

Third Symposium on  
**Computational Challenges and  
Tools for Nanotubes**  
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Organizers:

- **Rodrigo B. Capaz** (Universidade Federal do Rio de Janeiro - UFRJ)
- **Helio Chacham** (Universidade Federal de Minas Gerais - UFMG)
- **Hisashi Nakamura** (Research Org. for Inform. Sci. & Technology - RIST)
- **David Tomanek** (Michigan State University - MSU)

# Invited Talks

## Simulations of irradiation effects in carbon nanostructures

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The irradiation of solids with energetic particles such as electrons or ions is associated with disorder, normally an undesirable phenomenon. However, recent experiments on bombardment of carbon nanostructures with energetic particles demonstrate that irradiation can have beneficial effects and that electron or ion beams may serve as tools to change the structure and tailor mechanical, electronic and even magnetic properties of nanostructured carbon systems.

Atomistic computer simulations have provided lots of insight into irradiation damage creation in metals and semiconductors, as such simulations not only allow one to calculate the characteristic of the materials with defects but also model the defect production, which occurs on the picosecond time scale - a time interval too short to get the direct experimental information. Moreover, as in many cases the irradiation leads to self-assembly and self-organization, atomistic simulations make it possible to study these phenomena.

In this presentation, I will review the recent progress in our understanding of ion-irradiation-induced effects in carbon nanostructures and compare the simulation results [1] to the experimental data with a particular stress on the “beneficial” role of defects and impurities in nanotubes and related systems. Finally, I point out the issues which still lack complete comprehension and further outline the simulation challenges in the field.

[1] <http://www.acclab.helsinki.fi/~akrashen/publist.html>

# Electron-Ion Dynamics throughout Collision of Highly-Charged Ar on Stacked Graphite and Subsequent Structural Change

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Irradiation of highly charged ion has become a new tool for inducing structural change on solid surfaces with aid of electro-static forces. Although several experimental approaches were made, mechanisms of the structural change on the surface have not been fully understood. Recently, experimental group of RIKEN has found significant structural change of the surface upon irradiation of Ar<sup>8+</sup> ions [T. Meguro, *et al.*, Appl. Phys. Lett. **79**, 3866 (2001)]. Measurements of scanning tunneling spectroscopy and infrared absorption strongly suggested creation of nano-scaled diamond on the surface. To challenge atomic scale understanding of this result, charge flow and ion-ion collision throughout the irradiation must be treated simultaneously in first-principles simulation.

In this presentation, I would like to show my recent first-principles approach based on the time-dependent density functional theory (TDDFT) on this phenomenon. Experimentally it was expected that the high-charge-state of Ar<sup>8+</sup> played a major role in determining surface structure upon irradiation through the steep electro-static potential of Ar<sup>8+</sup>. However, my molecular dynamics (MD) simulation within TDDFT shows variety of surface structures from *sp*<sup>3</sup>-like structure to wrapped graphene sheets depending on incidence energy of the Ar<sup>8+</sup>. To address importance of the high-charged state, I will also show fictitious computer simulations of irradiation of neutral Ar on graphite surface, and will discuss the difference in kinetics of surface structural change.

All of the present calculations were done by using the Earth Simulator under the support from the Next Generation Supercomputing Project, Nanoscience Program, MEXT Japan.

# Large Scale Density functional simulation of Hydrogen adsorption on Carbon

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Nano carbon materials as carbon nanotubes (CNTs) and fullerenes in nanotechnology have a lot of potential for industrial applications. On the efforts of developing the theoretical modeling and super computer, it has been recognized that computational simulations are powerful and efficient tools to find and create new materials on nano scale. Aiming at realistic simulations for nano materials, we have optimized the PWscf (Plane-Wave Self-Consistent Field) code [1] for a large-scale calculation. In my talk I discuss the application of CNT to Hydrogen Adsorption. For the automotive industry, the success of hydrogen and fuel-cell technologies is critically dependent upon discoveries of novel materials that can store and extract large amounts of hydrogen under economical and ambient conditions. The NIST group demonstrated how hydrogen molecules are adsorbed on single Ti metal atom which is bound to carbon nanotubes (CNT) or fullerenes by use of MD simulation [2]. In the case of single transition metal atom on the CNT, their simulations of Hydrogen molecule adsorption agree to ours in terms of binding energy, the number of adsorbent Hydrogen molecule. On the other hand, in case of many Ti metal atoms on the CNT, our results show aggregation of Ti metal atoms on energetically relaxation technique. This is difference from their results showing Ti metal segregation. We carried out large-scale simulations to consider direct Ti-Ti interaction. It shows that Ti metal aggregates at urface of CNT forming small size of Ti cluster and hydrogen is well adsorbed into the Ti cluster as both states of Hydrogen atom and molecule.

## References:

[1] <http://www.pwscf.org/>

[2] T. Yildirim and S. Ciraci, Cond-mat/054694 v1 26 Apr 2005

# Simulation of Inorganic Nanotubes

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Motivated by the high application potential of carbon nanotubes, the search for other quasi one-dimensional nanostructures has been pursued both by theoretical and experimental approaches. The investigations soon concentrated on layered inorganic materials, which may be exfoliated and rolled up to tubular and scroll-type forms. The talk reviews the basic design principles, which govern the search for novel inorganic nanostructures on the basis of energy- and strain related stability criteria. These principles are then applied to the prediction and characterisation of the properties of non-carbon, elemental and binary nanotubes derived from layered boride, nitride, and sulfide bulk phases. Finally, examples of one-dimensional nanostructures such as tubes and scrolls have successfully been constructed from non-layered materials, especially from oxides. Examples for the experimental verification of the predicted structures are given throughout the discussion and impressively underline the predictive power of today's materials modelling.

## Electronic and transport properties of CN<sub>x</sub>-system: the self-interaction correction and disorder effects

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CN<sub>x</sub> nanotubes can display a measurable variation in resistance upon exposure to ammonia. We present a microscopic model for the origin of these variations. We studied, using Total Energy DFT calculations, a (5,5) CNT containing pyridine-like N atoms replacing C atoms, and how the NH<sub>3</sub> molecule binds to these sites. We find that a divacancy surrounded by 4 pyridine-like defects is the most stable N-defect in CN<sub>x</sub> nanotubes. Upon interaction with these defects, the ammonia dissociates into NH<sub>2</sub> and H. For isolated defects we investigate how they affect the charge transport properties using our code (TranSampa) based on a Non-Equilibrium Greens Function formalism, which also includes self-interaction corrections. We find that the binding of ammonia decreases the conductance, providing the correct trend when compared to the experimental results. We will also present conductance results where disorder effects are included.

This work was performed in collaboration with the following researchers: Antonio J. R. da Silva, Mariana Rossi, Frederico D. Novaes, Alexandre R. Rocha, Matheus P. Lima. We acknowledge FAPESP, CNPq and CENAPAD-SP.

# 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.



# Non-adiabatic effects in the vibrational properties of carbon nanotubes and related systems

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The tangential vibrational modes of metallic single-walled carbon nanotubes (SWNTs) are thought to be characterized by Kohn anomalies resulting from the combination of their intrinsic one-dimensional nature and a significant electron-phonon coupling. These properties are modified by the doping-induced tuning of the Fermi energy level  $\epsilon_F$ , obtained through the intercalation of SWNTs with alkali atoms or the application of a gate potential. We present a Density-Functional Theory (DFT) study of the vibrational properties of a (n,n) 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, but we also use time-dependent perturbation theory to explore non-adiabatic effects beyond this approximation. We find that these effects are very important in nanotubes, and likely to have even more dramatic effects in other nanotube-related systems. We compare our results with existing measurements and suggest features to be explored in future experiments.

# Quantum Transport in Carbon Nanotubes Devices: Role of Magnetic Field and Chemical Doping

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In this talk, the role of chemical doping and magnetic field on quantum transport is addressed in clean and disordered carbon nanotubes. 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-Buttiker transport formalisms, and the Thouless relationship between both quantity is well satisfied.

The effect of a magnetic field is shown to alter localization phenomena, as well as carbon nanotubes based devices characteristics and performances, with the demonstration of a magnetic-dependent Schottky Barrier formation at the metal/nanotube contact [2]

A novel inelastic backscattering mechanism, mediated by electron-(optic)phonon interaction, is also briefly mentioned. This many-body mechanism, which can be seen as the removal of degeneracies in the electron-phonon 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 [3].

[1] R. Avriller, S. Latil, F. Triozon, X. Blase and S. Roche, Phys. Rev. B 74, 121406R (2006).

[2] G. Fedorov, A. Tselev, D. Jimenez, S. Latil, N. Kalugin, P. Barbara, and S. Roche, Nano Lett. 7 (4), 960 (2007) B. Lassagne, J-P. Cleuziou, S. Nanot, W. Escofier, R. Avriller, S. Roche, L. Forro, B. Raquet, J.-M Broto, Physical Review Letters (in press)

[3] L. E. F. Foa Torres and S. Roche, Phys. Rev. Lett. 97 (2006) 076804; Appl. Phys. A: Mater. Sci. Process. 86, 283 (2007); see also S. Roche, J. Jiang, L.E.F. Foa-Torres, R. Saito, J. Phys. Condens. Matter 19, 183203 (2007). L. E. F. Foa Torres and S. Roche, Phys. Rev. B. 75, 153402 (2007).

# Contributed Presentations

# SWCNT interference devices: Synthesis and electronic properties of Y-junction rings and quantum dots

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Molecular nanostructures such as single wall carbon nanotubes (SWCNT) are promise candidates for prospective nano-scale electronic devices. A variety of geometrical shapes, like X-, T-, and Y-junctions, quantum dots and crossing objects are needed for a successful incorporation into 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.

[1] "Synthesis and interferometric properties of single wall carbon nanotube rings formed by two Y-junctions", D. Grimm, P. Venezuela, F. Banhart, N. Grobert, H. Terrones, P. M. Ajayan, M. Terrones, and A. Latge, submitted to Small

# 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% of the exciton state, as in the 3D hydrogen atom). On the other hand, first-principles calculations give much smaller splittings, around 40% of the binding energy. 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  $E_{11}$  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.

# 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.

# 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 appearance 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.

# 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 anti-ferro 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.

- [1] T. L. Makarova *et al.*, *Nature*, **2001**, 413, 716: Retraction **2006** 440, 707.
- [2] R. Höhne et P. Esquinazi, *Adv. Mat.*, **2002**, 14, 753.
- [3] O. Lehtinen *et al.*, *Phys. Rev. B*, **2004**, 69, 155422.
- [4] P. Esquinazi *et al.*, *Phys. Rev. Lett.*, **2003**, 91, 227201.
- [5] J. Heyd *et al.*, *J. Chem. Phys.*, **2003**, 118, 8207.
- [6] J. Paier *et al.*, *J. Chem. Phys.*, **2006**, 124, 154709.



# 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].

- [1] F. Abild-Petersen *et al.*, *Phys. Rev. B*, **2006**, 73, 11519.
- [2] G. Bertoni *et al.*, *Phys. Rev. B*, **2005**, 71, 075402.
- [3] Y. Gamo *et al.*, *Surf. Sci.*, **1997**, 374, 61.
- [4] H. Hamara *et al.*, *Phys. Rev. B*, **2006**, 73, 113404.
- [5] F. Banhart *et al.*, *Nature Nanotechnology*, **2007**, in press.

# Ab-initio electronic structure and optical transitions of graphene nano-ribbons

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The electronic properties of nanotubes of different chirality and diameters are usually represented by the so called Kataura-plot [1]. This provided a roadmap for the understanding of the optical and spectroscopic properties of nanotubes and was the starting point for more refined investigations of their electronic structure. Here we present a detailed theoretical investigation of the band-structure of 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]. In particular, we focus our study on the construction of a Kataura-like plot for armchairs and zigzag GNRs. For armchair GNRs, a strong family-dependence of the optical transitions is observed. Our calculations also show that zigzag GNRs are characterized by an antiferromagnetic ground state, which results in the opening of an electronic band-gap. This is in agreement with other recent DFT calculations [3,4].

We also investigate the modification in the electronic structure of GNRs induced by edge functionalization and by substitutional defects. In particular, we investigate the onset of defect states in the ribbons bandstructure and the possible n and p doping of GNRs [5].

1. H. Kataura et al., *Synth Met*, 103, 2555 (1999).
2. D. Prezzi, A. Ruini, E. Molinari, S. Piscanec, A. V. Osadchy, A. Gruneis, T. Pichler, C. Attaccalite, A. Rubio, A. C. Ferrari, submitted (2007).
3. Y. W. Son, M. L. Cohen, S. G. Louie, *Phys. Rev. Lett.*, 97, 216803 (2006).
4. Y. W. Son, M. L. Cohen, S. G. Louie, *Nature*, 444, 347 (2006).
5. F. Cervantes-Sodi, G. Csanyi, S. Piscanec, A. C. Ferrari, submitted (2007)

# Kohn Anomalies and Non-adiabatic Effects in Single Wall Carbon Nanotubes and Doped Graphene

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We present a detailed study of the vibrational properties of Single Wall Carbon Nanotubes (SWNTs) and doped graphene. The phonon dispersions of SWNTs are strongly shaped by the effects of electron-phonon coupling. In SWNTs, we analyze the separate contributions of curvature and confinement. Confinement plays a major role in modifying SWNT phonons and is often more relevant than curvature. Due to their one-dimensional character, metallic tubes are expected to undergo Peierls distortions (PD) at  $T=0\text{K}$ . At finite temperature, PD are no longer present, but phonons with atomic displacements similar to those of the PD are affected by strong Kohn anomalies (KA) [1]. We investigate by Density Functional Theory (DFT) KA and PD in metallic SWNTs with diameters up to 3 nm, in the electronic temperature range from 4K to 3000 K. Calculations are performed by using an electronic zone folding (EZF) approach, which simultaneously allows a precise description of the confinement effects and a high computational throughput. The effects of curvature are investigated by comparing results from EZF with calculations performed on the curved tubes, and are shown to be negligible for tubes larger than 1 nm. We then derive a set of simple formulas accounting for all the DFT results. Finally, we prove that the static approach, commonly used for the evaluation of phonon frequencies in solids, fails because of the SWNTs reduced dimensionality. The correct description of KA in metallic SWNTs can be obtained only by using a dynamical approach, beyond Born-Oppenheimer, by taking into account non-adiabatic contributions. Dynamic effects induce significant changes in the occurrence and shape of Kohn anomalies. We show that the SWNT Raman G peak can only be interpreted considering the combined dynamic, curvature and confinement effects. We assign the G+ and G- peaks of metallic SWNTs to TO (circumferential) and LO (axial) modes, respectively, the opposite of semiconducting SWNTs [2,3]. Dynamic effects are also proven to play a fundamental role in the determination of the frequency and the life-time of the  $\Gamma - E_{2g}$  mode of doped graphene, and are necessary to explain the evolution of the Raman G peak of graphene as a function of doping [4,5].

1. S. Piscanec et al., Phys. Rev. Lett. 93, 185503 (2004)
2. S. Piscanec et al., Phys. Rev. B, 75 035427 (2007)
3. M. Lazzeri et al. Phys. Rev. Lett. 95, 336802 (2005)
4. S. Pisana et al Nature Materials 6, 198 (2007)
5. M. Lazzeri et F. Mauri, Phys. Rev. Lett. 97, 266407 (2007)

# 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-homogeneous and depend on the nanotube chirality. We also find that extra electrons are localized around the impurity, giving rise to defect states.

[1] G. Chen et al., Phys. Rev. B 72, 155406 (2005).

# 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 dispersionless and are always single-degenerate. We ascribe the removal of degeneracy to the electron interaction, which is automatically included in the *ab initio* calculations. We study the origin of the superlattice bands by comparing our results to tight-binding calculations for superlattices and for  $N(12, 0)$  [ $N(6, 6)$ ] quantum dots, either isolated or connected to metallic semi-infinite  $(6, 6)$  [ $(12, 0)$ ] leads. This comparison allows to determine the origin of flat localized bands. Furthermore, it allows also for the identification of interface states, which we find to appear close to the Fermi energy.

# Modelling the effect of randomly dispersed doping agents in carbon 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.

# 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 carbon-polymer 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<sub>2</sub>O<sub>2</sub>-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 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/cm<sup>2</sup> 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/cm<sup>2</sup>), 2 wt% of MWNT (5077±742 cells/cm<sup>2</sup>) and 2 wt% of SWNT (5405±910 cells/cm<sup>2</sup>) in comparison with control polystyrene dish (11300±2569 cells/cm<sup>2</sup>). 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 ( $66.0 \pm 2.1\%$  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 ( $43\,029 \pm 9746$  cells/cm<sup>2</sup> compared to  $108421 \pm 7801$  cells/cm<sup>2</sup> on polystyrene,  $p = 0.001$ , 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  $99.8 \pm 0.2\%$  and  $99.9 \pm 0.1\%$ , respectively, which was significantly higher than on the control polystyrene ( $95.6 \pm 1.7\%$ ).

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 multi-walled 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 ( $1774 \pm 94$   $\mu\text{m}^2$  compared to  $1402 \pm 113$   $\mu\text{m}^2$  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 (Fig. 1, 2).

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.

#### References

- [1] Tan J, Saltzman WM: *Biomaterials* 25: 3593-3601, 2004
- [2] Harrison BS, Atala A: *Biomaterials* 28: 344-353, 2007
- [3] Bacakova L, Filova E, Rypacek F, Svorcik V, Stary V: *Physiol Res.* 53 (Suppl 1): S35-45, 2004.

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# Quantum-chemical modeling of X-ray photoelectron and X-ray absorption spectra of nitrogen occurred in CN<sub>x</sub> nanotubes

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X-ray photoelectron spectra of nitrogen-doped carbon (CN<sub>x</sub>) nanotubes show a splitting of N1s line, which is changed in the dependence of synthetic conditions. For example, we found the N 1s spectra of CN<sub>x</sub> nanotubes synthesized in the result of acetonitrile decomposition over metal particles formed from Ni and Co bimaleates and their mutual solid solutions can be fitted to three components. The ab initio calculations on the fragments of nitrogen-doped carbon nanotubes indicated the low-energy spectral component corresponds to the pyridinic nitrogen. The electronic state of three-coordinated nitrogen atoms was found to be largely sensitive to the atomic arrangement of carbon nanotube that leads to appearance of two high-energy components in N 1s spectrum of CN<sub>x</sub> nanotubes. The relative intensity of these components varies with change of a catalyst and could be a mark for indication of chiral tubes formation. Comparison of theoretical binding energies of nitrogen with the experimental data revealed that argon ion bombardment of CN<sub>x</sub> nanotubes results to formation of atomic vacancies with nitrogen atoms at the edges. X-ray absorption spectra measured near NK-edge of CN<sub>x</sub> nanotube samples prepared using iron catalysts exhibited three well-separated peaks indicating existence of additional form of nitrogen in the outer space of nanotubes. Assignment of the peaks was made using the results of quantum-chemical calculation of nitrogen-doped carbon nanotubes incorporated N<sub>2</sub> molecule in a tube cavity. Preferable orientation of N<sub>2</sub> molecule relative to the tube axis was determined.

# 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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