for, (ii) it is compatible with full quantum mechanics, and (iii) the implementation can be done in a general framework, allowing for simulations of a larger class of structures. In addition (iv) the scheme is ideal for obtaining nanomechanical responses since it allows for applying various mechanical deformations. The method is illustrated by simulations of carbon nanotubes.

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E13 - DFT study of a possible ferromagnetism in carbon-based nanostructures

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Based on first-principles calculations of carbon-based nanostructures, the existence of a possible ferromagnetic coupling between magnetic adatoms is shown. Even if experimentally the question of a spontaneous magnetism is still under debate [1, 2], various DFT calculations have demonstrated the role played by non-magnetic intrinsic defects and impurities in nanotubes and graphene [3]. Recently, irradiation experiments have confirmed this possibility [4]. Besides, in the more general context of electronic transport, understanding the influence of these defects is of first importance. Here we present DFT studies of structural stability, electronic properties and magnetism of carbon adatoms on nanotubes and graphene sheets. In particular, it is shown that a ferromagnetic ordering is, in most cases, a stable configuration. Depending on the exchange-correlation approximations used, the energy difference between antiferro and ferromagnetic states can be largely enhanced. The special case of the hybrid functionals [5,6], which are known to provide better magnetic properties than standard functionals do, will also be reviewed.

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E14 - Zero-Temperature and Elastic Weak-Localization Correction to the Conductance of Infinite Metallic Single Wall Carbon Nanotubes

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Using a pi-orbital tight-binding (TB) model within a perturbative formalism, the effects of substitutional impurities on the conductance of infinite metallic single-wall carbon nanotubes (MSWCNTs) are studied. The perturbative scheme is based on the energy dissipation of electrons travelling through the nanotube. A general expression for the differential conductance (DC) is presented, and scattering processes are investigated. It is demonstrated how the DC depends sensitively on the nature of the electronic band structure and velocity of carriers moving in the nanotube.We have shown that the quantum interference (QI) of electronic waves scattered by impurities plays a meaningful role. In particular, for the case of a couple of impurities the DC exhibits periodic oscillations comprising both positive and negative values. The negative differential conductance (NDC) stemming from the QI and rotational symmetry selection rule is very sensitive to the relative distance and symmetry of two impurities. This signature is absent for the case of a single impurity. In fact, the NDC can be attributed to the zero-temperature/elastic weak-localization correction to the conductance. As a result, the faster/higher and slower/shorter oscillations can then effectively be achieved by metallic zigzag and armchair nanotubes, respectively [1].

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E15 - Aharonov-Bohm conductance modulation in Ballistic Carbon Nanotubes

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When a magnetic field is applied parallel to the axis of mesoscopic rings or cylinders, the phase of the wave functions for each of the ring's arms are out of phase one to each other which in turns modulates the electronic transmission coefficients of the system. This quantum phenomenon, referred as the Aharonov-Bohm effect, is responsible for Phi_0=h/e periodic oscillations of the conductance. In this context, systems of particular interest are ballistic carbon nanotubes (CNT) since they can be viewed as mesoscopic cylinders made from concentric rolled graphene sheets. The so-called Aharonov-Bohm effect is expected to drastically alter the allowed **k**-vectors along the circumference of the nanotubes resulting in a periodic energy gap modulation. We report on magnetoconductance experiments in ballistic multiwalled carbon nanotubes threaded by magnetic fields as large as 60 Tesla [1]. In the high temperature regime (100K), giant quantum flux modulations of the conductance, mediated by electrostatic gating, are unveiled. Evidence is given for an unambiguous manifestation of the Aharonov-Bohm modulation of the electronic band structure. We infer an energy gap opening for the external shell from a simple tight binding calculation. A quantitative interpretation of experimental data is achieved by computing the electronic transmission properties within the Landauer/Büttiker theoretical framework and assuming a field dependent band bending profile at the nonatube/metal interface.

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E16 - Ultra-Large Scale Directed Assembly of Single-Walled Carbon Nanotube Devices

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We present the ultra-large scale assembly of individually addressable carbon nanotube devices, by dielectrophoretic deposition, where the nanotubes are self-limited to one per device. We establish that the accepted mechanism for single-nanotube self-assembly is incorrect due to the unique metal-nanotube contact properties. Instead, we propose, using experiments and numerical simulations, an alternate mechanism to explain this observed self-limiting behavior. We also demonstrate that using capacitively-coupled electrodes for dielectrophoretic deposition introduces the element of scalability in our deposition scheme, allowing us to increase the electrode array density, while maintaining the ability to electrically address each device individually. Combining these two advances, we demonstrate the fabrication and characterization of a high-density array of individually-contacted single-walled carbon nanotube devices. We achieve densities of more than 1 million devices per cm2, which is at least three orders of magnitude higher then what has been possible before with carbon nanotube devices, and comparable to the current integration density in microelectronics, namely, 'ultra-large scale integration'. The results are significant in that they provide a one-step process to fabricate a large-density of independent single-nanotube electronic devices, which has been one of the biggest hurdles in the advancement of carbonnanotube based electronics.

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E17 - Improvement Of Contacts Formed Bewteen Carbon Nanotubes And Metal Electrodes By Dielectrophoresis

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Due to exceptional combination of electrical, mechanical, optical and other properties, carbon nanotubes (CNTs) are considered as building blocks for future nanoelelctronics and NEMS (nano-electromechanical systems) [1]. In order to realize high potential of this nanomaterial in nanodevices, it is necessary to develop methods of controlled deposition between pre-fabricated micro- or nanoelectrodes [2]. Here, a method of AC dielectrophoresis using aquous solutions of CNTs with SDS as a surfactant was applied to align and deposit individual multi-wall nanotubes (or bundles of single-wall nanotubes) between pre-fabricated metal (Au, Pd) electrodes with a micron scale separation [3]. Due to poor contact quality, the two-terminal resistances for as-deposited nanotubes were measured to vary widely, between dozens of kΩ to a few M, depending on the metal and the deposition conditions. No clear correlation was observed between the nanotube length and the resistance. Poorer contacts were observed for Au electrodes. For improvement of nanotube-electrode contacts, metal (Pd and Ni) electroless process was used. Significant improvement of 2 terminals resistances was demonstrated, especially after samples annealing at 150-300 °C. Besides the conventional annealing, dynamic annealing was observed while varying potential was applied between electrodes. Under these conditions, linear I-V dependence was measured indicating that contact resistance was improving as current through the contact areas was increasing. Further, using ion beam deposited Pt contacts, 4 terminals measurements have been performed to evaluate precisely the intrinsic nanotube resistances. The values between 30 and 130 kΩ/μm were obtained for nanotubes with diameters in the range from 40 to 15 nm, respectively. The contact resistance between multi-wall nanotube and metal (Pd, Ni) electrodes were evaluated to be as low as 15-20 kΩ.

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E18 - Low frequency 1/f noise of Single Walled Carbon Nanotube network transistors.

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The low frequency 1/f noise is studied with single walled carbon nanotube(SWNT) network field effect transistors. In spite of geometrical complexity of nanotube networks in the channel area, large number of tube-tube/tubemetal junctions and scattering centers due to adsorbed gases on the tube wall, the noise power shows about the same level with the single-SWNT transistors. Detailed analysis is performed in the point of number of mobile carriers and mobility by the different environment (i.e. ambient air and vacuum) during the measurement. This shows that change in the number of mobile carriers is more dominant factor to the 1/f noise level for CNT-network transistors.

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E19 - Nanotube based microelectronics interconnections

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Many applications are expected to take advantage of the outstanding properties of carbon nanotubes. Amongst extreme heat removal efficiency, enhanced composite strength or high surface capacities for batteries, carbon nanotubes are increasingly expected to be used in fluidic membranes and even more challenging is their applications as electronic transport wires in nanoelectronics industry. Our work is focused on integrating carbon nanotubes into microelectronic chips in order to build electronic pathways for future technological nodes dictated by the famous Moore's law. Interconnections are most critical features for increasing performance. Smaller vertical interconnects (called vias) to be achieved are about 30nm wide. In these conditions, carbon nanotubes therefore appear ideal for their high conductivity at this range. Our goal is to be industrially compatible meaning that all processes have to be achieved on at least 200mm Silicon wafers respecting limited thermal budgets.

The main issues are catalyst localization at the bottom of the vertical via openings, growth on copper lower electrodes, which means engineering steps to find proper diffusion barriers, and global low temperature achievement.

Two new integration schemes that counteract these issues will be presented. In these approaches, the catalyst localization is obtained without additional photolithography steps and interaction between etching plasma and catalyst. Moreover, the developed processes are compatible with microelectronics baseline. CVD growth on copper substrates is studied and a highly conductive Cu diffusion barrier is therefore required. We demonstrate an AlNi 10nm stack allowing CVD nanotube growth.

Finally, 140nm wide nanotube vias interconnects arrays obtained at 520°C using industrial reactors are exhibited. Nanotube density in each interconnection is equivalent to $5 \times 10^{10}/\text{cm}^2$ with densely packed nanotubes around 10nm in diameter. First electrical tests performed on 300nm via holes show resistances about 80 Ω.

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E20 - Diffusion of Fe in aligned multi-walled carbon nanotubes by high-temperature treatment

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Residual catalysts can be effectively removed from the multi-walled carbon nanotubes by high-temperature treatment. To understand the purification process clearly, aligned multi-walled carbon nanotubes (AMWNTs) with different length were heated in vacuum environment, and the escaping rate of Fe catalyst was analyzed. The rate of Fe removing in AMWNTs decreases with increasing the length of AMWNTs, which indicates that the residual catalyst, mainly Fe, is evaporated and diffused mainly along the axial direction. The diffusion coefficient of the Fe calculated from the experimental result is $5*10^{-6}$ cm^2/s, which is smaller than that of the theoretical calculation of the single-walled carbon nanotubes reported. The main reason of the low value of the diffusion coefficient is due to the presence of the curved graphene caps in the channel of AMWNTs.

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E21 - Through wafer via filling with carbon nanotubes, integration for packaging applications

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Carbon nanotubes promise great applications in many industrial fields including microelectronics, especially for thermal management and electrical conduction. It has been shown that Carbon Nanotubes are good candidates for device packaging improvement [1]. The aim of this work is to evaluate the feasibility of a 50 µm wide and at least 150 µm deep through wafer via filled with long multiwall carbon nanotubes. Dissociation of silicon substrate and carbon nanotubes electrical conduction contributions need to be achieved. Thus, an isolating barrier layer has to be deposited on the wafer to separate the different contributions. In the first part of the project, we studied different possibility to produce this barrier (silicon oxide SiO_2 or silicon nitride Si_3N_4 and its impact on carbon nanotubes growth on silicon wafers. The second part of the project deals with integration questions and feasibility for the final structure; difficulties to overcome will be discussed. This device is devoted to thermal and electrical tests. This work is sponsored by the French National Research Agency (ANR).

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E22 - Modelling the effect of randomly dispersed doping agents incarbon nanotubes

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Theoretical studies of how the electronic properties of carbon nanotubes are affected by one isolated doping agent are 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. It is based on suitable sum rules for the Green functions of the impurity-free nanotubes and does not rely on band-structure fitting. The resulting parametrization allows us to describe disordered systems without missing the important contributions due to charge transfer and screening. The method is illustrated with hydrogen atoms adsorbed to a nanotube, for which the transport properties are subsequently investigated.

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E23 - Torsional Electromechanics of Carbon Nanotubes

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Carbon nanotubes are known to be distinctly metallic or semiconducting depending on their diameter and chirality. Here we show that continuously varying the chirality by mechanical torsion can induce conductance oscillations, which can be attributed to metal-semiconductor periodic transitions. The phenomenon is observed in multi-walled carbon nanotubes, where both the torque and the current are shown to be carried predominantly by the outermost wall. The oscillation period with torsion is consistent with the theoretical shifting of the corners of the first Brillouin zone of graphene across different subbands allowed in the nanotube. Beyond a critical torsion, the conductance irreversibly drops due to torsional failure, allowing us to determine the torsional strength of carbon nanotubes. Our experiments indicate that carbon nanotubes could be used as self-sensing torsional springs for nanoelectromechanical systems (NEMS).

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E24 - Quantum transport in “real“ carbon nanotubes

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Carbon Nanotubes (CNTs) are constantly attracting the interest of researchers because they offer the opportunity of investigating fundamental physical properties at the nanoscale and being exploited as building blocks for nanoelectronic devices. Among the different possible applications of CNTs, the present work focuses on their use as nanosensors for gas detection thanks to the change in conductance of the nanodevice in presence of the gas to be detected. To reach this goal, the structural, electronic and transport properties of CNTs have been investigated for perfect tubes, tubes containing defects such as vacancy, di-vacancy, oxigenated vacancy, and tubes decorated with metal clusters.

Due to the “nano“ size of the systems under investigation, atomistic simulations become necessary for an accurate modelling of their structural, electronic, and transport properties. Indeed, effective bulk parameters cannot be used for the description of the electronic states since interfacial properties play a crucial role and semiclassical methods for transport calculations are not suitable at the typical scales where the device behavior is characterized by coherent tunnelling. Consequently, quantum-mechanical computations with atomic resolution can be achieved using localized basis sets for the description of the system Hamiltonian and can predict electronic and transport properties of nanostructures.

In the present work, the structural and electronic properties of CNTs are obtained via the *ab initio* method as implemented in the SIESTA code, *i.e.* the calculations are based on density functional theory (DFT), using norm-conserving pseudopotentials (Troullier-Martin) and atomic orbitals basis set. The quantum conductance of the system is achieved from electronic transport calculations performed with the SMEAGOL code. The latter is based on the non-equilibrium Green’s function (NEGF) formalism and uses the one-particle Hamiltonian obtained from the DFT calculations. Such approach, which combines NEGF and DFT, allows us to model real systems constituted by hundreds of atoms to a high degree of accuracy.

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E25 - Studies of electronic transport properties in topgated MWNTs

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There has been a vast amount of studies of electronic properties in single wall carbon nanotubes (SWNTs) and also multiwalled carbon nanotubes (MWNTs), but the area between large diameter MWNTs and SWNTs is not yet well mapped. Probing electronic properties of thin MWNTs can give insight to interesting phenomena like the interlayer conduction in carbon nanotubes. We fabricated devices with intermediate size MWNTs on a heavily doped Si-wafer, which was thermally oxidated and could then be used as a backgate. Some of the samples were fabricated with an additional local topgate which could be tuned separately from the backgate. We studied the effect of having separately adressable topgate and backgate on the conductance of the tubes. Measurements were done at temperatures ranging from room temperature to liquid helium temperature. Special attention was given to conductance in the gap region of the MWNTs. Also we observed a hysteresis in the gate depedence of the conductance at room temperature, which was gradually getting smaller with decreasing temperature. The hysteresis could be of interest for future memory applications.

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E26 - Transport properties of nanotube-based sensors: a general approach

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One remarkable characteristic of nanotubes is that their conductance may be strongly affected by the interaction with impurities, enabling them to be used as efficient nanoscopic sensors. From the theoretical point of view, the study of how a nanotube responds to the presence of a foreign object is usually carried out in two separate stages: one that addresses the conditions under which a single object adheres to the nanotube (often by ab-initio techniques), and another that investigates the subsequent effect that this interaction brings to the transport properties of the quantum device (usually by semi-empirical methods). These two stages are often performed separately, disconnectedly and with a reduced degree of transparency due to the heavy numerical calculations involved. Here we make use of a method that integrates both stages of the calculation by deriving a simple and transparent way of obtaining the change in the electronic density of states due to the interaction between tube and foreign object. This quantity is shown to be directly associated with both the binding energy and the charge transfer between the parts, establishing a link between these two latter measurable quantities. The method is sufficiently general and capable of treating different types of objects. Results are illustrated with atomic impurities adsorbed to the walls of a nanotube. We argue that this method can be used to provide general guidelines on the absorption process, including the ideal combination of tube and foreign object required to produce significant changes in the conductance of a sensor.

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E27 - Electrical characterization of a field-effect transistor based on a random network of single-wall carbon nanotubes

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In this work, we report on the fabrication and performance of field-effect transistors (FET) based on random networks of single-wall carbon nanotubes and their electrical transport properties. The network of nanotubes is located on the top of a Si/SiO$_2$ substrate and bridges the gap between two Ti/Au electrodes. An electrical contact is made to the doped silicon substrate that acts as a back gate. We have measured the current-voltage characteristics and the transconductance of the devices at different temperatures and with and applied magnetic field. The behavior of nanotubes network is similar to that of a p-type MOSFET. Immediately after biasing the gate, we observe a decrease of the source to drain current with time. This is tentatively assigned to a charging effect on the contacts between the metal and the bundle of nanotubes. At low temperatures we also observe a change in the drain source current versus drain source voltage - Ids x Vds curves - with a large decrease in the conductance at low (< 0.1 V) Vds and a turning on effect at larger (> 0.2 V) Vds. This behavior also depends on the gate voltage with a large suppression of current for lower gate voltages.

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E28 - Electronic and transport properties of phosphorus and nitrogen-phosphorus doped carbon nanotubes

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Carbon nanotubes have been an important subject of research for several years due to their mechanical and electronic properties, which makes them suitable in a wide range of applications, varying from reinforcement on composite materials to components in electronic circuits. Recent experimental work has shown that during the growth stage, carbon nanotubes can be doped with phosphorus, which can behave as an electron donor. In this work, we explore the electronic structure of phosphorus and nitrogen-phosphorus doped carbon nanotubes using density functional theory within the local spin density approximation (DFT-LSDA). The stability of the proposed structures is studied by molecular dynamics simulations. The electronic transport properties of these structures are also studied. Phosphorus doped nanotubes could lead to new applications as chemical sensors based on the reactivity of the doping atoms.

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E29 - Electronic and Transport Properties of Carbon Nanotube Double Quantum Dots

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The electronic and transport properties of carbon nanotube double quantum dots has been studied over the last years [1]. Recent experimental studies have shown that it is possible to modify locally a small segment of a SWCNT applying a gate voltage over the tube. By placing several of such local gate voltages on the SWCNT, a double quantum dot can be constructed which shows a tunable inter-dot coupling [2]. From the theoretical point of view, a double quantum dot can be model by joining several segment of different SWCNT using pentagonheptagon defects [3] or by simulating the confinement made by the gate potentials in specific regions of a pristine SWCNT.

In this work we show a theoretical study of the electronic and transport properties of carbon nanotube double quantum dots formed by zigzag nanotubes with different electronic behavior. The systems are described using a single band tight binding Hamiltonian. The electronic conductance and the density of states of the systems are calculated within the Green function formalism based in real-space renormalization techniques [4, 5]. The current curves are calculated using the Keldysh formalism [6]. Symmetry effects and gate voltages applied on the dots are investigated.

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E30 - Quantum Transport in Carbon Nanotubes : Role of Electron-Phonon coupling and chemical doping

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In this contribution we analyze the role of (i) chemical doping and (ii) electron-phonon coupling, on quantum transport in carbon nanotubes. In the first part, the different quantum transport phenomena in chemically doped carbon nanotubes is presented [1], exploring for the first time the transition from weak to strong localization regime at a quantitative level. The extraction of transport length scales such as elastic mean free path and localization lengths are performed by using both the Kubo and the Landauer-Buettiker transport formalisms, and the Thouless relationship between both quantity is well satisfied.

In the second part, we focus on the effects of electron-(optic)phonon interaction on transport through carbon nanotubes. A novel inelastic backscattering mechanism which suggests a different scenario in the high bias regime is presented. This many-body mechanism [2], which can be seen as the removal of degeneracies in the electronphonon Fock space, is fully activated when driving the system out of equilibrium, and is theoretically unravelled by means of a theoretical treatment beyond the commonly used mean field approach.

Specifically, we consider the case of a longitudinal optical phonon mode in metallic zig-zag and armchair carbon nanotubes. By using a full quantum description of the joined processes of tunneling and phonon-assisted transport, the interaction between electrons and optical A1(L) phonons is shown to result in nonequilibrium energygaps opening at half the phonon energy above (below) the charge neutrality point, owing to phonon emission (absorption) [2]. As a result, an onset of current saturation develops as soon as incoming electrons in the nanotube gain sufficient kinetic energy to explore the electron-phonon Fock space. The case of semiconducting nanotubes is further developed. It is shown that similar inelastic backscattering phenomena take place, but become strongly diameter-dependent [3].

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E31 - Field emission as a sensitive probe of nanotube geometry

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Many potential applications of single, isolated carbon nanotubes depend on a precise knowledge of their geometry, such as their length. While such knowledge may be obtained with electron microscopes or scanning probe techniques, an all-electrical method would be preferred for applications. Here, we demonstrate the use of field emission of electrons from the tip of an individual cantilevered carbon nanotube as a sensitive and practical means of measuring various properties of the nanotube's geometry.

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E32 - Electron field emission for a cylindrical emitter of single carbon nanotube

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We investigated the results of experimental and theoretical methods on the property of the enhancement factor from a cylindrical emitting surface. For the calculation of the tunneling probability, we used the Simpson integral formula in C programming language. And we get the equation of tunneling current density. The graph of I/V^2 vs I/V of our result is not linear. These results are nearly coincident with our experimental observation.

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E33 - Alignment Behavior of Magnetic Particle-SWNT hybrids and Their Emission Characteristics

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Carbon nanotubes (CNTs) have attracted considerable attentions to their potential applications in the emission materials, because of their high aspect ratio, high emission current density and chemical stability. [1] For such applications, it requires that CNTs be aligned over large-scale, and have long-time stability. Here, we investigate the effect of alignment and emission properties of a magnetic particle attached - CNTs (MP-CNTs), in which the magnetic nanoparticles were constructed via thermal decomposition in high boiling solvent by metal chloride and sodium oleate. [2] The nanoparticles were attached to the CNT surface during thermal reaction process. We show that the monodisperse magnetic particles are successfully attached to the surface of CNTs. Effect of the magnetic fields on the alignment of the MP-CNTs was investigated, showing that the MP-CNTs align perpendicular to the device surface. However, the magnetic particles on the CNT surfaces do not strongly affect their field emission properties. We also discuss the alignment behavior of the MP-CNTs incorporated into amorphous polymers.

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E34 - Electronic Structure and Field Emission Properties of Double-Walled Carbon Nanotubes

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We have synthesized high-purity double-walled carbon nanotubes (DWCNTs) using an arc-discharge method in hydrogen ambient. Fe catalyst and FeS promoter were used to synthesize the DWCNTs. It was possible to grow SWCNTs or DWCNTs selectively according to concentration of FeS promoter. The FeS promoter played a key role for the controlled growth of the DWCNTs. In this work, we studied the relationship between the field emission properties and electronic structures of DWCNTs. The DWCNTs showed low turn-on voltage of 3.0 V/μm at the current density of 0.1 μA/cm2, and the high emission-current density of 3.5 mA/cm^2 at the applied field of 6.0 V/μm. We observed that DWCNTs have larger density of states in the binding energy region between 3.88 and 13.23 eV below Fermi energy, presenting that DWCNTs have delocalized graphite σ and σ/π electrons. The high emission current densities of DWCNTs are attributed to all the emitted delocalized graphite σ and σ/π state electrons of DWCNTs.

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E35 - Field Emission Characteristics of MWNT tip and FIB modified tip

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Composite AC-DC dielectrophoresis (DEP) is used to assemble arrays of individual multi-walled nanotube (MWNT) onto a silicon tip for atomic force microscopy (AFM) and modified for the fabrication of the needed experimental device using by focused ion beam (FIB). The tips made by DEP as well as modified by FIB are evaluated their emission performance from the field emission experiment in high vacuum and compared for each other. Both tips had excellent field emission properties as well as large current density compared with previously reported results.We investigated why FIB-modified tip had different field emission property. Consequently, it was found that both tip would be applicable as a single electron source.

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E36 - Synthesis and field emission properties of carbon nanotubes on anodic aluminum oxide template

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Well-aligned crystalline carbon nanotubes (CNTs) were synthesized on anodic aluminum oxide (AAO) template using thermal chemical vapor deposition (TCVD). The AAO template was fabricated using two-step anodization process, and catalyst metal was electrochemically deposited inside the vast majority of pores on the AAO template. Additional pore widening and catalyst reduction were performed to separate the catalytic actions of the pore wall and catalysts. The enhancement of the catalytic reaction between C_2H_2 and the catalyst particles results in CNTs with good crystallinity and a high packing density without the deposition of amorphous carbon on the pore surface of the AAO template. The diameter and density of the CNTs were approximately 50 nm and 7×10^9 CNTs/cm^2 (70 % of pore density), respectively. The morphology, crystal structure, and density for the CNTs synthesized on AAO template were characterized by FESEM, Raman, and HRTEM. When the threshold voltage of the electron emission was measured with a gap of 300 μm, it showed a very low turn-on field of 0.87 V/μm and the field enhancement factor of about 5600.

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E37 - Combined Transistor and Field Emission Action From Single Walled Carbon Nanotubes

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Lateral in plane field emission - field effect transistors (FE-FET) using Single walled Carbon Nanotubes (SWCNTs) are reported. In-situ growth of single-walled carbon nanotubes oriented in plane from catalyst islands defined by e-beam lithography on an SOI substrate form the base structure. Further masking and metal contact formation is carried out as for the fabrication of a back gate transistor. However, the drain end of the SWCNT FET is suspended over a trench defined in the oxide and substrate. The drain contact is physically spaced from the SWCNT and placed on one edge of the trench. The SWCNT channel and the drain form a field emission diode. Side gates are located outside the trench to modulate the channel conductivity, thus to switch on/off and adjust the supply current to field emission diode at the drain through FET action. Several additional contacts are placed along the tube with defined spacings between them. These contacts are used as conventional drain contacts in an under gate FET structure to calibrate the SWCNT channel current dependency on electric field. The field emission characteristics of individual semiconducting SWCNTs are investigated. The device combines a field emitter and FET and has an exponential current characteristic with gate control.

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E38 - Field emission of BN-coated CNTs

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Field emission characteristics of BN-coated multiwalled carbon nanotubes (CNTs) were investigated by measuring energy distribution of emitted electrons. Vertically aligned CNTs were grown on the glass substrate using DC plasma enhanced chemical vapor deposition with C_2H_2 and NH_3 gases. A BN film was deposited on CNTs by radio-frequency unbalanced magnetron sputtering at room temperature and at a vacuum of 10^{-3} torr with the 400 W RF power. From transmission electron microscopy a partially crystallized BN layer coated mainly on tips of CNTs was observed with the thickness of around 10 nm. During the measurement of electron emission spectrum, the field emission current was measured at the same time. The shpae of field emission energy distribution curves change from one peak to two peaks after the buildup process of BN-coated CNT field emitters. Furthermore, the movement of the peaks does not agree with previous reports. The possible explanation for this peak movement is proposed here – thermal effect due to high emission current during the measurement. Finally, the field emission characteristics of BN-coated CNTs were compared with other semiconductor-coated CNTS.

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E39 - A new concept of carbon nanotube based photocathode

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We have developed a new concept of photocathode that is based on carbon nanotubes (CNTs) and that can operate at various wavelengths. This photocathode is an array of CNTs, each CNT being associated to one PIN photodiode. The device is highly efficient as it uses an optically controlled reconfiguration of the electric field at CNT location. When a large electric field is applied and for small absorbed optical powers, a voltage drop is developed within the PIN diode. This situation that we already observed for CNTs exhibiting a bad electrical contact between the substrate and their base leads to a significant reduction of the field enhancement at CNT apex and to a dramatic decrease of the emitted current [1]. On the opposite, for relatively high absorbed optical powers, the PIN diodes are highly conductive and the emitted current follows the Fowler-Nordheim law. The result is the possibility to efficiently modulate the emitted current with e.g. a laser diode.

Using silicon based PIN photodiodes we have demonstrated the first CNT based photocathode. For a 20 V/µm applied electric field, the emitted current increases from 16 µA to 0.5 mA for an absorbed optical (532 nm) power varying from 0 to 11.8mW. The associated quantum efficiency is 10%. The new photocathode combines significant current density (0.2 A/cm^2), high quantum efficiency (10%), and can operate continuously, a combination never before realized.

This breakthrough opens a new domain for photocathodes, that of microwave amplifier tubes. Their use as optically modulated electron sources could be particularly fruitful to design light and compact satellite telecommunication tubes. We would use GaInAs PIN photodiodes that can be modulated with large bandwidth 1.55 µm lasers already developed for optical fiber telecommunication.

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E40 - Enhancement of Field Emission Properties of Multi-Walled Carbon Nanotube

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It was considered the effect of plasma ion irradiation on the field emission properties of thermally grown multi-walled carbon nanotubes (MWNTs). The irradiation of plasma ions (argon or oxygen) were varied with energies, 30, 70, and 150 eV and the dose, 3.8 x 10^{16}, 7.6 x 10^{16}, and 15.2 x 10^{16} cm^{-2}, respectively. Ion energy and dose were precisely controlled by the sheath potential formed near the MWNT target. With increasing the irradiation energy and ion dose, the top tangled region of MWNTs could be trimmed out easily. The penetrated ions were experienced to sputtering the weak nanotubes and also the delivered energy by the irradiated ion did to weld the tips of the protruded MWNTs, remaining a conical shape of MWNT bundles. More conical shapes of MWNTs were obtained from the oxygen treatment. The deformations of MWNTs, as the spacing the intertube distance and the tip welding, may improve the turn-on voltage, the field emission current through the reduction of field screening effect and also the stability of field emission, respectively. This process will be applicable to the mass fabrication of MWNT field emission tip. The field emission properties were calculated with the hyperboloid model, having a good agreement with the measurement. Those results and the details of process procedures will be presented.

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E41 - Photoresponse of Suspended Carbon Nanotube Networks: Single-Walled Carbon Nanotube Infrared Bolometer

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The photoresponse of ultrathin single-walled carbon nanotube (SWNT) film is enhanced by more than 5 orders of magnitude when the SWNT film is suspended.[1] We show that the nature of enhanced photoresponse is bolometric: electron-phonon interactions lead to ultrafast relaxation of the photoexcited carriers and the energy of the incident infrared radiation is efficiently transferred to the crystal lattice. We conduct photo and absorption spectroscopy of the SWNT networks and discuss implication of the spectroscopic study on differentiation between the free carriers and exciton nature of photoexcitations in SWNTs.We suggest that suspended SWNT network can be utilized as the sensitive element of an infrared bolometric detector. The bolometer performance can be optimized by modifying the intertube junctions to enhance the temperature dependence of electrical conductivity and suppress heat flow along the SWNT network. To characterize the heat transport we develop a new bolometric technique for in-situ measurement of thermal conductivity of ultra-thin SWNT films in which the IR radiation is used as a heat source to generate a triangular temperature profile, and the SWNT film serves as a resistive thermometer.[2] The interplay between thermal and electrical transport in SWNT networks is analyzed in relation to thetype of intertube junctions and their optimization for application in IR detection. 1. M.E.Itkis, F.Borondics, A.Yu, R.C.Haddon, Science 312, 413 (2006)
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E42 - Photoluminescence imaging of freely suspended single SWNTs

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Pristine SWNTs freely suspended in air ambient emit strong near infrared photoluminescence (PL) [1] at quantum efficiencies approaching 10% [2]. We have been using PL to spatially and spectrally image extended suspended lengths (>10 micron) of single SWNTs with micron scale spatial resolution. Here we summarize the results from recent spectroscopy and imaging studies of over 25 different (n,m) species. By imaging the nanotube orientation and controlling the polarization of excitation, optical excitation spectra are cleanly separated into longitudinal (E11, E22, ...) and transverse (E12, ...) components. Several resonances are identified for either polarization and their (n,m) dependence and resulting family behavior is determined. The position of the strongest transverse resonance, assigned to E12, cannot be explained by simple conduction and valence band pictures, but can be explained by excitonic models. The very high signal-to-noise ratio possible by this method of single nanotube imaging spectroscopy allows for unambiguous identification of the many weaker satellite peaks. Some of these peaks are phonon related, while others are excited or unbound ("continuum") states of the exciton. From these PL experiments alone the SWNT exciton binding energy is estimated and its (n,m) dependence determined. In addition to fundamental spectroscopic studies, PL imaging is a valuable tool for nanotube electronics. We will demonstrate the use of PL on suspended nanotube field effect transistors (FETs) to detect and image single SWNTs in functioning devices. PL data enables diameter and chirality assignment, and makes essential contributions to the understanding SWNT FET performance.

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E43 - Anisotropic dielectric response and local field effects in single wall carbon nanotubes

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SWCNT are archetypical 1D systems, with peculiar anisotropic electronic properties. The depolarization effects concomitant with dielectric screening of electronic transitions are crucial in optical probes like Raman, optical absorption and luminescence. Only recently μm thick freestanding films of vertically aligned SWCNT became available and were characterized regarding the polarization dependent optical response[1]. The plasmon response in electron energy loss spectroscopy is a direct access to the full energy and momentum dependent dielectric function. The full plasmon dispersion allows distinguishing between the effective dielectric screening and depolarization effects. The sparse morphology of the aligned freestanding mats gives rise to a substantial increase in local field corrections as compared to earlier studies on bulk aligned SWCNT[2].We find two novel branches in the π and σ plasmon, respectively. Varying the effective transverse and parallel momentum transfer conclusively identifies the dispersive branches as parallel and non dispersive branches as perpendicular with respect to the SWCNT axis. These novel findings provide an unprecedented experimental insight into local field and depolarization effects in one dimensional electronic systems.

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E44 - Simultaneous Spectroscopy of Photoluminescence and Photocurrent of Individual Carbon Nanotube Channel in Field-Effect Transistor

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Photoluminescence (PL) spectroscopy is a useful technique to study not only 1-D exciton physics but also carrier transport phenomenon in single-walled carbon nanotubes (SWNTs).[1] In this study, we have simultaneously investigated PL and photocurrent (PC) of individual SWNT channel in field-effect transistor (FET). The device used in this study is the carbon nanotube FETs with SWNT channel bridging over a trench. We obtained good correlation between excitation spectra of the PL and PC of a SWNT at low drain bias. With increasing the drain bias, PL intensity collapsed and PC increased. We have estimated the optical absorption cross section of a single free-standing SWNT from the PC.

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E45 - Excitons in Carbon Nanotubes: Insights from Model Calculations

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Recent experimental determinations of exciton binding energies in carbon nanotubes rely on the energy splitting between 1s and 2p exciton states. This splitting can be measured by one-photon and two-photon optical absorption. To obtain the exciton binding energy from the splitting, it is often assumed, based on model calculations, that this splitting constitutes a substantial fraction (around 75 In order to understand this problem in a simple way, we explore effective one dimension hamiltonians that reproduce the first-principles and/or experimental eigenstates and eigenfunctions for the exciton states in semiconducting single wall carbon nanotubes. We focus on the ground state (1s) and first excited state (2p) of the E11 excitons in (10,0) and (8,0) nanotubes. We show that simple hamiltonians, based on the effective mass and a regularized Coulomb potential, can fit either experimental or theoretical results.

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E46 - Many body effects for E_{33} and E_{44} optical transition of single wall carbon nanotubes

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We calculate the exciton energy of E_{22}, E_{33} and E_{44} of single wall carbon nanotubes. The exciton energy is calculated by solving the Bethe-Salpeter equation within the extended tight-binding method [1]. The chirality dependence of the binding energy of E_{11} and E_{22} is almost canceled by the self-energy. The energy correction depends on diameter and follows the scaling low [2]. The $2n+m$ =const family spread of the exciton energy of E_{11} and E_{22} mainly comes from the single particle energy. In the case of the higher exciton energies of E_{33} and E_{44}, since the self-energy of E_{33} and E_{44} becomes larger than the binding energy, the chirality and diameter dependence are appeared in the energy corrections. The family spread of the exciton energy of E_{33} and E_{44} is mainly found to be from the excitonic effects. The chirality dependence of many body effects becomes important to analyze the exciton energies of E_{33} and E_{44} [3].

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[3] K. Sato *et al* ., submitted.

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E47 - Dependence of exciton transition energy of single-walled carbon nanotubes on surrounding dielectric materials

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Optical transition energies of single-walled carbon nanotubes (SWNTs) are strongly affected by the change of environment around SWNTs [1]. In this report, we theoretically investigate the dependence of exciton transition energies on dielectric constant of surrounding materials. We make a simple model for the relation between dielectric constant of environment and a static dielectric constant describing the effects of electrons in core states, σ bonds and surrounding materials [2]. Although the model is quite simple, calculated results well reproduce the feature of experimentally observed transition energy dependence on dielectric constant of various surroundingmaterials, and various *dt* and theta.

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E48 - Phonon-Induced Electron Relaxation and Dephasing Dynamics in Graphene and Single-Walled Carbon Nanotubes

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We investigate the influence of the electron-phonon coupling (EPC) in graphene and carbon nanotubes within the density-matrix formalism. To determine the EPC matrix elements Kohn anomalies in the phonon dispersions are used [1]. We study the influence of the EPC on the relaxation dynamics of photo-excited electrons in graphite. Similar to recent experiments [2], hot phonons lead to a delayed decay of the electronic temperature. Our numerical simulations reproduce these observations and give new insight into the ultrafast dynamics of the first 500 fs after excitation not yet accessible by the experiment. The qualitative agreement of our results with the experiment indicate the right order of magnitude for the EPC strength. With the electron-phonon coupling matrix elements [1] we can also microscopically calculate dephasing dynamics in carbon nanotubes. Our approach is a first step to determine the line width of free particle spectra for arbitrary tubes. The formalism allows a self-consistent inclusion of the electron-electron interaction and is therefore promising to investigate phonon-induced damping of excitons.

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E49 - Dependence of exciton transition energy of single-walled carbon nanotube on dielectric constant of surrounding material

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We have experimentally investigated the dependence of exciton transition energy of single-walled carbon nanotubes (SWNTs) on surrounding dielectric material, in the range of dielectric constant (ε) from 1.0 to 37, by means of photoluminescence spectroscopy [1]. The sample with SWNTs bridging over trenches was immersed in various organic solvent with different ε. With increasing _, both E_{11} and E_{22} exhibited a redshift by several tens meV and a tendency to saturate at ε/sim5 without an indication of significant (*n*,*m*) dependence. The redshifts can be explained by dielectric screening of the repulsive electron-electron interaction [2]. We have also measured the time-resolved photoluminescence in air and solvent, respectively, by utilizing the excitation intensity correlation technique [3]. When the sample was immersed in a solvent, the correlation signal collapsed and decay time decreased drastically.

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[2] Y. Ohno, S. Iwasaki, Y. Murakami, S. Kishimoto, S. Maruyama, and T. Mizutani, Phys. Rev. B **73**, 235427 (2006).
[3] Y. Ohno, T. Shimada, S. Kishimoto, S. Maruyama, and T. Mizutani, J. Physics: Conf. Series **38**, 5 (2006).

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E50 - Carbon-Nanotube Bloch Equations: A Many-Body Approach to Excitonic Spectra, Optical Gain and the Dynamical Stark Effect

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We derive and apply optical Bloch equations for arbitrary carbon nanotubes. Within the density matrix formalism, the equations of motion for the coherent interband transitions and electron band occupations are obtained. The electron-electron interaction is included within a screened Hartree-Fock approximation. Higher correlations and phonons can be included in a self-consistent way. The Carbon-Nanotube Bloch Equations are used to model linear (absorption and Rayleigh spectra) as well as ultrafast non-linear optical dynamics. Here, the linear absorption spectra are calculated to benchmark the derived equations of motion. Within the Carbon-Nanotube Bloch Equations approach, we reproduce the exchange shift leading to a renormalized blue-shifted band edge, whereas the excitonic contribution strongly alters both peak shape and position. Beyond linear optical properties, the Bloch equations can be used to describe ultrafast and non-equilibrium effects. First, for occupation inversion we observe a shift of the lowest excitonic resonance (E_{11}), including gain at large electron-hole densities. Second, we discuss the response of CNTs to an ultrafast pump pulse, treating the dynamics of the non-equilibrium density matrix. In particular, the dynamical Stark effect reveals the importance of ultrafast many-body non-linearities in CNTs.

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E51 - Transparent Conducting Carbon Nanotube Thin Films by Spray Coating

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Transparent conducting films are essential to several modern technologies such as photovoltaics, light emitting diodes, displays, etc. Recent works have shown that thin films of carbon nanotubes (<100nm) may present a combination of high electrical conductivity and high transparency which matches the performance of commercial transparent conducting oxides. However, the proposed fabrication processes for such films are not practical for large area deposition.

In this work, we have investigated spray coating methods for the formation of carbon nanotubes thin films. One of the main challenges in the optimization of such methods is the formation of stable, concentrated CNTs suspensions. Different routes for the “solubilization” of CNTs in water have been tested. These include noncovalent approaches by using surfactants, arabic gum, or ammonium hydroxide as well as covalent approaches (attachment of carboxylic groups). The films were characterized by UV-VIS and Raman spectroscopy, and 4- probe electrical measurements. The best films present sheet resistance of ~ kohms and transparency of ~80%.

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E52 - Rayleigh Scattering from Single-Walled Carbon Nanotubes

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We study Rayleigh scattering from single-walled carbon nanotubes. Combining density matrix formalism and tight-binding band structure calculations, we calculate the Rayleigh scattering cross section $\sigma(\omega)$for arbitrary nanotubes. In contrast to the optical absorption coefficient which is given by the imaginary part of the optical susceptibility, $\sigma(\omega)$ is determined by the full dielectric response of the investigated nanotube. Metallic tubes exhibit an asymmetric double-peak structure in their Rayleigh spectra, where the low-energy peak is always stronger in intensity. This characteristic arises from an interplay of the joint density of states and the optical matrix element $M(\mathbf{k})$. We obtain a fully analytical expression for $M(\mathbf{k})$ showing that the matrix element has a different behavior along the two high-symmetry lines ΓK and KM of graphene. As a result, the low-energy peak stemming from the KM-side has a stronger oscillator strength. Furthermore, we show that the lineshape in the Rayleigh spectra exhibits an symmetry towards lower energies, which can be explained by the ω^{-2}-dependence of the real part of the dielectric function. The latter also accounts for a red-shift of about 10meV in the Rayleigh spectra compared to the corresponding peaks in the absorption spectra. Our results are in good agreement with experiment. They will be useful for the optical characterization of metallic single-walled carbon nanotubes.

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E53 - Time-resolved photoluminescence from excitons in individual carbon nanotubes

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The photoluminescence lifetime of individual semiconducting single-walled carbon nanotubes (SWCNTs) dispersed on glass substrates has been measured using time correlated single photon counting (TCSPC). At room temperature transients show fast decay times in the range of few picoseconds (~10 ps) with small variations from nanotube to nanotube of the same chirality (n,m). Convolution of the data with the instrument response function (FWHM = 27 ps) confirms the mono-exponential decay behaviour of the exciton recombination over several orders of magnitude and does not indicate any long lived contribution [1]. In addition, we investigated the effect of the excitation energy and the nanotube environment for different nanotube chiralities and sample materials.

[1] A. Hagen et al., Phys. Rev. Lett. 95, 197401 (2005).

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E54 - Controlling Non-Equilibrium Phonon Populations in Single-Walled Carbon Nanotubes

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We studied spatially isolated single-walled carbon nanotubes (SWNT) immobilized in a quasi-planar optical λ/2-microresonator using confocal microscopy and spectroscopy. The modified photonic mode density within the resonator is used to selectively enhance or inhibit different Raman transitions of SWNT. Experimental spectra are presented that exhibit single Raman bands only. Calculations of the relative change in the Raman scattering cross sections underline the potential of our microresonator for the optical control of non-equilibrium phonon populations in SWNT.

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E55 - Exciton energy transfer in nanotube bundles

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Photoluminescence is commonly used to identify the electronic structure of individual nanotubes. But, nanotubes naturally occur in bundles. Thus, we investigate photoluminescence of nanotube bundles [1]. We show that their complex spectra are simply explained by exciton energy transfer between adjacent tubes, whereby excitation of large gap tubes induces emission from smaller gap ones via Forster interaction between excitons. The consequent relaxation rate is faster than non-radiative recombination, leading to enhanced photoluminescence of acceptor tubes. This fingerprints bundles with different compositions and opens opportunities to optimize them for opto-electronics.

1. P. H. Tan et al. submitted (2007)

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E56 - Nanotube Based Polymer Photonics

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Optical nonlinearity can be used for various photonic applications including to switch, route and regenerate optical signals, or form ultrashort laser pulses [1]. In any particular material whose output characteristics are determined by the intensity of input signal or by a separate control beam it is possible to achieve optical switching. Carbon nanotubes (CNTs) exhibit strong saturable absorption nonlinearities, i.e. they become transparent under sufficiently intense light [2,3]. The performance of CNTs based saturable absorbers strongly depends on concentration, size of CNT bundles, and transparency of the matrix [2]. Here, we present the fabrication and characterization of saturable absorber based on CNT - polymer optical composites [2,3]. We use strong ultrasonication to obtain CNT solutions. Such solutions with different nanotube bundle sizes are then studied by photoluminescence excitation spectroscopy [4]. We demonstrate picosecond pulse generation in a nanotube mode-locked waveguide laser [5], as well as 600 fs generation in an erbium doped fiber laser [6]. The integration of nanotube saturable absorbers into high speed data transmission systems will be discussed [7].

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7 A. G. Rozhin et al. submitted (2007)

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E57 - Resonance Raman study of polyynes encapsulated in single wall carbon nanotubes

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In this work we present a resonance Raman study of hydrogen-ended polyynes molecules encapsulated inside carbon nanotubes, using many different laser lines in the visible range.We observed that the Raman features of the polyynes exhibit a strong resonance behavior around 2.1 eV, and this energy is much lower than the first optical transition of the polyynes dispersed in solvents. We interpret our results as due to the symmetry lowering of the polyyne when encapsulated inside the carbon nanotube, allowing forbidden electronic states to be active. We also present Raman measurements on this sample dispersed in water with surfactants.

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E58 - Strain dependence of photoluminescense of individual carbon nanotubes

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We have investigated strain dependence of photoluminescense (PL) spectra of single wall carbon nanotubes (SWNT). Nanotubes were sparsely dispersed in a thin PMMA film applied to acrylic bar, and strained in both compression and extension by bending this bar in either direction in a homebuilt four-point bending rig. The average surface strain was measured with high accuracy by a resistive strain gage applied on top of the film. The near - infrared imaging and spectroscopy were performed on the inverted microscope equipped with high numerical aperture reflective objective lens and InGaAs CCD cameras. PL was excited with a diode laser at either 658, 730 or 785 nm, linearly polarized in the direction of the strain. We were able to measure (n,m) types and orientation of individual nanotubes with respect to strain direction and strain dependence of their PL maxima. It was found that PL peak shifts with respect to the values measured in SDS micelles are a sum of three components. First, a small environmental shift due to difference in the dielectric constant of the surrounding media, that is constant and independent of the nanotube type. Second, shift due to isotropic compression of the film during drying. Third, shifts produced by the uniaxial loading of the film in the experiment. Second and third shifts follow expression based on the first-order expansion of the TB hamiltonian. Their magnitude is proportional to the nanotube chiral angle and strain, and direction is determined by the nanotube quantum number. PL strain dependence measured for a number of various nanotube types allow to estimate TB carbon-carbon transfer integral.

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E59 - Memory Effects In Carbon Nanotubes

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We investigate potential solutions for the fabrication of future molecular scale memory elements based on single-walled carbon nanotube field-effect transistors (CNT-FETs). CNT-FETs are known to sometimes display undesirable hysteresis in their transfer characteristics. For a memory element, this is on the contrary a favorable feature that can be utilized. The gate insulator film has here a crucial influence on the operation of the CNT-FET. For an effective capacitive coupling between the CNT and the gate electrode, a thin and dielectrically strong film is required. On the other hand, in order to achieve the desired hysteretic behavior for a non-volatile memory, the gate-nanotube coupling has to include mobile charges within the gate insulator or at some interface close to the nanotube.

The studied devices are all CNT-FETs fabricated from semiconducting single-walled carbon nanotubes with a diameter close to 2 nm. Measurements were carried out at various ambient conditions for more than 70 CNT-FETs with differing gate insulators. the observed memory effects, and our conclusions thereof, will be presented.

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CONTRIBUTED ABSTRACTS

POSTER SESSION F

JUNE 28 (Thursday)

F01 - Tuning electronic and magnetic properties of multi-layered graphene ribbons

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We report results of spin density functional calculations for multi-layered graphene ribbons. Each ribbon layer consists of a finite width graphite monolayer with well-defined, parallel edges. Monolayer graphene ribbons with zigzag edges exhibit a peculiar electronic structure, resulting in spin polarized states at the two edges that couple antiferromagnetically. The only way to exploit the magnetization to generate a spin polarized current involves breaking the symmetry of the ribbon, such as applying a large electric field across the ribbon. Here, we explore an alternative approach to modify the electronic structure of a graphene ribbon, namely by forming bi-ribbons containing graphene or BN layers. Our calculations suggest that the electronic structure and magnetic ordering in bi-ribbons differ significantly from monolayer ribbons. Depending on the stacking geometry, the "flat bands" underlying the spin polarized edge states can be modified in a way to yield net spin polarization of the ribbons, making them attractive for spintronics applications.

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F02 - Fabrication of LSI via interconnect using a bundle of multi-walled carbon nanotubes synthesized at a temperature as low as 400 ^oC

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MIRAI-Selete

Due to their excellent electrical, mechanical and thermal properties, carbon nanotubes (CNTs) are considered to be a promising candidate for interconnect materials of LSIs in the hp32 nm technology node and beyond. We have actually been trying to use bundles of multi-walled carbon nanotubes (MWNTs) for vertical wiring, namely, vias in LSI, instead of W or Cu. In the previous study [1], we developed a method to grow high-density MWNTs using size-controlled catalyst particles. CNT vias with a diameter of 2μm made of MWNTs grown at 450 ^oC had a resistance as low as 0.59Ω, which is of the same order as that of W plugs.

In this work, we have reduced the growth temperature down to 400 ^oC [2] and fabricated CNT vias with diameters as small as 160 nm using a newly-developed via process. Both the growth temperature and the process are compatible with the conventional LSI process. The new via process is as follows [3]. First, a substrate composed of a Cu interconnect and a SiOC dielectric layer was prepared. Via holes were made using conventional photolithography and subsequent dry etching. A TaN/Ta barrier layer and a TiN contact layer were deposited using an anisotropic physical vapor deposition (PVD). Size-controlled Co particles with an average diameter of about 4 nm were then deposited all over the substrate using a catalyst nanoparticle deposition system [1]. Subsequently, MWNTs were grown all over the substrate, in contrast to the previous study where MWNTs were grown only in via holes [1]. The synthesis was done by thermal chemical vapor deposition using acetylene diluted by Ar as the source gas with a substrate temperature of 400 ^oC. After the CNT growth, chemical mechanical polishing (CMP) process was used to eliminate the excess MWNTs and planarize the substrate, leaving MWNTs only in via holes. Finally, the Ti top contact layer, Ta barrier layer and Cu wire were connected to CNT vias by PVD without subsequent annealing.

Synthesis of high-quality MWNTs at 400 ^oC was confirmed by transmission electron microscopy. The electrical properties of CNT vias were measured using the Kelvin pattern and via chains. The details of the electrical properties will be given in the presentation.

This work was completed as part of the MIRAI Project supported by NEDO.

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F03 - Defects Engineering in Ordered Networks based on CNTs

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Assemblying nanostructures into ordered micro-networks remains a challenge in modern nanotechnology. Carbon nanotubes (CNTs) are excellent candidates as building blocks, due to their extremely high Young's modulus and remarkable flexibility, their ballistic conductor or semiconductor behaviour and their high surface area. Recently, there has been proposed 2D and 3D ordered networks built from 1D nanostructures, showing intriguing mechanical and electronic properties of the assembled array when CNTs are used [1-2]. These type of networks represent excellent candidates for complex integrated nanoelectronic circuits. Here we propose to use defect patches (graphene layer pieces composed by heptagons, pentagons and hexagon carbon rings; i.e. Haeckelite pieces) in strategic zones of an Ordered Network built from CNTs (ON-CNTs) in order to guide the electronic current trough specific paths along the network.

Based on a SuperGraphene ON-CNTs we have incorporated Haeckelite pieces in strategic zones resulting in guiding the electronic current through specific paths. To understand in full detail the phenomenon, we have incorporated one by one Stone Wales defects until a Haeckelite patch is obtained, to systematically investigate the electronic transport properties of the network. These calculations have been carried out in the framework of the Landauer-Buttiker formalism and equilibrium Green functions. To take curvature into account, we employed a semi-empirical Hamiltonian based on 4 orbitals (s,px,py,pz) per carbon atom. Further insight into the transport mechanism was obtained by analyzing the electron pathways from a scattering point of view, which allows for a real-space analysis of the wave function corresponding to transmitted electrons across the structure.

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[2] Coluci V.R., et.al. Nanotechnology, 17: 617-621 (2006).

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F04 - Spectroscopic evidence for hot-phonon generation in single-walled carbon nanotubes

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We provide spectroscopic evidence for hot phonon generation in biased single-walled carbon nanotubes by simultaneously measuring the Stokes and Antistokes Raman G-mode lines as a function of voltage bias. Using the Bose-Einstein statistics we can directly calculate the phonon occupation number from the intensity ratio of the Antistokes to Stokes lines and observe an increase of the effective phonon temperature with voltage. We do not observe shifts of the G-mode lines and can therefore exclude thermal heating of the nanotube [1]. To the best of our knowledge this is the first direct spectroscopic evidence for hot phonon generation in singlewalled carbon nanotubes. The data qualitatively confirms previous estimates on the effective phonon temperature as derived from modelling of electron transport characteristics. The samples were prepared by single-nanotube dielectrophoresis, a method that we have recently developed into a scalable technique for making single-nanotube devices with a density beyond 1 Mio. devices per cm^2 [2]. If time allows I will explain the underlying basics and how single-nanotube dielectrophoresis is related to dielectrophoretic nanotube separation [3].

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F05 - Fabrication of n-type single-walled carbon nanotube field effect transistors by Al decoration

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We have fabricated single-walled carbon nanotube n-type field effect transistors (FET) by controlled in-situ Al decoration technique. Three different device configurations were used for Al decoration; contact-decoration, channel decoration, and open devices. All three types of devices turned into n-type transistors after decoration, and goes back to p-transistor again in ambient atmosphere. While contact-decorated devices show improved p-type characteristics in air, channel-decorated devices show decreased conductance and negative shift of gate threshold voltages. In case of open device or channel-decorated devices, doping control was possible by controlling the amount of Al particles. Recovery to the p-type FET can be explained by oxidation of Al nanoparticles and subsequent work function increase, and improved performance of the channel shielded device can be attributed to the formation of n-p-n junction in carbon nanotube.

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F06 - Observation of negative differential resistance in superlattice structure of C_{60}, C_{70}, and C_{84} encapsulated double-walled carbon nanotubes

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Fullerene and carbon nanotubes (CNTs) have widely been investigated in nanoelectronics due to their remarkable electrical properties. In this study, we demonstrate the observation of negative differential resistance (NDR) in nanodevices fabricated with various fullerenes (C_{60}, C_{70}, and C_{84}) encapsulated metallic double-walled carbon nanotubes (DWNTs) [1]. It is found that the observed NDR behavior keeps stable throughout the ambient condition from 400 K to 10 K. In addition, a very high peak-to-valley current ratio of $10^2 \sim 10^4$ is observed for most fabricated devices, which is much higher than those reported in previous NDR devices fabricated with conventional semiconducting materials. The type of encapsulated fullerenes displays an important effect on the NDR characteristic, and the peak voltages of NDR are interestingly found to show a linear downshift with increasing the diameter of fullerenes. More importantly, the observed current-voltage curves are proved to be highly reproducible during measurements, and fully reversible upon a change in bias sweep direction or rate.

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F07 - Novel properties of magnetic-atom encapsulated single-walled carbon nanotubes

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Magnetic Fe nanoparticles less than 1 nm have been successfully filled in single walled carbon nanotubes (SWNTs) by using ferrocene as a staring material. Samples of both ferrocene-filled SWNTs and Fe-filled SWNTs are characterized in detail by a Hitachi HF-2000 transmission electron microscope (TEM) operated at 200 kV, equipped with energy dispersive X-ray spectrometry (EDX, Noran Instruments). The amount of Fe nanoparticles in SWNTs is analyzed by X-Ray Fluorescence Spectroscopy (XRF, RIX2100). Magnetic properties of samples are characterized by using a Quantum Design MPMS-5 superconducting quantum interference devices (SQUID) magnetometer. Our results indicate that most of the encapsulated Fe particles are in the metallic phase, and superparamagnetic behavior is observed due to their small size [1]. In addition, electrical transport measurements indicate that Fe-filled SWNTs at high filling fractions exhibit high performance n-type semiconducting characteristics at room temperature and Coulomb blockade behavior at low temperatures [2]. By comparison, at low filling fractions p-n junction diode behavior is significantly observed in many of Fe-filled SWNTs. More importantly, we prove that the observed rectifying characteristic of p-n devices maintains high reproducibility even after exposure to air [3].

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F08 - Electronic transport properties of alkali-metal/halogen encapsulated single-walled carbon nanotubes formed by plasma ion irradiation method

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Single-walled carbon nanotubes (SWNTs) have a strong potential for fabricating novel nano electronic devices in combination with other foreign molecules or atoms, owing to their unique one-dimensional structure and electronic properties. Up to now, our group has demonstrated that electrical features of SWNTs can drastically be modified by various alkali-metal atoms encapsulation, and hence an air-stable n-type semiconducting behavior has been obtained. This result motivates us to develop a nano-pn junction diode by encapsulating both electron donor and acceptor in a same individual SWNT. Here, we present unique electron transport properties of Cs and I encapsulated SWNT (Cs/I@SWNT), which is prepared by a novel alkali-halogen plasma irradiation technique. Transport measurements under a field-effect transistor (FET) configuration reveal that the Cs/I@SWNTs show a diode like rectification behavior due to selective encapsulation of these electron donor and acceptor. In addition to this rectification behavior, source-drain current (I_{DS}) vs gate voltage (V_G) characteristics are observed to be different from the usual p-type or n-type behavior, which can be explained as a unique feature of the p-n junction structure.

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F09 - Hetero-Channel CMOS with single-walled CNT and ZnO nanowires

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Single-walled carbon nanotubes (SWCNT)Field Effect Transistors (CNTFET), mostly exhibit p-type behaviour. Zinc Oxide (ZnO) Nanowires also have promising electrical characteristics which have recently been exploited in high performance n-type transistors1. Here we report the integration of CNTFET and ZnOFET on the same substrate.We have fabricated the CNTFET with SWNTs that have been grown by CVD method with 2-5μm length. The disadvantage of the uncertainty of whether the SWNTs are semiconducting or conducting has been addressed by the fabrication of multiple devices. As the yield of semiconducting SWNTs is 70%, the CNTFET is realised on a statistical basis. For the ZnOFET, we have used ZnO nanowires that have been grown with CVD method with 5-10 μm length and has n-type behaviour. This novel approach for combining the ZnOFET and CNTFET is being explored as an alternative solution for CMOS technology where both n-channel and p-channel transistors are required to define binary logic levels. Although the ZnOFET does not display ballistic electron transport, which the CNTFET can, the important parameter is that the total current per channel. Though the channel current density in the CNTFET (1.4nm diameter) is much higher than that of a ZnOFET (60nm diameter), the overall transistor current density is the same. This is because the total area occupied by a nanotube/nanowire transistor is not governed by the tube/wire diameter. It is rather the contact dimensions, common to both, which determine area. One of the main limitations in scaling CMOS Silicon (Si) transistors is that they suffer from short channel effects that diminish the control of the channel through the gate and increase the power losses due to excessive leakage current. By having high mobility CNT and ZnO tube/wires the channel geometry can be changed to avoid short channel effects, effectively by making long channels, while maintaining the overall transistor area and current. Experimentally, the SWCNT were grown in situ on an SOI substrate with the ZnO nanowires grown ex-situ and dispersed subsequently. The positions of the SWNT and ZnO were located using a Scanning Electron Microscope (SEM) and combined with an electron beam lithrography tool for device fabrication. The source and drain of the CNTFET were formed by sputtered by Palladium (Pd). The ZnOFET has a chromium (Cr) with air dielectric. The source-drain has sputtered Niobium (Nb) contacts. Electrical characteristics of this new hetero-channel CMOS transistor are presented.

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F10 - Gas sensor built with iron oxide-filled multi-walled carbon nanotubes

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The development of solid state sensors for several kinds of gases has a great importance for the industry in general. As many factors play an important role on the analysis and detection of gases, the search for a versatile, cheap and low-sized gas detector has become essential. Recent studies prove that carbon nanotubes present variations regarding their electrical resistance when they are in contact with some sorts of organic gases; therefore, they can be detected. The possibility of obtaining carbon nanotubes filled with other materials allow the addition of new properties to build sensitive sensors either to the gases which interact with the carbon nanotubes or with the gases which interact with the filling. That is why it is possible to build versatile sensors in solid state, relatively cheap and with a proper size. This study presents the results for a gas detector that works the variation of the electric current which passes through the iron oxide-filled multi-walled carbon nanotube. We identified conductivity changes when there was contact with some organic gases. The results showed that is possible to build a device that works as an electric sensor for gases of easy identification which is stable, without presenting any signs of degradation or saturation and with a quick response to atmosphere changes.

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F11 - Characteristics of individually suspended single-walled carbon nanotube based nanodevices

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Presented in this study are of the morphological, structural, optical, and electrical properties of individually suspended single-walled carbon nanotubes (SWCNTs) synthesized by microwave plasma chemical vapor deposition (MPCVD) and the characteristics are achieved by means of field-emission scanning electron microscopy (FESEM), high-resolution transmission electron microscopy (HRTEM), micro-Raman spectroscopy, photoluminescence (PL), and I -V analyzer techniques. The preliminary results demonstrate that the laterally suspended SWCNTs could successfully cross several micrometer length scales trenches of the patterned Si wafer, which is fabricated by focused ion beam (FIB) technique. The results also indicate that several PL-peaks locate at about 1.6-1.8 eV, and the intensity of radial breading mode (RBM) peaks of the SWCNTs is varied by temperature from micro-Raman observations. In addition, electrical characteristics of the individually suspended SWCNTs are also presented in this work. Therefore, this approach is a simple yet valuable method for the fabrication of suspended SWCNTs particularly well suited for application in nanodevices. Keyword: suspended SWCNT; MPCVD, photoluminescence (PL); focused ion beam (FIB), radial breading mode (RBM).

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F12 - A new approach for designable carbon nanotube based transistor

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It is generally admitted that the miniaturisation of silicon-based transistors will reach some fundamental limit before the end of the decade. This is currently motivating an intense research activity for alternative devices and materials. In particular, molecular electronics is an emerging area, where essentially single molecules are used for the active part of the devices. Moreover, molecular electronics could bring higher device performance than conventional electronics because of possible ballistic transport and better gate coupling. Today, the most widely studied molecular systems are single wall carbon nanotubes (SWNTs), which exhibit unique electrical properties.

The integration of such nanostructures in transistors is currently restrained by two crucial issues : i) the SWNT manipulation and positioning and ii) the chirality control to obtain same electrical properties for each CNT.

Manipulation and positioning can be settled using a nanometer-sized template whose features will determined the carbon nanotubes characteristics (diameter, length, orientation, position ...). For this purpose, we have two different approaches : the vertical and the lateral templates. The first one is fabricated with a process combining conventional microelectronics methods with dedicated growth conditions while the second one uses the well known aluminum anodization method to create nanometer-sized pores. In the case of lateral templates, the anodization has to be performed parallel to the substrate. At this aim, a dedicated process is use leading to a configuration where the electric field is parallel to the substrate during anodization and therefore nanopores created are also laterally orientated. This leads to a perfect organisation with nanopores perfectly organised in parallel. This configuration is highly desirable in order to increase the current delivered by each devices. Process fabrication and growth inside lateral and vertical templates will be presented.

For the second issue, we know that the carbon nanotube growth is essentially a surface-driven process and therefore is highly dependent on the catalyst structure. We plan to control the chirality by a perfect tailoring of the catalyst particle crystalline structure. This is done by epitaxially depositing the catalyst particles and growing the SWNTs at low temperature (i.e. lower than the melting point of the catalyst material) to preserve the crystallographic structure. First results performed on different kind of substrates and substrate orientations (Si, quartz, sapphire, MgO (100) and (111)) have shown that the SWNT chirality/diameter is depending on the choice of the substrate material and/or substrate orientation. This has been brought to light by Raman measurements.

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F13 - Network Transistors of Carbon Nanotubes Directly Grown on Glass

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Random network tansistors of carbon nanotubes were fabricated on glass. Single-walled carbon nanotubes (SWNTs) were directly grown on glass by using a water assisted remote plasma chemical vapor deposition (CVD). The carbon nanotube networks acting as the active components of the thin film transistor were selectively formed on the transistor channel areas that were previously patterned with catalysts. Even though the density of grown nanotubes is much higher than the percolation threshold, it shows high on/off ratio of $\sim 10^4$. It is understood that the remote plasma CVD seems to be an effective method for a preferential growth of semiconducting SWNTs. This achievement suggests that the nanotube active devices may be fitted to thin film applications for future optoelectronics.

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F14 - A Novel Mono-layer Shell-Etching Process Using Vacuum-ultraviolet Light for Double-walled Carbon Nanotube Transistors

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We developed a mono-layer etching process of double-walled carbon nanotubes (DWNTs) using the vacuumultraviolet light (VUV) dry reaction system. By utilizing the system, we successfully etched the outer-shell of DWNTs remaining the inner-shell.

Carbon nanotube (CNT) field effect transistors (FETs) are the candidate of post-Si channel for CMOS devices because of their high carrier mobility and miniaturization feature. In order to obtain the stable operation of such nanotube or nano-wire FETs, the surface passivation technique for the channel is very important. We propose a new structure of DWNT-FETs, consisting of the inner semiconductor shell as a channel and the outer-shell as a passivation layer. At the gate region, the outer-shell will be removed and the inner semiconducting shell will be covered with an insulator and a metal electrode, forming MIS structure. In this structure, the ideal passivation by the outer-shell can be expected at the source-gate and gate-drain regions.

To realize them, the mono-layer etching of outer-shell remaining the semiconducting inner-shell is the key process. Then, we tried to develop the mono-layer etching process utilizing VUV treatment. First, we fabricated back-gate type CNT-FETs with DWNT channel on a SiO_2/Si substrate. The diameter of DWNTs is about 1 to 3 nm. Then, the FETs were exposed to the VUV (λ= 172nm) in oxygen gas diluted by nitrogen [1]. Before and after the VUV treatment, the drain current (I_{ds}) vs. the gate voltage (V_{gs})) characteristics was measured. The I_{ds} dependence on V_{gs}, i.e. the transconductance gm was very small before the VUV-treatment, which means that the I_{ds} is mainly consisted of the current flowing in the metallic outer-shell and the contribution of the current flowing in semiconducting inner-shell was very small. However, after the VUV treatment, the gm becomes about twice, which means that the I_{ds} attributed to the current flowing in semiconducting inner-shell became two times larger than that before the treatment. This indicates the etching of the metallic outer-shell of DWNTs remaining the semiconducting inner-shell. We believe that the VUV dry reaction system will be very useful for fabricating not only this FET structure but also several DWNT-based novel devices.

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F15 - Crossed Carbon Nanotube Devices

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Cross junctions of carbon nanotubes (CNTs) separated by thin oxide layers have 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 CNTs at low temperatures. The gating field from the upper CNT is seen to modulate the band structure in the lower CNT, producing double quantum dot systems [1]. The ability to modulate the electronic structure of CNTs in such a way opens up many possibilities for future electronic and logical nanodevices. The oxide deposition step is a crucial one and we illustrate that this is best carried out by Atomic Layer Deposition.We will report some new measurements on related systems and also illustrate the improvement of carbon nanotube transistor characteristics when using metallic nanotubes as the electrical leads instead of larger metallic electrodes.

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F16 - Dynamic exchange coupling and spin pumping in carbon nanotubes

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Motivated by the growing evidence of spin-dependent interactions in carbon-based structures, we investigate the pumping of spin currents into a nanotube and how this may affect the magnetic response of these materials. The spin pumping that results from precessing magnetic moments in contact to a nanotube is used here to explain (a) the finite lifetime of magnetic excitations on nanotubes even in the absence of spin-orbit interaction and (b) the appearence of a dynamic magnetic coupling between localized moments in nanotubes. Both features are illustrated by calculations of the spin excitation spectra of nanotubes in the presence of magnetic adatoms. In this context, we show that the calculated dynamic coupling may be either long- or short-ranged, depending on the geometry of the adatom adsorption as well as on the doping level of the nanotube. We argue that changes in the range of this dynamic interaction may be externally controlled or carefully selected. Furthermore, we point to the dominant role played by the loss of coherence in the magnetic excitations, a.k.a Stoner excitations, and how influential this can be in determining the range of the dynamic interaction. Finally we stress the fundamental differences between spin pumping in three-dimensional systems with planar symmetry and quasi-one-dimensional materials with broken translational symmetry.

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F17 - Double Wall Carbon Nanotubes filled with α-Fe

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Double Wall Carbon Nanotubes, DWCNT's, whose preparation has been described elsewhere (E. Flahaut et al. Chem. Commun. (2003)1442), by CCVD, were filled with iron using a simple method based in the chemical wetting with an FeCl3 oversaturated solution. The pristine CNT's were constituted of ca. 75% DWCNT's, with 1.5 nm internal diameter and 2.2 nm external diameter. The characterizations made by TEM, HRTEM, SAED, Mössbauer spectroscopy (MS) and VSM allow to say: -the observed iron in the DWCNT's is α-Fe (95% according to MS and ~5% a superparamagnetic oxide), with a hyperfine field ~5% larger than in bulk iron at room temperature. -HRTEM indicate that DWNT's were partially filled (diameter of the wire 1.37 nm), and TEM allow to estimate length in some nanowires ~40 nm. -SAED made on a bundle of NTC's confirm the presence of α-Fe, which due to non continuous rings in the 110 reflection indicate a clear orientation of the wires. -VSM show a hysteresis cycle with a coercive field 190 gauss, indicating the clear ferromagnetic behaviour of the sample. It is to be underlined that comparing with previous experiments in MWCNT's, where a mixture of cementite, γ-Fe and α-Fe was reported, we almost only find α-Fe. The most striking result is perhaps the increase of the hyperfine field certainly due to the confinement of the α-Fe in the interior of the nanotube.

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F18 - Mössbauer and Raman spectroscopies studies in Double Wall Carbon Nanotubes filled with α-Fe.

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Elsewhere in this conference we present the synthesis and characterization of DWCNT's filled with α-Fe. In this complimentary work we study the physical properties by Mössbauer (MS) and Raman spectroscopies. The Mossbauer spectra obtained from room temperature (RT) to 26K, indicate increases of the hyperfine fields from 341 kG to 353 kG respectively, which with respect to bulk α-Fe are 11 and 16 kG above. Those values are considerable higher compared with other authors when studying α-Fe in MWCNT's. In addition, the thermal evolution of the resonnant absorptions allowed us to determine the Debye temperature equivalent, $\theta D=241$ K, which is extremely low compared with bulk iron (467 K). The Raman spectra were also particularly rich, indicating the features of the DWCNT's (tangential and radial modes) as well as the appearance, due to the confinement, of characteristic iron modes in the range of radial modes of the nanotubes. It is to be underlined that the magnetic enhancement and the mechanical softening are new features observed in those systems.

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F19 - Noncollinear coupling between magnetic adatoms in carbon nanotubes

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The long range character of the exchange coupling between localized magnetic moments indirectly mediated by the conduction electrons of metallic hosts often plays a significant role in determining the magnetic order of low-dimensional structures. In addition to this indirect coupling, here we show that the direct exchange interation that arises when the moments are not too far apart may induce a non-collinear magnetic order that cannot be characterized by a Heisenberg-like interaction between the magnetic moments. We argue that this effect can be manipulated to control the magnetization alignment of magnetic dimers adsorbed to the walls of carbon nanotubes.

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F20 - Transport properties of nanotubes with randomly distributed magnetic impurities

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We calculate how the conductance of a carbon nanotube is affected by the dispersion of randomly distributed magnetic adatoms. The first stage of the calculation involves obtaining the most favourable alignment of the atomic magnetizations both with and without an external magnetic field. Whereas the former saturates the overall magnetization by aligning the individual moments, the latter follows from a Monte Carlo study showing that the magnetization may depend rather sensitively on the concentration of magnetic adatoms. The second stage of the calculation consists of evaluating the quantum conductance from which we can extract the values for the magnetoresistance. A systematic study shows the concentration dependence of the magnetoresistance.

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F21 - First observation of magnetic interaction between metal-filled carbon nanotubes

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We present a growth and characterization of self-assembled aligned Pd_xCo_{1-x} alloy encapsulated into multiwalled carbon nanotube (MWCNT) arrays on Pd/Co thin layers coated Si substrate by dc bias-enhanced plasma chemical vapor deposition method during the growth of MWCNTs with C_2H_2 and NH_3 as the reaction gasses at various temperatures.

The magnetic properties of large area Pd_xCo_{1-x} alloy encapsulated into MWCNTs were investigated by a vibrating sample magnetometry (VSM). Off-axis electron holography in the transmission electron microscope (TEM) was used to correlate the magnetic microstructure of magnetite Pd_xCo_{1-x} alloy in individual MWCNTs. As the growth temperature increases from 700 ^{o}C to 750 ^{o}C, both the coercive fields and the loop squareness coefficient defined as the remanence-to-saturation magnetization ratio, S, based on VSM results increase when the applied fields both in perpendicularly (Coercive fields: from 104 to 267 Oe, S: from 0.060 to 0.095) and parallelly (Coercive fields: from 177 to 674 Oe, S: from 0.143 to 0.684) to the metal-filled MWCNTs. This magnetic anisotropy of the metal-filled MWCNTs results from the interplay of a series of effective fields, such as crystalline anisotropy energy, shape anisotropy effect and demagnetization field. The powerful technique of the electron holography in the TEM enabled us to obtain the saturation magnetization of each Pd_xCo_{1-x} alloy in the metal-filled MWCNTs and the magnetic interaction between metal-filled MWCNTs by calculating the magnetic field lines. We observed an interaction between metal-filled MWCNTs, with saturation magnetization of 1.12 T and 0.9 T, which were separated by about 340 nm. The external fields among metal-filled MWCNTs were clearly observed. Each metal-filled MWCNT was seen to have independently, however there was some transfer of magnetic flux between adjacent metal-filled MWCNTs. Although many adjacent magnetic materials are oriented magnetically anti-parallel in each other, it is apparent from our results that both the Pd_xCo_{1-x} alloy in each metal-filled MWCNTs are the magnetic particles with parallel local magnetization along the MWCNT direction.

Our results demonstrate significant progress towards the goal of producing spinelectronic devices from ferromagnetic Pd_xCo_{1-x} alloy encapsulated MWCNTs.

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F22 - Spin-orbit interaction in carbon nanotubes

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Transport experiments [1,2] in carbon nanotubes show that spin plays an important role in their transport properties, although certain results are in apparent contradiction. We have studied the effect of spin-orbit (SO) interactions in carbon nanotubes of different geometries within an empirical tight-binding model. We have found that chiral nanotubes present spin splitting, whereas achiral (i.e., zigzag or armchair) tubes preserve spin degeneracy. This may yield different spin transport properties depending on chirality. This different behavior can be understood by noticing that achiral tubes have inversion symmetry, whereas chiral tubes lack an inversion center [3].

In achiral nanotubes, fourfold degenerate bands can present a partial removal of degeneracy when including spin-orbit effects. In particular, this band splitting is present in the valence and conduction bands of zigzag nanotubes. Zigzag tubes can be classified into three families, metallic (3N,0) tubes and the semiconducting (3N-1,0) and (3N+1,0). We have found a different behavior for the semiconducting families: in (3N-1,0) tubes, the band splitting is larger for the valence band than for the conduction band, as it happens for metallic (3N,0) tubes. However, in the (3N+1,0) family, the splitting is larger for the conduction band [4]. This distinct behavior for the zigzag families has been noticed before with respect to other physical properties and can be related to the trigonal warping effect [5].

We have also explored the role of curvature in spin-orbit interaction: spin-orbit splitting is enhanced with curvature, and we have studied its dependence for different chiralities [4].

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F23 - Magnetism in carbon nanotubes with line defects: first-principles calculations

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We apply first-principles calculations to investigate the interplay between electronic and magnetic properties in carbon nanotubes with line defects.We show that, depending on the diameter, oxygen line defects, which could appear as a consequence of a cooperative oxidation process, may lead to flat bands close to the Fermi energy with similar characteristics than those at nanoribbon edges.We also show that the antiferromagnetic state with a narrow band gap, which is the ground state solution for a specific diameter, may undergo a metallic transition upon application of a transverse electric field. The dependence of the results with the nanotube diameter and with the nature of the defect is also discussed.

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F24 - Spin Switching in Carbon Clusters

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Electronic and magnetic properties of all sp^2 carbon clusters with 10-14 atoms and carbon rings are investigated using many-body schemes. The correlated pi-electrons are treated by means of the single band Hubbard model. The ground-state energy, wave function and the total spin are calculated exactly using the Lanczos numerical diagonalization method. The clusters exhibit a spin switching when the electron-electron interaction is increased (a transition from singlet to triplet state). Among the clusters found with non-null spin, it has observed carbon chain morphologies containing two interconnect clusters joined by one or two bonds. Also, one hole or electron doping effect in the magnetic properties of carbon clusters is investigated. Finally, armchair and zigzag carbon ribbons results are discussed.

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F25 - Magnetic Properties of Carbon Nanostructures

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We investigate the magnetic response and the ring currents induced by the presence of an external magnetic field in different carbon nanostructures using a pi-electron tight binding model in conjunction with the London approximation.We consider fullerenes, corrugated and non-corrugated carbon nanotori, and finite graphene sheets. For corrugated carbon nanotori, we have constructed the structures in two different ways: (1) by joining the ends of carbon nanotubes containing pentagonal, hexagonal and heptagonal carbon rings (rectangular and hexagonal Haeckelites), and (2) by coalescing C_{60} molecules along of the three different axes of symmetry (C2, C3 and C5). The non-corrugated carbon nanototori have been constructed by joining the ends of standard carbon nanotubes containing hexagonal rings only. For the graphene ribbons, we considered those exhibiting armchair or zig-zag edges. Our results reveal strong paramagnetic signals in structures containing non-hexagonal carbon rings. For carbon nanotori, the presence of strong paramagnetism causes the electrons to flow around the torous. We also observed that the ring currents of graphene ribbons are small and localized at the edges. Finally, the magnetic moment of nanotori constructed from Haeckelite structures is also described as a function of doping (adding additional electrons or holes).

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F26 - Electron Holography of Ferromagnetic Nanoparticles Encapsulated in Three-dimensional Arrays of Aligned Carbon Nanotubes

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Arrays of closely-spaced ferromagnetic nanoparticles are of interest for applications that include data storage, magnetic imaging and drug delivery. Here, we use electron holography and micromagnetic simulations to study the magnetic properties and interaction of ferromagnetic metal nanoparticles that are encapsulated in threedimensional arrays of closely-spaced carbon nanotubes. The nanotubes are used to tailor the shapes, sizes and compositions of the nanoparticles, as well as to protect them from oxidation. Magnetic induction maps are recorded from individual nanoparticles that have sizes of between 10 and 40 nm, the magnetic moments of the nanoparticles are measured, and the strengths of magnetostatic interactions between adjacent particles are quantified.

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F27 - Theoretical studies doped double-wall carbon nanotubes

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Carbon nanotubes are promising in a wide variety of electronic applications from nanotransistores to sensors. Most studies of carbon nanotubes are realized on single-wall carbon nanotubes (SWCNTs). Recently it has been an increasing substantial interest in double-wall carbon nanotubes (DWCNTs). The DWCNTs are interesting cause it is an intermediate structure between SWCNTs and multi-wall carbon nanotubes (MWCNTs). The control of properties of these nanotubes is a key for their potential applications in technology. A way to control is through doping nanotubes with atoms of other chemical species. The addition of dopants within the lattice of carbon nanotubes has suggested that application can be realized. It has been shown that B-doping of MWCNTs results in the addition of acceptor states near the valence band [1]. In this work we have doped the DWCNTs with B and N atoms and observed how the electronic properties are changed.

[1] Blasé, X., et. al. Phys. Rev. Lett., 81, 2332 (1998).

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F28 - Hydrogen storage in carbon nanoscrolls

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Hydrogen (H_2) has been recently object of intense research as an energy source. Among the problems that have to be solved for the wide use of hydrogen energy, the most important one is how to store H_2 easily and cheaply. The target of the U.S. Department of Energy for hydrogen storage is a gravimetric capacity (weight of stored H_2/system weight) of 6.5 wt% and a volumetric density of 62 kg H_2 m^{-3}. Graphite and carbon nanotubes have been both theoretical and experimentally investigated as potential adsorbent structures. Recently, a lowtemperature synthesis method was developed to produce a different type of carbon nanostructure, the so called carbon nanoscroll (CNS). This structure is formed by wrapped graphite sheets.

In contrast to carbon nanotubes, CNSs provide inter-layer galleries that can be intercalated with different agents, and the CNS diameter can expand to accommodate the volume of the intercalant. This feature is potentially important for hydrogen storage. In this work we have used molecular dynamics simulations to investigate the hydrogen uptake mechanism and the gas sorption/desorption cycle, and grand-canonical Monte Carlo simulations to estimate the storage capacity of CNSs. The scroll adsorption capacity was explored by changing the space between scroll layers. At equilibrium geometries (interlayer spacing about 3.4 angstrom the scroll storage capacity can reach 2.5 wt% which is higher than the values obtained for crystallographically packed carbon nanotubes at 150 K and 1 MPa. Higher capacities were reached when interlayer spacings were increased. The value of 5.5 wt% hydrogen was obtained when the interlayer spacing was 6.4 angstrom. While our Monte Carlo simulations were performed at low pressure (1 MPa) and relatively high temperatures (150-350 K), we expect an increase in the storage capacity of CNSs for pressures available in experimental setups (~10 MPa). The sorption/desorption in an isolated CNS was investigated through a temperature-controlled cycle. After the scroll had been loaded reaching about 4 wt%, the desorption process was carried out by heating up the system. During this process, the absorbed H_2 amount decreased to 1 wt% when almost all the H_2 molecules were released. A recharging process was then performed through cooling, that can lead to even higher wt% values than the ones obtained before the desorption process. Our simulations suggest that CNSs can be promising systems for hydrogen storage especially when intercalants are present, and that temperature can be used as a charging/releasing variable.

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F29 - ALKALINE METALS ADSORBED ON GRAPHENE

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Graphene layers have been proposed as alternative materials for replacing carbon nanotubes in some applications, due to its easy synthesis and low costs. In case of double layer recent experiments shown that is possible to achieve the control of the electronic band gap by adjusting the carrier concentration in the layers and controlling the gate potential. In this work we study the interaction between graphene layer and alkaline metals aiming to understand the modification on the electronic band structure and how the gap can be tuned.We used first principle calculations based on the Density Functional Theory (DFT). We have investigated different configurations for the alkaline metals on the layer. Optimized parameters such as minimal distances, energy, electronic band structure and charge transference is discussed.

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F30 - Electronic and Magnetic Properties of Fe Atomic and Wires Adsorbed on Graphene and Nanotube Surfaces

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Materials based on carbon have found an enormously wide range of potential applications. Although buckyballs, nanotubes, and others structures can all be viewed as derivatives of graphene but only recently the graphene has been experimentally obtained by micromechanical cleavage of graphite. Many reasons make the graphene a promising candidate for potential applications, such as our scalability, chemical stability, and ballistic transport at room temperature, among others. Moreover, there is an extraordinary interest about the magnetic order in low-dimensional systems that can be used in recording media, magnetic inks, and spintronics devices. For such purpose, it is interesting to understand the interaction of transition metals with graphene and nanotube surfaces. In this work the structural, electronic and magnetic properties of adsorbed Fe atomic and linear chains on graphene surface are investigated by using total energy ab initio calculations based on the density functional theory. A systematic study of several configurations of a Fe atomic and wires interacting with graphene surface will be presented. The most stable configurations will be compared with previous results obtained for Fe atomic and wires interacting with carbon nanotubes.

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F31 - Topological defects and grain boundaries in graphene

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We constructed theoretical models to study the modifications in electronic structure and energetics of graphene, introduced by the presence of various topological defects: pentagon-heptagon pairs, Stone-Wale (SW) defects made of two adjacent heptagon-pentagon pairs, and a grain boundary observed in a recent scanning tunneling microscopy study [1]. The grain boundary (GB) geometry is formed by pentagon-heptagon pairs extended along the GB line. Theoretical studies indicate that substitution of an hexagon by an n-membered ring introduces important modifications in the electronic structure of graphene. Pentagon-heptagon pairs and SW defects are commonly present in graphene samples or carbon nanotubes because they are stable defects from the energetic viewpoint [2,3]. The presence of pentagon or heptagon in graphene without changing the threefold coordination of the carbon atoms induces positive and negative curvature, respectively. In presence of a pentagon-heptagon pair,the mean a remains zero curvature. Calculations of charge from the local density of states of graphene with single n-membered ring showed that pentagon is attractive and the heptagon is repulsive to electrons while the even - membered rings are neutral [4,5].

Using first principles calculations, we find that SW defects, two heptagon-pentagon separate pairs and GBs do not introduce resonant states at the Fermi level in graphene. Resonance energies are at least ~0.3 eV above from the Fermi level. We find also that vacancies in grain boundaries can lead to localized to Fermi-level resonances and magnetic moments on graphene. Preliminary results on the interaction between impurities (N and B) and topological defects will also be presented.

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F32 - Graphite and Carbon Compounds Nuclear Purity Control by Total Neutron Cross-Section Determinations

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The neutron crystal spectrometer installed at the 1 kW Argonaut research reactor of the Instituto de Engenharia Nuclear(IEN)-CNEN-Rio de Janeiro, is used as one of quality control of materials at level of nuclear purity, both applied to nuclear and pharmaceutical industries. In order that the property and parameters of graphite from several origins could be determined, neutron total cross-sections were measured. For the carbon nanotubes fabrication by UFMG/ICEX-Instituto de Física, and its purification in the CNEN/Centro de Desenvolvimento da Tecnologia Nuclear (CDTN) - Belo Horizonte, the instrument is disposable for measurements to accompany the processes, complemented by chemical physics techniques and other methods for control fabrication, characterization and analysis for these materials. Joined to neutron transmission and diffraction techniques, the total neutron cross-sections, a parameter related to atomic nucleus area, can be determined. By the use of rather sophisticated technique, the cross-sections grouping and parceling processes, is possible the neutron cross-section determinations for chemical compounds and big molecules. Total neutron cross-sections for graphite samples from Brazil, Japan an USA were measured. French graphite samples from Pechiney were used as reference, with a value of 4,7 barn for the energy of neutrons of 0,05 eV and recommended in the international literature. The results are here discussed with the objective of application in the carbon nanotubes technology (CNT).

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F33 - Electrostatics of individual SWNTs investigated by EFM

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We report an experimental study of static charge distribution in individual single-walled carbon nanotubes grown on Si+115nm SiO_2 substrate. From these experiments, we conclude that charges are distributed uniformly along the nanotubes. We demonstrate that electrostatic force microscopy can accurately measure the amount of charges per unit length. We found that this amount is diameter dependent and in the range of 1 electron per nanometer for a 2.5 nm nanotube at a potential of + 3.5V.

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F34 - A Molecular Structural Mechanics Investigation on Single-Walled Carbon Nanotubes

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Since their discovery in the earlies 90's carbon nanotubes (CNT) have being the center of attention of many research groups. CNTs exhibit exceptionally high stiffness, strength and resilience. As the size, mechanical strength, and electrical properties of nanotubes are highly dependent on their atomic architectures, the traditional "mechanics of materials" has to be expanded to accommodate the atomistic formulation. Based of mechanics of materials the finite element method is one of the most used "tools" for stress/strain analysis. This paper will focus its attention on numerical simulation of single walled carbon nanotubes (SWCNT) based on a three-dimensional finite element analysis associated to molecular dynamics (MD). Following Tserpes and Papanikos (2005), three SWCNTs configurations were simulated, i.e. armchair, zigzag and chiral. The model development is based on the assumption that carbon nanotubes, when subjected to loading, behave like space-frame structures. The bonds between carbon atoms are considered as connecting load-carrying members, while the carbon atoms as joints of the members. To be able to create the finite element models, nodes are placed at the locations of carbon atoms and the bonds between them are modeled using three-dimensional elastic beam elements. The elastic moduli of beam elements are determined by using a linkage between molecular and continuum mechanics. Compression, tension, torsion and shear are simulated and the SWCNT stress and strain fields are obtained. Furthermore, based on the concept of representative volume element developed by Tamma and Avila (1999) the SWCNT stiffnesses are obtained and compared against experimental and numerical data. The results showed are in good agreement with those published in literature.

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F35 - Inner-shell charging of multi-walled carbon nanotubes

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Carbon nanotubes (CNTs) have been studied by Electrostatic Force Microscopy (EFM). Electrostatic properties of individually separated single-walled and multi-walled carbon nanotubes deposited on insulating layers have been investigated by charge injection and EFM experiments [1,2]. Delocalized charge patterns are observed along the CNTs upon local injection from the EFM tip, and correspond to charge storage in the nanotubes and to charge trapping in the oxide layer along the nanotubes. Both effects are dissociated experimentally. The continuous and abrupt discharge processes of CNTs are discussed, as well as the field-enhancement of electron emission patterns at the CNT caps [3]. In the case of multi-walled CNTs, quantitatively measured linear charge densities are found to deviate from classical electrostatics by more than one order of magnitude. From the analysis of charge densities as a function of CNT diameters, we demonstrate that multi-walled carbon nanotubes develop an develop an internal response to the biased tip probe, allowing an inner-shell charging as a result of intershell tunnelling processes.

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F36 - Carbon nanotubes filled with ferrocene: charge transfer, hybridization, and possible strong bonding

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We present calculations on the inter-molecular interaction between the components of ferrocene filled single walled carbon nanotubes. We find that there is charge transfer between the subsystems in agreement with photoemission spectroscopy measurements. We consider the possibility of a strong binding between the ferrocene and the nanotube in light of the charge transfer data.

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F37 - Engineering the structure and properties of carbon nanotubes with electron and ion beams

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As recent experimental and theoretical studies demonstrate [1], beams of energetic particles such as electrons or ions can have beneficial effects on mechanical, electronic and even magnetic properties of carbon nanotubes and other nano-structured carbon systems. Self-organization effects in graphitic lattices under a particle beam lead to the formation of new nanostructures that cannot be obtained otherwise. This is an unusual behaviour that comes from the ability of the graphitic network to reorganize its structure and from the inherent nanometer size of the systems which affects the dissipation of the energy brought in by the energetic particles. Irradiation can give rise to extreme pressure inside nanotubes [2], so that these systems can be used as nanolaboratories for studying pressure-induced transformations at the smallest scale. We report on the recent progress [3] in our understanding of ion-irradiation-induced phenomena in carbon nanotubes obtained from atomistic computer simulations. The production, annealing and further evolution of defects is simulated at various levels of theory ranging from ab initio to kinetic Monte-Carlo methods. Our simulations open new avenues for defect and impurity-mediated engineering of the atomic and electronic structure of carbon nanotubes.

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F38 - Interaction of molecular hydrogen with carbon nanomaterials

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One of the biggest drawbacks of current density functional theory is its inability to account properly for the dispersion interactions. DFT is probably the only ab initio method directly applicable to complex molecular systems, and, therefore, there is an ongoing research aimed to include the dispersion interaction into the DFT. In this work we employ a novel DFT-D approach based on the Reciprocal Power Reproducing Kernel Hilbert Space (RP-RKHS) interpolation (M.Rubeš, P.Soldán, P.Nachtigall, and O.Bludský, Phys. Chem. Chem. Phys., submitted) to describe interactions of molecular hydrogen with various carbon nanomaterials. The reliability and accuracy of our method is tested on systems where high-level ab initio calculations are available.

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F39 - Control of the structure and properties of carbon nanotube fibres

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We have previously introduced a continuous single-step gas-phase CVD process for carbon nanotube 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 nanotubes continuously as pure fibres or films. In this work we present the effects of several process parameters on the morphology and properties of the individual nanotubes as well as the fibres, which were produced from a feedstock containing ethanol, ferrocene and thiophene as the carbon and catalyst sources and the growth modifying additive, respectively. A variety of nanotube morphologies, from pure multiwall to double wall nanotubes or mixtures of “thin wall” nanotubes (1 to 3 walls) can be selectively produced by controlling the furnace temperature, carrier gas (hydrogen) flow rate and relative concentrations of iron, carbon and sulphur in the process. The morphology changes have a significant effect on the optical properties of the nanotubes, namely the Raman intensity ratio of the D- and G-bands, which ranges from 1 to 0.05. Furthermore, the mechanical properties of the nanotube fibres vary, the strength being from 0.1 to more than 2 N/tex, the highest performance found with the large diameter double wall tubes. In this paper we aim to present a comprehensive study to the factors governing the nanotube properties during their bulk production.

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F40 - Auto-collapse of single, double and triple-walledcarbon nanotubes is diameter dependent

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Large diameters single and double-wall carbon nanotubes are can be continuously produced in the process of direct-spinning fibres from the gas-phase in a CVD reactor. The individual tubes are mainly double-walled of surprisingly large diameter, in the 4-9 nm range. In line with theoretical predictions, these tubes collapse to give a “dog-bone” cross-section. Images from high resolution electron microscopy show that all of those with a diameter larger than 5 nm have collapsed, including the single, double and triple-walled. Recent results from classical molecular dynamics simulation have shown that single-wall carbon nanotubes with diameters larger than 4.16 nm should auto-collapse under atmospheric pressures (Elliott et al. Phys Rev Lett 92, 2004). The extra strain energy associated with the higher curvature at the dog-bone ends of the collapsed tubes is more than compensated for by the energy of bonding between the inner surfaces of the graphene sheets. Both X-ray and electron diffraction also show clear evidence of the auto-collapse. In X-ray diffraction, The position of 002 is 26.3° corresponding to 0.340 nm is typical of multiwall CNTs and very close to the turbostratic graphene layer spacing of 0.344 nm. However, there is a broad smearing of the 002 peak towards lower angles which correlates with the regions of the collapsed structure where the walls of adjacent nanotubes are not quite in contact. In electron diffraction, there is also significant streaking of the 002 maxima towards the centre of the pattern. The compatibility of the diffraction evidence with the high resolution electron microscopy images underlines that the collapse of the tubes, was not caused by sample preparation for microscopy. Therefore, the microstructure of the direct-spun fibres which show properties in the high-performance range consists of very long bundles of collapsed large diameter carbon nanotubes.

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F41 - Orientation development and liquid-densification of carbon nanotube fibres

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Kilometres of fibres with outstanding physical properties can be obtained at a rate of 70 m/min by the direct spinning of carbon nanotube aerogels from the CVD reaction zone. Data are reported which show that the properties and degree of orientation increase with wind up speed. Induced interaction between CNT macro assemblies and suitable liquids results in densified fibres with controlled diameter ranging from 100 to 5 mm. The densification by capillary forces and liquid evaporation increases their mechanical integrity, tensile strength (e.g 3.4 N/tex), electrical and the thermal conductivity. These properties are related to the inter-tube distance and high degree of alignment within the nanotube network, as has been observed by Raman spectroscopy and small angle X-ray scattering.

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F42 - Fibres of carbon nanotube systems via a liquid crystalline route

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Processing of carbon nanotubes is a significant challenge due to highly hydrophobic character of the nanotubes. Stable suspensions of carbon nanotubes in different media have been achieved by surface functionalisation, which typically causes changes to the structure of nanotubes, or by appropriate surfactants. Furthermore precise control of morphology of the nanotubes and their electronic properties is yet to be seen. It has been shown that nanotubes form liquid crystalline phase in aqueous systems where the equilibrium behaviour is in accord with the rigid-rod/solvent lyotropic phase diagram first predicted by Flory. In this paper we demonstrate that carbon nanotubes form liquid crystalline phases at sufficiently high concentration in other non aqueous matrices. The liquid crystalline suspension of nanotubes can then be used to continuously spin fibres of carbon nanotubes with desire diameters, aspect ratios and morphology. Fibres of single-, multi-walled with cylindrical and herringbone arrangements of the graphene layers as well as nitrogen doped isochiral nanotubes were made. The nanotubes were found to be very well orientation in the fibres and among the different nanotubes examined, the highly crystalline isochiral nanotubes formed fibres with the highest level of orientation and packing density. Using the crystalline isochiral nanotubes areas with pure armchair and zigzag nanotubes were found. Mechanical and electrical properties of these fibres will be discussed.

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F43 - Continuous spinning of high performance carbon nanotube fibres: structure control and properties

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The process of direct spinning of carbon nanotube fibres from the CVD reaction zone (Li et al. Science 304, 2004, 276-278) is yielding fibres with distinctly encouraging mechanical properties. While the best strength (2.2 N/tex) and stiffness (160 N/tex) promise competition for established carbon fibres, the maximum energy absorbed at fracture (46 J/g) is higher than for Kevlar and considerably higher than carbon fibres. The paper will briefly review the process and describe the process parameter set for the production of continuous lengths of fibre wound up at 20 m per minute. The structure of the nanotubes forming these high performance fibres is unique, consisting of double walled tubes of unusually large diameter which have autocollapsed to give a ‘dog-bone’ cross section. The collapsed tubes stack in layers and maximise their contact areas. The length of the individual nanotubes is at least 10,000 times their diameter. The key parameters for the synthesis of such nanotubes and their spinning into continuous fibre would appear to be the high temperature of the process and addition of a small amount of sulphur with the feedstock. Evidence is presented which shows that the sulphur forms a separate phase on the surface of the iron particles and enables the formation of thin walled tubes of relatively large diameter. The mechanical properties of the fibres are assessed as a function of wind up speed and condensation process. Statistical analysis as a function of gauge length indicate that the strength is defect limited, and that the intrinsic strengths can be expected to be at the high end of current carbon fibre technology. The observed properties are related to the microstructure, and the prospect for future developments explored.

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F44 - Carbon nanoribbons under electric fields: magnetic and transport features

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Recent first principle calculations [1] show that zigzag nanoribbons are magnetic and can be tuned to produce highly polarized electrical currents under the presence of an electric field. Here we study the transverse dynamic spin response of the ribbon within the linear regime, using a tight-binding model to describe the electronic structure. Magnetism is driven by an effective intra-atomic Coulomb repulsion treated in a self-consistent mean-field approximation. The properties of such excitations allow us to investigate the robustness of magnetic order in these systems. An interesting behavior is found for the excited mode relation dispersion with the field momentum, mixing ferro and antiferromagnetism signatures. We also investigate the ribbon´s transport properties with and without applied transverse electric fields using the Landauer formalism.

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F45 - Gap modulations in graphene nanoribbons under electric and magnetic fields

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We present a theoretical analysis of graphene nanoribbons under the action of a transversal electric field and a perpendicular applied magnetic field. A simple one -band tight-binding model is adopted following the realspace Green function formalism and the Peirls phase approach. A self consistent treatment is performed for the charge occupation in the nanoribbon using the Poisson equation.We have studied the gap modulation of armchair, zigzag and chiral nanoribbons due to an transversal electric field and determined the induced metal-insulator - like transition. This may be useful for potential applications of graphene ribbons in electronic devices. Special attention is devoted to the possible metallicity of zigzag-edge nanoribbons, depending upon the passivation at the dangling bonds at the ribbons edges. Different schemes are proposed, varying the intensity of the coupling between carbon and foreign atoms and the nature of them. They are guided by ab initio calculations using density functional theory, trying to obtain more realistic models for the ribbons. The ballistic transport behavior has been examined under the external perturbations by calculating conductance.We also analyze the transport properties in the non-equilibrium regime to study the current-voltage characteristics of the ribbons.

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F46 - Disorder and segregation effects on the electronic properties of graphene-like BCN layers

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Materials with sp2 covalent bonds can present distinct electronic structures. For instance, a graphite layer (graphene) is a zero-gap semiconductor while an analogous boron nitride (BN) layer is a wide gap insulator. Experimentally, it is possible to make partial substitutions of carbon atoms by boron and nitrogen leading to the formation of $B_xC_yN_z$ layered compouds of distinct stoichiometries. These structures present intermediate electronic properties between those of those of pure carbon or BN structures, which could be useful, for instance, in applications that require optical absorption in the visible region. In the present work, we investigate electronic and structural properties of $B_xC_yN_z$ layers with several configurations and stoichiometries using a combination of first-principles calculations and a recently developed firstneighbor valence-bond model. The model is based on the parametrization of binding energies obtained from first-principles calculations [Mazzoni, Nunes, Azevedo, and Chacham.Phys. Rev. B, 73, 073108 (2006)] and generates results similar to the first-principles ones, with a much lower computational cost. We apply this model to obtain the total energies and the lower energy conformations of $B_xC_yN_z$ layers, by means of a simulated annealing program. The electronic and structural properties of selected structures (generated by the simulated annealing procedure) are also investigated by means of first-principle calculations. We find that the annealing procedure leads to the segregation of the $B_xC_yN_z$ layers into graphene islands within a BN layer. As the segregation progresses during the simulation, we also find that the electronic density of states D(E) evolves from a featureless one towards one that has a strong depletion of D(E) near the Fermi energy. This is associated with the formation of localized electronic states at the graphene islands.

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F47 - First-Principles Calculations of Carbon Nanotube Superlattices

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We report on first-principle calculations for metallic carbon nanotube superlattices N(12,0)/N(6,6) with N=1-4. The calculated band structures show a good overall agreement with the results of the simpler tight-binding pi-electron approximation. In particular, some peculiar flat bands, localized in the N(12,0) or N(6,6) sections, found previously with the tight-binding model [W. Jaskólski and L. Chico, Phys. Rev. B 71, 155405 (2005)] are present also in the *ab-initio* calculation. However, in contrast to previous results, these bands are no longer dispersionlees and are always single-degenerate.We ascribe the removal of degeneracy to the electron interaction, which is automatically included in the *ab-initio*.

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F48 - Determination of LA and TO Phonon Dispersion of Graphene and 2D Disordered Graphite by Double Resonance Raman Spectroscopy

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Phonon dispersion relation is a fundamental physical property of a solid. In this work Raman spectroscopy was used to determine the dispersion of the longitudinal acoustic (LA) and in-plane transversal optic (iTO) branch near the *K* point in the Brillouin zone (BZ) of a graphene monolayer and of a two-dimensional (2D) turbostratic graphite by the analysis of two second-order peaks: the *G'* band and another band around 2450 cm^{-1}. The *G'* peak comes from a double resonance intervalley Raman process involving two in-plane transverse optical (iTO) phonons with $q = 2\ k$, where q and k are the phonon and electron wavevectors, respectively, measured from the *K* point [1]. The 2450 cm^{-1} band also is explained by two $q = 2\ k$ phonons, but involving the iTO and the LA phonon branches [2]. Therefore, the LA and TO frequencies can be obtained by this two peaks frequencies. The experimental results were compared with theoretical phonon dispersion relation of graphene.

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F49 - Structural and Electronic Properties of the Boronand Nitrogen-Doped Graphene

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We study the structural, electronic and vibrational properties of substitutional boron- and nitrogen-doped graphene using density-functional theory and pseudopotential approaches. As expected, both dopants introduce sharp donor-like and acceptor-like resonance levels in the graphene electronic structure. Regarding structural properties, in the large concentration regime 5lattice constant of graphene. We also analyze the modifications in the phonon spectrum of graphene introduced by the doping.

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F50 - Raman Spectroscopy of Doped Graphene

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Raman spectroscopy can identify and count graphene and graphene layers [1]. The G and 2D Raman peaks change in shape, position and relative intensity with number of layers. This reflects the evolution of the electronic structure and electron-phonon interactions [1,2].We present the effect of doping on the Raman spectra of graphene [3]. The Fermi energy is tuned by applying a gate-voltage to produce both electron and holes doping at different ambient temperatures. We show that this induces a stiffening of the Raman G peak for both holes and electrons doping [3]. This cannot be explained within the standard adiabatic Born-Oppenheimer approximation [4]. Indeed, in graphene the electron-momentum relaxation is much slower than the phonon pulsation, thus electrons cannot relax to their instantaneous ground states, invalidating Born-Oppenheimer [3]. On the contrary, the 2D peak shows a different response to electron and hole doping. This can only be explained considering the double resonant nature of the 2D peak [5]. Thus Raman spectroscopy can also be used to monitor the doping level. The combination of G and 2D allows to distinguish electron from hole doping. This is key to interpret the variation of the Raman spectra on a given substrate or on different substrates. Finally we discuss the implications for the interpretation of the Raman spectra of nanotubes [6].

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F51 - Probing the phonon and electronic dispersion of a graphene layers by Resonance Raman Scattering

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Graphene is the building block for all kinds of graphite materials. It forms a unique material for basic research, since it provides relativistic electrons for quantum electrodynamics research, being interesting for new applications. The number of graphene layers have different Raman features related to the Double Resonance (DR) process, when compared to three-dimensional graphite.In this work we measured the G0 Raman band which is related with the DR in graphene layers. By using several laser lines we could map the dispersion of the G0 Raman band in the range of the visible and probe both phonon and electronic dispersion of different number of graphene layers.

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F52 - Rayleigh Imaging of Graphene and Graphene layers

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Developing tools for the quick, non-destructive identification of Graphene layers is imperative to enable graphene technology. Raman scattering has emerged as an ideal, non-destructive technique for the identification of graphene and its doping [1, 2]. However, the Raman scattered photons are a minority compared to those elastically scattered. Elastic scattering (Rayleigh scattering) can provide a much quicker means of identification of single and multi-layer samples. Here we report an extensive investigation of graphene by monochromatic and white-light Rayleigh scattering and the theoretical understanding of the experimental data [3]. Samples consisting of increasing number of layers are identified by a combination of AFM and Raman Spectroscopy. Confocal Rayleigh maps are obtained by raster scanning the sample with a piezoelectric stage. The scattered light depends on the dielectric function of the samples and their geometry. The intensity varies with the number of layers. Large graphene layers can be mapped and identified in a few minutes. The dependence from sample geometry of the elastically scattered light makes Rayleigh spectroscopy a promising tool for the identification of graphene nano-ribbons.

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F53 – Raman Mapping of Graphene Edges

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The identification of graphene edges is of particular interest, since their “chirality” determines the electronic properties of the flake. Furthermore edges are preferred doping sites. Here we present a detailed far field and near field Raman mapping of graphene layers and graphene edges oriented at diffierent relative angles [1]. Very large graphene flakes (~100um^2) with sharp edges are produced by micromechanical cleavage of graphite [2,3]. Single-layer flakes are then identified by Raman Spectroscopy [3,4]. The angle between the edges is determined by optical microscopy, scanning electron microscopy and atomic force microscopy. Raman spectra are measured for different excitation wavelengths. The D and G peaks are studied as a function of the polarization of the incident light. The D-band intensity is strongest for light polarized parallel to the edge and minimum for perpendicular orientation [5]. Raman mapping shows that the D peak intensity is very small or absent inside graphene flakes. The I(D)/I(G) ratio significantly increases close to the edge, becoming as large as 0.3-0.5 for parallel polarization. This increase is due to the relaxation of the Raman fundamental selection rule at the crystal edges [6].

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F54 - Transport Properties of Graphene Nanoribbon Heterostructures

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The fabrication under controlled experimental conditions of graphene nanoribbons (GNRs) has attracted a lot of scientific interest in the last decade [1]. GNRs are single atomic layers which can be understood as na infinite unrolled carbon nanotube. The special electronic behavior of graphene ribbons defined by their quasi one dimensional electronic confinement and the shape of the ribbons ends (two cases of maximum symmetries can be obtained: zigzag and armchair ends [2]), suggest remarkable applications in graphene-based devices [3]. Moreover, due to the flat structure GNRs seem to be easier to manipulate than carbon nanotubes. The transport properties of these structures have been studied with special interest by several scientific groups. Peres et al find that, for clean systems, the quantization condition for the electronic conductance is different for zigzag and armchair GNRs. [4], Shi et al show that, applying a gate voltage to the ribbons, it is possible to obtain an electronic switch very useful to study the Klein paradox. [3]. In this work we study the electronic and transport properties of heterostructures formed by armchair graphene nanoribbons with intersections of finite length. We describe the system by a tight-binding model and calculate the density of states and the conductance of the system within the Green function formalism based on real-space renormalization techniques. The current is calculated within the Landauer-Büttiker formalism.We show the appearance of interface states and bound states in the continuum which present a strongly dependence of the heterostructure geometry [5]. We investigate the effects on the conductance and the characteristic curves of currents versus voltages of an external perturbation applied on the edges atoms of the intersection region.

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F55 - Electronic structure and edge doping in graphene nano-ribbons

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The recent discovery of single layer graphene [1] provides carbon electronics with a new material compatible with planar top-down processing. In particular, graphene nanoribbons (GNRs) are the ideal counterpart of carbon nanotubes.We present a detailed theoretical investigation of the band-structure of GNRs, focusing in particular on the construction of a Kataura-like plot for armchairs and zigzag GNRs. Here we compare calculations performed on hydrogen-terminated GNRs using a number of different techniques, ranging from simple first-neighbors tight binding, to density functional theory and GW. Each technique sheds light on different and complementary aspects of the electronic structure of GNRs, and only their combined use enables a full description of the GNR band structure [2]. By means of DFT calculations, we also investigate the modification in the electronic structure of GNRs induced by the presence of various chemical groups at the ribbons edges. In particular, we investigate the onset of defect states in the bandgap of zigzag ribbons when an H atom is replaced by a NH_2 or a COOH groups, and thus the possible n and p doping of GNRs.

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F56 - Deposition of Pt nanoparticles on CNx explointing its inherent chemical properties

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IPICyT

We describe a simple process to deposit transition metals on the surface of N-doped multiwalled carbon nanotubes (MWNTs-CN*x*) exploiting its inherent chemical properties that makes them different from the undoped ones. In this research, we describe one of the first approaches to use the chemical properties of the N dopant site "naturally" obtained in the surface of CN*x*. First we proved the different response that both, undoped and N-doped CNTs, exhibit to be dispersed in different protic solvents, which is indicative of a distinct chemical behavior of every kind of nanotube. In second place, we took advantage of such properties and developed a simple method for depositing Pt nanoclusters on the surface of MWNTs-CN*x* which were not previously submitted to any treatment of chemical functionalization. In this context, we have also developed two different methods for depositing iron (Fe). This is the first time that the distinctive chemical properties of N-doped carbon nanotubes are illustrated by a simple experiment and open the ways to make more specific research focused in specific and complex chemical reactions. In this way we have started to study the reaction of CN*x* with specific reagents and obtained some initial results.

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F57 - Electronic and Mechanical Properties of 'Super'-Carbon Nanotubes

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Carbon based materials present an enormous variety of forms and properties. Among these structures we can mention graphite, diamond, fullerenes and nanotubes. But in principle other carbon-based structures are possible. In this work we present the electronic and mechanical properties of a new family of structures called 'super'- carbon nanotubes. The starting structure, generically named the super-graphene (SG), is heuristically constructed replacing the carbon-carbon bonds of the graphene architecture by single walled carbon nanotubes (SWNTs), andthe carbon atoms by Y-like junctions. From the SG a new tubular structure can be generated.We named this tubular structure super-nanotube (ST) which represents a carbon nanotube made of carbon nanotubes. Such procedure can be repeated several times, generating a fractal structure. This procedure is not limited to carbon nanotubes, and can be easily modified to be applied to other materials. Tight-binding total energy (TROCADERO) and density of states calculations showed that the 'super'- sheets and tubes are thermodynamically stable and predicted to present metallic and semiconducting behaviour. Also, molecular dynamics simulations, using Brener-Tersoff type potentials for nets built from STs showed that these materials could exhibit remarkable mechanical properties and could be the basis to new classes of super-hard and elastic carbon-based materials.

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F58 - DFT modeling of growth of SWCNT on iron catalyst

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We performed simulations of initial stages of carbon nanotube growth catalyzed by iron particles using allelectron density functional theory with generalized gradient approximation for the exchange-correlation functional. We computed $Fe_4 + C_n$ for n=7-25, $Fe_{10} + C_{15}$, and $Fe_{10}C_{15} + 10C$. In addition, we performed a detailed study of the development of different isomers in the C_n series, for n=7-25. Our simulations show that the prime role of a catalyst is to assemble carbon atoms in the optimal gas-phase configuration of C_n that corresponds to a ring configuration for a rather large n. The surface topology of a catalyst particle is most likely responsible for the chirality of a carbon nanotube grown from a seed ring.

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F59 - A Carbon Nanotube Hybrid Filter for Removal of Microbial Contaminants

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Carbon nanotubes (CNTs) are known for their high surface areas, exceptional strength properties, extreme thermal stability, and other novel characteristics. Previous research has also indicated that CNTs might be affective in inactivating microbial pathogens. Our work studies the development of a CNT-hybrid filter by incorporating a thin CNT layer on various microporous base filters. The development of a CNT-hybrid filter shows promise in several drinking water applications. It could provide bacterial inactivation, and viral removal at gravity-driven or low pressures. The thin CNT layer on the filter surface is effective in filtering 100%, and inactivating more than 80% of bacteria (E. coli) deposited on the filter, suggesting an ability to eliminate or reduce biofouling of the filter. Viral removal experiments using the CNT layer of the hybrid as a depth filter have also been performed, demonstrating removal of 99.93% - 99.98% of MS-2 virus applied to the filter.

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F60 - Defects in Carbon Nanotubes

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Even though pristine carbon nanotubes (CNTs) have exceptional material properties, defects can be used to tailor or improve their mechanical and/or electrical characteristics. In this work we study a variety defects in CNTs with ab initio Density Functional Theory (DFT) calculations. For CNTs in bundles we investigate two different configurations, V12 and V22, which correspond to distinct arrangements of the vacancies in two nearest neighbor tubes. For a double walled CNT we investigate the Wigner defect as well as the V12 and V22 configurations. In all these cases the defects are such that a link is formed between the tubes, either in a bundle or in the doublewall. We will present results for formation energies and barriers of formation and recombination of these defects. We compare these results with the graphite, and study how these defects can alter the mechanical properties. We also study the electronic, structural and transport properties of divacancies in single-walled CNTs. Two structures were investigated, one that has two pentagons side by side with an octagon (585) and another composed of three pentagons and three heptagons (555777).We investigate their stability as a function of tube diameter, and calculate their charge transport properties. The 585 defect is less stable only in graphene due to two ´´broken´´ bonds in the pentagons.We estimate that the 555777 becomes more stable than the 585 for a diameter of about 40 Å (53 Å) for an armchair (zigzag) SWNTs, indicating that they will prevail in large diameter multi-walled carbon nanotubes and graphene ribbons.

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F61 - Theoretical study of anomalous Moiré patterns on HOPG

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We have calculated the electronic structure of a HOPG surface which has its surface layer missoriented with respect the internal ones and we have reproduced the well known Moiré patterns observed frequently in Scanning Tunneling Microscopy experiments. Besides this it is possible to introduce vacancies of carbon atoms in the surface layer and to study how these defects modify the surface electronic structures. Consequently this effect could be observed using the STM technique. This calculations were made applying the Density Functional Theory in the local density approximation (LDA) and using LMTO (Linear Muffin-Tin Orbitals) method in the Atomic Sphere Approximation (ASA).
On the other hand, the Tersoff-Hamman theory was used to generate artificial STM images.

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