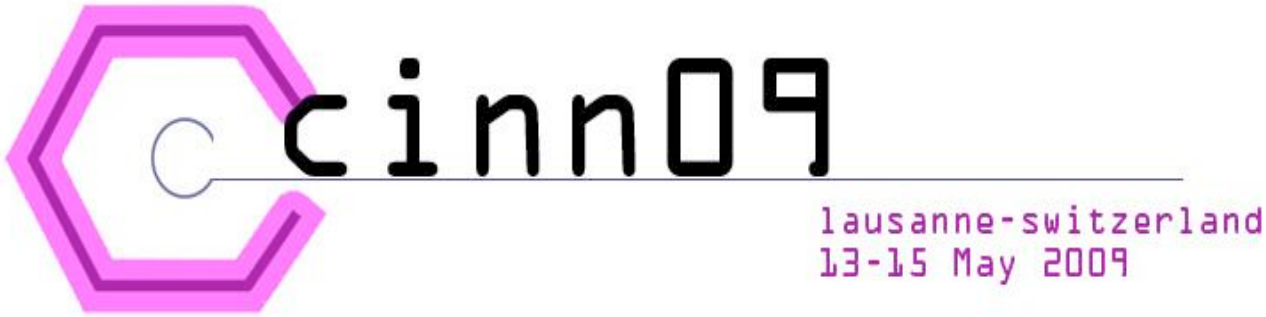
# Modeling of Carbon and Inorganic Nanotubes and Nanostructures




## Final Report

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Centre Européen de Calcul Atomique et Moléculaire

EUROPEAN SCIENCE FOUNDATION
SETTING SCIENCE AGENDAS FOR EUROPE

Organizers:
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## General remarks

The CECAM/SimBioMa workshop on "Modeling of Carbon and Inorganic Nanotubes and Nanostructures" (CINN09), held at the CECAM HQ in Lausanne, Switzerland, constituted a great opportunity to gather leading experts in the subject, allowing a fruitful exchange of ideas. The workshop has focused especially on computational and theoretical studies of low-dimensional structures of interest in nanotechnology and their relationship with state-of-the-art experiments.

The compact format of the workshop, structured as a 3-day program including oral contributions and a poster session, allowed a tight interaction among a total of 37 participants, thus achieving the planned objectives. The chosen format for oral contributions, organized as 30' talks followed by 15' of discussion, proved extremely useful in providing both a comprehensive description of novel research works and in-depth analysis of results and of eventual consequences on applications and future directions of development. Moreover, the poster session represented a useful opportunity to discuss topics of interest of the workshop and tighten the interaction among participants.

The merging of CINN09 with the previous workshop on "Defects on Carbon Nanostructures" (DNC09) allowed to establish links between similar research fields within the same week. The link between the two workshops ensured significant continuity between the research topics discussed and resulted in remarkable logistics advantages, due to the presence of common participants. Moreover, both communities benefitted from the continuity between the CINN09 and DNC09 workshops by extending the respective domain of competencies and knowledge.

It is worth noting that a great contribution to the success of the workshop was due to the excellent management of both local organization duties and administrative and logistics aspects, which were covered by the CECAM staff, in particular Mrs. Emilie Bernard (CECAM program manager and secretary) and Mr. Jordi Brusa (CECAM system manager and administrator), and supervised by the CECAM directors, Prof. Wanda Andreoni and Prof. Mauro Ferrario.

## Discussion

The work presented at the CINN09 focused on different aspects of the modeling of carbon and inorganic nanotubes and nanostructures, addressing also experimental progresses, in the attempt of providing a comprehensive picture of the state of the art in the field. The contributions presented during the workshop can be classified as follows:

- **Functionalization of low-dimensional nanostructures**:
  Chemical functionalization constitutes an effective route for the tailoring of the properties of nanostructures and for the production of novel nanostructured materials. Such issues have been addressed in detail within the workshop, focusing in particular on the modeling of chemical functionalization processes in fullerenes (**Berber**) and nanotubes (**Bettinger**) to obtain novel carbon nanostructures with tailored chemical properties. Indeed, theoretical models and accurate calculations demonstrate the possibility of applying with success traditional chemistry concepts to the case of low-dimensional carbon nanosystems. Such concepts can be also extended to different interaction schemes, as in the case of non-covalent interactions (**Basiuk**), and applied to the study of complex interactions occurring in nanostructured gas sensors (**Furlan**). Moreover, similar considerations can also be applied to the modeling of functionalized inorganic nanostructures (**Da Rosa**), a class of systems which has recently attracted a lot of interest in view of its applications in the development of biological-inorganic interfaces.

- **Low-dimensional inorganic and hybrid structures**:
  Computational modeling studies presented within the workshop addressed the characterization of low-dimensional crystalline inorganic compounds obtained by encapsulation into carbon nanotubes. This concerns both the assessment of structural and electronic properties of the hybrid carbon-inorganic assembly (**Green**) and fundamental investigations on the structural and dynamical properties of the low-dimensional inorganic system (**Wilson**). Besides, quasi-one-dimensional inorganic compounds exhibit interesting chemical properties, which can be used in the development of applications (**Da**

**Rosa**). The research presented indicated the possibility of computational design of novel compounds, based on quasi-one-dimensional phases of inorganic crystals.

- **Complex structures and applications**:
  The interest on carbon and inorganic nanotubes and nanostructures relies on their potential use in real applications and devices. Recent research presented at CINN09 addressed this topic, focusing on the assessment of the possibility of using carbon nanostructures for the production of clean energy and in environmental applications (**Buongiorno Nardelli**) and developing novel complex carbon nanostructures with potential use as energy storage media (**Froudakis**, **Linnolahti**). Moreover, the computational design of novel phases of carbon and functionalized carbon nanosystems suggest a large variety of structures (**Crespi**, **Nieminen**, **Melchor**) exhibiting interesting structural and electronic properties.

- **Transport properties**:
  One of the most promising applications of carbon and inorganic nanotubes and nanostructures is constituted by the realization of nanostructured electronic devices. Therefore, the evaluation of the electron transport properties of a nanosystem is a crucial step in the evaluation of its potential in the development of real applications. Moreover, present experimental techniques are still far from obtaining an accurate structure/property correlation at the atomistic level of detail. Research work presented at the workshop demonstrated the considerable contribution of modeling in this field. In particular, theoretical investigations are able to provide an accurate description of transport properties in nanostructures (**Charlier**) and in complex nanostructured assemblies (**Ordejon**), thus providing a comprehensive link between theory and experiments.

- **Beyond idealized structures**:
  As one can expect, non-ideal structures often exhibit a very different behavior with respect to their ideal counterparts. On the one hand, the presence of defects in complex nanostructures is expected to affect their properties and computational modeling provides a valuable tool to investigate on the changes occurring upon deviation from ideality (**Tomanek**). On the other hand, the controlled formation of defects can be viewed as an effective way to produce novel nanostructures

with interesting properties (**Krasheninnikov**), as also demonstrated by recent experimental work.

- **Computational techniques and evaluation of properties**
  The modeling of generic nanostructures is often hindered by their intrinsic complexity, which requires the application of accurate theoretical methods and calls for intensive numerical computations. Therefore, the choice of suitable modeling techniques is a crucial prerequisite to obtain reliable data, with experimental accuracy, yet keeping the calculation feasible. Generally speaking, density functional theory represents the method of choice in the study of the electronic properties of nanostructured systems. However, results can be strongly biased by the use of the proper exchange-correlation functionals (**Scuseria**), which are expected to provide the required agreement with the experiments. Moreover, depending on the computational approach applied, a variety of properties of the system under study can be evaluated, including electronic response (**Sebastiani**). Beside electronic structure calculations, techniques based on simplified potentials (**van Duin**) can be also applied with success to the study of low-dimensional nanostructured systems.

- **Experiments**
  The comparison of the outcome of calculations with available experimental data represents a crucial step for the assessment of modeling techniques. Moreover, state-of-the-art experimental research provides the required input to develop new modeling strategies. These aspects have been addressed in contributions concerning both chemical properties and functionalization of carbon nanostructures (**Basiuk**) and atomic-resolution microscopy of low-dimensional inorganic nanosystems (**Bar-Sadan**).

Overall, the research work presented at the CINN09 workshop provided a comprehensive account of the state of the art in the modeling of carbon and inorganic nanotubes and nanostructures. In particular, the presented contributions demonstrated the possibility of applying a common approach to the study of both carbon and inorganic nanotubes and nanostructures. Moreover, the work discussed demonstrated as the application of accurate theoretical methods on models of complex nanostructured systems constitutes a useful tool to achieve a realistic description of their properties and rationalize the outcome of experiments. The findings discussed can be

applied to the development of devices and applications based on nanostructured systems and in the design of novel materials at the nanoscale. The complexity of systems presented suggests further advancements in the field, thus paving new ways in the advancement of nanotechnology and related fields. Remarkably, the participation of leading scientists in the field is expected to strengthen current collaborations, to give rise to fruitful future partnerships and opens new perspectives to the foundation of research networks.

## Program

### Day 1 - May, 13th 2009

- 9.00 – 9.45**Jean-Christophe Charlier** (Université Catholique de Louvain, Belgium)
  *Quantum Transport in Carbon Nanostructures including Defects*

  (Contribution from the CECAM/Psi-k workshop on *Computational Studies of Defects in Nanoscale Carbon Materials*)

- 13.30 – 14.00 Registration and opening remarks

- 14.00 – 14.45 **Savas Berber** (Gebze Institute of Technology, Turkey)
  *Modifying physical properties of carbon nanostructures by chemical functionalization*

- 14.45 – 15.30 **Arkady Krasheninnikov** (University of Helsinki, Finland)
  *Irradiation of carbon nanomaterials with electrons and ions: from defects to self-organization*

- 15.30 – 16.15 **David Tomanek** (Michigan State University, USA)
  *Defects in nanotubes: Blessing and curse*

- 16.15 – 16.45 Coffee break

- 16.45 – 17.30 **Gustavo E. Scuseria** (Department of Chemistry and Department of Physics & Astronomy, Rice University, USA)
  *Carbon Nanotubes and Grapheme Nanoribbons: Screened Hybrid Theoretical Studies*

- 17.30 – 18.00 **Andreia L. Da Rosa** (Bremen Universitaet, Germany)
  *First-principles investigations on the functionalization of ZnO nanowires and nanotubes*

- 18.00 – 19.00 Poster session

## Day 2 - May, 14th 2009

- 9.00 – 9.45 **Adri van Duin** (Penn State University, Department of Mechanical and Nuclear Engineering, USA)
  *Development and applications of a reactive force field (ReaxFF) for surface catalysis*

- 9.45 – 10.30 **Marco Buongiorno Nardelli** (North Carolina State University, USA)
  *Carbon Nanostructures for Energy and Environmental Application*

- 10.30 – 11.00 Coffee break

- 11.00 – 11.45 **Vincent H. Crespi** (Department of Physics Penn State University, USA)
  *A new energetic regime for carbon nanostructures: the bi-ribbon, and also incommensurate stacking in graphenic bi-layers and graphene as a bi-continuum*

- 11.45 – 12.30 **Vladimir A. Basiuk** (Universidad Nacional Autónoma, Mexico)
  *Non-covalent interactions of porphyrins and carbon nanoclusters*

- 12.30 – 14.00 Lunch

- 14.00 – 14.45 **Georgios Froudakis** (University of Crete, Greece)
  *Pillared Graphene: A Novel Nanostructured Material with Enhanced Hydrogen Storage Capacity*

- 14.45 – 15.30 **Jennifer C. Green** (University of Oxford, UK)
  *Quantum mechanical modelling of crystals and molecules encapsulated within single walled nanotubes*

- 15.30 – 16.15 **Daniel Sebastiani** (Max-Planck Institute for Polymer Research, Germany)
  *Electronic response properties in organic nanotubes*

- 16.15 – 16.45 Coffee break

- 16.45 – 17.30 **Mark Wilson** (University of Oxford, UK)
  *The Growth and Structure Inorganic Nanotubes from Computer Simulation*

- 17.30 – 18.00 **Maya Bar-Sadan** (Weizmann Institute of Science, Israel)
  *HRTEM and modeling of closed-cage structures: imaging the atomic scale*

- 19.00 Conference Dinner

## Day 3 - May, 15th 2009

- 9.00 – 9.45**Pablo Ordejon** (CIN2 (CSIC-ICN), Spain)
  *Electron transport between graphene layers connected by nanotubes*

- 9.45 – 10.30 **Holger F. Bettinger** (University Tuebingen, Germany)
  *Simulation of the Chemical Modification of Carbon Nanotubes*

- 10.30 – 11.00 Coffee break

- 11.00 – 11.45 **Santiago Melchor** (University of Granada, Spain)
  *Construction and Analysis of Carbon Nanotube Structures: Shapes and Ripples*

- 11.45 – 12.30 **Risto Nieminen** (Helsinki University of Technology, Finland)
  *Quasi-graphite: a new carbon-based structure*

- 12.30 – 14.00 Lunch

- 14.00 – 14.45 **Mikko Linnolahti** (University of Joensuu, Finland)
  *Structural characteristics of the fulleranes and related main group nanostructures*

- 14.45 – 15.15 **Sara Furlan** (University of Udine, Italy)
  *Car-Parrinello molecular dynamics of inorganic gas molecules and graphene system with Rh intermediation*

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## *Abstracts*

## *HRTEM and modeling of closed-cage structures: imaging the atomic scale*

**Maya Bar-Sadan**
Weizmann Institute of Science, Israel

### Abstract

Modeling, synthesis and characterization progress hand in hand, as the dimensions of interest shrink to the nano scale. It is necessary to work iteratively in suggesting models, adapting them to fit the experimental data and vice versa.

Experimental characterization data is commonly achieved via ensemble techniques, such as Raman and XRD. However, by using them, one assumes that the particles are a homogeneous mixture, which in many cases is not correct.

The state-of-the-art aberration-corrected transmission electron microscopes allow imaging of structures in atomic resolution. Several imaging and measurement techniques allow direct comparison with calculated models, down to the atomic-scale.

I will present several case studies including carbon nanotubes, inorganic nanotubes and nanooctahedra. I will also address mainly the collaborated research of modeling, microscopy and synthesis and the accumulated information which is gained in the process.

## *Non-covalent interactions of porphyrins and carbon nanoclusters*

**Vladimir Basiuk**
Universidad Nacional Autónoma, Mexico
**Coauthor(s) :** Oscar Amelines-Sarria, Yevgeniy Kolokoltsev, and Maria Bassiouk

### Abstract

A rational approach to the design and preparation of new nanohybrids and nanoassemblies based on porphyrins and carbon nanomaterials (fullerenes and carbon nanotubes) requires a detailed understanding of the forces governing interactions between the components.

Here, as in many other areas of modern science and technology, the role of computational techniques cannot be overestimated, especially when obtaining relevant experimental information is complicated or impossible at all. Molecular mechanics calculations can provide some insight into the mechanisms and geometry of porphyrin□carbon nanomaterial assemblies.

At the same time, the electronic structure calculations on such nanohybrids are a challenging task due to their large molecular size, as well as due to imperfections of the available theoretical approaches. In the present work, the non-covalent interactions between porphyrins and carbon nanoclusters (mainly C60 fullerene as model system) are discussed.

The emphasis is made on the comparative study of several DFT functionals incorporated into the Materials Studio package from Accelrys in the calculations of binding energies, geometries, plots of molecular electrostatic potential, HOMO, LUMO, etc., for the non-covalent bonded complexes of C60 with meso-tetraphenylporphine and its transition metal complexes.

To validate the functionals employed (PW91, PBE and BLYP GGA, as well as PWC and VWN LDA), the theoretical results obtained are compared, when possible, with relevant experimental data.

## *Modifying physical properties of carbon nanostructures by chemical functionalization*

**Savas Berber**
Gebze Institute of Technology

### Abstract

The physical properties of carbon nanostructures are diverse owing to the ability of C atom to show different bindings. But, this is also an obstacle for controlling the synthesis of nanocarbon materials with desired properties. However, chemical functionalization is another way for engineering carbon nanostructures. In addition, unintentional chemical functionalization is always present due to the cleaning process, which may involve halogens as well as strong acids. We used ab initio density functional theory calculations to investigate the
chemical activity of defective and pristine nanostructures.

In the first part, we have considered the effect of halogens, which we consider as cleaning agents for purification, on physical properties of carbon nanotubes. Since our adsorption energies indicated that the physisorption of chlorine is as likely as its chemisorption, it can be used as a less invasive cleaning agent.

In the second part, we aim to demonstrate the chemical reactivity at defect sites of carbon nanotubes. In general, defects on carbon nanotubes self-heal. We have investigated the adsorption of H and SiHn radicals at defect sites. We found that both the defect and the radicals go through structural transformations due to the increased reactivity of defective region of the nanotube, compared to pristine tube walls.

Finally, we searched how the hydrogen adsorption outside C60 molecules affect the species encapsulated inside the fullerene. The modification of the environment outside the fullerene changes the reactivity of the fullerene inside. The hydrogen molecule that is encapsulated inside C60 fullerene may dissociate with lower activation energies when the fullerenes are exohedrally hydrogenated.

## *Simulation of the Chemical Modification of Carbon Nanotubes*

**Holger F. Bettinger**
University Tuebingen, Germany

### Abstract

The interaction of small molecules resulting in covalent and non-covalent modification of single-walled carbon nanotubes (CNT) is investigated by theoretical methods. We present model studies for the reaction with the highly reactive dichlorocarbene CCl2 molecule and an investigation of the mechanism of the CCl2 addition to the CNT. Furthermore, the magnitude and nature of interactions between small aromatic systems (benzene and naphthalene) and various single-wall carbon nanotubes are examined by MP2 theory.

### Key References

1. Bettinger, H. F. Chem. Eur. J. 2006, 12, 4372-4379.
2. Kar, T.; Bettinger, H. F.; Scheiner, S.; Roy, A. K.; J. Phys. Chem. C 2008, 112, 20070-20075.

## *Carbon Nanostructures for Energy and Environmental Application*

**Marco Buongiorno Nardelli**
North Carolina State University, USA

### Abstract

Hydrogen generation and purification, carbon monoxide sequestration and solar energy conversion are key problems that need to be resolved to achieve a sustainable energy economy and reduce, if not reverse, global warming.

Using first principles calculations based on Density Functional Theory (DFT) we have demonstrated that key reactions involved in these processes can be achieved using carbon nanostructures, where the reactive sites can be regenerated by the deposition of carbon decomposed from the reactants (methane or carbon monoxide) to make the reactions self-sustained.

Moreover, using a novel time-dependent DFT approach, we have explored ways to improve the adsorption spectra of molecular assemblies for optimal solar energy conversion.

Our results indicate that carbon nanostructures hold great promise for clean energy and environmental technology applications.

## *Quantum Transport in Carbon Nanostructures including Defects*

**Jean-Christophe Charlier**
Université Catholique de Louvain (UCL)

### Abstract

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 nanosized 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~T 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].

## Key References

[1] Electronic and transport properties of nanotubes, J.-C. Charlier, X. Blase, and S. Roche, Reviews of Modern Physics 79, 677-732 (2007)
[2] Scanning tunneling microscopy fingerprints of point defects in graphene : a theoretical prediction, H. Amara, S. Latil, V. Meunier, Ph. Lambin, and J.-C. Charlier, Physical Review B 76, 115423 (2007)
[3] Defective carbon nanotubes for single molecule sensing,
Z. Zanolli and J.-C. Charlier, submitted for publication (2009)

## *A new energetic regime for carbon nanostructures: the bi-ribbon, and also incommensurate stacking in graphenic bi-layers and graphene as a bi-continuum*

**Vincent Crespi**
Department of Physics Penn State University, USA
**Coauthor(s) :** D. Stojkovic, P. Zhang, C. Nisoli, P. Lammert, Y. Tang

### Abstract

Conversion of two diametrically opposed atomic rows on a carbon nanotube to sp3 hybridization produces two identical weakly coupled one-dimensional electronic systems within a single robust covalently bonded package: a biribbon.

Arm-chair tubes, when so divided, acquire a pair of narrow spin-polarized bands at the Fermi energy; interaction across the sp3 dividers produces a tunable band splitting in the THz range.

For semiconducting tubes, the eigenvalues of the low-energy electronic states are surprisingly unaffected by the bifurcation; however, the tubes' response functions to external electric fields are dramatically altered.

These modified tubes could be produced by uniaxial compression transverse to the tube axis followed by site-selective chemisorption.

As time permits, I will also discuss how recent results on incommensurately stacked gaphenic bilayers reveal signs of Bragg scattering in the Raman response, and how a bicontinuum model of grapheme can describe optical phonons within a continuum framework.

## *First-principles investigations on the functionalization of ZnO nanowires and nanotubes*

**Andreia Luisa da Rosa**
Bremen Universitaet, Germany

### Abstract

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.

## *Pillared Graphene: A Novel Nanostructured Material with Enhanced Hydrogen Storage Capacity*

**Georgios Froudakis**
University of Crete, Greece

### Abstract

A multiscale theoretical approach is used for designing novel materials with enhanced storage capacity. A combination of ab-initio and Monte Carlo techniques was employed to investigate hydrogen storage in a three-dimensional carbon nanostructure named Pillared Graphene.
Pillared Graphene is the combination of two allotropes of carbon, CNTs and graphene sheets [Dimitrakakis, G. K.; Tylianakis, E.; Froudakis, G. E. Nano Letters 2008, 8, (10), 3166-3170]. The entire structure looks like a building on its early stages of construction where CNTs can be considered as the pillars and graphene sheets as the floors. CNTs and graphene sheets have been combined in such a way to create a 3-D material with tunable pores, as the length, the width and the intertube distance of the CNTs can be changed at will. Tunable porosity is the key aspect of our material as it is crucial for efficient hydrogen storage.
This novel nanoporous material has by design tunable pore sizes and surface areas. Its interaction with hydrogen was studied thoroughly via ab-initio and Grand Canonical Monte Carlo calculations. Our results show that, if this material is doped with lithium cations, it can store up to 41 g H2/L under ambient conditions, almost reaching the DOE volumetric requirement for mobile applications.

## *Car-Parrinello molecular dynamics of inorganic gas molecules and graphene system with Rh intermediation*

**Sara Furlan**
Università di Udine, Dipartimento di Fisica, Italy

### Abstract

Carbon nanotubes (CNTs) are promising candidates for extremely sensitive gas sensors because of the variation of their electron transport properties when toxic gas molecules are adsorbed on surface. Several experimental evidences reveal that residual contaminants, e.g. metal catalyzer particles, can provide a major contribution to the sensor response [1]. On the other hand, CTNs have been widely studied as supports for nanoscopic metal catalysts even for gas-phase reagents, an example among all: the conversion of syngas in ethanol over Rh-loaded CNTs [2].
We proposed to investigate the role played by transition metals within interaction between small gas molecules and CNTs in the two different contexts: gas adsorption and gas-phase catalysis. In particular we are interested in CNTs/NOx/Rh and CNTs/COx/Rh systems. Since the graphene layer is a good approximate model for large radius single walled CNT, we have performed Car-Parrinello molecular dynamics of gas molecules on graphene in absence or presence of single atom or small cluster of Rh. We are going to discuss the wide range of behaviours discovered.

### Key References

[1] R. Larciprete, L. Petaccia, S. Lizzit and A. Goldoni, J. Phys. Chem. C, 111, 12169-12174, (2007)
[2] X. Pan, Z. Fan, W. Chen, Y. Ding, H. Luo and X. Bao, Nature Materiels, 6, 507-511, (2007)

## *Quantum mechanical modelling of crystals and molecules encapsulated within single walled nanotubes.*

**Jennifer Green**
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**Coauthor(s) :** Emma Sceats, Navaratnarajah Kuganathan

### Abstract

Density functional calculations on a series of pseudo one-dimensional crystals encapsulated within single walled nanotubes are presented. The inorganic materials include KI, HgTe, PbI2, and group 13 halides.

The computed structures help refine models for the fitting of transmission electron microscopy images and provide energetic and electronic information on the encapsulates.

Modelling a series of transition metal sandwich compounds with known ionization energies enables definition of the redox properties of single walled nanotubes as a function of their size and morphology.

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## *Irradiation of carbon nanomaterials with electrons and ions: from defects to self-organization*

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### Abstract

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 morphology and tailor mechanical, electronic and even magnetic properties of nanostructured carbon systems, and first of all, carbon nanotubes.

We systematically study irradiation effects [1] in carbon nanotubes and other forms of nano-structured carbon. By employing various atomistic models ranging from empirical potentials [2] to time-dependent density functional theory [3] we simulate collisions of energetic particles with carbon nanostructures, and calculate the properties of the irradiated systems.

In my presentation, I briefly review the recent progress in our understanding of ion-irradiationinduced phenomena in nano-structured carbon and compare the simulation results to the experimental data. I dwell on the "beneficial" role of defects and impurities in nanotubes and related systems.

Finally, I will present the results of simulations of irradiation-induced pressure build-up inside nanotubes [4] and onions [5] encapsulated with metals. Electron irradiation of such composite systems in the transmission electron microscope gives rise to contraction of nanotube shells and thus to pressure in the encapsulate. In such systems, irradiation-stimulated pressure can be as high as 40 GPa, which makes it possible to study phase transformations at the nanoscale with high spatial resolution.

I will also address the interaction of transition metal atoms with pristine and defected grapheme sheets [6]. I will discuss the electronic structure of defected graphene sheets with adsorbed metal atoms and identify possible

avenues for tailoring the electronic structure of graphene by irradiation induced defects and metal atoms. Finally I will touch upon the response to irradiation of mechanically strained carbon nanotubes and some other low-dimensional materials.

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## *Structural characteristics of the fulleranes and related main group Nanostructures*

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### Abstract

Perhydrogenation of icosahedral fullerenes larger than C60 is predicted to produce thermodynamically stable fulleranes, i.e. perhydrogenated fullerenes.

Demonstrated by B3LYP and MP2 calculations, the fulleranes are significantly stabilized by partial endo-hydrogenation, allowing nearly optimal sp3-hybridization for each carbon atom.

The in–out isomeric structural motif of the fulleranes is extended to other main group compounds, with the focus on Group 14 hydrides, icosahedral diamondoids and heavier Group 14 analogues, novel nanostructural modifications of Group 15 elements, and Group 13–15 binary hydrides, revealing their distinct structural characteristics.

The studies include both cage structures and nanotubes. Concerning the latter, by taking advantage of line group symmetries, periodic B3LYP-level calculations are shown to be practical for nanotubes with diameters of 10 nm and above.

## *Construction and Analysis of Carbon Nanotube Structures: Shapes and Ripples*

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### Abstract

The number of structures based on nanotubes is increasing constantly, and they show an amazing variety of shapes. Particularly, connection of nanotubes is of high interest because the possibility of building tube-only nanocircuits.

However, for exploring these possibilities, computation and modelling is required, and prior to that, 3D models of such structures have to be built. These structures are hard to get manually, specially considering the presence of disclinations and dislocations that messes up the orientation reference in the graphitic network.

Here, we will show how to account for the geometry of multiple-tube structures, arising from the presence of various non-hexagonal rings. Starting from the concepts of dislocations and disclinations, we will explain the strip algebra as a method to identify the position of non-hexagonal rings, and even calculate the indices of the nanotubes arising from two and three nanotube junctions.

The resulting strip notation allows the precise identification of any particular geometry, and in some cases, guess which structures (could be more than one) fits any particular set of indices. These procedures are continuously being incorporated into CoNTub, a software which automates all the process, making easy the construction of complex structures that otherwise could be even impossible to construct.

In addition, analysis tools are required to inspect easily the resulting geometries. To illustrate these needs, we will present the results of theoretical calculations on finite nanotubes of distinct length and chirality, and will discuss how to evidence small geometric changes that have consequences in the electronic structure.

For most nanotubes, if they are long enough, all rings usually converge to the same geometry, with uniform bonds. However, for armchair nanotubes, even capped or not, we
have not yet seen the tendence to uniformity. Instead, small, although measurable oscillations between two distinct regimes (Clar and Kekulé) appear, which are evidenced with our visualization software TubeAnalyzer.

Each of these regimes is characterized by an opposed tendence in geometry: Clar areas present uniform and smaller rings inside bigger ones, which indicate the local aromaticity is enhanced in determined areas. The effect of these oscillations is confirmed with NICS calculations, and the causes and relevance of this phenomenon will be discussed.

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## *Quasi-graphite: a new carbon-based structure*

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### Abstract

We propose a new carbon-based nanostructure, the quasi-graphite phase (QGP). The phase resembles carbon nanotubes welded into planes, in turn arranged similarly to carbon layers in graphite. The QGP exhibits strong stability with respect to temperature and external strain. The elastic and electronic properties of the proposed structure are discussed.

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## *Electron transport between graphene layers connected by nanotubes*

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### Abstract

The study of electronic transport both in graphene and in carbon nanotubes has attracted a great deal of work, due to the interesting fundamental phenomena that these materials display and to the promise of outstanding applications in nanoelectronics. The two- and one-dimensional character of the two materials, respectively, confer them with sharply different electronic transport properties, and therefore different potential applications are envisioned.

In this work, we have considered the possibility of future devices that may use combinations of graphene layers and carbon nanotubes for electronic applications. For instance, nanotubes might be used to transmit electronic signals between two graphene-based devices, in the same way as copper wires do between traditional silicon-based transistors.

We present first-principles studies of the transport properties of a system consisting on two graphene sheets connected by a carbon nanotube. We consider different nanotubes with different chiralities and lengths, and also different types of connections between the tube and the sheet. We compute the ballistic transport between the two sheets through the nanotube, and show that the behavior of the conductance is qualitatively different for metallic and semiconducting nanotubes. We also show how the conductance depends on the link between the nanotube and the graphene sheet.

## *Carbon Nanotubes and Grapheme Nanoribbons: Screened Hybrid Theoretical Studies*

**Gustavo Scuseria**
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### Abstract

I will present some of our recent calculations on carbon nanotubes and graphene nanoribbons, and the theoretical tools used in these studies, in particular, the HSE screened hybrid functional for systems with periodic boundary conditions.

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## *Electronic response properties in organic nanotubes*

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### Abstract

We elucidate electronic response effects in carbon nanotubes and self-assembled (non-covalent) organic nanotubes, which can be observed spectroscopically as a host-induced change in the guest's spectroscopic properties.

This effect can be useful for analyzing the host structure alone [1,3], but also for understanding biomimetic processes like molecular recognition [2]. Specifically, we consider the electronic response on an external magnetic field, which is closely related to nuclear magnetic resonance (NMR) spectroscopy.

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## *Defects in nanotubes: Blessing and curse*

**David Tomanek**
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### Abstract

Defects in carbon nanotubes, including atomic vacancies and Stone-Wales defects, are known to significantly degrade the stability, electrical and thermal conductance of these unique nanostructures. Location of defects can be detected spectroscopically [1] or by probing the topography or local damping in dynamic Atomic Force Microscopy [2]. Carbon nanotubes exhibit an unusual capability for healing by reconstruction at defect sites, induced thermally or by monochromatic light [3,4].

On the other hand, presence of structural defects may be a desirable pre-requisite to induce large-scale structural changes, including fusion of nanotubes [5] and nanotube peapods [6].

Since direct observation of atomic-scale processes associated with self-healing at defect sites or defect-assisted structural changes is very hard by experimental means, computer simulations offer unique insight into the underlying Physics.

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## *Development and applications of a reactive force field (ReaxFF) for surface catalysis*

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### Abstract

In order to enable large-scale (>>1000 atoms) simulations on metal and metal oxide surface catalysis we have developed ReaxFF reactive force fields for metal/metal oxide materials and their interactions with hydrocarbons, oxidants and water.

In this presentation we will describe the force field development process, which involves parameter training against quantum mechanical data describing reaction energies and barriers, and applications of these force field to metal/hydrocarbon, metal oxide/hydrocarbon [1] and metal oxide/water systems.

We believe that these force fields have unique applications for describing the dynamics of surface chemistry for organic and inorganic nanosctructures and will demonstrate applications of surface structure effects on catalytic reactivity.

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## *The Growth and Structure Inorganic Nanotubes from Computer Simulation*

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### Abstract

A range of materials have been observed to form nanotubular structures (inorganic nanotubes -INTs) analogous to those well known for carbon. These INTs, which may have unique low-dimensional morphologies not simply related to known bulk polymorphs, potentially offer unique mechanical and electronic properties.

Controlled synthesis is difficult to achieve as direct methods often require extreme reaction conditions. A potentially useful synthetic pathway is to use carbon nanotubes as templates and grow the INTs internally.

Molten salts represent a useful class of filling materials as typical surface tensions are low enough so as not to crush the nanotubes. In this talk, atomistic simulation models, in which the atom interactions are treated utilizing relatively simple potential energy functions, will be developed and applied to understand the INT formation and stability.

INT morphologies will be classified by reference to folding two dimensional sheets. The ion transport mechanisms (not directly available from experimental HRTEM observations) by which the INTs form will be discussed.

The respective roles of thermodynamics and kinetics in determining INT morphology will be outlined and the atomistic results used to develop an analytic model to predict INT diameters.

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

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### Abstract

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 nanocrystallytes[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) singlewalled 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 nanoregime.

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.

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## *Effect of the Chemical Functionalization on Charge Transport in Carbon-Based Materials at the Mesoscopic Scale*

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### Abstract

The chemical attachment of groups on single-walled carbon nanotubes (CNTs) and grapheme nanoribbons (GNRs) has attracted much attention as it provides an efficient way for tuning their electronic properties.

These carbon based systems are being widely investigated as potential candidates for nanoelectronic interconnects and transistors. The control of electric current is, therefore, an important challenge in nanostructures engineering[1].

Here we present a theoretical methodology and study of charge transport through GNRs [2], as well as in metallic and semiconducting CNTs [3], with randomly distributed functional groups covalently attached to the system surface.

We resort to both first principles calculations, to obtain a suitable parametrization of the electronic structure, and a fully ab initio transport approach calculation to explore conduction regimes through large and disordered systems.

The quantum transport modeling is based on the Green's function formalism, combining an iterative scheme for the calculation of transmission coefficients with the Landauer's formula for the coherent conductance.

Our results describe how the conductance of the hybrid systems is altered as a function of incident electron energy and molecules coverage density. We explore the transport regimes comparing two different types of functional groups. Phenyls and hydroxyl groups induce a local rehybridization from sp2-type to sp3-type orbital of the carbon atoms yielding a localized transport regime.

On the other hand, carbene groups do not disrupt the original sp2 network which allows a good conductance preservation.

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

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### Abstract

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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## *Ab initio quantum mechanical simulation of systems with helical symmetry: carbon and chrysotile nanotubes*

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### Abstract

Nanotubes can be characterized by a very high point symmetry (helical groups), comparable or even larger than the one of cubic systems.1 The helical symmetry is now fully exploited in the CRYSTAL code, so that the computational cost of large unit-cell nanotubes dramatically decreases.2
The nanotube symmetry is exploited at three levels: (a) for the automatic generation of the nanotube starting from a two-dymensional structure; (b) for the calculation of the mono- and bi-electronic integrals; (c) for the diagonalization of the Fock matrix in the reciprocal space.
The modified CRYSTAL code was used for the study (structure, stability, band gap) of a set of carbon nanotubes at different DFT levels (LDA, GGA, hybrids) with Gaussian type basis sets of increasing complexity (from STO-3G to 6-1111(2d1f)), and the results compared with the available experiments and other simulations.1,3
A preliminar quantum mechanical ab initio analysis of chrysotile4 nanotubes ($Mg_3Si_2O_5(OH)_4$, phyllosilicate cylindrically wrapped that can contain hundreds of atoms in the unit cell) was also performed for the first time (DFT, 6-31G* basis sets). The relationship between structure (i.e. radius of the tube and rolling direction of the flat layer) and stability is discussed.5
Keywords: helical symmetry, carbon nanotubes, chrysotile.

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## *Polyhedral fullerenes of group 15 elements*

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### Abstract

Group 15 elements phosphorus, arsenic, antimony, and bismuth are all known to appear as layered materials. The layered bulk materials are composed of sheets of puckered six-membered rings, being structurally related to graphite.

In analogy to the structural relationship between the single layers of graphite and carbon fullerenes, the individual puckered sheets of the layered group 15 materials can be folded into fullerene-like polyhedral cages [1-3].

We have investigated the structural and electronic characteristics of tetrahedral, octahedral, and icosahedral fullerenes composed of group 15 elements P, As, Sb, and Bi.

Systematic quantum chemical studies at the DFT and MP2 levels of theory were performed to obtain periodic trends for the stabilities, structural principles, and electronic properties of the elemental nanostructures.

The structures and stabilities of the studied group 15 fullerenes converge smoothly towards their experimental bulk counterparts. Comparisons with experimentally known allotropes of the studied elements suggest the predicted polyhedral cages to be thermodynamically stable.

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## *Density Functional Tight-Binding calculations on ZnO surfaces and nanostructures*

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### Abstract

Over the last few years, several ZnO nanostructures have been successfully synthesized and often suggested for new applications in optoelectronics and sensing devices1,2. Therefore, theoretical modeling is required in order to better understand these structures and guide the development of new technologies based on ZnO complex materials. However, realistic electronic structure simulations on complex ZnO systems – such as defective and functionalized nanostructures – are still computationally very demanding and therefore using efficient computational schemes is mandatory. In this talk we present our recently developed Self-Consistent-Charge Density Functional based Tight-Binding (SCC-DFTB) model for describing Zn-X interactions (X=H, C, N, O, S and Zn), which is a promising time-efficient method for simulating ZnO-based complex materials. The model has been derived based on Density Functional Theory (DFT) calculations, and validated for Zn-X in different chemical environments, including solids, surfaces, nanostructures and molecular complexes. We were able to accurately reproduce ab initio DFT results for ZnO surfaces and nanowires3, and also predict the stability of ZnO nanobelts. Besides, we have employed our method to investigate adsorption of small organic molecules on ZnO surfaces, which is the first step towards functionalization of nanostructures.

### Key References

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## *First principle modeling of initial stage of CNT growth on nanostructured Ni(111) catalyst*

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### Abstract

The chemical vapor deposition (CVD) growth of CNTs above the particles of metallic catalyst is believed to be the most promising approach for gaining a control over the geometry and the electronic properties of nanotubes which demonstrates to yield limited distributions of their chiralities [1].

In dependence of the surface area of catalytic particle, not only separated each from other single-walled (SW) nanotubes can be synthesized but also SW CNT bundles, which may contain hundreds of closely-packed nanotubes, and multi-walled (MW) CNTs.

In the current study, we simulate 2D periodic models of the Ni(111)-SW CNT nanostructures, which can describe peculiarities of growth for the SW CNT bundle upon the nanostructured catalytic particle comparable with the diameter of bundle.

In the current study, we observe the transfer of electronic charge from the nickel catalyst towards the CNTs (about 1.5 e per C atom in carbon ring contacting to substrate, somewhat smaller for ac- and larger for zz-nanotube chirality, respectively).

We analyze here 2D plots of the electron charge distributions in the CNT/Ni interconnects in planes both parallel and perpendicular to the Ni(111) slab. We also estimate adhesion energies of CNTs in all interconnects considered and analyze both total and projected densities of one-electron states (DOS).

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## *Atomic and electronic structure of model SrTiO3 nanotube: First-principle calculations*

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### Abstract

Among a large variety of modern inorganic compounds, the class of ABO3 perovskites exhibits an enormous number of properties that make nanotubes produced from these compounds highly promising materials for future applications in many exciting electronic and electromagnetic devices. Nowadays, many different monophasic perovskite ABO3 nanotubes having an outer diameter from about 8 nm to about 500 nm, and a length from about 10 nm to about 10 um can be synthesized via the low-temperature hydrothermal reaction route [1]. On the other hand the results of theoretical simulations on perovskite nanostructure are very scarce in the literature. In our study we have performed ab initio simulation of nanotubes made from SrTiO3 perovskite, which bulk and surface properties are well studied both theoretically and from experiment. We have examined both SrO- and TiO2-terminated SrTiO3 nanotubes of outer diameter ~3 nm taking into account their possible nonstoichiometry. The calculated energetics, atomic and electronic structures of SrTiO3 nanotubes are thoroughly discussed in our presentation.

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## *Quantum confinement and electronic properties of single-crystalline silicon nanotubes*

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### Abstract

We studied the quantum confinement and electronic properties of single-crystalline silicon nanotubes (sc-SiNTs) with both uniform (ideal) and nonuniform (more practical for experiments) thickness.
(i) These pristine sc-SiNTs with sp3 hybridization are found to be energetically stable. The electronic property is sensitive to the external diameter, tube-wall thickness, and tube-axis orientation due to quantum confinement effects.
(ii) For sc-SiNTs with nonuniform thickness, the distributions of wavefunctions of the valence band maximum and conduction band minimum show that the carriers (electrons and holes) are mainly confined in the thicker sides, supplying an advantage to spatially separate the doping impurities (thinner side) from the conducting channel (thicker side ) in doped sc-SiNTs.
(iii) We proposed a new modulation doping method through the nonuniformity of nanostructures instead of heterostructures. The performance of the SiNT-based transistors may be substantially improved by selective p/n doping in the thinner side to reduce the impurity scattering.

## *Unraveling the strong interaction between graphene monolayer and Ru(0001) : a DFT study*

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### Abstract

Epitaxial graphene on Ru (0001) surface has led to recent scientific activities [1-2], since it is thought to be a smart way to obtain large-scale graphene. We refer to recently published experimental Scanning Tunneling Microscopy experiments resolving the (12x12)C / (11x11)Ru Moiré superstructure [1] and propose a detailed comparison with an extensive density functional theory (DFT) calculation.

In contrast to expectations, we show that the measured electronic corrugation of the Moiré pattern mainly originates from a geometric buckling of the graphene sheet of 1.5 Å, induced by alternating weak and strong chemical interactions with Ru [3].

The chemical bonding in the strong contact regions, leads to three measurable properties nicely reproduced by our calculations:
- the asymmetry between low and high –lying carbons electronic states probed by STS spectroscopy [4-5]
- the considerable band gap opening in the graphene states [6]
- the work function decrease [7]

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## *Electric-field-induced deformations of graphene nanoribbons and carbon nanotubes*

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### Abstract

We developed analytical approaches to predict deformations of graphene nanoribbons and carbon nanotubes induced by electric fields. These approaches were validated through molecular simulations using a constitutive atomic electrostatic model combined with an empirical potential.

Our results reveal that graphene's field-oriented bending angle is roughly proportional to the square of either field strength or graphene length for small deformations, while is independent of grapheme width.

The effective bending stiffness and longitudinal polarizability were also found to be approximately proportional to the square of graphene length. Compared with carbon nanotubes, graphene nanoribbons were found to be more mechanically sensitive to external electric field.

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