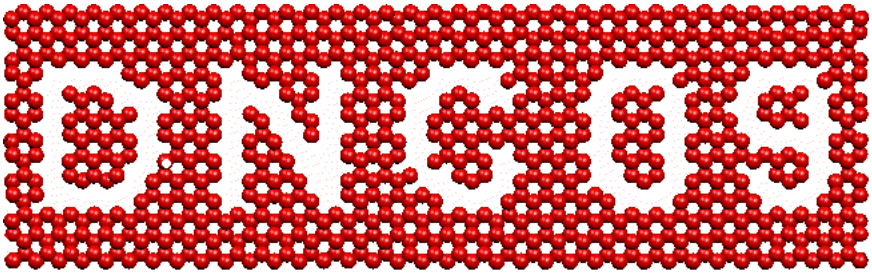
Computational Studies of Defects in Nanoscale Carbon Materials



May 11-13, 2009

CECAM-HQ-EPFL, Lausanne, Switzerland

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DNC09 Program Schedule

Time	Monday 11 May 2009	Tuesday 12 May 2009	Wednesday 13 May 2009
08:30	Registration and Opening Remarks		
09:00	A01 **Florian Banhart**	E01 **Laszlo Forro**	J01 **Jean-Christophe Charlier**
09:45	A02 **Steven G. Louie**	E02 **Chris Ewels**	J02 **Francesco Mercuri**
10:30	Coffee Break		
11:00	Summary Presentations B	Summary Presentations F	L01 **Gotthard Seifert**
11:45	Contributed session B	Contributed session F	Closing Remarks
12:30	Lunch		
14:00	C01 **Dmitri Golberg**	G01 **Oleg Yazyev**	CINN09 Workshop on Modeling of Carbon and Inorganic Nanotubes and Nanostructures
14:45	C02 **Susumu Saito**	G02 **Daniel Sanchez-Portal**	
15:30	Coffee Break		
16:00	D01 **Irene Suarez-Martinez**	H01 **Oliver Gröning**	
16:30	D02 **Gueorgui Gueorguiev**		
16:45		H02 **Giulio Biddau**	
17:00	D03 **Sami Malola**		
17:15		H03 **Andres Ayuela**	
18:30		Conference Dinner	

Color Legend:

Invited
Contributed
General contribution

Workshop description

Defects in nanoscale carbon materials such as carbon nanotubes and graphene may fully govern their mechanical and electronic properties. Moreover, defects may cause intriguing behavior including magnetism. Presence of defects is believed to be mostly detrimental, by weakening the mechanical toughness. Beneficial effects of defects, including stiffening of loosely-connected nanotube networks or nucleation sites for structural transformations, have been mostly overlooked. By the vice or virtue, defects in carbon nanomaterials require complete understanding at the microscopic level. The aim of the proposed workshop is to bring together representatives of solid-state physics and materials science communities who use theoretical computational tools to discuss the state of our understanding of defects in carbon nanostructures. The participants will present the state of the art to students and newcomers to the field in tutorial presentations and discuss ongoing developments and perspectives of various computational techniques for modeling of non-ideal nanoscale carbon materials.

Topics receiving special attention include:

- Mechanical properties of defective carbon nanostructures
- Electronic and magnetic properties of defective carbon nanostructures
- Electronic and thermal transport in defective carbon nanostructures
- Chemical modification and tailoring of defective carbon nanostructures

Format of the Workshop:

Combination of invited and contributed presentations.

Program

Day 1 - May 11th, 2009

08:30 to 09:00 - Registration and Opening Remarks

09:00 to 09:45 A01-invited

Florian Banhart

The formation and observation of individual vacancies in carbon nanotubes by a focused electron beam

09:45 to 10:30 A02 - invited

Steven G Louie

Graphene nanostructures: Edges, ribbons, superlattices, and defective tubes

10:30 to 11:00 - Coffee Break

11:00 to 11:45 B - Summary Contributed Presentations

11:45 to 12:30 – Contributed Session B

12:30 to 14:00 - Lunch Break

14:00 to 14:45 C01- invited

Dmitri Golberg

Engineering of filled carbon nanotubes in a transmission electron microscope

14:45 to 15:30 C02 - invited

Susumu Saito

Energetics and Electronic Properties of Doped Carbon Nanotubes

15:30 to 16:00 - Coffee Break

16:00 to 16:30 D01- contributed

Irene Suarez-Martinez

Chemistry of different carbon nanoforms

16:30 to 17:00 D02 - contributed

Gueorgui Gueorguiev

Defects as structure-defining features in Fullerene-like Carbon Nitride and Phosphorus-Carbide

17:00 to 17:30 D03 - contributed

Sami Malola

Edge reconstructions and gold in-plane of graphene

Day 2 - May 12th, 2009

09:00 to 09:45 E01- invited

Laszlo Forro

Extended defects in carbon nanotubes and graphene

09:45 to 10:30 E02 - invited

Chris Ewels

Metals on Carbon Nanotubes

10:30 to 11:00 - Coffee Break

11:00 to 11:45 F-Summary Contributed Presentations

11:45 to 12:30 - Contributed Session F

12:30 to 14:00 - Lunch Break

14:00 to 14:45 - G01 - invited

Oleg Yazyev

Defects in graphene and graphite: formation and magnetism

14:45 to 15:30 G02 - invited

Daniel Sanchez Portal

Substitutional Transition-Metal Impurities in Graphenic Nanostructures

15:30 to 16:00 - Coffee Break

16:00 to 16:45 - H01 - invited

Oliver Gröning

Electron scattering observed by STM/STS at artificially created defects on single-walled carbon nanotubes

16:45 to 17:15 - H02 - contributed

Giulio Biddau

Atomic Pathways Towards the Synthesis of Fullerenes and Triazafullerenes from Polycyclic Aromatic Hydrocarbons

17:15 to 17:30 H03 - contributed

Andres Ayuela

Interface States in Carbon Nanotube Junctions: Rolling up graphene

18:30 to 23:00 - Conference Dinner

Day 3 - May 13th, 2009

09:00 to 09:45 J01 - invited

Jean-Christophe Charlier

Quantum Transport in Carbon Nanostructures including Defects

09:45 to 10:30 J02 - invited

Francesco Mercuri

Modeling of low-dimensional carbon nanostructures: an efficient approach based on chemical criteria

10:30 to 11:00 - Coffee Break

11:00 to 11:45 L01 – invited

Gotthard Seifert

The influence of Defects in Inorganic Nanotubes on Electronic and Mechanical Properties

11:45 to 12:30 - Closing remarks

12:45 to 14:00 - Lunch Break

CINN09 Workshop

14:00 to 18:00

List of all DNC09 presentations

Session A

A01 The formation and observation of individual vacancies in carbon nanotubes by a focused electron beam
Florian Banhart, J. A. Rodriguez-Manzo

A02 Graphene nanostructures: Edges, ribbons, superlattices, and defective tubes
Steven G Louie

Session B

B01 Chemistry of different carbon nanoforms
Irene Suarez-Martinez, Christopher Ewels, Gregory Van Lier, Marc Monthioux

B02 Atomic Pathways Towards the Synthesis of Fullerenes and Triazafullerenes from Polycyclic Aromatic Hydrocarbons
Giulio Biddau, Gonzalo Otero, Pablo Pou, Carlos Sánchez-Sánchez, Renaud Caillard, Celia Rogero, Javier Méndez, Antonio M. Echavarren, Berta Gómez-Lor, Jose Angel Martin-Gago and Ruben Perez

B03 Theoretical Investigations on the Formation and Structure of Nanocrystallites by Encapsulation in Carbon Nanotubes and Carbon Nanotube Junctions.
Matteo Baldoni, S. Leoni, A. Sgamellotti, G. Seifert, F. Mercuri

B04 Formation of defect structures on graphene and CNTs
Oguz Gulseren, Rasim Volga Ovali

B05 Defects as structure-defining features in Fullerene-like Carbon Nitride and Phosphorus-Carbide
Gueorgui Gueorguiev, S. Stafström, A. Furlan, L. Hultman

B06 Edge reconstructions and gold in-plane of graphene
Sami Malola, Hannu Häkkinen, Pekka Koskinen

B07 Interface States in Carbon Nanotube Junctions: Rolling up graphene
Andres Ayuela, H. Santos, W. Jaskolski, M. Pelc, L. Chico

B08 Synthesis, Experimental Research and Modeling of Structure of Carbon Nanotubes for Formation of Fuel Hydrogen Elements
Natalya Voronova, Anatoly Kupchishin

Session C

C01 Engineering of filled carbon nanotubes in a transmission electron microscope
Dmitri Golberg, Pedro M.F.J. Costa, Mingsheng Wang, Zhi Xu, Yoshio Bando

C02 Energetics and Electronic Properties of Doped Carbon Nanotubes
Susumu Saito

Session D

D01 Chemistry of different carbon nanoforms
Irene Suarez-Martinez, Christopher Ewels, Gregory Van Lier, Marc Monthioux

D02 Defects as structure-defining features in Fullerene-like Carbon Nitride and Phosphorus-Carbide
Gueorgui Gueorguiev, S. Stafström, A. Furlan, L. Hultman

D03 Edge reconstructions and gold in-plane of graphene
Sami Malola, Hannu Häkkinen, Pekka Koskinen

Session E

E01 Extended defects in carbon nanotubes and graphene
Laszlo Forro

E02 Metals on Carbon Nanotubes
Chris Ewels, I. Suarez Martinez, A. Felten, J. –J. Pireax, M. Hecq, C. Bittencourt

Session F

F01 Nonlinear conductance reveals positions of carbon atoms in finite metallic SWCNTs
Pouya Partovi-Azar, Afshin Namiranian

F02 Transport properties of N and B doped Nanotubes
Hafid Khalfoun, P. Hermet, S. Latil, and L. Henrard

F03 Electron scattering observed by STM/STS at artificially created defects on single-walled carbon nanotubes
Oliver Gröning, Gilles Buchs, Pascal Ruffieux, Dario Bercioux, and Hermann Grabert

F04 Suppression of size-quantization steps by lattice defects in graphene nanoribbons
Florian Libisch, Stefan Rotter, Joachim Burgdörfer

F05 Optical properties of defects in carbon nanotubes
Gilles Buchs

F06 Catastrophic model of destruction of polymer materials irradiated by electrons and formation of nanostructures based on carbon
Natalya Voronova, Anatoly Kupchishin

F07 Binding Energy of Fullerene to Q120C Mutant of Cytochrome C Oxidase
Markus Kaukonen, V. Ruiz, D. Bloch, M. Verkhovsky and E. Kauppinen

F08 First-principles investigations on the functionalization of ZnO nanowires
Andreia L. da Rosa, Thomas Frauenheim

Session G

G01 Defects in graphene and graphite: formation and magnetism
Oleg Yazyev

G02 Substitutional Transition-Metal Impurities in Graphenic Nanostructures
Daniel Sanchez Portal, E. J. G. Santos, A. Ayuela

Session H

H01 Electron scattering observed by STM/STS at artificially created defects on single-walled carbon nanotubes
Oliver Gröning, Gilles Buchs, Pascal Ruffieux, Dario Bercioux, and Hermann Grabert

H02 Atomic Pathways Towards the Synthesis of Fullerenes and Triazafullerenes from Polycyclic Aromatic Hydrocarbons
Giulio Biddau, Gonzalo Otero, Pablo Pou, Carlos Sánchez-Sánchez, Renaud Caillard, Celia Rogero, Javier Méndez, Antonio M. Echavarren, Berta Gómez-Lor, Jose Angel Martin-Gago and Ruben Perez

H03 Interface States in Carbon Nanotube Junctions: Rolling up graphene
Andres Ayuela, H. Santos, W. Jaskolski, M. Pelc, L. Chico

Session J

J01 Quantum Transport in Carbon Nanostructures including Defects
Jean-Christophe Charlier

J02 Modeling of low-dimensional carbon nanostructures: an efficient approach based on chemical criteria
Francesco Mercuri

Session L

L01 The influence of Defects in Inorganic Nanotubes on Electronic and Mechanical Properties
Gotthard Seifert, Th. Lorenz, A. Enyashin

Abstracts

Invited and Contributed Oral Presentations

A01. The formation and observation of individual vacancies in carbon nanotubes by a focused electron beam

Florian Banhart

University of Strasbourg, France

Coauthor(s) : J. A. Rodriguez-Manzo

Modern scanning transmission electron microscopes (STEM) with aberration correctors enable us to focus an extremely intense electron beam onto an Angstrom-size spot. The highly focused electron beam gives us the possibility of carrying out in-situ electron irradiation on the atomic scale and to displace ballistically pre-selected atoms in the lattice. This technique is applied to single- and multi-wall carbon nanotubes. Irradiation experiments within a wide temperature range show the particular relaxation behavior of different types of nanotubes. Single or multiple vacancies are created in desired positions with the focused beam. This gives us, for the first time, the possibility of observing in real time the response of graphitic materials to the creation of individual point defects. It is shown how the reconstruction of the graphitic lattice after the creation of point defects determines the behavior of carbon nanostructures upon the removal of atoms.

A02 Graphene nanostructures: Edges, ribbons, superlattices, and defective tubes

Steven G Louie

University of California, Berkeley, USA

In this talk, I discuss some of our recent work using theory and computation to study the electronic, optical and transport properties of sp2-bonded carbon nanostructures, including those with defects and under external perturbations. Systems investigated include defective carbon nanotubes, graphene, graphene nanoribbons, and graphene subjected to nanoscale external periodic potentials (called graphene superlattices). These nanostructures exhibit a number of unexpected behaviors – novel conductance characteristics, magnetic defect states, extraordinarily large excitonic effects in their optical response, anomalous behaviors in the dynamics of carriers (the 2D massless Dirac fermions) in graphene superlattices, and an electric field-induced half-metallic state for zigzag graphene nanoribbons, among others. Moreover, under specific conditions, graphene superlattices are predicted to be electron supercollimators and new generation of 2D massless Dirac fermions may be created. The physical origins of these interesting properties and phenomena are discussed.

C01. Engineering of filled carbon nanotubes in a transmission electron microscope

Dmitri Golberg

National Institute for Materials Science, Tsukuba, Japan

Coauthor(s) : Pedro M.F.J. Costa, Mingsheng Wang, Zhi Xu, Yoshio Bando

Carbon nanotubes (CNTs) filled with metals, semiconductors and ceramics were manipulated and their transport and mechanical properties were engineered in a high-resolution transmission electron microscope (HRTEM) equipped with scanning tunneling microscope (STM) or atomic force microscope (AFM) units. Electrical resistance of the tubes was found to be proportional to the length ratio between filled and unfilled (or on-demand emptied) nanotube segments in a style peculiar to a rheostat. The sign of the conductivity change was dependent on the transport properties of the filled matter [1,2]. The release/transport of filled masses from inside of the tubes can be tuned with a femtogram or even attogram precision. In-situ TEM recorded kinetics of nanotube/metal interactions, and interface dynamics under current flow were thoroughly analyzed [3]. Mechanical response of filled nanotubes, e.g. rigidity, ductility, was found to be primarily dependent on the existence or absence of core fillings [4]. The examples discussed include CNT-Cu,[1] CNT-Au,[3] CNT-W,[3] CNT-ZnS,[4] CNT-CuI [2] nanoscale systems. Finally, the in-situ TEM electrical and mechanical probing, and engineering of the sister nanotube system – Boron Nitride – will be briefly demonstrated. [5-8]

Key References

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C02 Energetics and Electronic Properties of Doped Carbon Nanotubes

Susumu Saito

Tokyo Institute of Technology, Japan

Doping into semiconducting nanotubes should be an important process to make p-type and n-type semiconductor nanotubes. Experimentally, however, the atomically controlled substitutional doping into nanoscale materials including carbon nanotubes remains to be realized in the future.

In the present work, we study the energetics and geometries of B and N-doped carbon nanotubes in the framework of the density functional theory. Interestingly, it is found from the energetics study that it is easier to dope B atoms into thin nanotubes than into thick nanotubes. This preference can be understand from the geometrical strain energy by substitutional B doping which causes the outward displacement of the B atom. It is also found that the energetics of the B doping depends systematically on the metallic versus semiconducting electronic properties of the host nanotube.

We have also studied electronic properties of impurity-induced states ("impurity levels") in B and N doped semiconducting carbon nanotubes in detail. Their spatial distribution is found to correlate well with the depth of the state from the top (bottom) of the valence (conduction) band. Deep states show rather narrow spatial distribution, while shallow states show wider distribution. Finally, the limit of the density-functional theory to predict the depth of the impurity levels and the necessary corrections will be discussed.

Key References

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D01 Chemistry of different carbon nanoforms

Irene Suarez-Martinez

Institut des Matériaux Jean Rouxel (IMN/CNRS), France

Coauthor(s) : Christopher Ewels, Gregory Van Lier, Marc Monthioux

Between 0D fullerenes and 2D graphene there exists a wide range of exotic carbon nanoforms. The underlying structural differences of such materials can fundamentally alter their reaction chemistry and mechanical and electronic properties. As well as showing different local curvature these can also show variation in edge sites and continuity. Variations in inter-layer interaction and curvature can in some forms compete energetically. Other forms can also be constructed via combinations of dislocations ('rolling') and disclinations ('coning').

Using first principles calculations we examine specific examples where these effects modify the underlying chemistry properties of these materials, such as their oxidation behavior and mutual interaction. Structures such as carbon nanohorns can exhibit hybrid chemistry (both fullerene- and graphene- like) which can be exploited to control their functionalization chemistry.

Key References

I. Suarez-Martinez, M. Monthioux, C.P. Ewels. Fullerenes interaction with nanohorns. J. Nanosci. Nanotechnol. Accepted

G. Van Lier, C.P. Ewels, M. Cases-Amat, I. Suarez-Martinez, P. Geerlings. Comparison between early stage oxygenation behavior of fullerenes and carbon nanotubes. J. Nanosci. Nanotechnol. Accepted

D02 Defects as structure-defining features in Fullerene-like Carbon Nitride and Phosphorus-Carbide

Gueorgui Gueorguiev

Linkoping University, Sweden

Coauthor(s) : S. Stafström, A. Furlan, L. Hultman

Contrarily to most fullerene allotropes, fullerene-like carbon nitride (FL-CN) can be synthesized in compound form by vapor phase deposition of thin solid films at a relatively low temperature [1]. In FL-CN , the substitutional N at C sites in graphene layers promotes bending due to incorporation of shapes other than hexagons and cross-linkage, dramatically improving the properties of the CN.

By developing the Density Functional Theory (DFT)-based Synthetic Growth Concept (SGC) understood as structural evolution by sequential steps where each one is defined by the previous relaxed state, we addressed the defects and structural evolution of FL-CN [2].

Perceiving the FL solid compounds as an entirely new class of materials, we employed SGC to predict the feasibility of solid phosphorus-carbide FL-CP. In the case of FL-CP , phosphorus is seen as an alternative dopant to nitrogen in the graphene network. In comparison with FL-CN, higher curvature of the graphene sheets and higher density of cross-linkages (some of which with a character of inter-linkages) between them were predicted and explained by stability and prevalence of P-containing tetragon defects. Cage-like and onion-like structures both containing tetragons are determined as typical for FL-CP [3].

The purpose of the present presentation is to discuss and compare typical defects in FL-CN and FL-CP and their essential role as structure-defining features of these compounds [4]. Remarkable agreement of these theoretical results with results from characterization of FL-CN and (recently deposited by us) FL-CP will be also commented.

Key References

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[4] G. K. Gueorguiev, E. Broitman, A. Furlan, S. Stafström, L. Hultman, manuscript in final stage of preparation

D03 Edge reconstructions and gold in-plane of graphene

Sami Malola

University of Jyväskylä, Department of Physics, Finland

Coauthor(s) : Hannu Häkkinen, Pekka Koskinen

In applications for nanoscale materials and devices, it is often the atomic and electronic structure of boundaries and surfaces that is responsible for mechanical, electronic, and chemical properties. Also interactions of carbon nanostructures with metal atoms is interesting because of their fundamental relevance to many applications. This presentation combines two separate studies related to defects in graphene, the first concentrates on edge reconstructions in graphene [1] and the second on gold atom adsorption and diffusion in plane of graphene [2].

In the first study [1], we investigated planar reconstruction patterns at the zigzag and armchair edges of graphene with density-functional theory. We unexpectedly found that the zigzag edge is metastable and a planar reconstruction spontaneously takes place at room temperature. The reconstruction changes electronic structure and self-passivates the edge with respect to adsorption of atomic hydrogen from a molecular atmosphere. With help of recent TEAM-images [3], the existence of this reconstructed zigzag edge can be also seen experimentally.

In the second study [2], we investigated the bonding and diffusion of Au in graphene vacancies using density-functional theory. Energetics show that Au adsorbs preferably to double vacancies, steadily in-plane with graphene. All diffusion barriers for the complex of Au in double vacancy are above 4 eV, whereas the barriers for larger vacancies are below 2 eV. Our results support the main results of a recent experiment [4], but suggest that the observed diffusion mechanism is not thermally activated but radiation enhanced.

Key References

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E01 Extended defects in carbon nanotubes and graphene

Laszlo Forro

Ecole Polytechnique Fédérale de Lausanne, Switzerland

We have studied experimentally the influence of defects on the physical properties on two carbon based nanostructures: carbon nanotubes and graphene. In carbon nanotubes Young's modulus measurements show that with nanotube diameter the number of extended defects strongly increases weakening the structure of the tube. We believe that this is due to instabilities in the catalysis of hydrocarbons in CVD grown nanotubes.

In the case of graphene we report the results of the characterization of graphene oxide and reduced graphene oxide flakes, putting a great emphasis on the latter ones, since they represent the starting material for future applications. Our ESR data bring information on the defect density in these flakes. The electrical resistivity studies through the charge transport mechanism give a further insight into the influence of defects on the extended electronic states.

Acknowledgments. All the collaborators in these topics are gratefully acknowledged. The work in Lausanne is supported by the Swiss NSF and a European network "IMPRESS".

E02 Metals on Carbon Nanotubes

Chris Ewels

CNRS, Institute of Materials, Nantes, France

Coauthor(s) : I. Suarez Martinez, A. Felten, J.–J. Pireax, M. Hecq, C. Bittencourt

The interface between metals and carbon nanotubes is of interest in a wide range of domains: metallic contacts for nanoelectronics applications, interfaces between metallic nanoparticles and carbon nanotubes for catalysis or gas sensing, etc.

One area of potential application for carbon nanotubes (CNTs) is in gas sensing. However pristine nanotubes typically show low sensitivity, which has been ascribed to lack of reactivity of the CNT surfaces. In order to overcome this, cold low-pressure RF plasma methods have been shown to efficiently ‘activate’ the surface of CNTs through the introduction of surface defects, or “active sites”. The deposition and growth behavior of metal nanoclusters on CNTs differs dramatically depending on whether the surface of the tube has been ‘activated’ by such a plasma treatment. Metal cluster morphology is dictated by interactions between the deposited atoms and the CNT surface. Thus, .ne control of the local defects (type: structural or chemical; density) can be used to tune the interfacial properties of the metal clusters, that will determine their size and shape, diffusion (or not) avoiding aggregation, coalescence and complete wetting.

Modern theoretical modeling provides an unprecedented tool for realistic simulations of complex and ‘messy’ experimental systems such as these. In particular a detailed understanding of the atomic structure and behavior of the plasma induced surface active sites is required, as well as the resultant interaction with metal atoms and nanoparticles. Using DFT (AIMPRO) and DFTB+ codes we examine both graphene and CNTs with a variety of oxygen and fluorine plasma induced defects, as well as their interaction with a variety of metal species, notably Au, Pd and Ti. We correlate our results with experimental HRTEM, XPS and X-ray and Ultraviolet photoemission spectroscopy results of both plasma- treated and non-treated CNTs. Modeling successfully provides a complete picture of surface binding, diffusion and aggregation properties for these metals, notably highlighting fundamental differences in their surface chemical and electronic behavior.

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G01 Defects in graphene and graphite: formation and magnetism

Oleg Yazyev

Swiss Federal Institute of Technology Lausanne (EPFL), Switzerland

Magnetic materials and nanostructures based on carbon and other light elements provide a number of attractive opportunities for future information technologies such as spintronics and quantum information processing. In this talk, I review the first-principles studies of the magnetism induced by defects and edges in graphene and graphite. Particular attention is devoted to single-atom point defects (e.g. vacancies and hydrogen chemisorption) responsible for the high-temperature ferromagnetism in proton-irradiated graphite. Formation of irradiation-induced defects is further discussed in the light of first-principles molecular dynamics simulations.

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G02 Substitutional Transition-Metal Impurities in Graphenic Nanostructures

Daniel Sanchez Portal

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Coauthor(s) : E. J. G. Santos, A. Ayuela

We report a theoretical study of substitutional Ni, Co and Fe impurities in graphene. Only Cosub defect is magnetic with a magnetic moment of ~1μ_B for the isolated impurity. However, when the Co substitution takes place in more than one site, the total magnetic moment of the system exhibits a strong dependency on the relative position of the Cosub impurities. More precisely the magnetic moment depends on the number of Co substitutions in A and B sublattices. This behavior is better understood when we realize that the electronic structure of a substitutional Co impurity nearby the Fermi energy is equivalent to that of a carbon vacancy in a simple π-tight-biding model of graphene. Therefore, we can expect the Lieb's[1] theorem to apply to this situation and the total magnetic moment to behave as |CoA-CoB|, where CoA and CoB are, respectively, the number Co substitutions in the A and B graphene sublattices [2].

In contrast to Co impurities, Nisub defects, which have been recently detected in carbon nanotubes by Ushiro et al.[3] using extended x-ray absorption fine structure (EXAFS) and x-ray absorption near edge structure (XANES) data, show a zero magnetic moment in flat graphene. However, Nisub impurities develop a non-zero magnetic moment in metallic carbon nanotubes [4]. This surprising behavior stems from the peculiar curvature dependence of the electronic structure

of Nisub. A similar magnetic/nonmagnetic transition of Nisub can be expected by applying other kinds of anisotropic strain to a flat graphene layer [5].

In general, we have found that we can draw an analogy between the electronic structure in the neighborhood of the Fermi energy, and its strain dependence, of substitutional Co, Ni and Fe atoms in graphenic systems and that of an unreconstructed carbon vacancy in graphene with different charge states. With this analogy at hand we can easily understand and predict many complex and interesting phenomena for graphenic nanostructures substitutionally doped with transition metals.

Key References

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H01 Electron scattering observed by STM/STS at artificially created defects on single-walled carbon nanotubes

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We have investigated the effects of local atomic defects on the electronic structure of single-walled carbon nanotubes (SWNT) by means of low-temperature scanning tunneling microscopy (STM) and spectroscopy (STS). The defects have been created by irradiation of the samples with low energy hydrogen ions (2 eV mean ion energy), medium energy argon ions (200 -1500 eV) or by cutting the SWNT with the STM tip. Besides significant changes in the local density of states (LDOS) at the defect sites, we observe pronounced signatures of electron standing waves, which result from electron scattering at the defect sites.

We will show that quasi bound states can be created between two closely spaced (10-20 nm) defects in metallic SWNTs, with regular energy spacing above 100 meV. This observation demonstrates the feasibility of room temperature active intra tube quantum dots by using ion irradiation. Fourier-transform scanning tunneling spectroscopy reveals that the observed electron standing waves are composed of multiple high and low spatial frequency components, which can be attributed to large (inter-valley) and small (intra-valley) momentum scattering, respectively. The position of these components in reciprocal space is chirality dependent and can be obtained by projection of the possible electron scattering vectors in the extended zone scheme onto the direction of the tube axis. The experimental results will be compared to the results from a Fabry-Perot electron resonator model, where we are able to describe in detail the scattering dynamics and to identify contributions from inter- and intra-valley scattering.

The experimental data show significant anisotropies in the scattering strength of the defects with regard to energy. In particular, we observe a pronounced asymmetry regarding the parity of the states participating in the scattering event. This behavior is at the moment not fully understood. Since our observations are of pivotal importance for electronic transport properties in defective carbon nanostructures, this issue certainly deserves further in-depth experimental characterization and theoretical explanation.

H02 Atomic Pathways Towards the Synthesis of Fullerenes and Triazafullerenes from Polycyclic Aromatic Hydrocarbons

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True fullerene-based molecular electronics are limited by the current production methods. Standard techniques, such as graphite vaporization, do not permit a real control on size, and, particularly, on doping (e.g. heterofullerenes and endohedral fullerene). This has promoted an intense research activity directed towards more rational and efficient synthesis methods. We have recently achieved the formation of closed fullerenes (C60) and triazafullerenes (C57N3) by thermal annealing using polycyclic aromatic hydrocarbons (PAHs) adsorbed on Pt(111) surfaces with efficiency of ~100%, as we recently report [1]. The PAHs (C60H30 and C57N3H33) chosen as precursors for fullerenes and triazafullerenes (C60 and C57N3), are characterized by easy synthesis and doping processes, paving the way to the formation of doped fullerene with specific characteristics.

We have combined STM, XPS, NEXAFS and thermal desorption measurements with first principles calculations, to study the adsorption of C60H30 and C57N3H33) on Au(111) and Pt(111) surfaces, and the possibility of closed fullerene formation by thermal annealing using these molecules as precursors. In this work, we focus our attention on both experimental and theoretical results.

Large scale first principles DFT calculations have been carried out, using both an efficient local orbital basis[2-3] and standard plane-wave approaches[4-5] . These simulations give support for the interpretation of experiments that confirm the feasibility of the formation process and provide insight into the atomic pathways leading from the planar PAHs to the closed fullerenes and triazafullerenes. In particular, we characterize the adsorption and STM images of both the planar precursors and the final closed molecules, considering different coverages and the influence of surface defects (like surface vacancies). Furthermore, we explore the closure process for partially and fully dehydrogenated precursors with the NEB method [6], identifying the relevant steps and showing that the energy barriers are low enough so they can be overcome with the available thermal energy during the annealing process.

In this work, we have reached an efficient fullerene and heterofullerene size controlled production method via surface catalyzed cyclo dehydrogenation; furthermore our method opens to other possibilities, such as encapsulation (endohedral fullerene) and formation of other carbon nanostructures.

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H03 Interface States in Carbon Nanotube Junctions: Rolling up graphene

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Carbon nanotubes are currently regarded as one of the most promising materials to develop future nanoelectronics, with an impressive combination of robustness and ideal electronic properties. At present, it is well established that further progress towards real applications depends on the ability to form junctions between different nanotubes [1]. Recently, the controlled synthesis of several carbon nanotube intramolecular junctions has been reported, either by current injection between nanotubes [2] or by temperature changes during growth [3]. These intramolecular junctions, which often present interface states, are typically made of topological defects arising from the connection between tubes of different chirality (Fig. 1). Although interface states are commonly regarded as a drawback in device performance, they may actually provide a means of achieving diode behavior at the nanoscale, as proposed in Ref. [4]. Therefore, understanding the physics of CNT intramolecular junctions, for which interface states may dominate transport properties, has been a subject of growing activity in the last few years [5–7].

We study the origin of interface states in carbon nanotube intramolecular junctions between achiral tubes. By applying the Born-von Karman boundary condition to an interface between armchair- and zigzag-terminated graphene layers, we are able to explain their number and energies. We show that these interface states, customarily attributed to the presence of topological defects, are actually related to zigzag edge states, as those of graphene zigzag nanoribbons. Spatial localization of interface states is seen to vary greatly, and may extend appreciably into either side of the junction. Our results give an alternative explanation to the unusual decay length measured for interface states of semiconductor nanotube junctions, and could be further tested by local probe spectroscopies.

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J01 Quantum Transport in Carbon Nanostructures including Defects

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Their unusual electronic and structural physical properties promote carbon nanostructures as promising candidates for a wide range of nanoscience and nanotechnology applications. Not only can carbon 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 nanosize devices. Further, the intrinsic semiconducting character of other tubes and graphene nanoribbons, 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 [1], 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 quantum transport properties of both nanotubes and nanoribbons in relation with their atomic structures. Since quantum effects are prominent in carbon nanostructure 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, like in most materials, the presence of defects in carbon nanotube and graphene has been demonstrated experimentally. These defects may take different forms: vacancy, bi-vacancy, Stone-Wales defect, 5/7 pair, atom in substitution, ~E and are known to modify the electronic properties of the host graphene material [2]. 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 carbon nanostructure 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 [3].

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J02 Modeling of low-dimensional carbon nanostructures: an efficient approach based on chemical criteria

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Recently, the properties of nanostructured carbon materials, like carbon nanotubes (CNTs) and graphene, have been the subject of in-depth investigations in view of their potential use in nanotechnology. Most of the interest concerning nanostructured carbon materials is related to the peculiarities of their electronic structure, which is constituted mainly by a complex network of pi-conjugated bonds. Details of the electronic structure play a crucial role in the application of such materials as nanostructured building-blocks for molecular electronics and in functionalization processes, where the CNTs and graphenes undergo chemical reactions[1]. However, the particular structural and electronic features of nanostructured carbon poses significant problems to their computational modeling. Recent studies indicate the extension of classical organic chemistry concepts to the case of low-dimensional nanostructured carbon materials as a successful approach to obtain an accurate and consistent description of the electronic structure of the hexagonal carbon atom network[2-4]. In particular, the application of ideas borrowed from the study of polycyclic aromatic compounds, like Clar's theory of the aromatic sextet, proved markedly effective for the quantitative assessment and the analysis of the properties of nanostructured carbon materials. In this work we apply state-of-the-art numerical techniques to investigations on the stability and on electronic and chemical properties of nanotubes and graphenes and related compounds[4-6]. Our approach is based on the definition of suitable models of the system under study starting from chemical considerations. Results indicate unprecedented accuracy in the prediction of properties for a large variety of systems, obtained at a relatively cheap computational cost.

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L01 The Influence of Defects in Inorganic Nanotubes on Electronic and Mechanical Properties

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The theory of defects in inorganic nanotubes is presented and illustrated by results from Density Functional theory based calculations of the electronic structure, the energetics and the mechanical properties. The results are discussed with respect to a comparison with Carbon nanotubes and with available experimental data.

Contributed Presentations

B01 Chemistry of different carbon nanoforms

Irene Suarez-Martinez

See abstract D01

B02 Atomic Pathways Towards the Synthesis of Fullerenes and Triazafullerenes from Polycyclic Aromatic Hydrocarbons

Giulio Biddau

See abstract H02

B03 Theoretical Investigations on the Formation and Structure of Nanocrystallites by Encapsulation in Carbon Nanotubes and Carbon Nanotube Junctions

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The ability to encapsulate different materials has constituted one of the first applications of carbon nanotubes[1](CNTs). Besides the possibility of creating intrinsically monodimensional materials through nanotube-driven template syntheses, one of the most interesting aspects of encapsulation concerns the formation of ordered structures in the hollow of CNTs, in the form of nanocrystallites[2]. The one-dimensional confined growth of different compounds has been viewed as a suitable route to the development of new low-dimensional materials, like nanowires. In recent experimental studies metal halides were inserted into the nanotube hollow in excellent yields[3]. As a result of the filling process, the properties of both the filler and the nanotube are generally modified. In a previous work[4], the morphologies of AgI nanocrystallites grown inside (n,n) single-walled CNTs are investigated by means of molecular dynamics simulations. All crystal structures found are formally constituted by (n,m) AgI nanotubes, with chiral vectors n and m depending on the CNT diameter and on the local environment. In particular, for narrow CNTs unprecedented low-dimensional AgI nanoribbons appear, actively stabilized by a deformation of the CNT, as observed in experiments. In larger diameter CNTs, inorganic (n,m) AgI nanotubes are typically formed. Hence, the filling of large diameter CNTs can eventually lead to the concurrent formation of different AgI aggregates, depending on the nanotube diameter and on the environment, like local instantaneous pressure, giving rise to a scenario of polymorphism in the nano-regime. Moreover, interfaces between different confined nanocrystallites are likely to be observed, as well as a variety of defective structures. As a further assessment we analyze the possibility to simulate the growth of monodimensional nanocrystallites of AgI inside CNTs junctions[5]. Structural features very similar to those observed in the case of simple CNTs can be recognized relatively far from the junction between the two CNTs of different diameter. More interestingly new inter-phase structures, which allow the transition between different AgI phases, are observed in the region of

the CNTs junctions. The possibility to exploit the intrinsic AgI superionic conducting properties to achieve monodimensional superionic conducting devices is analyzed in the cases of both pristine CNTs and CNTs junctions[5]. Due to the potential interest of hybrid inorganic-carbon low-dimensional nanostructures in the fabrication of technological devices, the electronic properties of the encapsulated nanocrystallites are also analyzed by means of first-principle calculations. The application of density functional theory (DFT), though requiring extensive computing resources, is able to shed light on the properties of the systems under investigation at an unprecedented level of detail.

B04 Formation of defect structures on graphene and CNTs

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Various defect structures of graphene are investigated by using first principles calculations based on density functional theory. Our motivation is to investigate the possible mechanisms behind the junction formation on carbon nanotubes (CNTs). Some of our candidate defect structures are single and double vacancies, Stone-Wales defects, 4-5-7-8 rings of carbon, and combinations of these rings. Initially, these defect structures are formed within graphene nanoribbons where edges are saturated by hydrogen atoms and placed in a supercell such that with a 10 A vacuum along all directions in order to avoid defect-defect interaction because of periodic boundary conditions. By using plane-wave pseudopotential calculations implemented in simulation package VASP, these defect structures are relaxed by conjugate gradient geometry optimizations. In order to quantify various defect structures, then the cohesive energies and formation energies are calculate from the total energies. For point defects, the relaxed structures remain almost planar with a little local distortion; hence these structures might not be an appropriate initial structure for Y-junction formation on CNTs. Similarly, we observed that Stones Wales, single 8-ring and single 7-ring type defect structures are resulted almost planar relaxed geometry. However, defect structures with single 4-ring and 5-ring combinations (single, double and triple 5-ring) are results highly curved final geometries around defect and it becomes sharper from single to triple ring structures. Hence, these type of defect structures are good candidate for initial structure for junction formation on CNTs. The studies on the effects that might lead such defect structures on graphene, such as foreign atoms, and mechanisms behind Y-junction formation on CNTs are in progress.

B05 Defects as structure-defining features in Fullerene-like Carbon Nitride and Phosphorus-Carbide

Gueorgui Gueorguiev

See abstract D02

B06 Edge reconstructions and gold in-plane of graphene

Sami Malola

See abstract D03

B07 Interface States in Carbon Nanotube Junctions: Rolling up graphene

Andres Ayuela

See abstract H03

B08 Synthesis, Experimental Research and Modeling of Structure of Carbon Nanotubes for Formation of Fuel Hydrogen Elements

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Methods have been developed and carbon nanotubes have been synthesized by means of carbon oxide degradation at high temperatures and pressures in reactor with adding Fe(CO)5 as catalyst and further purification from admixtures. Electronic and microscopic research and modeling of nanostructure of the obtained material have been done. It is obtained that main part of nanotubes are formed inside biners of up to 10nm in diameter and several microns long. Synthesized materials may be applied as catalytic electrode or a medium for fuel hydrogen accumulation.

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Physical and mechanical properties of polymer composites based on polyimide with nanostructures.

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F01 Nonlinear conductance reveals positions of carbon atoms in finite metallic SWCNTs

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Nonlinear quantum conductance in finite metallic Single-Wall Carbon Nanotubes (SWCNTs) due to presence of a single defect has been studied theoretically using real-space ┌-orbital nearest neighbors tight-binding method. The correction to the conductance is sensitively dependent on wavefunction amplitude of contributing electronic states at the point on which the defect is placed. It has been shown that calculation of the first correction to the conductance can be used to specify the type of SWCNT in hand, delineate level spacing and provide detailed data about band structure near the Fermi level in linear response regime. More importantly, sensitive dependence of nonlinear conductance on defect position provides a method for imaging carbon atoms positions throughout the tube. In proposed method, AFM/STM tip is introduced as a provider of a single point-like defect at each instance of time. While intrinsic curvature of tubes causes difficulties in analyzing the results provided by STM, this problem can be overcame in proposed approach since no tunneling procedure is necessary. This method can be also used in any other low-dimensional metallic structures e.g. graphene nano-ribbons.

F02 Transport properties of N and B doped Nanotubes

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The nanoscale electronic properties of carbon nanotubes have been studied for a long time. If electronic quantum transport of pristine nanotubes have been extensively studied as well as Nitrogen and Boron substitutional doping, other configurations (i.e. pyridine-like for N doping) have not been fully investigated despite experimental evidence that several atomic configuration may coexist in experimentally produced samples.

We present here quantum transport simulations based on *ab initio* calculation and Green's function formalism for several N and B doping configuration that are found in experimental produced nanotubes. Our simulations are a first step towards simulation of realistic systems with distribution of dopant positions and species.

F03 Electron scattering observed by STM/STS at artificially created defects on single-walled carbon nanotubes

Oliver Gröning

See abstract H01

F04 Suppression of size-quantization steps by lattice defects in graphene nanoribbons

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We numerically study impurity scattering in graphene nanoribbons as a function of defect density and ribbon length. For long ribbons (ribbon length up to 3 micrometers) we observe exponential (Anderson) localization of the wave function over eight orders of magnitude. By calculating the scattering wave function on the A and B sublattice, we can directly visualize broken pseudo-spin conservation. To contrast the role of AB and K-K' scattering, we compare impurities that either break or conserve pseudo-spin. Using a Fourier transformation allows us to quantitatively assess, for different impurity types, the amount of AB and K-K' scattering. For perfect ribbons, the conductance features size quantization steps due to the transverse confinement. We find that these steps are strongly suppressed in disordered ribbons for impurities that break the AB-symmetry. In contrast, short-range impurities that conserve pseudo-spin result in K-K' scattering and preserve size quantization steps. Comparison of our results with recent experimental data suggests that broken AB symmetry plays an important role in realistic graphene devices.

F05 Optical properties of defects in carbon nanotubes

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Carbon nanotubes are a remarkable material that has been the subject of intensive research since their discovery in 1991 [1]. The achievement of optical emission from isolated semiconducting single-walled carbon nanotubes (SWNTs) with direct band gaps has stimulated considerable efforts in understanding optical properties of SWNTs [2,3]. Especially, it has been shown that the characteristic optical properties of SWNTs are determined by the dynamics of 1D excitons with very large binding energies up to ~700 meV [4,5]. The recent report of defect-induced midgap luminescence centers [6] and the striking demonstration of photon antibunching in the photoluminescence (PL) spectra of functionalized semiconducting SWNTs, most probably due to disorder-induced exciton localization [7], have stimulated the study of the effects of structural defects on the optical properties of semiconducting SWNTs.

In this project, we will investigate the optical properties of medium energy argon ions-induced defects in suspended SWNTs devices by means of photoluminescence excitation (PLE) techniques [6]. Such devices have shown high quantum ef.ciencies (~ 7% [3]) in comparison to functionalized nanotubes (~ 0.01 – 0.1 %) used in the experiments cited above. We will analyze our results on the base of our recent low temperature scanning tunneling spectroscopy investigations where we have shown that medium energy argon ions give rise to narrow states in the band gap of semiconducting SWNTs [8]. Furthermore, signatures of electrons and holes confinement between adjacent defects have been observed (results not published yet for semiconducting SWNTs, see [9]).

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F06 Catastrophic model of destruction of polymer materials irradiated by electrons and formation of nanostructures based on carbon

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Dependence of deformation ε on stress σ for polyimide films irradiated by electrons with energy of 2 MeV up to different integral doses by using cascade-probability method have been calculated. Catastrophic model of polymer materials has been suggested. It has been shown that at irradiation complex nanostructures in the line C – C bonds, which are essential for mechanical properties have been formed. Within the model a series of experimental data for dependence ε on σ has been explained.

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F07 Binding Energy of Fullerene to Q120C Mutant of Cytochrome C Oxidase

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Cytochrome c Oxidase is an enzyme that catalyses the fuel cell cathode reaction: 4e┌ + 4H+ + O2 ┌ 2H2 O. In practice it has turned out that the reaction limiting step in biofuel cells is the cathode, and especially the electron transfer rate from the electrode to the enzyme[1]. The ultimate motivation of this study is to connect the enzyme electroni-cally as well as possible to the cathode made of carbon nanotubes. In this study the binding energy of C60 fullerene to Cytochrome C Oxidase is calculated using QM/MM GBSA method [2]. The connection is made to cystein mutant close to the first metal (CuA) in the electron transfer chain of Cytochrome c Oxidase. The binding is found to be strongly favorable with respect to an isolated fullerene in water but one must keep in mind that the solubility of C60 in water is extremely poor. Additionally, the binding energy of a more soluble fullerene-derivative f N-(3-maleimidopropionyl)-3,4-fulleropyrrolidine to cytochrome c oxidase is studied.

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F08 First-principles investigations on the functionalization of ZnO nanowires

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There is an increasing demand for portable, reliable and cost-effective integrated systems for biological. This type of sensor has the potential to provide immediate analysis of blood samples so allowing early detection of diseases. Nanostructures offer novel and unique properties to fabricate such sensors, because the dimension of such structures are similar to those of the target chemical and biological molecules. On the other hand, well-ordered ZnO nanowire arrays can be grown, making them promising for such functional devices. In this work we employ density functional theory to investigate ZnO nanowires and nanotubes. Bare wires are found to have semiconducting behavior, with band gaps larger than the ones in bulk ZnO, suggesting strong quantum confinement effects. As a first step towards surface modification we have investigated ZnO nanowires functionalized with H and water. We find that the band gaps of these wires can be tuned depending on how the species are adsorbed on the nanowire surfaces. We have further investigated atomic and electronic properties of ZnO nanotubes. We find that the formation energies of single and thick-walled ZnO nanotubes are mainly dependent on the thickness of the wall and almost insensitive to the diameter. Besides, thick-walled ZnO nanotubes are energetically more favorable than single-walled ZnO nanotubes. We also show that confinement strongly affects the shape and energies of the conduction bands, while the valence band maximum seems not to be sensitive to a change of the tubes thickness.

F09 Magnetism of Graphene and Carbon Nanotubes Substitutionally Doped with Ni

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Most popular CNT growth methods rely on the use of catalyst based on transition metals (particularly Ni, Co and Fe). Even after many hours of acid treatment the catalyst is not completely removed. Several works show that remnant metal is in the form of isolated atoms [1] and strongly bound to the carbon layer occupying substitutional positions [2]. Therefore is of paramount importance to study the magnetism of substitutional species in graphenic systems. Here, we report a first-principles study of the structural, electronic and magnetic properties of substitutionated Ni atoms in graphenic systems by making spin-polarized calculations [3]. We have observed that the magnetic moment of Ni-doped graphene layers can be controlled applying mechanical deformations that break the hexagonal symmetry of the graphene layer in the appropriate way. We analyze in detail the response of the curvature of the layer with the doping. We do this by comparing the results obtained for graphene and single-walled carbon nanotubes, and analyzing the changes of the electronic structure. We find that flat graphene layers doped with substitutional Ni present a zero magnetic moment. This is already an unexpected result. However, the magnetic moment of Ni can be switched on by applying curvature to the structure[4]. It is interesting to note here that curvature is the parameter connecting two, in principle topologically equivalent, nanostructures of carbon: carbon nanotubes and graphene nanoribbons. Furthermore, we find that the Ni magnetic moment becomes also a signature of the metallicity of the structure: only metallic structures develop a magnetic moment. We think that these results are of great interest for a large number of scientists working in the field of magnetic and electronic properties of graphene and related materials.

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