GRANADA'12

Graphene Nanoscience: from Dirac Physics to Aplications

Granada, Spain
9-13 September 2012

Book of Abstracts

Edited by Blanca Biel, María J. López and Elvira Romera

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ISBN: 978-84-695-4635-2

Preface

Graphene nanoscience is a vigorous and a topical issue in the last years. The contributions to the conference **GRANADA'12** represent a broad range of the current research in graphene nanoscience at the highest scientific level, from fundamental principles to applications and industrial developments. **GRANADA'12** is aimed to be a mosaic of expertise and young talent, counting with a number of the leader scientists in the field together with emerging young talented researchers.

This book contains the abstracts of the contributions to this Conference: invited talks, selected oral contributions (hot topics) and poster contributions. All the talks (invited and hot topics) are arranged chronologically according to the Program. The poster contributions have been ordered according to the surname of the presenting author. An author index is provided at the end of the Book.

Topics

- Synthesis and large scale production techniques
- Spectroscopic characterization methods and microscopies (HRTEM, STM, AFM)
- Electronic properties, magnetism and spintronics
- Quantum transport
- Graphene oxide and the chemistry of graphene
- Simulation of graphene based materials and devices
- Electronic, sensing and energy applications
- Graphene in industry

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Sunday, 9th		Monday, 10th		Tuesday, 11th		Wednesday, 12th		Thursday, 13th	
		8:30	*Conference Opening*						
			Chairman:Stephan Roche		*Chairman: Florian Barnhart*		*Chairwoman: Irene Suárez-Martínez*		*Chairman: Frank Koppens*
		9:00	*Opening Session:* Francisco Guinea	9:00	Antonio Castro Neto (I)	9:00	David Jiménez (I)	9:00	Rodolfo Miranda (I)
		9:40	*Graphene Flagship* Francisco Guinea	9:40	Juan José Palacios (I)	9:40	François Triozon (I)	9:40	Amaia Zurutuza (I)
		10:00	Cristina Gómez-Navarro (I)	10:20	John Schliemann (I)	10:20	Stijn Goossens (O)	10:20	Julio Alonso (I)
						10:40	Dinh Tuan (O)		
		10:40	Coffee break	11:00	Coffee break	11:00	Coffee break	11:00	Coffee break
			Chairman:Julio Gómez		*Chairman: Ignacio Paredes*		*Chairman: Fernando Magaña*		*Chairman: Iván Cabria*
		11:10	Pablo Pou (I)	11:30	Irene Suárez-Martínez(I)	11:30	Alessandro Cresti (I)	11:30	Nicolás A. Cordero (O)
		11:50	Florian Barnhart (I)	12:10	Francisco Domínguez Adame (O)	12:10	Mark Auslender (O)	11:50	Shengjun Yuan (O)
		12:30	Amadeo Vázquez de Parga (O)	12:30	César González (I)	12:30	Ralph H. Scheicher (O)	12:10	Rafael Roldán (O)
								12:30	Guy Le Lay (O)
		12:50	Enrico Gnecco (O)	13:10	Stefano Bellucci (O)	12:50	Jürgen Schiefele (O)	12:50	Andrés Castellanos (O)
						13:10	Frank Ortmann (O)	13:10	*Concluding Remarks*
		13:10	Lunch	13:30	Lunch	13:30	Lunch		
			Chairman:Julio Alonso				*Chairman: Juan José Palacios*		
		15:00	Arben Merkoçi (I)			15:30	Frank Koppens (I)		
17:00-21:00	Registration	15:40	Sergio Valenzuela (I)			16:10	Andrés Ayuela (O)		
		16:20	Jan M. Michalik (O)			16:30	Yannick Dappe (O)		
		16:40	Enrique Burzuri (O)	17:00	Visit to the Alhambra	16:50	Yoshihiro Gohda (O)		
20:00-	Welcome reception	17:00 -19:00	Coffee and **Poster Session**			17:10-19:00	Coffee and **Poster Session**		
		21:00	Conference Dinner						

Monday, September 10th 2012

8:30 Wellcome and Opening Ceremony

9:00 Session 1. Chairman: Stephan Roche

Opening Sesion: F. Guinea
Models for graphene

Graphene Flagship: F. Guinea

C. Gómez-Navarro (Invited 1)
Chemically derived graphene, electronic, structural and mechanical properties

10:40 Cofee Break

11:10 Session 2. Chairman: Julio Gómez

P. Pou (Invited 2)
Graphene on weakly interacting metals: pristine surfaces and point defects

F. Banhart (Invited 3)
In-situ growth of graphene and related structures in the electron microscope

A.L. Vázquez de Parga (Oral 1)
Localized states on graphene quantum dots

E. Gnecco (Oral 2)
Elastic Response of Graphene Nanodomes by AFM microscopy and spectroscopy in UHV

13:10 Lunch

15:00 Session 3. Chairman: Julio A. Alonso

A. Merkoçi (Invited 4)
Graphene Based Platforms for Biosensing Applications

S.O. Valenzuela (Invited 5)
Spin precession in freely-suspended graphene nonlocal spin valves

J.M. Michalik (Oral 3)
Spin transport in graphene based devices with magnetic Co electrodes

E. Burzuri (Oral 4)
Graphene electrodes for molecular spintronics

17:00 Coffee and Poster Session

21:00 Conference Dinner

Models for graphene

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Graphene presents a number of unique properties, not found in other materials. Models are important for the understanding of these unusual features. We present the basic ingredients of graphene models, and review applications to the study of electron-electron interactions, and lattice properties.

Graphene Flagship

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Presentation of the Flagship on Graphene.

Chemically derived graphene, electronic, structural and mechanical properties

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J. Meyer[4], U. Kaiser[4]

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The promising electronic, mechanical and thermal properties of graphene for high demanding applications call for the need of approaches that provide access to large amounts of graphene monolayers.
In this talk I will talk about the electronic and mechanical properties of single graphene sheets obtained via chemical reduction of graphite oxide, a promising route for the large scale production of graphene that offers the possibility to assemble them on insulating substrates.

Chemically reduced single graphene oxide layers exhibit moderate conductivities due to the presence of defects or residual functional groups remaining after reduction [1,2]. This moderate electrical performance can be extraordinarily improved by a CVD process to heal defects contained within the monolayers. In this manner, sheets with two orders of magnitude conductivity enhancement can be obtained [3], reaching mobilities that exceed those of the molecular semiconductors currently used in organic electronics.
From the mechanical point of view, AFM indentation experiments on suspended chemically derived layers reveal a Young modulus closely approaching that of pristine graphene [4].

[1] Gomez-Navarro *et al* ***Nano Letters*** 2007, 7, 3499-3503
[2] Gomez-Navarro *et al* ***Nano Letters*** 2010, 10, 1144-1148
[3] López *et al* ***Advanced Materials*** 2009, 21 , 46 -50
[4] Gomez-Navarro *et al* ***Nano Letters*** 2008, 8, 2045-2049

Graphene on weakly interacting metals: pristine surfaces and point defects

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Understanding the coupling of graphene with its local environment is critical to integrate it in tomorrow's electronic devices. Previous studies have shown that highly perfect sheets of graphene can be obtained by epitaxial growth on metal surfaces, and for some transition elements, like Cu or Pt, the interaction is very weak and many characteristic properties of graphene are preserved [1,2]. In this work, we show: i) how the presence of these two metallic substrates affects the properties of an atomically tailored graphene layer, and ii) the structure of graphene grown on Pt close to the steps where the flakes start to nucleate. To this end, we combine scanning tunneling microscopy (STM) experiments with density functional theory calculations (DFT) and non-equilibrium Green's functions (NEGF) methods to model the electronic transport. For the non-defective graphene adsorbed on Pt(111), our calculations show that the periodic modulations typically observed by STM on the Moiré patterns can be explained as a purely electronic effect. For graphene on Cu(111), topographic effects are larger. When vacancies are present on graphene/Pt(111), the calculations help us associate the observed STM images with the positions of the atoms (Fig. 1a,b). Vacancy sites become reactive, leading to an increase of the coupling between the graphene layer and the metal substrate at these points (Fig. 1c,d). This gives rise to a rapid decay of the localized state and the quenching of the magnetic moment associated with carbon vacancies in free-standing graphene layers [3]. We have also studied the competition between the interaction of graphene with a Pt step and with the metal surface that controls the structure and chirality of the flake edge and the observed Moiré structures (Fig. 1e).

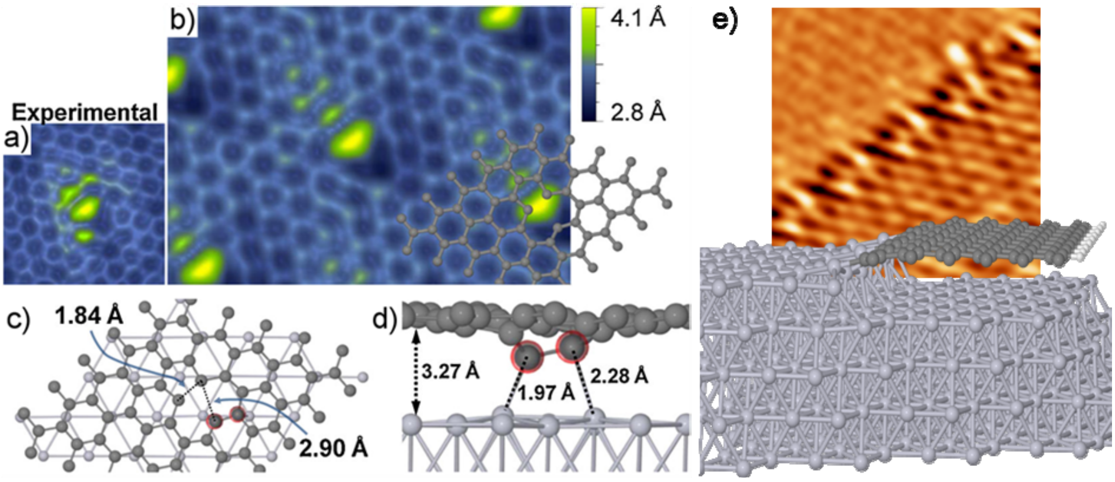

Figure 1: (a) Experimental LT-STM image of a single vacancy in graphene/Pt(111). (b) Calculated STM image of the same system. (c,d) An adsorption site for a single vacancy in graphene on Pt. (e) RT-STM image and the atomic structure of graphene grown on a Pt step.

[1] A.J. Martínez-Galera et al., Nano Letters, 11 (2011) 3576.
[2] P. Sutter et al, Phys. Rev. B, 80 (2009) 245411.
[3] M.M. Ugeda et al, Phys. Rev. Lett., 107 (2011) 116803.

In-situ growth of graphene and related structures in the electron microscope

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The growth of graphene and other carbon nanophases is often carried out on catalytically active metal surfaces. The topography and crystallographic orientation of the metal substrate determines the morphology of the growing carbon phase. The growth of carbon nanomaterials can be realized from a solid metal-carbon composite in vacuum. This became the basis for *in-situ* electron microscopy experiments where metal-carbon composite structures are heated in the high-temperature stage of a TEM. The nucleation and growth of carbon nanostructures can hence be monitored in real time and at high spatial resolution. The shaping of the metallic precursor can be carried out by dedicated heating or electron irradiation experiments.

The procedure of heating composites of transition metals (e.g., Fe, Co, Ni) and carbon in the vacuum of the TEM has first been successful in the *in-situ* nucleation and growth of carbon nanotubes. Multi-wall carbon nanotubes grow from metal crystals that were encapsulated in the interior of larger multi-wall tubes [1]. Growth occurred in the inner hollow of the large host tubes. The experiment showed that bulk diffusion of carbon atoms through the metal determines the growth process. For the growth of single-wall carbon nanotubes, a sharp metal tip had to be generated. This was realized by the electron beam-induced thinning of nano-sized metallic cylinders so that a double-cone shape was obtained. After the breakage of the cone at the bottleneck, the nucleation and growth of a single-wall nanotube was observed on the tips of the cones [2].

For the catalytic growth of graphene layers, flat metallic surfaces are needed. This was achieved by depositing thin layers of transition metals onto amorphous carbon films. A careful heating procedure was used to induce an uptake of carbon in the metal layer and, later, the coalescence of metal islands by ripening. During the thermally induced retraction of the metal layer, the growth of graphene layers became visible [3]. A structuring of the metal layer is possible by writing patterns with a focused electron beam and was used to grow patterns of graphene [4].

Part of the work has been funded by the French *Agence Nationale de Recherche* (project NT09 507527, NANOCONTACTS).

[1] J. A. Rodriguez-Manzo, M. Terrones, H. Terrones, H. W. Kroto, L. Sun, F. Banhart, *Nature Nanotech*. **2**, 307 (2007).

[2] J. A. Rodríguez-Manzo, A. Tolvanen, A. V. Krasheninnikov, K. Nordlund, A. Demortière, F. Banhart, *Nanoscale* **2**, 901 (2010).

[3] J. A. Rodríguez-Manzo, C. Pham-Huu, F. Banhart, *ACS Nano* **5**, 1529 (2011).

[4] J. A. Rodríguez-Manzo, F. Banhart, *Appl. Phys. Lett.* **98**, 183105 (2011).

Localized states on graphene quantum dots

[1,2]S. Barja, [2,3]D. Stradi, [1,2]M. Garnica, [3]C. Díaz, [1]B. Borca, [4]A. Arnau, [5]D., Sánchez-Portal,
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Graphene epitaxially grown on Ru(0001) displays a remarkably ordered pattern of hills and valleys in Scanning Tunneling Microscopy (STM) images. The origin of this ordered array of bumps is the difference in lattice parameters between graphene and the Ru(0001) surface that in turn produces a spatial modulation of the interaction between the graphene overlayer and the substrate.

The interpretation of the STM/STS data measured for graphene grown on Ru(0001) is a challenge due to the entanglement between the geometric corrugation of the moiré pattern and its electronic structure. The experimental measurements of the apparent corrugation of the moiré pattern as function of the bias voltage [1] are a clear evidence of this entanglement. Spatially resolved dI/dV spectra around the Fermi level measured at room temperature on the gr/Ru(0001) [2] show an asymmetry on the LDOS measured on the high and low areas of the moiré pattern, presenting a higher occupied density of states on the high areas of the moiré. We employ a realistic model for monolayer graphene adsorbed on Ru(0001), based on density functional theory including van der Waals interactions, to describe accurately its electronic structure. The results of the calculations shown that the peaks appearing in STS spectra close to the Fermi level are the result of the periodic modulation in the electronic properties induced by the formation of the moiré. The peaks observed in the L-area STS spectrum close to the Fermi level are due to residual charge density from Ru accumulated below the ripple. The only role of graphene is to modulate the electronic density of the underlying Ru surface

The spectroscopic data measured at high positive bias voltage shows a peak at +3eV in the low areas of the moiré. Based on a simple theoretical model that makes use of 1x1 flat graphene, Borca et al. [3] have conjectured that the STS peak observed at +3 eV in the low areas of the moiré is due to an interface state. Our density functional theory calculations including van der Waals interactions describes accurately the interfacial state that is at the origin of the inversion of contrast observed in the STM topographies of the graphene moiré pattern for bias voltages higher thna +2.6V. At these energies the graphene layer plays an active role in the formation of an interface band [3,4] strongly localized in the low regions of the moiré. This interfacial state is strongly localized in the low area of the moiré. The agreement between our calculations and the experimental measurements is excellent, supporting the validity of our calculation [4].

[1] B. Borca et al. New J. Phys. **12**, 093018 (2010)
[2] A.L. Vazquez de Parga et al, Phys. Rev. Lett. **100**, 056807 (2008)
[3] B. Borca et al. Phys. Rev. Lett. 105, 036804 (2010)
[4] D. Stradi et al. Phys. Rev. Lett. 106, 186102 (2011)

Elastic Response of Graphene Nanodomes by AFM microscopy and spectroscopy in UHV

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A key feature of ulltra perfect graphene monolayers is their exceptional mechanical strength. We have measured the elastic response of the nanosized structures that appear in graphene monolayers epitaxially grown on single crystal metal surfaces under Ultra High Vacuum (UHV) conditions. Specifically, a single graphene monolayer on Ru(0001) [1] is spontaneously nanostructured in an hexagonal array of 100 pm high nanodomes with a periodicity of 3 nm [2,3]. The periodic array of hills and valleys display localized electronic states and conductivity [4]. By means of non-contact Atomic Force Microscopy and Spectroscopy in UHV conditions we have determined that the nanodomes response is perfectly elastic up to extraordinary large normal displacements of 120 pm [4]. This conclusion has been confirmed by Density Functional Theory simulations [5]. These elastic nanodomes have great potential for acting as antennas for TeraHz radiation using their variable conductivity for the read-out.

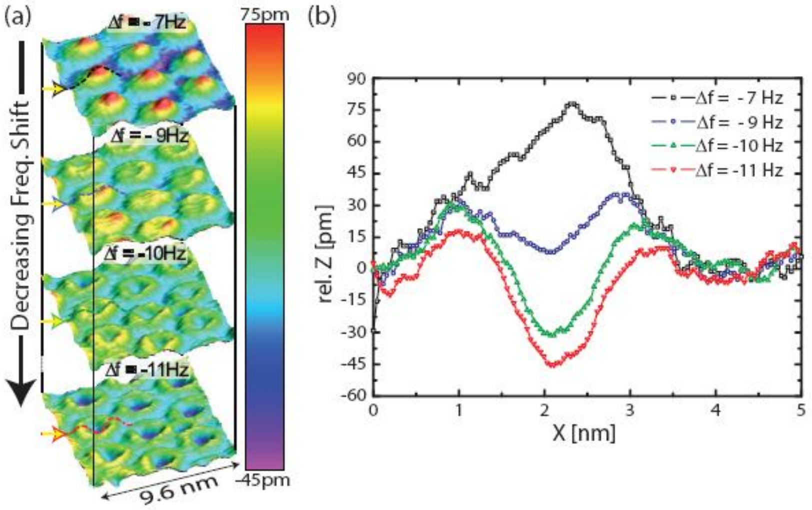

Figure 1: AFM images of ripples on epitaxial graphene grown on Ru(0001)(left) recorded at increasing forces under UHV conditions and corresponding profiles of the indentation of the nanodomes.

[1] A.L. Vázquez de Parga et al, Phys. Rev. Lett. **100,** 056807 (2008)
[2] A.L. Vázquez de Parga et al, Phys. Rev. Lett. **101**, 099704 (2008)
[3] R. Miranda and A.L. Vázquez de Parga, Nature Nanotechnology **4**, 549 (2009)
[4] B. Borca et al, Phys. Rev. Lett. **105**, 036804 (2010)
[5] S. Koch et al, to be published

Graphene Based Platforms for Biosensing Applications

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Since graphene exhibits innovative mechanical, electrical, thermal and optical properties this two-dimensional material is increasingly attracting attention and it is under active research in various fields including that of biosensors. Graphene displays advantageous characteristics as a biosensing platform due to its excellent capabilities for direct wiring with biomolecules, heterogeneous chemical and electronic structure, the possibility to be processed in solution and the availability to be tuned as insulator, semiconductor or semi-metal. Between the various graphene forms, graphene oxide (GO) shows the photoluminescence property with energy transfer donor/acceptor molecules exposed in a planar surface. It can even be proposed as a universal highly efficient long-range quencher, which is opening the way to several biosensing strategies. We will discuss the various reasons of the use of graphene in optical and electrochemical biosensing applications by describing several potentially exploitable properties and present an overview of the current approaches along with future perspectives and challenges with interest for DNA, protein and cells sensing. These graphene biosensing applications are showing unprecedented advantages with interest for clinical diagnostics, environmental monitoring and safety and security applications.

References

1. Eden Morales-Narváez, Arben Merkoçi, “Graphene Oxide as an Optical Biosensing Platform”, Advanced Materials, 2012, 24, 3298–3308
2. Briza Pérez-López, Arben Merkoçi, “Carbon nanotubes and graphene in analytical sciences”, Microchimica Acta, 2012, Published on-line, DOI: 10.1007/s00604-012-0871-9

Spin precession in freely-suspended graphene nonlocal spin valves

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We achieve spin injection and detection in freely-suspended graphene using cobalt electrodes and a nonlocal spin-valve geometry. The devices are fabricated with a single electron-beam-resist process that minimizes both the fabrication steps and the number of (aggressive) chemicals used, greatly reducing contamination and increasing the yield of high-quality, mechanically stable devices. As-grown devices can present mobilities exceeding 10^4 cm^2 V^{-1} s^{-1} at room temperature and, because the contacts deposited on graphene are only exposed to acetone and isopropanol, the method is compatible with almost any contacting material. We study spin accumulation and spin precession in our nonlocal spin valves. Fitting of Hanle spin precession data in bilayer and multilayer graphene yields a spin relaxation time of ~ 125-250 ps and a spin diffusion length of 1.7-1.9 µm at room temperature.

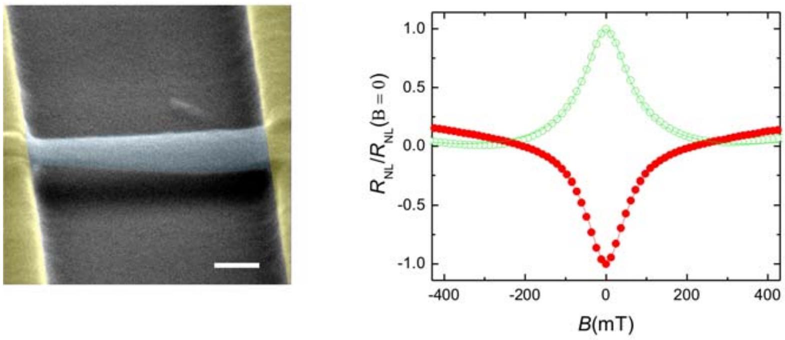

Figure 1: Scanning electron image (left, bar is 100 nm) and electrical detection of spin precession in freely-suspended graphene spin valves.

Spin transport in graphene based devices with magnetic Co electrodes

J. M. Michalik[1,2], I.Serrano-Esparza[1,2], S. Roddaro[2,3], R. Córdoba[3], L. Casado[3], M.R. Ibarra[2,3]
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Graphene – a single-layer hexagonal lattice of carbon atoms displays unique electronic transport properties such as very high and tunable conductivity at room temperature together with a spin polarized transport up to room temperature. Those make graphene a promising material for applications in Spintronics. One of the key issues in the investigation of the spin polarized transport in graphene is the distinction between charge and spin signals possibly via a “non-local” technique combined with the use of magnetic contacts

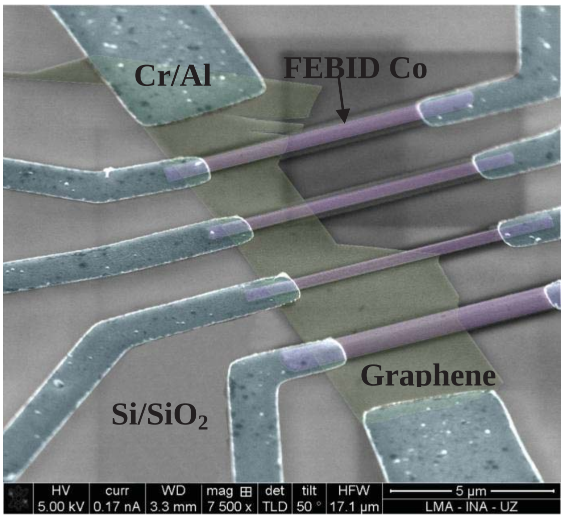

Fig. 1. SEM image of a complete graphene based device: flake with four Cobalt FEBID grown electrodes and EBL fabricated Cr/Al connections.

We investigate the adoption of focused-electron-beam-induced deposition (FEBID) technique as an alternative route to grow resistance-matched contacts for the investigation of spin transport in graphene. We have recently discussed [1] the influence of the FEBID process on graphene flakes. We showed that the deposition process, although up to some extent harmful for this material, is a good way of preparing complex graphene based devices (see fig. 1). We have also reported the influence of the lithography processes (both Electron Beam and UV) on graphene [2].

Here we aim to present a complete fabrication process and preliminary results of spin dependent transport in graphene based devices.

[1] J.M. Michalik, S. Roddaro, L. Casado, M.R. Ibarra and J.M. De Teresa, *Quantification and minimization of disorder caused by focused electron beam induced deposition of cobalt on graphene*, Microelectronic Engineering 88 (2011) 2063-2065

[2] Jiyu Fan, J.M. Michalik, L. Casado, S. Roddaro, M.R. Ibarra and J.M. De Teresa, *Investigation of the influence on graphene by using electron-beam and photo-lithography*, Solid State Communications 151 (2011) 1574-1578

Graphene electrodes for molecular spintronics

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Spintronics, which aims at using the spin state of the electrons to process information, is a promising technology to complement conventional electronics based on the control of the electrical charge of the electrons. The field is rapidly evolving into molecular spintronics where electrical transport takes place through individual molecules advancing in miniaturization and spin-state preservation. Gold electrodes, traditionally used to address the molecules, are not stable at room temperature hindering any possible application. Different from gold, graphene electrodes are stable at room temperature and can be combined with ferromagnetic materials enabling the molecular spin to be addressed by spin-polarized electrons. To fabricate such a device, we open a nanometric gap (1-2 nm) on a few-layers graphene flake using a carbon electroburning technique [1]. The target molecules are afterwards trapped from solution bridging both electrodes. We present preliminary electronic transport measurements through individual spin crossover molecules attached to graphene electrodes.

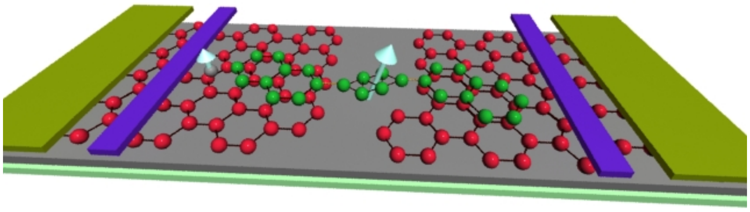

Figure 1: Sketch of a three-terminal transistor based on graphene electrodes linked by a single molecule.

[1] F. Prins et al., Nano Letters 11, 4607 (2011)

Tuesday, September 11th 2012

9:00 Session 4. Chairman: Florian Barnhart

A.H. Castro Neto (Invited 6)
New Directions in Materials Science and Technology: Two-Dimensional Crystals

J.J. Palacios (Invited 7)
Quantum spin Hall insulators: Graphene and Bi bilayers

J. Schliemann (Invited 8)
Hartree-Fock Theory for Graphene

11:00 Cofee Break

11:30 Session 5. Chairman: Ignacio Paredes

I. Suárez-Martínez (Invited 9)
Thermal conductivity of graphitic materials

F. Domínguez-Adame (Oral 5)
Spin-dependent transport in graphene superlattices

C. González (Invited 10)
Ordered vacancy network induced by the growth of epitaxial graphene on Pt(111)

S. Bellucci (Oral 6)
Microwave probing of graphitic materials filled composites

13:30 Lunch

17:00 Visit to the Alhambra

New Directions in Materials Science and Technology: Two-Dimensional Crystals

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Smart advanced materials that are flexible (for transparent wearable electronics), adaptable (that change structure depending on exterior conditions), multifunctional (that can be tuned by application of electric and magnetic fields, pressure or strain), and at the same time are environmentally friendly (that do not waste energy and are low power consuming), are the ultimate dream of materials scientists and engineers. Such materials hold the key to the next generation of devices with deep incursions into new markets. The discovery of graphene and other twodimensional crystals in 2004 has finally brought materials with the promise of such properties to light. More importantly, the recent breakthrough in their industrial scale fabrication is paving the way towards a new era in materials science and technology. A shift in such a key economic sector will provide unprecedented opportunities in transforming the industry with impact in several fundamental areas: energy, defense, communications, electronics, artificial intelligence, and information technology. I will describe the latest developments, the opportunities, and future challenges in this new field and the plans at the Graphene Research Centre at the National University of Singapore to develop and study, theoretically and experimentally, a large family of advance materials, which do not exist in nature (and certainly are not yet available commercially) with new functionalities that can meet the needs of an ever-demanding market.

Quantum spin Hall insulators: Graphene and Bi bilayers

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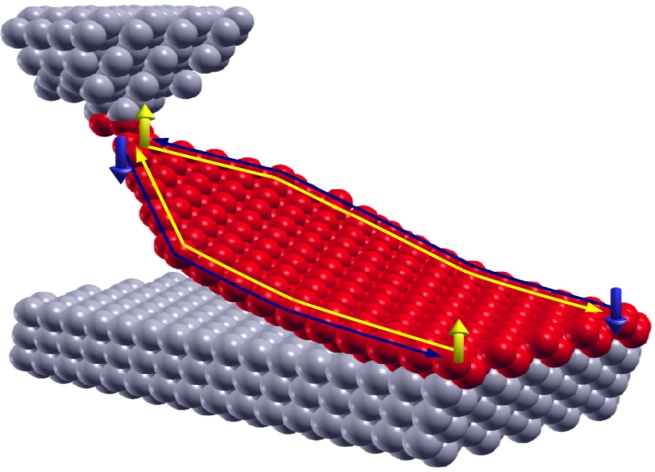
The non-trivial band structure of bidimensional topological insulators, also known as quantum spin Hall insulators (QSHI), is expected to manifest itself through a robust universal quantum of conductance $G = 2e^2/h$, which is supported by helical edge states. In the first part of my presentation I will explore the consequences of time-reversal symmetry preserving edge reconstructions in nominally single-branched quantum spin Hall systems (QSHI's). To this end we consider a prototypical zigzag graphene nanoribbon with enhanced spin-orbit coupling. We show that a well-known edge reconstruction increases the number of pairs of helical edge states in the gap from 1 to 3. While disorder opens the way to intra-edge backscattering, it also induces inter-edge backscattering in one of the new channels, which largely extends into the bulk. This turns the conductance sample-dependent, masking the most direct experimental manifestation of the topological invariant.

This result contrast to the one in another proposed QSHI, a Bi(111) bilayer, which also features three pairs of helical branches, but presents strong edge confinement and very short localization lengths. In this case the quantized conductance becomes a topological invariant even for very small sample sizes. In the second part of my talk I will report conductance measurements of Bi nanocontacts created by repeated tip-surface indentation using a scanning tunneling microscope at temperatures of 4 K and 300 K. As a function of the elongation of the nanocontact we measure stable, nanometer-long conductance plateaus at $2e^2/h$ at room temperature. This observation can be accounted for by the mechanical exfoliation of a Bi(111) bilayer in the retracing process following a tip-surface contact (see figure). This is further supported by the additional observation of conductance steps below $2e^2/h$ before break-up at both temperatures. Our finding is extraordinary on three accounts, namely, it provides the first experimental evidence of the possibility of mechanical exfolation of Bi bilayers, of the existence of the QSHI phase in a two-dimensional crystal, and, most importantly, of the observation of this novel phase at room temperature [1].



[1] *Evidence of the quantum spin Hall phase in mechanically exfoliated Bismuth at room temperature,* C. Sabater, D. Gosálbez, J. Fernández-Rossier, J. G. Rodrigo, C. Untiedt, and J. J. Palacios, Submitted to Science.

Hartree-Fock Theory for Graphene

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We study Coulomb repulsion among charge carriers in monolayer as well as multilayer graphene within Hartree-Fock approximation. Apart from in-plane solutions given by the single-particle states of the non-interacting system, we find further solutions with the sublatttice spin pointing out of the plane. At sufficienntly strong interactions, the latter configurations are lower in energy than the in-plane solutions. We point out physical (and measureable) consequences of such out-of-plane solutions in terms of symmetry breaking and optical as well as transport properties.

References:

Pseudospin in optical and transport properties of graphene, Maxim Trushin and John Schliemann, Phys. Rev. Lett. 107, 156801 (2011).

Polarization-sensitive absorption of THz radiation by interacting electrons in chirally stacked multilayer graphene, Maxim Trushin, John Schliemann, arXiv:1202.2302v1 [cond-mat.mes-hall], to appear in New J. Phys.

Thermal conductivity of graphitic materials

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The thermal properties of carbon materials varies from the best thermal conductor to insulator materials. Highly ordered carbons such as crystalline diamond and graphite have extremely high thermal conductivities (thousands of $Wm^{-1}K^{-1}$). At this end, thermal conductivity is limited by defects and isotope concentration. At the opposite end of the spectrum, amorphous carbons, glassy carbons and chars have much lower thermal conductivity, of the order of several $Wm^{-1}K^{-1}$. Experimental determination of thermal conductivity is often complicated by uncertainties in characterisation (e.g. the density and thickness of thin films) and the absence of a comprehensive sets of samples. Computational studies are valuable, as they allow precise control over density, microstructure, defect and isotopic content.

We compute the thermal conductivity of a range of carbon materials from amorphous carbons to graphitic structures with different degrees of structural order and isotopic abundance. Our results reproduce experimental data for amorphous and glassy carbons and confirm previously proposed structural models for vitreous carbons, demonstrating that the nanostructure of the solid influences the thermal properties more strongly than the density [1]. The isotope effect on the thermal conductivity of highly-ordered carbons such as graphene and carbon nanotubes will be compared to the effect of defects and loss of ordering.

[1] I. Suarez-Martinez, N.A. Marks, *Effect of microstructure on the thermal conductivity of disordered carbon*, Applied Physics Letters 99, 2011, p. 033101-1-3

Spin-dependent transport in graphene superlattices

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The occurrence of large spin-coherence lengths [1] has spurred the interest in graphene as a material of choice for spintronic devices. In this contribution, we show the occurrence of a spin-dependent negative differential resistance (NDR) in superlattices based on armchair graphene nanoribbon. We consider nanoribbons with a set of ferromagnetic insulating stripes grown on top of it. The ferromagnets induce the exchange splitting of the electronic levels in the regions of the ribbon located just below the stripes. This results in a spin-dependent potential profile. One can choose the system geometry to produce a resonant mode close to the energy of the band edge for spin up electrons, paving the way for obtaining spin-dependent NDR.

Numerical simulations were carried out using the standard tight-binding model for π electrons, taking into account up to the third nearest neighbor interaction and the hydrogenation of carbon atoms in the edge of the nanoribbon. We used the quantum transmission boundary method (see Ref. [2] for details) to obtain the spin-dependent transmission coefficient for a given energy and source-drain voltage (V_{SD}). Using the Landauer-Buttiker formalism we calculated the current-voltage characteristics. Figure 1 demonstrates that the current-voltage curves shows regions of well-defined NDR. The spin dependence of the the transmission spectrum leads to different voltage intervals at which highly transmitting channels are open, which makes the NDR be spin-dependent too. We believe that the latter can be useful for spintronic applications.

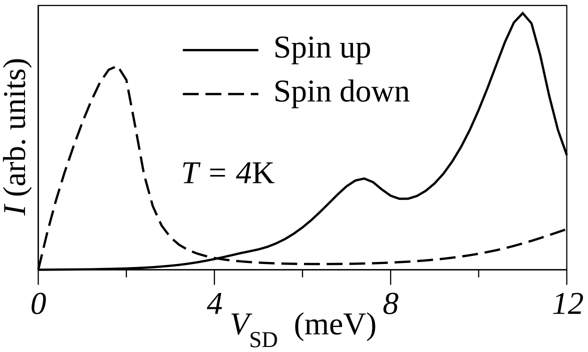

Figure 1: Spin-dependent current-voltage characteristics in a superlattice with five ferromagnetic stripes. The nanoribbon width is 10 nm. The size of the stripes along the source-drain direction and their separation are 21 nm and 49 nm, respectively. The Fermi energy at the source is set at 28.25 meV.

[1] C. L. Kane and E. J. Mele, Phys. Rev. Lett. **95** 226801 (2005).
[2] J. Munárriz, F. Domínguez-Adame and A. V. Malyshev, Nanotech. **22** 365201 (2011).

Ordered vacancy network induced by the growth of epitaxial graphene on Pt(111)

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We have studied large areas of (√3x√3)R30º graphene commensurate with a Pt(111) substrate. A combination of different experimental techniques with *ab-initio* density functional theory [1] leads us to conclude that this structure is originated by the formation of a surface reconstruction at the Pt surface, which consists in the creation of an ordered vacancy network at the outermost Pt layer and a covalently bound graphene layer. The formation of this reconstruction is enhanced when polycyclic aromatic hydrocarbons are used as molecular precursors for the epitaxial growth of the graphene layers [2].

In this talk, thanks to the comparison between experimental and theoretical STM images [3], it will be explained how the final (√3x√3)R30º reconstruction is obtained.

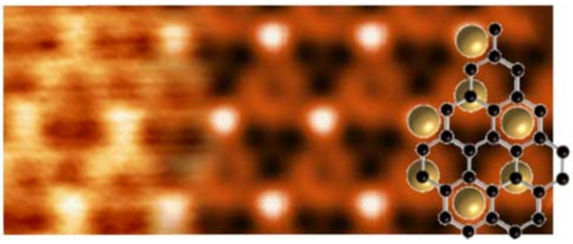

Figure 1. STM comparison between theory and experiment for the (√3x√3) R30^0 graphene/ Pt(111)

[1] J. P. Lewis, P. Jelínek, J. Ortega, A. A. Demkov, D. G. Trabada, B. Haycock, H. Wang, G. Adams, J. K. Tomfohr, E. Abad, H. Wang and D. A. Drabold, Phys. Status Solidi B 248, No. 9, 1989–2007 (2011)

[2] G. Otero, G. Biddau, C. Sánchez-Sánchez, R. Caillard, M. F. López, C. Rogero, F. J. Palomares, N. Cabello, M. A. Basanta, J. Ortega, J. Méndez, A. M. Echavarren, R. Pérez, B. Gómez-Lor and J. A. Martín-Gago., Nature **454**, 865 (2008)

[3] J. M. Blanco, F. Flores, and R. Perez, Progress in Surface Science **81**, 403 (2006)

Microwave probing of graphitic materials – filled composites

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The main goal of the present communication is to optimize the way of producing electromagnetic (EM) materials of coating-type providing high EM interference (EMI) shielding effectiveness in microwave frequency range caused by as low as possible content of conductive graphitic inclusions (up to 2 wt.%). For that purpose, a series of composite samples were prepared, based on epoxy resin (Epikote 828), a curing agent called A1 (a modified TEPA) and 0.25, 0.5, 1.0 and 2.0 wt.% content of exfoliated graphite (EG), thick graphene (TG) and commercial single-walled carbon nanotubes (CNT) from Heji for reference. EG was obtained by intercalation of natural graphite flakes, subsequently submitted to a thermal shock. Accordion-like particles were thus produced, leading to a material of low packing density, around 3 g/L [1]. EG particles have the form of distorted accordion-like cylinders, with a typical diameter in the range 0.3 - 0.5 mm, and an aspect ratio around 20. TG was prepared by suspending EG particles in cyclohexane, and submitting the suspension to a series of grinding and ultrasonic dispersion steps [2]. After freeze-drying, disk-shaped particles, having diameter and thickness around 10 and 0.1 µm, respectively, were obtained.

The spectra of S–parameters of epoxy/carbon composites were measured in microwave range (26-37 GHz) with scalar network analyzer. It was found that the highest EMI shielding effectiveness similar to that provided by 20 wt. % of carbon fibers, 7 wt.% of carbon filaments, and 12-20 wt.% of single-walled and multi-walled CNTs [3-4] embedded into polymer matrix, corresponds to epoxy/EG composites. The average value of power transmitted through the samples is 60%, 30%, and close to 0 for 0.25, 1 and 2 wt.% of EG embedded, respectively. Along with relatively high EM performance in microwave range, graphene platelets are much more easily processable than composites filled with CNTs [5]. Concluding, giving the benefit of being lightweight, graphitic materials, especially EG, lead to exceptionally good EM attenuation ability to epoxy resin matrix, along with high electrical conductivity (3 orders of magnitude higher than epoxy filled with single-walled CNTs [6]).

This work was partially supported by the ISTC project B-1708, the EU FP7 project FP7-266529 BY-NanoERA and the Italian Ministry PRIN 2008 research program Development and Electromagnetic Characterization of Nano Structured Carbon Based Polymer CompositEs (DENSE).

[1] A. Celzard, J.F. Marêché, G. Furdin, Progress in Materials Science 50 (2005) 93-179.
[2] French Patent CNRS N° PCT/EP 92 / 023117.
[3] D.D.L. Chung, Carbon 39 (2001) 279–285
[4] Y. Yang, M. C. Gupta, K. L. Dudley and R. W. Lawrence, NANO LETTERS 5 (2005) 2131-2134
[5] G.D. Bellis, A. Tamburrano, A.Dinescu, M. L. Santarelli, M. S. Sarto, Carbon 49 (2011) 4291–4300
[6] A. Paddubskaya, D. Bychanok, A. Plyushch, et al., Journal of Nanoelectronics and Optoelectronics 7 (2012) 1–6

Wednesday, September 12th 2012

9:00 Session 6. Chairwoman: Irene Suárez-Martínez

D. Jiménez (Invited 11)
Compact modelling of graphene field-effect transistors targeting RF applications

F. Triozon (Invited 12)
Simulation of quantum transport in doped graphene ribbons

S. Goossens (Oral 7)
Electrostatically induced Coulomb blockade and quantized conductance in bilayer graphene/hBN sandwiches

D. Van Tuan (Oral 8)
Electronic Transport in Amorphous Graphene

11:00 Cofee Break

11:30 Session 7. Chairman: Fernando Magaña

A. Cresti (Invited 13)
Aspects of high field magnetotransport in graphene nanoribbons: a numerical perspective

M. Auslender (Oral 9)
Impurity scattering limited quantum transport in monolayer graphene

R.H. Scheicher (Oral 10)
DNA sequencing with graphene nano-electrodes

J. Schiefele (Oral 11)
Boron nitride, graphene, and finite temperature the effect of substrate phonons

F. Ortmann (Oral 12)
Magnetotransport in Disordered Graphene: Crossover between Localization Regimes and Competition between Disorder and Magnetic-Field Effects

13:30 Lunch

15:30 Session 8. Chairman: Juan José Palacios

F. Koppens (Invited 14)
Graphene nano-optoelectronics for capturing and manipulating light at the nanoscale

A. Ayuela (Oral 13)
Magnetism of Graphene with Defects: Vacancies, Substitutional Metals, and Covalent Functionalization

Y.J. Dappe (Oral 14)
Cohesion in sp2 - systems mediated by weak interactions

Y. Gohda (Oral 15)
Structural phase transition of graphene caused by GaN epitaxy predicted by ab-initio calculations

17:10 Coffee and Poster Session

Compact modelling of graphene field-effect transistors targeting RF applications

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Graphene has emerged as a material of special interest to make nanoelectronic integrated circuits beyond silicon based technology. This is due to remarkable electronic properties, like high mobility (~10^5 cm^2/V-s) and saturation velocity (~10^8 cm/s), together with a promising ability to scale to short gate lengths and high speeds by virtue of its thinness. Besides, advances on synthesis of large-scale graphene sheets of high quality and low cost using chemical vapor deposition techniques (CVD), are creating an appropiate framework for a new technology based on graphene to be introduced. The main concern with graphene is the absence of a gap, which results in a poor ON-OFF current ratio, therefore limiting the usefulness of graphene in digital applications. However, zero gap graphene could still be very useful in analog and radiofrequency (RF) applications where high ON/OFF current ratios are not required. In small signal amplifiers, for instance, the transistor is operated in the ON-state and small RF signals that are to be amplified are superimposed onto the DC gate-source voltage. Instead, what is needed to push the limits of many analog/RF figures of merit, for instance the cut-off frequency or the intrinsic gain, is an operation region where high transconductance together with a small output conductance is accomplished. These conditions are realized for state-of-the-art graphene field-effect transistors (GFETs). Specifically, for large-area GFETs, the output characteristic shows saturation like behavior that could be exploited for analog/RF applications. Recently, important progress for obtaining a saturated output characteristic has been made based on CVD graphene. Using GFET technology, cut-off frequencies in the THz range are envisioned. It is worth noting that cut-off frequencies in the range of hundreds of GHz have been demonstrated with a non-optimized technology [1].

To boost the development of GFET technology, modeling of the electrical characteristics is essential to cover aspects as device design optimization, projection of performances, and exploration of analog / RF circuits providing new or improved functionalities. Recently, an explicit compact model for the current-voltage (I-V) characteristics of GFET was proposed [2]. Taking this work as a basis, which provides the DC behavior, we further develop a compact physics-based model of the charge and capacitances of GFETs. This is necessary to address AC and transient simulations of graphene based circuits. The physical framework is a field-effect model and drift-diffusion carrier transport with saturation velocity effects, which is accurate in explaining the I-V behavior of GFETs [3]. A Ward-Dutton's charge partition scheme provides the technique to model the terminal charges together with self-capacitances and transcapacitances of GFET. Explicit closed-form expressions have been derived for these quantities continuosly covering all operation regions. The model is intended to be the kernel to build up CAD simulators of graphene based circuits

[1] Y. Wu et al., "High-frequency, scaled graphene transistors on diamond-like carbon", Nature 472, pp. 74-78 (2011).
[2] D. Jiménez et al., "Explicit drain-current model of graphene field-effect transistors targeting analog and radio-frequency applications", IEEE Transactions on Electron Devices, vol. 58, no. 11, pp. 4049-4052 (2011).
[3] I. Meric et al., "Current saturation in zero-bandgap, top-gated graphene field-effect transistors", Nature Nanotechnology, vol. 3, pp. 654-659, (2008)

Simulation of quantum transport in doped graphene ribbons.

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In previous studies, electronic transport in boron and nitrogen doped graphene layers and nanoribbons was studied using *ab initio* simulation and the Landauer-Büttiker formalism for quantum transport [1-3]. A simple but realistic tight-binding model was elaborated, which allowed the simulation of transport in long ribbons with random distributions of impurities. Carrier scattering shows a strong electron-hole asymmetry, leading to a "mobility gap" in some energy interval. For instance, boron doped armchair ribbons exhibit a very low conductance for holes and a high conductance for electrons. This opens the perspective of obtaining field-effect switching in ribbons of large width, in spite of the absence of a significant energy gap. Recently, this idea was tested at the device level, using non-equilibrium Green's functions (NEGF) [4]. It was shown that enhanced screening of the boron impurities at negative gate voltage leads to a reduction of hole scattering and to a poor Ion/Ioff ratio of the envisioned devices.

In the first part of this talk, these results are discussed in details. In a second part, the NEGF module recently developed at CEA is presented [5]. This code includes electron-phonon coupling, opening perspectives for the simulation of graphene devices at room temperature. The capacities of the code are illustrated by a few examples, and short-term applications for graphene are listed.

[1] A. Lherbier, X. Blase, Y.M. Niquet, F. Triozon, and S. Roche, *Charge transport in chemically doped 2D graphene*, Phys. Rev. Lett. **101**, 036808 (2008).
[2] B. Biel, X. Blase, F. Triozon, and S. Roche, *Anomalous doping effects on charge transport in graphene nanoribbons*, Phys. Rev. Lett. **102**, 096803 (2009).
[3] B. Biel, F. Triozon, X. Blase, and S. Roche, *Chemically induced mobility gaps in graphene nanoribbons: a route for upscaling device performances*, Nano Letters **9**, 2725 (2009).
[4] P. Marconcini, A. Cresti, F. Triozon, G. Fiori, B. Biel, Y.M. Niquet, M. Macucci, and S. Roche, *Atomistic boron-doped graphene field-effect transistors: a route toward unipolar* characteristics, ACS Nano, Article ASAP (2012). http://dx.doi.org/10.1021/nn3024046
[5] Developed within the code TB_Sim: http://inac.cea.fr/L_Sim/TB_Sim/index.html

Electrostatically induced Coulomb blockade and quantized conductance in bilayer graphene/hBN sandwiches

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We report quantized conductance and Coulomb blockade in split-gate bilayer graphene devices with hexagonal boron nitride as a top and bottom gate dielectric [1]. Compared to earlier work where constrictions and island were etched in graphene, this approach avoids edge disorder and induces a smooth potential landscape, improving device tunability and control.

Using the gate voltages, we apply an electric field perpendicular to the bilayer in order to open a band gap, and set the Fermi level near mid gap underneath the top gates, suppressing transport. In between two split top gates, a narrow ballistic channel is formed containing only a few transverse modes. By varying the voltage on the split gates we tune the width of the channel and observe quantized steps in the conductance. Just before pinch-off of the channel, a tunnel barrier is formed in the constriction.

Two tunnel barriers in series create an island in between, in which a discrete number of electrons can be confined. When sweeping the voltage on one of the top gates, we observe regular Coulomb blockade. Finite-bias measurements gave Coulomb diamonds. Addition energies are around 0.25 meV.

Ballistic transport through the constrictions requires devices with a high electronic quality. This is the reason why we encapsulate the bilayer graphene between two hexagonal boron nitride (hBN) layers. Furthermore, we use a newly developed mechanical cleaning technique in order to remove fabrication residues [2]. In this method, scanning a contact mode AFM (CM AFM) tip over a graphene surface removes residues, removes doping and improves the electronic mobility without damaging the graphene. Our dual-gated bilayer graphene transistors with hBN dielectrics show mobilities up to ~36,000 cm^2/Vs at low temperature.

[1] Unpublished
[2] A.M. Goossens et al., *Mechanical cleaning of graphene*, Appl. Phys. Lett. **100**, 073110 (2012).

Electronic Transport in Amorphous Graphene

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In this talk, I will present our results of the charge transport properties of topologically disordered graphene, in the form of sp^2 lattices consisting predominantly of hexagonal rings, but also including many pentagons and heptagons distributed in a random fashion. Using the Kubo transport methodology and the Lanczos method, the density of states, mean free paths and semiclassical conductivities of such amorphous graphene sample are explored. Despite a huge increase in the density of states close to the charge neutrality point, all electronic properties are dramatically damaged, evidencing an Anderson insulating state. These results are supported by Landauer-Büttiker conductance calculations, which allow us to extract a localization length smaller than 10 nm.

[1] N. Leconte *et al.*,ACS Nano **4** (7), 4033 (2010).
[2] V. Kapko, D.A. Drabold, and M.F. Thorpe, Phys. Status Solidi B **247**, 1197 (2010).
[3] R Kubo, Rep. Prog. Phys. **29**, 255 (1966).
[4] M. Büttiker *et al.*, Phys. Rev. B **31**, 6207 (1985); Y. Meir, and N. S. Wingreen, Phys. Rev. Lett. **68**, 2512 (1992).
[5] S. Roche, and D. Mayou, Phys. Rev. Lett. **79**, 2518 (1997); S. Roche, Phys. Rev. B **59**, 2284 (1999); S. Roche and R. Saito, Phys. Rev. Lett. **87**, 246803 (2001).
[6] Ph. Kim et al., Phys. Rev. Lett. **99**, 246803 (2007).
[7] A. Lherbier *et al.*, Phys. Rev. Lett. **101**, 036808 (2008).
[8] N.H. Shon, and T. Ando, J. Phys. Soc. Jpn. **67**, 2421 (1998).
[9] P. A. Lee and T. V. Ramakrishnan, Rev. Mod. Phys. **57**, 2 (1985).

Aspects of high field magnetotransport in graphene nanoribbons: a numerical perspective

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This contribution focuses on the role of the spatial chirality of the magnetic edge states in the observation of the integer quantum Hall effect in graphene nanoribbons. We investigate the spatial distribution of the electron flow and the extension of the magnetic edge channels in disordered narrow [1] and wide [2] ribbons and in the presence of scrolled edges [3]. Our simulations clarify the interplay between magnetic length, ribbon width and disorder range.

Our results for narrow ribbons (~10 nm-wide) allow us to interpret some experimental outcomes obtained by the group of prof. Raquet (LNCMI-T, Toulouse, France) and to identify edge roughness and charged defects trapped in the substrate as the most likely sources of disorder. The emerging of chiral edge channels at high fields is shown to play a central role in determining the positive magnetoconductance experimentally observed at high field (~60 T).

As concerns larger ribbons (~100 nm-wide), our simulations relate the spatial extension of the magnetic edge channels to the conductance quantization in the integer quantum Hall regime (fig.1) and, thanks to the progressive magnetic confinement of the states toward the ribbon edges at high fields, allow us to gain significant information on the geometry of the edges.

Finally, the results for magnetotransport on samples with scrolled edges show the raise of non-chiral channels in the region of the scrolls (fig.2), thus providing a consistent and meaningful interpretation of the possible suppression of the quantum Hall regime in suspended graphene and rationalizing its complicate experimental observation.

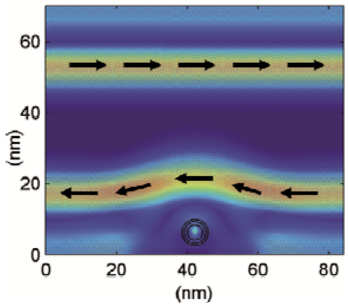

Figure 1: Spatial distribution of the edge currents in the presence of an impurity close to the lower edge of a 70 nm-wide ribbon.

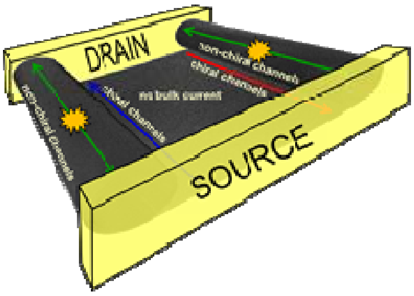

Figure 2: Scheme of the chiral and non-chiral edge channels in a graphene sample with scrolled edges.

[1] J.-M. Poumirol, A. Cresti, S. Roche, W. Escoffier, M. Goiran, X. Wang, X. Lin, H. Dai and B. Raquet, Phys. Rev. B **82**, 041413(R) (2010)

[2] R. Ribeiro, J.-M. Poumirol, A. Cresti, W. Escoffier, M. Goiran, J.-M. Broto, S. Roche and B. Raquet, Phys. Rev. Lett. **107**, 086601 (2011)

[3] A. Cresti, M. Fogler, F. Guinea, A.H. Castro Neto and S. Roche, Phys. Rev. Lett. **108**, 166602 (2012)

Impurity scattering limited quantum transport in monolayer graphene

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Very important for device applications is the impurity scattering limiting the carriers' mobility. As monolayer graphene (MLG) is *true* 2D zero-bangap semiconductor with chiral electron-hole coherence [1], quasi-classical description may break down for it [1, 2]. Though at present numerical techniques are successfully used to compute quantum transport properties, analytical and semi-analytical approaches still remain valuable. Here we report on a derivation of quantum kinetic equations (QKEs) for MLG in the presence of impurities of arbitrary kind with a density n_i and electric field, and estimation on their base of Ohmic conductivity σ for point-like [3] and charged impurities. Other QKEs were published concurrently with and after [3]. Contrary to those, the terms describing electron-hole coupling in our QKEs [3] contain both Golden-Rule and recoil Principal-Value integral terms which are crucial near the neutrality point $n = 0$, where n is the electron density. Our results for σ per spin and valley, in the units of e^2/h, are summarized as follows. For the point-like impurities, we have

$$\frac{\sigma}{\sigma_{\mathrm{B}}} = 1 + \frac{\pi^2}{16} - \frac{\pi}{8}\arctan\left(\frac{1}{\pi}\ln\frac{n}{n_{\mathrm{K}}}\right) + \frac{\pi^2}{4}\left(\pi^2 + \ln^2\frac{n}{n_{\mathrm{K}}}\right)^{-1}, \; n_{\mathrm{K}} = \frac{\varepsilon_c^2}{\pi v^2 \hbar^2} e^{-2\pi\sigma_{\mathrm{B}}}, \tag{1}$$

where σ_{B} is the n-independent Boltzmann conductivity, ε_c is an ultraviolet cutoff energy and v is the velocity at the cone point. Due to Eq.(1), $\sigma/\sigma_{\mathrm{B}} \simeq 1$ and $\sigma/\sigma_{\mathrm{B}} \simeq 1 + \pi^2/8$ at $n \gg n_{\mathrm{K}}$ and $n \ll n_{\mathrm{K}}$, respectively. In excellent agreement with a diagrammatic approach [4], Eq.(1) handles the logarithmic divergencies to all orders and predicts the increase of σ above σ_{B} at $n \to 0$.

For the charged impurities, we have asymptotic expressions agreeing with numerics of [5]

$$\sigma \simeq (n/n_i)\,\sigma_{\mathrm{B}} + \sigma_\infty, \; n \gg n_i; \quad \sigma \sim \sigma_0, \; n \ll n_i. \tag{2}$$

Here σ_{B} is the Boltzmann conductivity at $n = n_i$, while σ_∞ and σ_0 is a quantum correction to σ far from and near $n = 0$, respectively. Both σ_{B} and σ_∞ are well defined numbers depending only on substrate dielectric permittivity, while σ_0 is either a number or very weakly divergent function of n_i/n. Our σ_{B} fully agrees with literature data, while accurate assessing of σ_0 needs a revision of the charged-impurity screening. Computation of σ_∞ and σ_0 will be presented.

[1] M.I. Katsnelson, *Graphene: Carbon in two dimensions*, Materials Today **10**, 20-27 (2007)

[2] S. Das Sarma et al, *Electronic transport in two-dimensional graphene*, Rev. Mod. Phys. **83**, 407470 (2011)

[3] M. Auslender and M. I. Katsnelson, *Generalized kinetic equations for charge carriers in graphene* Phys. Rev. B **76**, 235425: 1-15 (2007)

[4] A. Sinner and K. Ziegler, *Perturbative analysis of the conductivity in disordered mono- and bilayer graphene*, arXiv:cond-mat 1110.3065v1

[5] K. Nomura and A.H. MacDonald, *Quantum transport of massless Dirac fermions*, Phys. Rev. Lett. **98** 076602: 1-4 (2007)

DNA sequencing with graphene nano-electrodes

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Atomically-thin electrodes made from graphene could overcome the issue of achieving single-nucleobase resolution and were therefore proposed [1] for use as probes to measure the transverse conductance of nucleotides in DNA. Experimentally, it was demonstrated [2–4] that the characteristic drop in ionic current associated with translocation events of DNA passing through a graphene nanopore can be detected.

Using ab initio methods, we evaluated different aspects of the performance of two graphene nano-electrodes configurations for nucleobase identification. In the first study [5], we investigated the electronic transport properties of nucleotides when located in a graphene nanogap, in particular how the electrical current varies at finite bias due to changes in the nucleotides orientation and lateral position.

Our second study [6] utilized molecular dynamics simulations in conjunction with electronic transport calculations to explore the effect of hydrogenated graphene edges on the translocating DNA. It is found that edge-hydrogenated graphene electrodes facilitate the formation of H-bonds with the nucleotides and raises the average conductivity by three orders of magnitude while reducing statistical variance.

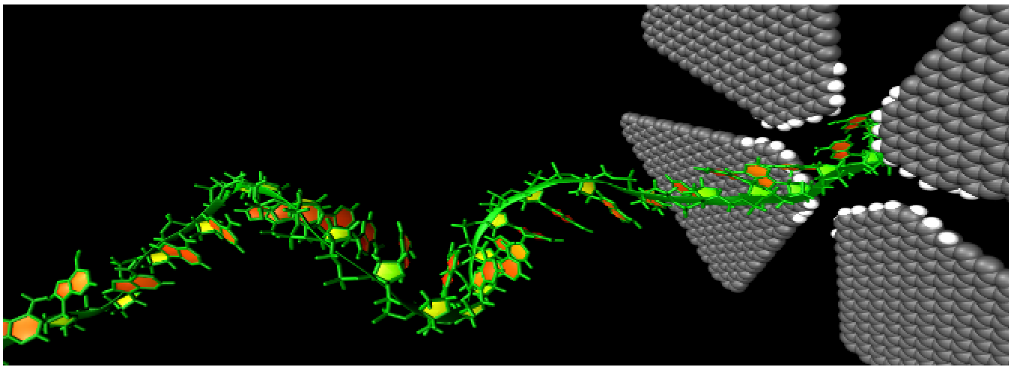

Figure 1: Illustration of DNA strand pulled through nanopore between graphene electrodes.

[1] H. W. Ch. Postma, *Nano Lett.* 10, 420 (2010).
[2] C. A. Merchant, K. Healy, M. Wanunu, V. Ray, N. Peterman, J. Bartel, M. D. Fischbein, K. Venta, Z. Luo, A. T. C. Johnson, and M. Drndić, *Nano Lett.* 10, 2915 (2010).
[3] G. F. Schneider, S. W. Kowalczyk, V. E. Calado, G. Pandraud, H. W. Zandbergen, L. M. K. Vandersypen, and C. Dekker, *Nano Lett.* 10, 3163 (2010).
[4] S. Garaj, W. Hubbard, A. Reina, J. Kong, D. Branton, and J. A. Golovchenko. *Nature* 467, 190 (2010).
[5] J. Prasongkit, A. Grigoriev, B. Pathak, R. Ahuja, and R. H. Scheicher, *Nano Lett.* 11, 1941 (2011).
[6] Y. He, R. H. Scheicher, A. Grigoriev, R. Ahuja, S. Long, Z. L. Huo, and M. Liu, *Adv. Funct. Mater.* 21, 2674 (2011).

Boron nitride, graphene, and finite temperature – the effect of substrate phonons

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At finite temperatures, scattering of charge carriers with phonons limits the carrier mobility in graphene. While this is true for any conventional bulk material, the charge carriers in a single atom thick graphene layer –which is usually not free standing– also interact with phonons of the surrounding material (remote phonon scattering).

A prominent candidate for such a substrate or spacer material in future graphene based electronic devices is the piezoelectric hexagonal boron nitride (hBN). Similar to graphite, single or few layer hBN can be produced by exfoliation, allowing for the production of layered graphene – hBN heterostructures.

We theoretically studied the effect of remote phonon scattering on the transport properties of graphene – hBN heterostructures. Specifically, we present our results on the influence of hBN substrate and spacer materials on the electrical conductivity of monolayer graphene and on the bilayer Coulomb drag effect.

[1] J. Schiefele, F. Sols and F. Guinea, *Temperature dependence of the conductivity of graphene on boron nitride*, PRB, **85** 195420 (2012)

[2] B. Amorim, J. Schiefele, F. Sols and F. Guinea, *Coulomb drag in graphene – boron nitride heterostructures: the effect of virtual phonon exchange*, arXiv:1206.0308

Magnetotransport in Disordered Graphene: Crossover between Localization Regimes and Competition between Disorder and Magnetic-Field Effects

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In graphene the interaction of electrons with any kind of disorder governs their signature in a variety of conductivity/mobility measurements. In such transport experiments the magnetic field can serve as an additional probe ranging from the low-field limit (millitesla) of weak antilocalization [1,2] to high fields defining the quantum Hall regime (~10T). Being under study ever since the discovery of graphene [3], magnetic fields may unveil some interesting physics hidden otherwise or generate new effects [4].

We are calculating the Kubo conductivity of graphene in the presence of both weak and strong disorder and magnetic fields using a linear scaling method. This allows us to model realistic samples up to micrometer size. Here we present our recent work on electric transport in the quantum-Hall regime and compare to previous results obtained for much lower magnetic fields. Particular emphasize is put towards the non-trivial interference of disorder and magnetic-field strength on transport.

[1] F.V. Tikhonenko et al. Phys. Rev. Lett. **103**, 226801 (2009)
[2] F. Ortmann et al. EPL **94**, 47006 (2011)
[3] K.S. Novoselov et al. Nature **438**, 197 (2005)
[4] D.A. Abanin et al. Science **332**, 328 (2011)

Graphene nano-optoelectronics for capturing and manipulating light at the nanoscale

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CIC nanoGUNE, San Sebastian (Spain)

Alba Centeno, Amaia Pesquera, Amaia Zurutuza
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Philippe Godignon, Nicolas Camara
CNM-IMB, Barcelona (Spain) and GREMAN, Tours (France)

Suko Thongrattanasiri, Javier Garcia de Abajo
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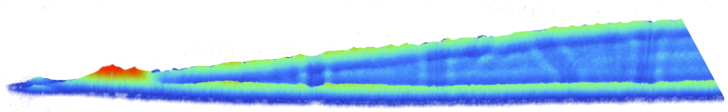
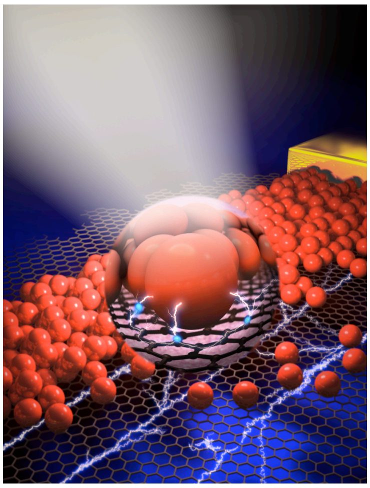


Graphene, a two-dimensional sheet of carbon atoms, has recently emerged as a novel material with unique electrical and optical properties, with great potential for opto-electronic applications, such as ultrafast photo-detection and optical switches.In this talk, I will review recent experimental work on exploiting graphene as a host for guiding, switching and manipulating light and electrons at the nanoscale [1,2]. This is achieved by exploiting surface plasmons: surface waves coupled to the charge carrier excitations of the conducting sheet. Due to the unique characteristics of graphene, light can be squeezed into extremely small volumes and thus facilitate strongly enhanced light-matter interactions. I will discuss recent observations of propagating and localized optical plasmons in graphene nano-structures. The plasmon wavelength can be tuned and plasmon propagation can even be switched on and off in-situ, simply by tuning the carrier density by electrostatic gates. These results pave the way towards ultrafast modulation of nanoscale optical fields, resonantly confined in graphene nano-structures or propagating along graphene ribbons.



The second part of the talk is devoted to a novel hybrid graphene-quantum dot photodetector [3] which exhibits a gain mechanism that can generate multiple charge carriers from one incident photon. Strong and tunable light absorption in the quantum-

Magnetism of Graphene with Defects: Vacancies, Substitutional Metals, and Covalent Functionalization

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Future spintronics applications of grapheme will depend crucially on the magnetism induced by defects and dopants. We start by reviewing the role of intrinsic defects, such as vacancies [1]. We mainly focus on extrinsic defects in graphene, by depositing metals in substitutional positions [2-4] or by functionalizing covalently with organic and inorganic molecules, and even polymers [5-6]. We have theoretically studied all these defects looking especially at their electronic and magnetic properties using first principles calculations.

Concerning the induced spin polarization our main findings are summarized as:

a) When we allow for rippling, the magnetic signal of monovacancies in graphene strongly decreases under small compressions, and even disappears at a strain of 3%. The magnetism of reconstructed monovacancies in planar graphene is well known to be due to dangling sigma orbitals. We found that the non-magnetic solutions have been associated to an increase of sp3 hybrization arising from graphene ripples.

b) Within traditional magnets, cobalt atoms in substitutional positions of graphene present spin polarization, while Ni cancels its spin signal. We have explained it with a model where the d states of the metal atom hybridize with the levels associated to an unreconstructed D_{3h} carbon vacancy. We have indeed determined that the occupation of levels explains the induced magnetism.

c) Adsorbates attached to graphene with a single covalent bond induce spin moments of 1.0 Bohr. This value can be explained by the saturation of a p_z orbital by each adsorbate, similar to H adsorption.

For metals and adsorbates we have also studied the magnetic couplings [3,5,6]. We have found that the magnetic ordering depends on the sublattice sites, and the exchange parameters show a power law decay with an exponent about 2.5, clearly different from metal atoms on graphene. Our results could provide key information about the magnetism induced in graphene by defects.

References

[1] Elton J. G. Santos, S. Riikonen, D. Sánchez-Portal and A. Ayuela, *J. Phys. Chem. C 116 (2012), 7602.*
[2] Elton J. G. Santos, A. Ayuela and D. Sánchez-Portal, *New Journal of Physics*, **12** (2010) 053012.
[3] Elton J. G. Santos, D. Sánchez-Portal and A. Ayuela, *Phys. Rev. B*, **81** (2010) 125433.
[4] Elton J. G. Santos et al. *Phys. Rev. B*, **78** (2008) 195420.
[5] Elton J. G. Santos, A. Ayuela and D. Sánchez-Portal, *New Journal of Physics (2012), in press.*

Cohesion in sp2 - systems mediated by weak interactions

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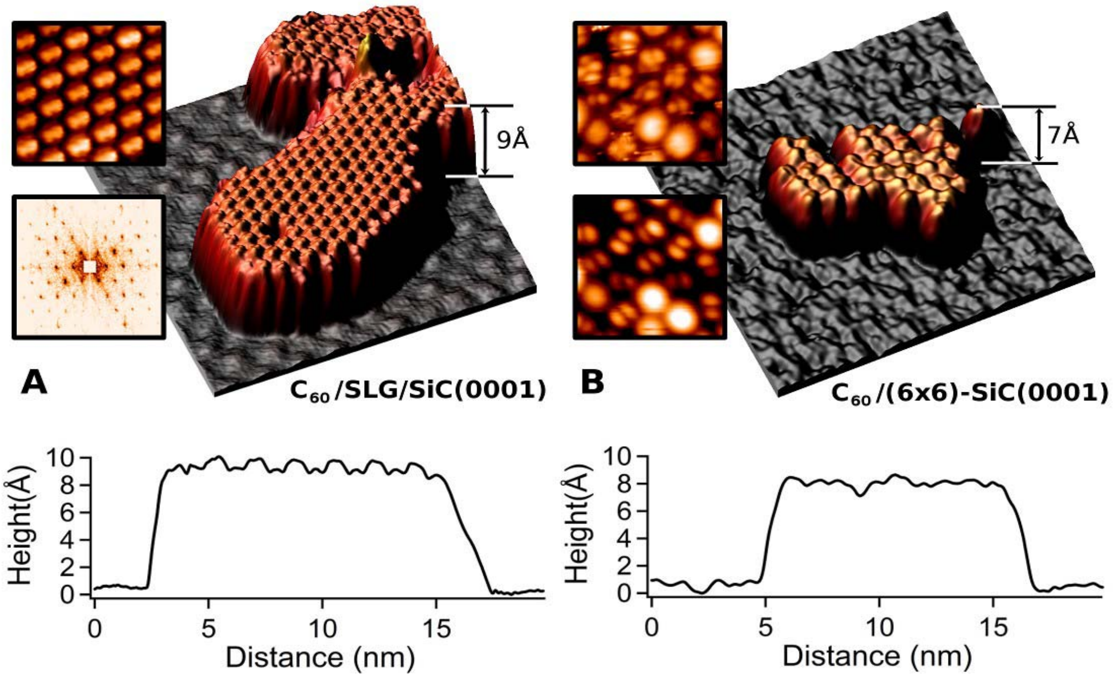
Fullerenes on single-layer epitaxial graphene are a model system where to study very faint interactions at a molecular level. By means of variable temperature scanning tunneling microscopy from 40K to ambient temperatures we have been able to grow ordered fullerene layers exclusively bound by van der Waals interactions. The adsorption geometry of the molecules was computationally confirmed only if van der Waals and weak interactions had been included in the calculation formalism. In the context of these interactions, mutual orientation of fullerenes in their close-packed arrangement is found to be an important factor for the total energy. Observation of collective movements of some islands point out the weak coupling to the substrate and the important role of the Van der Waals cohesion forces within.

Figure 1: 3D representation of 20x20 nm2 STM topography on C60 islands and their corresponding profiles.



[1] M. Švec, P. Merino, Y. J. Dappe, C. González, E. Abad, P. Jelínek, J.-A. M. Gago, *submitted to Phys. Rev. Lett. (2012).*
[2] Y.J. Dappe, J. Ortega and F. Flores, *Physical Review B 79, 165409 (2009).*

Structural phase transition of graphene caused by GaN epitaxy predicted by ab-initio calculations

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Graphene has potential to be a substrate of semiconductor devices. Indeed, GaN has been grown epitaxially by using pulsed laser deposition on graphite [1]. Thus, cleaving graphite layers after depositing nitrides by e.g. photoexfoliation [2] should provide graphene as a two-dimensional substrate. Such a structure can also be used as a release layer for mechanical transfer of semiconductor devices from graphite to a foreign substrate [3]. Theoretical studies have suggested that the GaN-graphene interface has a well-defined 1×1 structure [4]. However, the lattice mismatch between graphene and GaN is extraordinary large, c.a. 30%, encouraging to explore other stable interface structures.
Here, we report ab-initio predictions where the structure of graphene changes drastically with the epitaxial growth of GaN, by examining various non-1×1 superstructures for GaN- and AlN-graphene interfaces [5]. Among those, GaN-$4\sqrt{3}\times4\sqrt{3}$/graphene-9×9 and AlN-$5\sqrt{3}\times5\sqrt{3}$/graphene-11×11 superstructures have practically no lattice-mismatch. However, while the AlN-$5\sqrt{3}\times5\sqrt{3}$/graphene-11×11 superstructure is most stable as expected, the GaN-$\sqrt{3}\times\sqrt{3}$/graphene-2×2 interface is more stable than GaN-$4\sqrt{3}\times4\sqrt{3}$/graphene-9×9. As the GaN epitaxy proceeds expanding graphene gradually, the tensile strain for graphene is released suddenly by partial breaking of the C-bond network (Fig. 1). The interface exhibits spin polarization, even though ferromagnetic coupling is very weak in contrast with the AlN/MgB_2 interface [6].

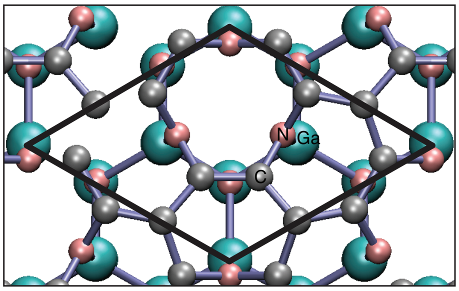

Figure 1: Optimized atomic structures of nitride-$\sqrt{3}\times\sqrt{3}$/graphene-2×2 interfaces obtained for lattice constants larger than 5.46 Å. The largest balls represent group-III elements, either Al or Ga. The primitive unit cell is indicated by the solid rhombus.

[1] J. Ohta and H. Fujioka, unpublished.
[2] Y. Miyamoto, H. Zhang, and D. Tomanek, Phys. Rev. Lett. **104**, 208302 (2010).
[3] Y. Kobayashi, K. Kumakura, T. Akasaka, and T. Makimoto, Nature **484**, 223 (2012).
[4] A. Ishii *et al.*, Phys. Status Solidi C **7**, 347 (2010); *ibid.* **8**, 1585 (2011).
[5] Y. Gohda and S. Tsuneyuki, Appl. Phys. Lett. **100**, 053111 (2012).
[6] Y. Gohda and S. Tsuneyuki, Phys. Rev. Lett. **106**, 047201 (2011).

Thursday, September 13th 2012

9:00 Session 9. Chairman: Frank Koppens

R. Miranda (Invited 15)
Experimental Evidence for Acoustic Plasmons in Graphene/Pt(111)

A. Zurutuza (Invited 16)
High Quality Graphene Films

J.A. Alonso (Invited 17)
Adsorption and storage of hydrogen in graphene materials

11:00 Cofee Break

11:30 Session 10. Chairman: Iván Cabria

N.A. Cordero (Oral 16)
Interaction of molecules containing a sulfuric group with graphene nanostructures. A DFT study

S. Yuan (Oral 17)
Modeling Electronic Properties of Single-layer and Multilayer Graphene

R. Roldán (Oral 18)
Graphene as a two-dimensional crystalline membrane

G. Le Lay (Oral 19)
Silicene and germanene graphenes cousins

A. Castellanos Gómez (Oral 20)
Laser-thinning of MoS2: on demand generation of a semiconducting analogue to graphene

13:10 Concluding Remarks: R. Miranda

Experimental Evidence for Acoustic Plasmons in Graphene/Pt(111)

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[2] Instituto Madrileño de Estudios Avanzados en Nanociencia (IMDEA-Nanociencia). Madrid. Spain
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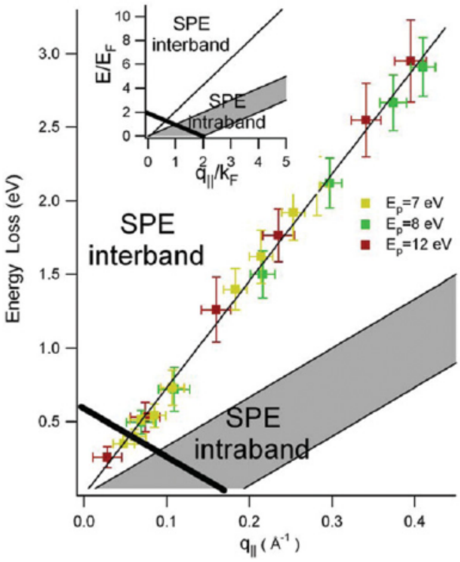
Ultra perfect graphene monolayers can be epitaxially grown on many single crystal metal surfaces under Ultra High Vacuum conditions [1,2]. The dispersion and damping of the sheet plasmon in a graphene monolayer grown on Pt(111) have been studied by angle-resolved High Resolution Electron Energy Loss Spectroscopy and found to be strictly *linear* [3] as a consequence of the screening by the metal substrate [4]. The Landau damping essentially occurs via interband excitationsabove the Fermi wavevector. Intraband transitions do not havea significant influence on the collective mode.

In order to transmit signals by means of plasmons it is crucial to have materials showing a linear dispersion relation, so that the phase velocity and the group velocity are the same, thereby avoiding the distorsion of the signal. Two dimensional materials, in principle, are expected to show a non linear, quadratic dispersion relation. The plasmon linear dispersion described here for graphene monolayers grown on metal substrates might be essential in the future or using plasmons to transmit information.

[1] A.L. Vázquez de Parga et al, Phys. Rev. Lett. 100, 056807 (2008)
[2] R. Miranda and A.L. Vazquez de Parga, Nature Nanotechnology, 4, 549 (2009)
[3] B. Diaconescu et al, Nature 448, 57 (2007).
[4] A. Politano et al, Phys. Rev. B 84, 033401 **(**2011)



Energy dispersion relation for plasmons excited by low energy electrons in graphene/Pt(111)

High Quality Graphene Films

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Graphene's unique and outstanding properties could make possible the application of graphene in many different fields. At present there are no products in the market that contain graphene, therefore, it is clearly at a research stage. In Graphenea we manufacture graphene for research laboratories. Depending on the application the required graphene format can vary from powder/flake to homogeneous film form. The powder form could meet large volume/weight requirements and it is typically obtained from graphite. While the large area graphene films can be obtained using chemical vapor deposition (CVD) methods on top of a metal catalyst. The synthesized graphene has to be typically transferred onto insulating or similar substrates for subsequent characterization or device fabrication. In this talk, the synthesis and characterization of high quality graphene films produced via CVD will be described.

Adsorption and storage of hydrogen in graphene materials

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Nanoporous carbons appear as promising candidate materials for hydrogen storage. The storage capacities depend on the characteristics of the pores. An interesting class of porous carbons can be synthesized by chemical extraction of the metal atoms from solid metallic carbides. However, the structure of these materials remains largely unknown. For this reason we have performed extensive computer simulations to investigate the form and the size distribution of the pores in these carbons and the atomistic structure of the pore walls. The simulations reveal a structure of interconnected pores of different sizes and shapes, forming a disordered three dimensional network [1]. The pores have planar or curved graphene-like walls with abundant defects. For this reason, the main features of the interaction of hydrogen with the pore walls can be studied by investigating the interaction of hydrogen with graphene. Calculations of the interaction of molecular hydrogen with a pure graphene layer and with the graphene-like walls of pores of different shape give adsorption energies which are not strong enough to deliver storage capacities of technological significance.

A promising strategy to increase the hydrogen storage capacity consists in doping these materials with metallic impurities and nanoparticles. The fundamental chemical interactions can be studied by modeling the adsorption of hydrogen on metallic clusters supported on graphene. In the case of doping with alkali metal impurities, like lithium, the charge transfer between lithium and graphene leads to charged Li impurities which polarize the electronic cloud of neighbor hydrogen molecules, increasing the binding energy of hydrogen to graphene. Adsorption of molecular hydrogen on graphene doped with palladium clusters leads to two different types of adsorption. In the first type, the bond distance between the two hydrogen atoms is elongated but the bond is not broken, and the adsorption energies are between 0.4 and 1 eV. In the second type, the hydrogen molecules dissociate, and the chemisorption of the hydrogen atoms shows stronger binding. The implications for hydrogen storage will be discussed.

[1] M. J. López, I. Cabria, J. A. Alonso, *Journal of Chemical Physics*, **135**, 104706 (2011).

Interaction of molecules containing a sulfuric group with graphene nanostructures. A DFT study

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One of the problems to be solved in order to use graphene and other carbon nanostructures in an industrial-scale environment is their insolubility in either water or organic solvents. Among the best surfactants for dispersing these structures are sodium dodecyl sulfate (SDS), sodium dodecylbenzenesulfonate (NaDDBS), and sodium polystyrene sulfonate (PSS), all of which have in common a sulfuric head group. Sulfuric acid itself is a good nanotube disperser and has been reported that mixed with chlorosulfuric acid it is capable of exfoliating graphene flakes from graphite.
We have simulated using the Density Functional Theory (DFT) the interaction of three molecules containing a sulfuric group (sulfuric acid, sodium bisulfate and sodium butyl sulfate) with three carbon nanostructures (mono- and bi-layer graphene as well as a (5,5) carbon nanotube) [1-4]. We have calculated equilibrium configurations, electron transfers, binding energies, and densities of states. Our results show the way these molecules change the conduction properties of the nanostructures and how they can separate them.

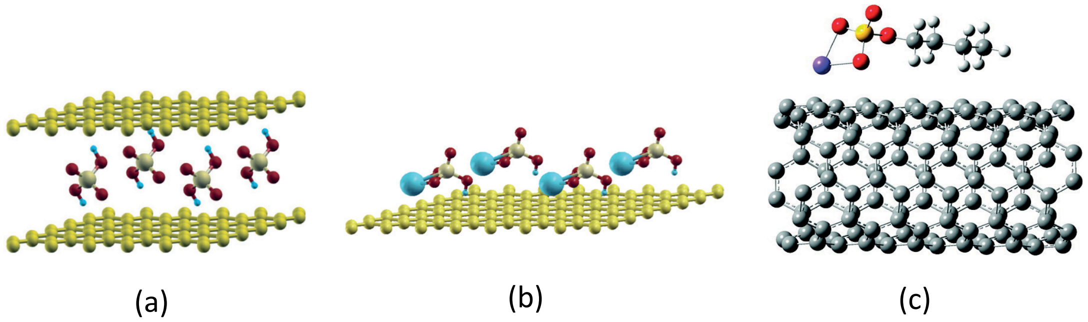

Figure 1: Molecules with a sulfuric group interacting with carbon nanostructures: (a) sulfuric acid intercalated inside bilayer graphene, (b) sodium bisulfate adsorbed on monolayer graphene and (c) sodium dodecyl sulfate adsorbed on a (5,5) carbon nnaotube.

[1] N.A. Cordero and J.A. Alonso *The interaction of sulfuric acid with graphene and formation of adsorbed crystals*, Nanotechnology **18** 485705 (2007).

[2] N.A. Cordero and J.A. Alonso *Interaction of surfactants containing a sulfuric group with a (5,5) carbon nanotube*, J. Phys. Chem. C **114** 17249 (2010).

[3] I.G. Ayala, N.A. Cordero, and J.A. Alonso *Surfactant effect of sulfuric acid on the exfoliation of bilayer graphene*, Phys. Rev. B **84** 165424 (2011).

[4] I.G. Ayala and N.A. Cordero, *Interaction of sodium bisulfate with mono- and bi-layer graphene*, J. Nanopart. Res. 2012 (submitted).

Modeling Electronic Properties of Single-layer and Multilayer Graphene

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Graphene in the real experiments always have different kinds of disorder or impurities, such as ripples, puddles, vacancies, adatoms, admolecules, etc. One of the most important problems in graphene physics is to understand the effect of these imperfections on the electronic structure and transport properties. Motivated by recent experiments, we performed a systemic study of the effects of different types of disorder or impurities to the electronic properties of single-layer and multilayer graphene [1-10].

We study this issue by direct numerical simulations of electrons on a honeycomb lattice in the framework of full pi-band tight-binding model. The magnetic field is introduced by means of the Peierls substitution. Numerical calculations based on exact diagonalization can only treat samples with relative small number of sites. For large graphene sheet with millions of atoms, the numerical calculation of an important property, the density of states (DOS), is performed by the time-evolution method. The time-evolution method is based on numerical solution of time-dependent Schrödinger equation with additional averaging over random superposition of basis states. We further extend this method to the calculation of various quantities by using the Kubo formula, such as polarization function, dielectric function, response function, energy loss function, static and dynamical (optical) conductivity, diffusion coefficients, mean free path, localization length, electron velocity and mobility. The effect of electron-electron interaction is considered within the random phase approximation (RPA). Another extension of the time-evolution method yields the quasieigenstate, a superposition of degenerate energy eigenstates. The Klein tunneling and quantum interference (Aharonov-Bohm effect) are studied by direct simulation of the wave packet propagation. Our numerical methods allow us to carry out calculations for rather large systems, up to hundreds of millions of atoms, with a computational effort that increases only linearly with the system size.

[1] S. Yuan, H. De Raedt, and M. I. Katsnelson, Phys. Rev. B **82**, 115448 (2010).
[2] S. Yuan, H. De Raedt, and M. I. Katsnelson, Phys. Rev. B **82**, 235409 (2010).
[3] S. Yuan, R. Roldán, and M. I. Katsnelson, Phys. Rev. B **84**, 035439 (2011).
[4] S. Yuan, R. Roldán, and M. I. Katsnelson, Phys. Rev. B **84**, 125455 (2011).
[5] S. Yuan *et al*, Phys. Rev. B **84**, 195418 (2011).
[6] S. Yuan, R. Roldán, and M. I. Katsnelson, arXiv:1201.4454
[7] S. Yuan *et al*, arXiv:1205.2782
[8] T. O. Wehling *et al*, Phys. Rev. Lett. **105**, 056802 (2010).
[9] R. R. Nair *et al*, Small **6**, 2877 (2010).
[10] A. Singha *et al*, Science **332**, 1176 (2011).

Graphene as a two-dimensional crystalline membrane

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Graphene is a two-dimensional (2D) crystalline membrane of carbon atoms, which unusual properties have attracted an enormous interest. Graphene has been demonstrated to be stable even for free-standing samples. Crystalline membranes at finite temperatures have an anomalous behavior of the bending rigidity that makes them more rigid in the long-wavelength limit. This issue is particularly relevant for applications of graphene in nanoelectromechanical and microelectromechanical systems. We calculate numerically the height-height correlation function of crystalline two-dimensional membranes, determining the renormalized bending rigidity in the self-consistent screening approximation (SCSA). For parameters appropriate to graphene, the calculated correlation function agrees reasonably with the results of atomistic Monte Carlo simulations for this material.

Furthermore, in practice, physical membranes are exposed to a certain amount of external strain (tension or compression) due to the environment where they are placed. As a result, the behavior of the phonon modes of the membrane is modified. We show that anharmonic effects in stiff two-dimensional membranes are highly suppressed under the application of tension. For this, we consider the anharmonic coupling between bending and stretching modes in the SCSA and compare the obtained height-height correlation function to the corresponding harmonic propagator. The elasticity theory results are compared to atomistic Monte Carlo simulations for a graphene membrane under tension. We find that, while rather high values of strain are needed to avoid anharmonicity in soft membranes, strain fields less than 1% are enough to suppress all the anharmonic effects in stiff membranes, as graphene. Finally we will consider the effect on the resistivity of electron interaction with flexural phonons. We will discuss the temperature and doping dependence of this contribution, treating the out of plane vibrations beyond the harmonic approximation.

Finally, we will study the generalization of the SCSA to the quantum dynamic case. I will show the frequency, wave-vector and temperature dependence of the correlation functions. These results will be used to compute thermodynamics properties of crystalline membranes as graphene, such as the temperature dependence of the specific heat [3].

[1] K. V. Zakharchenko, R. Roldán, A. Fasolino, and M. I. Katsnelson, *Phys. Rev. B* **82**, (2010) 125435.

[2] R. Roldán, A. Fasolino, K. V. Zakharchenko, and M. I. Katsnelson, *Phys. Rev. B* **83**, (2011) 174104.

[3] R. Roldán, E. Cappellutti, A. Fasolino, and M. I. Katsnelson, (in preparation).

Silicene and germanene graphene's cousins

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Silicene and graphene are the graphene equivalents for silicon. Free standing silicene and germanene have been theoretically predicted to have a buckled honeycomb atomic arrangement of sp^3/sp^2 hybridized Si atoms [1]. Still, they would share essentially the same electronic properties as graphene, namely, an electronic dispersion resembling that of massless relativistic Dirac fermions at the K points of the Brillouin-zone.
Recently, we have for the first time synthesized silicene as an epitaxial sheet on a silver (111) substrate; it shows an extremely high Fermi velocity of 1.3E6 ms^{-1} [2].
The demonstration that silicon can form sheets of silicene, a two dimensional honeycomb low buckled structure, which does not exist in nature, is tantalizing for new physics (especially, since silicene is predicted to have non-trivial topological properties [3]) and potential applications.
Since, silicon can be considered the workhorse of electronic industry, this synthesis should have a major impact for novel electronic devices because of the compatibility with existing Si technologies. Indeed, a key issue in this direction will be the transfer on an insulating substrate, like, possibly AlN [4].
Finally, the epitaxial growth of silicene has opened up the route to the synthesis of germanene, also with nontrivial band topology and a gap induced by effective spin orbit coupling for the π orbitals at the K point in low-buckled geometry corresponding nearly to room temperature [3].

[1] S. Cahangirov et al., Phys. Rev. Lett. 102, 236804 (2009).
[2] P. Vogt et al., Phys. Rev. Lett., 108, 155501 (2012).
[3] Cheng-Cheng Liu, Wanxiang Feng, and Yugui Yao, Phys. Rev. Lett. 107, 076802 (2011).
[4] M. Houssa et al. J. Electrochem. Soc. 158, H107 (2011).

Acknowledgements: *support from FET-Open grant number 270749 for the project "**2D-NANOLATTICES**"*

Laser-thinning of MoS_2: on demand generation of a semiconducting analogue to graphene

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Single-layer MoS_2 is an attractive semiconducting analogue of graphene [1] that combines high mechanical flexibility [2] with a large direct bandgap of 1.8 eV. On the other hand, bulk MoS_2 is an indirect bandgap semiconductor similar to silicon, with a gap of 1.2 eV, and therefore deterministic preparation of single MoS_2 layers is a crucial step towards exploiting the large direct bandgap of monolayer MoS_2 in electronic, optoelectronic, and photovoltaic applications. Although mechanical and chemical exfoliation methods can be used to obtain high quality MoS_2 single-layers [3], the lack of control in the thickness, shape, size, and position of the flakes limits their usefulness.

Here we present a technique for controllably thinning multilayered MoS_2 down to a single-layer two-dimensional crystal using a laser. We generate single layers in arbitrary shapes and patterns with feature sizes down to 200 nm, and show that the resulting two-dimensional crystals have optical and electronic properties comparable to that of pristine exfoliated MoS_2 single layers.

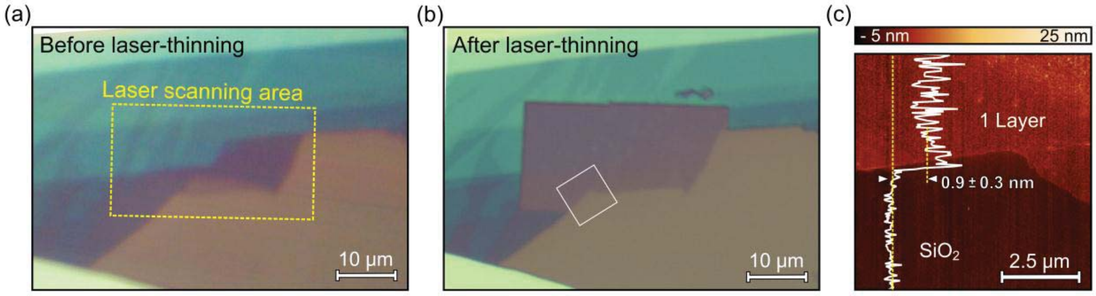

Figure 1: (a) Optical microscopy image of a multilayered MoS_2 flake deposited onto a 285 nm SiO_2/Si substrate. (b) Same as in (a) after scanning a laser in the area marked by a dashed rectangle in (a). (c) Topographic AFM images of the region marked by the square in (b). A vertical topographic line profile is included in (c) to indicate the thickness of the laser-thinned layer.

[1] B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, A. Kis, Nature Nanotechnology 2011, 6, 147.
[2] A. Castellanos-Gomez, M. Poot, G. A. Steele, H. S. J. van der Zant, N. Agraït, G. Rubio-Bollinger, Advanced Materials 2012, 24, 772.
[3] A. Castellanos-Gomez, N. Agraït, G. Rubio-Bollinger, Applied Physics Letters 2010, 96, 213116.

Posters

Chemical modification of exfoliated graphene

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Graphene is a two-dimensional single-layer sheet of sp^2 hybridized carbon atom with the hexagonal packed structure. Its extraordinary properties, such as high carrier mobility, half-integer quantum Hall effect at room temperature, spin transport, high elasticity, electromechanical modulation, and ferromagnetism, have made graphene a very promising candidate as a robust atomic-scale scaffold in the design of new nanomaterials. Up until now, versatile methods have been developed for fabrication, growth, or synthesis of graphene and its derivatives such as the mechanical exfoliation of graphite using adhesive tapes or the chemical vapor deposition method. Graphene can also be produced by liquid phase exfoliation in organic solvent without chemical modification by simple ultrasonication assistance. This methodology opens the way to carry out different organic reactions on graphene in order to produce specific structures for functional devices.

Our group have already successfully produced functionalized graphene layers using two well-established organic reactions: 1,3-dipolar cycloaddition and amide-condensation reactions.[1-2] We propose here different way of functionalization of graphene layers, after dispersion and exfoliation in organic solvent, such as the cyclopropanation and the aryl diazonium salt-based reactions.

[1] Mildred Quintana, Konstantinos Spyrou, Marek Grzelczak, Wesley R. Browne, Petra Rudolf, Maurizio Prato, *ACS nano*, 2010, 4(6), 3527-3533.

[2] Mildred Quintana, Alejandro Montellano, Antonio Esau del Rio Castillo, Gustaaf Van Tendeloo, Carla Bittencourt, Maurizio Prato, *Chem. Commun.*, 2011, 47, 9330-9332.

GRANADA'12 (09-13 September 2012)

Electrodeposition of Zn-Fe alloy from a chloride élecrolyte

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Keywords: Materials, Zn-Fe alloy, chloride electrolyte, anomalous codeposition, électrocristalisation, steel, transient, cyclic voltammetry, high temperature, structure and morphology, impedances, electroplating, ALSV, SEM, XRD, corrosion.

Abstract

Study of the kinetics of electrodeposition of Zn-Fe alloys from a chloride electrolyte was performed using transient methods. We have inferred, from the techniques of cyclic voltammetry and potentiostatic elements on the kinetics of nucleation and growth of germs on a steel substrate E24. The influence of different parameters (current density, concentration ratio of Zn (II) / Fe (II), temperature) on the morphology and structure of deposits was discussed.

The EDS analysis for determining the composition of the alloys obtained gives an increase in the atomic percent of iron in the composition of the alloy with the elevation of the density and an increase in the run atomic percent oxygen with increasing temperature.

Anodic dissolution of electrodeposited coatings by the method ALSV allowed to see that the deposits formed in the electrolyte or ionic concentration ratio is 1/3 are uniform and especially single-phase, while when the ratio Zn (II) / Fe (II) is 1/6 the coatings are biphasic. The electrodeposition of the alloy Fe-Zn nucleation occurs via multiple 3D with a diffusion controlled by growth following the theoretical response of a nucleation instant.

The XRD analysis coupled with SEM microscopic observations showed that the elevation of temperature causes a change in the structure of deposits, a refinement of grain size and the presence of three phases η, ζ, and Γ.

Finally, potantiodynamiques curves and impedance measurements, in a corrosive NaCl 3%, that gave resistance to corrosion is maximalle for alloys made from an electrolyte or the concentration ratio of Zn (II) / Fe (II) is 1/3 and at a temperature of 50 ° C.

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Interaction of water molecules with bilayer graphene nanoribbons.

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One of the ways of producing graphene is the reduction of graphene oxide. In order to improve this process it is necessary to understand how oxygen and hydrogen atoms interact with the reactive areas (defects and edges) of graphene nanostructures.

We have simulated the interaction of water molecules with the edges of bilayer graphene nanoribbons using a Tight-Binding code (DFTB+). We have changed the water concentration and the kind of edge (zig-zag or armchair). Besides, we have studied the difference between using pure carbon nanoribbons and nanoribbons with their dangling bonds passivated with hydrogen atoms.

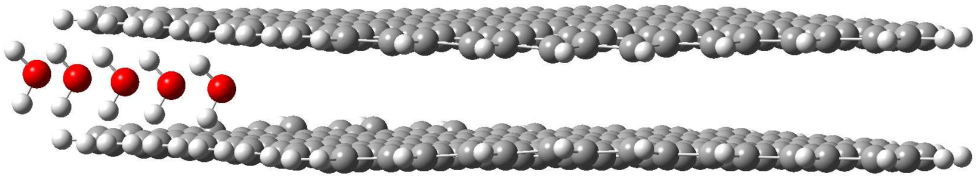

Figure 1: Water molecules close to a bilayer armchair graphene nanoribbon passivated with hydrogen atoms.

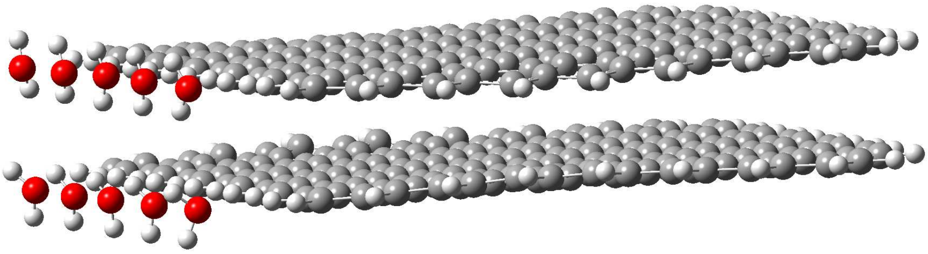

Figure 2: Water molecules on the edges of a bilayer armchair graphene nanoribbon passivated with hydrogen atoms.

Electrodeposition of nickel by pulse current from conventional Watt's baths.

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Metallic coatings are used for protection against corrosion of metal structures. The protection provided depends on the physico-chemical coatings. Three factors are crucial to have good resistance to corrosion morphology, crystallographic orientation and composition of layers. These can be modified in view of improving the corrosion resistance [1] by using appropriate organic additives. A promising alternative is also possible by the dedicated implementation of the electrodeposition technique in pulsed mode [2]. This technique allows an improvement of the characteristics of metals and alloys deposited compared to coatings obtained by conventional routes. This work is part of that objective. Thus we propose to optimize the parameters of development, pulsed coatings of nickel. We thus specifically linking the morphological characteristics and structural behavior of coatings to immersion of coated parts morphology of coatings was characterized by observations in scanning electron microscopy (SEM-FEG). The X-ray diffraction in symmetric mode was used to evaluate the structure and the main crystallographic orientations of the deposits. The results obtained, we conclude that the development in pulsed induced a marked improvement in the morphology and grain refinement.

[1].Kh. M. S. Yousef, C. C. Koch, P. S. Fedkiw, *Improved corrosion behavior of nanocrystalline zinc produced by pulse-current electrodeposition, Corros. Sci. 46(2004) 51.*
[2] A.M. El-Sherik, U.Erb , J.Page, *Surf. Coat. Technol.88(1997) 70-78.*

Adsorption and Storage of Hydrogen Molecules on Small Palladium Clusters, Pd-Pd_6, Supported on Graphene

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Palladium might enhance hydrogen storage in nanoporous carbons by surface reactions, especially by hydrogen spillover, which consists in the dissociation-storage-recombination of hydrogen in the material [1]. A first step to understand that enhancement of hydrogen storage was the simulation of the interaction and stability of Pd clusters deposited on graphene by means Density Functional calculations [2]. The second step is the present investigation of the adsorption and the dissociation of molecular hydrogen on the deposited Pd clusters as a function of cluster size, from a single Pd adatom to the Pd_6 cluster. We analyze the mechanisms for the activation of a single hydrogen molecule and for the possible subsequent dissociation, as well as the activation-dissociation barriers. According to the present Density Functional calculations, a single Pd atom does not dissociate the molecule, Pd_2 and Pd_3 clusters dissociate the molecule with no barriers and larger clusters dissociate the molecule with barriers of 0.3 and 0.8 eV. We have also simulated the adsorption of additional hydrogen molecules, up to four, with Pd clusters deposited on graphene. We discuss the implications for the hydrogen storage capacity of Pd-doped nanoporous carbon materials.

[1] C.I. Contescu, C.M. Brown, Y. Liu, V.V. Bhat and N.C. Gallego, J. Phys. Chem. C **113**, 5886 (2009)

[2] I. Cabria, M.J. López, and J.A. Alonso, Phys. Rev. B **81**, 035403 (2010)

Simple analytical potentials for the interaction between rare gases and graphene- based surfaces

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The interaction between atoms and molecules with graphene type surfaces is a topic of great interest given the potential new applications of these materials. For example it is in principle possible to detect with high resolution the presence of a single atom adsorbed on these surfaces[1]; also its porous sheets synthesized with atomic precision[2] have been proposed as a nano-scale membrane which could be used as an atmospheric nanofilter[3].

Thus in this kind of studies it is necessary not only a reliable and accurate description of the interaction potential but it is also very important to develop a convenient parametrization of the involved non-covalent interaction to support dynamical studies on the physisorption of atoms and molecules.

We report reliable interaction potentials for the physisorption of rare gases (He, Ne, Ar, Kr) with graphene and graphite surfaces which have been expressed in a very simple functional form suitable for pursuing further dynamical studies.

The interaction potentials have been obtained by combining the high level ab initio DFT-SAPT[4] and MP2C[5] methods with the empirical atom-bond approach[6]. Specifically, ab initio calculations using very large basis sets have been performed to obtain accurate interaction potentials for coronene—rare gas systems (coronene is the largest computationally affordable and planar polycyclic aromatic hydrocarbon sharing a hexagonal unit cell with graphene). The obtained potentials have been used as benchmarks for a fine tuning of the analytical atom-bond (rare gas—C-C) pair interactions. Then, the optimized atom-bond interactions are summed up to model the interaction between the atom and an infinite graphene (or graphite) surface.

We obtain binding energies for physisorption that are in good agreement with the experimental findings[7]. In addition, the interaction between the rare gas atoms and porous graphenes is modeled and barriers for penetration through the pores have been obtained.

[1] F. Schedin et al., *Nat. Mater.* **6**, 652 (2007).
[2] M. Bieri et al., *Chem. Comm.* **45**, 6919 (2009).
[3] S. Blankenburg et al., *Small.* **6**, 2266 (2010).
[4] A. Hesselmann et al., *J. Chem. Phys.* **122**, 014103 (2005);
R. Podeszwa and K. Szalewicz, *Chem. Phys. Lett.* **412**, 488 (2005).
[5] M. Pitonak and A. Hesselmann, *J. Chem. Theory Comput.* **6**, 168 (2010).
[6] F. Pirani et al., *Chem. Phys. Lett.* **394**, 37 (2004).
[7] G. Vidali et al., *Surf. Sci. Rep.* **12**, 133 (1991).

Use of the D'' band for the analysis of Raman spectra of graphene oxide

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Chemical exfoliation of graphite [1] is a potential candidate for the production of graphene-like material at industrial level. In spite of that the product of this chemical exfoliation usually is the insulator material graphene oxide (GO), with a reduction process we can obtain a reduced graphene oxide (rGO) with conductivity enough for some advanced applications. So, the understanding and control these reduction processes are crucial. In this work we propose the use of a band not previously used in graphene oxide, the D'' band, for fully understanding the Raman spectra of GO and rGO. This band is associated with stacking defects between the graphene layers [2]. Moreover, these measurements are correlated with X-ray diffraction analysis of the same samples.

The graphene oxide (GO) samples were synthesised at Grupo Antolín using a modified Hummers method, using as a precursor material carbon nanofibers. Reduced graphene oxide samples were obtained after an annealing process in air. The morphology of the samples was characterized by field emission SEM in a FEI Nova NanoSEM 230. Structural characteristics were obtained by X-Ray diffraction and Raman, in a PANalytical XPert PRO MPD and a Jobin Yvon HR800 LabRam, respectively.

We found that using the D'' band we obtain an accurate deconvolution of the Raman spectra, with the position of the other peaks (G, D and D') in accordance with the bibliography. Moreover, we monitor the evolution of the D'' band position during the reduction process at different temperatures (from 500 to 800ºC) and we found that there is a linear correlation between the D'' Raman shift and the variation of the interlayer distance measured with XRD, indicative of the elimination of oxygen functional groups. This indicates that the D'' band can be used a marker for knowing the reduction state of the sample.

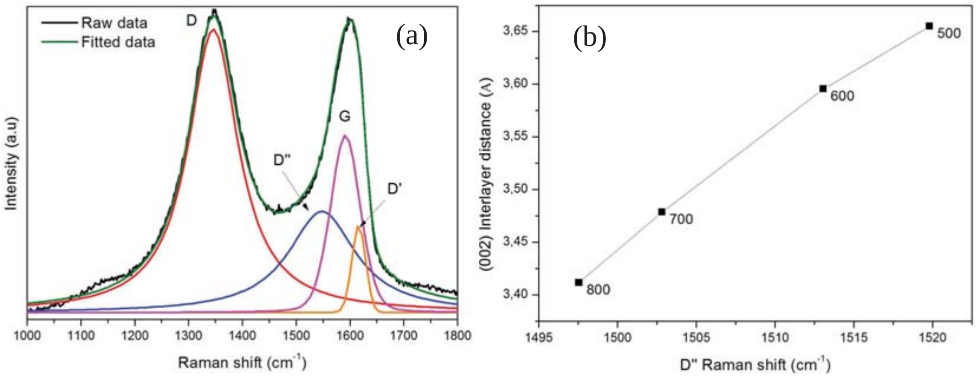

Figure 1. (a) Deconvolution of the Raman spectra of GO. (b) Evolution of the (002) interlayer distance vs the position of the D'' band, showing an almost lineal dependence.

[1] G. Eda, M. Chhowalla, *Advanced Materials* 2010, 22, 2392

[2]] T. Sharifi, F. Nitze, H. R. Barzegar, C.W. Tai, M. Mazurkiewicz, A. Malolepszy, L. Stobinski, T. Wagberg, *Carbon* 2012, 50, 3535

Magnetic Study of Spin Transition in a Dinuclear Iron(II)

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Abstract

From its discovery in the 1930's till now, spin crossover has been the subject of extensive applications. One of the problems remaining is the ability to organize at will spin crossover systems with the desired properties, since spin crossover remains an elusive property very much depending on the surroundings of the metallic center.

In this context, a very interesting family is the bis(pyrazolyl)pyridine one. With these analogues of the widely-used terpyridine system, many of their homoleptic complexes show spin crossover behaviour [1]. It has also been shown in our laboratory that many complexes can be photoconverted at low temperatures, with long lifetimes of photoexcited high-spin state [2a,b]. They constitute thus interesting building blocks for the obtention of organized systems.

During the course of our present investigations of functionalized subunits of the kind, we have also looked at the possibility of controlling the coordination behaviour of bis(pyrazolyl)pyridine ligands through the use of blocking ancillary ligands. This poster will show the results we have found with pseudohalogens in particular thiocyanate and selenocyanate.

The complexes $\{[Fe(3\text{-}bpp)(NCS)_2]_2 4,4'\text{-}bpy\}$ was synthesized in good yield. The infrared spectrum of the powder showed only one absorption in the cyanide region at 2079 cm^{-1}. The complex crystallizes in the centrosymmetric $P2_1/n$ space group with an inversion center lying in the middle of the 4.4_-bipyridine moiety. On the high-energy end, a strong absorption takes place below 600 nm, which corresponds to both the MLCT (metal-to-ligand charge transfer) and the d–d bands of the LS (low-spin) state of the complex. The other absorption band centered around 820 nm is very likely to be the d–d transition band of the HS (high-spin) state. A further decrease in the temperature to 80 K led to some changes in the valley around 700 nm and an apparent shift in the high-energy.

References:

[1]: M.A. Halcrow, *Coord. Chem. Rev.* 49, **(2005),** 2880

[2a,b]: a) V. A. Money, J. Sanchez Costa, S. Marcen, G. Chastanet, J. Elhaik, M. A. Halcrow, J. A. K. Howard, J.-F. Letard, *Chem. Phys. Lett.* 391, **(2004)** 273-277. b) J.-F. Letard, J. Sanchez Costa, S. Marcen, C. Carbonera, C. Desplanches, A. Kobayashi, N. Daro, P. Guionneau, J.-P. Ader, *J. Phys. Conf. Ser* 21, **(2005),** 23

Keywords:
Spin transition, iron (II), magnetism.

Structural characterization of CVD few layers graphene by Raman

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Few layers graphene (FLG) has been synthesized by chemical vapor deposition (CVD) at 1000ºC on copper and using methane as a precursor gas at low pressure. Oxygen coming from the residual gas was controlled to avoid the oxidation during the formation of graphene layer. Copper was deposited on a polished silicon wafer, which was previously coated by a nickel film acting as diffusion barrier layer. We have studied the surface structure of the substrate before and after the deposition of graphene. Raman shift shows the peaks G, D and 2D. The D band refers to disordered carbon and to the fraction of edge carbons, which serve as defects by breaking the translational symmetry of the lattice.[1,2] G band indicates the presence of graphitic carbon and 2D peak shows the formation of graphene. The I_{2D}/I_G ratio higher than unity demonstrates the formation of few layers graphene on copper. The surface distribution of graphene is provided by a Raman mapping of the sample, which shows the presence of a continuous graphene layer on copper crystals (3 µm of dimension) with defects. Figure b), corresponding to Raman shift mapping, shows the existence of 0.25 - 0.50 µm domains of few graphene layers.

1. Ferrari, A. C.; Meyer, J. C.; Scardaci, V.; Casiraghi, C.; Lazzeri, M.; Mauri, F.; Piscanec, S.; Jiang, D.; Novoselov, K. S.; Roth, S.; et al. Raman Spectrum of Graphene and Graphene Layers. Phys. Rev. Lett. 2006, 97, 187401/1–187401/4.
2. Ferrari, A. C.; Robertson, J. Interpretation of Raman Spectra of Disordered and Amorphous Carbon. Phys. Rev. B 2000, 61, 14095–14107.

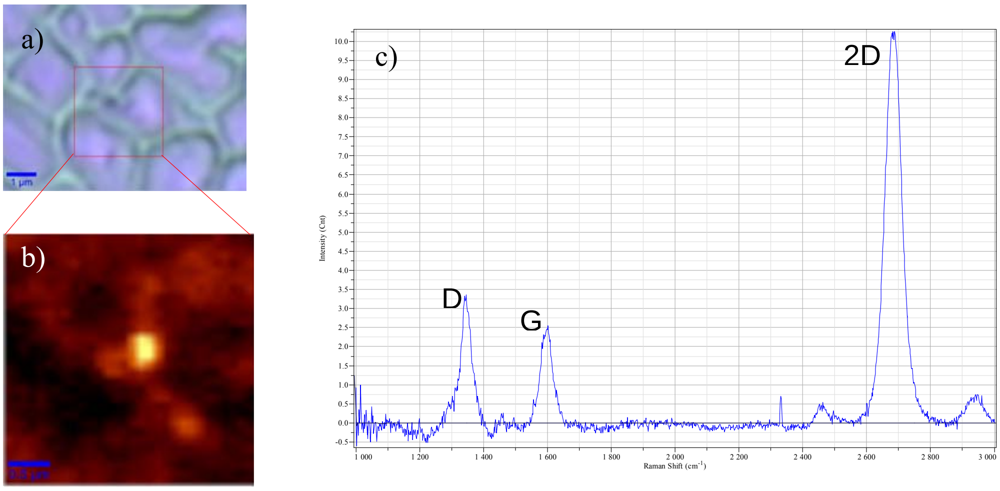

Figure. a) Cu/Ni/c-Si structure after annealing of 1000ºC. Copper crystalline domains appear by dewetting of copper on nickel during thermal treatment at high vacuum conditions. b) Raman shift map of the red framed region shown in figure a). c) Raman shift spectrum corresponding to the bright region of figure b).

Wave packet revivals in graphene quantum rings

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Graphene (a one-atom-thick gaphite monolayer) has attracted a lot of attention in recent years from both theoretical and experimental points of view due to its extraordinary mechanical, electronic and transport properties. These properties are due to the honeycomb-like geometry of the carbon atoms that, for instance, makes this material a zero-band-gap semiconductor. Besides, the dispersion relation at low energies for the electrons in this system does not obey the typical parabolic band structure but a conical one that translates into electrons behaving like massless Dirac fermions.

The quantum evolution of wave functions in confined systems exhibits some interesting properties. One of them is the revival of the wave packet. Revivals appear when wave packets return in their temporal evolution to a shape that is very similar to the initial shape. Assuming an initial wave packet that is a superposition of eigenstates sharply peaked around some level, this wave packet evolves oscillating and spreading out until the delocalization is so big that the packet nearly collapses. But at a later time the packet starts to regenerate itself and finally reaches a state in which it recovers approximately its initial shape. The time it takes for this phenomenon to occur depends on the energy eigenvalue spectrum.

We present examples of this kind of behaviour in small mono- and bi-layer graphene rings and disks. We have used three different models (a continuum model, Density Functional Theory and Tight-Binding) to calculate the energy spectrum of these systems and studied the difference in revival times among these nanostructures

Carbon-based Venetian blinds: a new class of materials with controlled anisotropic conductance

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Graphene has become a promising material for the near future development of molecular electronics. It is a 2D carbon-based material with unique properties. Interestingly, graphene basic structure can be modified to introduce new functionalities. Beyond doping processes, other boundless arrangements have been proposed: tri-wings graphenes,[1] graphynes and graphenynes.[2] On the other hand, 1D graphene-based materials have been also proposed, such as graphene nanoribbons, presenting interesting properties. In this work we propose a new graphyne-like structure based on a set of parallel nanoribbons having an appearance similar to a Venetian blind. The nanoribbons are attached to two parallel nanoribbons acting as a support of the set. The angle of the nanoribbons in the "blind" affects the conductance of the system because of the different coupling between orbitals. The control of conductance in such an anisotropic material could have some interesting applications. Moreover, the control of conductivity could be achieved by external stimuli such as pressure and/or electric fields (gate electrode). To carry out this control we need a molecular change capable of affecting strongly the conductivity in at least one of the pathways with a minor energy cost. [3] In this case we propose a conformational change of phenyl rings at suitable positions.

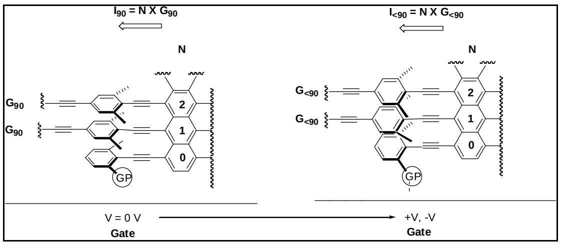

Fig 1: An example of proposed Venetian blind-like systems with gate control

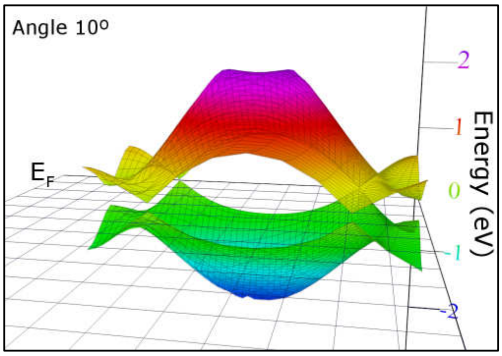

Fig. 2: Band structure of the system with angle=10º (slat-nanoribbons turned 10º with respect to support-nanoribbons). Typical grapheme details are observed in the bands. The Fermi energy is the reference at 0 eV.

[1] Y. Wang, Y. Ding, J. Ni, *J. Phys. Chem. C*, **2012**, *116*, 5995-6003 and references cited therein.
[2] D. Malko, C. Neiss, F. Viñes, A. Görling, *Physical Review Letters*, 2012, **108**, 086804.
[3] N. Fuentes, A. Martín-Lasanta, L. Álvarez de Cienfuegos, M. Ribagorda, A. Parra, J. M. Cuerva *Nanoscale,* **2011**, *3*, 4003-4014.

Electronic transport in 'circle-like' graphene structures with a topological defect

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We investigate the transport properties of graphene layers with circle-like geometries with a topological defect as the structure shown in the Figure 1. We use a nanostructure of graphene with a circular shape (quantum dot) that includes a pentagonal defect at its centre. After dynamical relaxation using a Tersoff-Brenner potential we obtained its 3D arrangement where we obtain variations in bond lengths lower than 5%. In our calculations we therefore employ a tight-binding model and calculate electronic properties such as density of states and transmission function. We use the Green's function method [1] and the formalism developed by López Sancho *et al*. [2]. The density of states of this structure shows several peaks associated with both the presence of quasi-bound states (due to the circular confinement) and localized edge states due to circular boundaries of the finite lattice. These results are manifested in the peak structure in the transmission function and are checked calculating directly the local density of states and participation number obtained directly from the eigenstates. We observe a change in the available quasi-bound states due to the defect presence and new peak of the transmission. Other authors have made similar studies but considering different geometries: Zhang *et al.* [3] worked on transport with narrow ballistic ribbon of graphene with zigzag edges including topological defects. Carpio *et al.* [4] studied just electronic properties in a similar structure but with dislocations consisting of heptagon–pentagon pairs in an hexagon lattice.

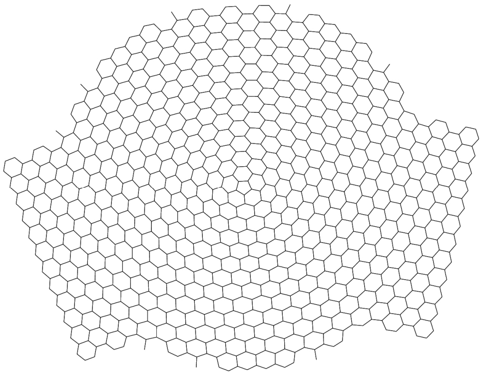

Figure 1: Geometry of the circle-like graphene sheet studied in this work. The pentagonal defect is placed at its centre. This structure is connected to 2 semi-infinite graphene leads, which are partially shown in the figure.

Thanks to DGAPA project PAPPIT IN112012 for financial support and sabbatical scholarship

[1] S. Datta, Electronic *Transport in Mesoscopic Systems* (Cambridge University Press, Cambridge 1995)
[2] M. P. López Sancho, J. M. López Sancho, J. Rubio, *J. Phys. F:Met. Phys.* **14**, 1205 (1984)
[3] Yanyang Zhang , Jiang-Ping Hu, B. A. Bernevig, X. R. Wang, X. C. Xie and W. M. Liu, *Phys. Rev. B* **78**, 155413 (2008). *Phys. Status Solidi A* **207**, 2726 (2010)
[4] Ana Carpio, Luis L. Bonilla, Fernando de Juan and María A. H. Vozmediano, *New Journal of Physics* **10**, 053021 (2008)

Spin Entanglement between a magnetic impurity and the electron in graphene: Thermal Effects

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Entanglement is a valuable resource in quantum information and represent a non local quantum correlation among two or more subsystem with no classical counterpart and has been an active subject of study [1]. Due to the graphene is represented as massles dirac fermions, this produces unique physical properties in the electronic and transport properties, klein tunneling etc [2]. However, less is known of what are the effects on the induced entangled properties of interacting particles embedded in a graphene layer. In this work we address this problem and study the spin entanglement between a magnetic impurity and the electron in a graphene layer. In this work, we consider the model of an electron in a graphene structure, within the tight binding approximation, that interact with the spin of a magnetic impurity localized in a graphene site through the Heisenberg exchange spin interaction. We present results for the entanglement properties of the ground state and the thermal effect. We characterize the degree of entanglement using the property of concurrence [3] and is computed as a function of the temperature and spin-spin amplitude interaction. We observe (see figure 1), in addition the known lineal behavior of the critical temperature (null entanglement) with the exchange Heisenberg coupling (EC), a critical EC where the temperature decreases or increases non-linearly. These are associated with existence of defect states, which are mixtures of singlet S and triplet T_0 spin states and not just the expected singlet S.

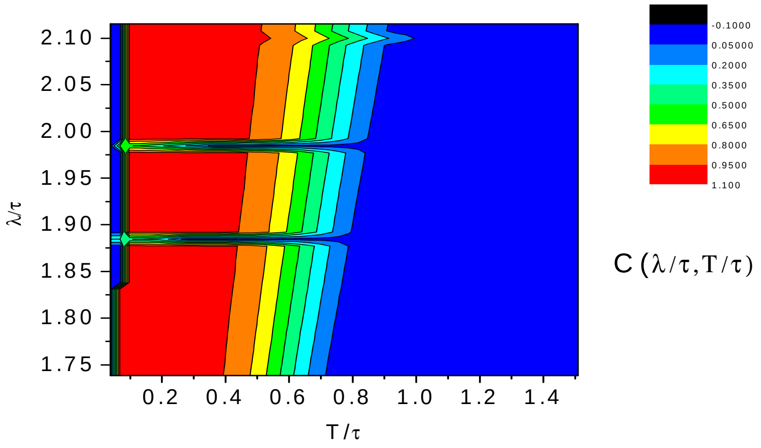

Figure 1: Contour plot of Concurrence C (degree of entanglement) as a function of temperature T (x-axis) and exchange coupling EC (y-axis). We observe a non-lineal decrease at certain values of EC. For a fixed temperature, around 0.2, C as a function of EC has maximum of 1 and two specific points (1.88, 1.96) with a sudden decreases of entanglement that is almost null

[1] R Hodorecki et tal , *Rev. Mod. Phys*. **81** 865 (2009)
[2] H. Castro Neto et al, *Rev. Mod. Phys,* **81** 109(2009)
[3]W. K. Wootter *Phys. Rev. Lett*. **80**, 22245(1998)

Thanks to DGAPA, project PAPPIT IN112012 for financial support and sabbatical scholarship for F. Rojas

Self-organization of addatoms in graphene: the Monte Carlo approach

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Thank to its remarkable properties graphene has been one of the most explored material in a recent few years. Very high carrier mobility, zero effective mass and long mean free path place graphene as a material for future electronics. Recent research shows that doped graphene becomes semiconducting even for a low concentration of adatoms [1,2]. In this regime one may not expect direct interaction between the adatoms. However, it turns out that the presence of mobile electrons, interacting with the adatoms, leads to an effective long range interaction between the dopants. This, in turn, may lead to their ordering or phase separation. In particular, the effective adatom-adatom interaction depends on whether they occupy the same or different sublattices. Because the dynamics of adatoms, compared to electrons, can be neglected and direct interaction (neglecting electronic correlations) exists only between the electrons and adatoms, doped graphene can be described by the Falicov-Kimball model [3] on a hexagonal lattice. We study this model with the Monte Carlo approach based on a modified Metropolis algorithm. It allows one to apply classical simulations for the systems with both classical and quantum degrees of freedom [4].

We consider the influence of doping on electronic properties of graphene. In particular, we demonstrate how formation of patterns of the addatoms leads to opening of a gap at the Fermi level in the electronic density of states.

Additionally, using the Reverse Monte Carlo method we calculate the effective interaction between the addatoms. We also perform DMFT calculations of intearction energy for two hydrogen adatoms on a graphene lattice as a function of their distance.

[1] A.V. Shytov, D.A. Abanin, L.S. Levitow, Phys. Rev. Lett. **103**, 016806 (2009).

[2] V.V. Cheianov, O. Syljuasen, B.L. Altshuler and V.I. Fal'ko, Europhys. Lett. **89**, 56003 (2010).

[3] L.M. Falicov and L.C. Kimball, Phys. Rev. Lett. **22**, 997 (1969).

[4]] M.M. Maśka and K. Czajka, Phys. Rev. B **74**, 035109 (2006).

Attractive interactions on graphene surface, a new steep to obtain new derivatives with potential applications

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The emergence of graphene has recently opened up a new field in the science and technology of two-dimensional nanomaterials with continuously growing interest. Graphene exhibits unique properties,[1] arising from its strictly single atomic layers of sp^2-bonded carbon atoms densely packed in a honeycomb crystal lattice. These properties generate huge interest from different application fields,[2] however they are also highly dependent on the number of layers of graphene. Unless well separated from each other, graphene tends to form irreversible agglomerates or recovers to form graphite through Van der Waals interactions.

Recently, our research group has developed a scalable and easy methodology for the exfoliation of graphite sheets through interactions with melamine (2,4,6-triamine-1,3,5-triazine) by ball milling processes in solvent free conditions. The milling treatments can be modulated in order to achieve graphene flakes with different sizes. Once graphite is exfoliated, the graphene layers can be dispersed in water and DMF at room temperature by means of soft sonication conditions. Moreover melamine can be removed by filtration and graphene samples are redispersed in fresh solvents forming stable dispersions during weeks.[4]

The methodology opens the way for an efficient processing of these materials. Once dispersions are obtained, it is possible to deposit graphene on different surfaces which could help to understand how this structure interacts with biological tissue/cells and how the biological targets respond to graphene. Ball-milling techniques can also help to prepare graphene sheets of different sizes and with a biocompatible coating. Moreover, once disperse in solvents, graphene can be functionalized by covalent or non covalent approaches providing multiple sites for the attachment of bioactive molecules or for the interaction with different polymers.

[1] (a) C. Lee, X. D. Wei, J. W. Kysar, J. Hone, *Science*, **2008**, *321*, 385-388. (b) K. S. Novoselov, A. K. Geim, *Nat. Mater*. **2007**, *6*, 183-191.
[2] P. Avouris, C. Dimitrakopoulos, *Materials Today,* **2012**, *15*, 86–97.
[3] H. Zhou, H. Dang, J. H. Yi, A. Nanci, A. Rochefort, J. D. Wuest, *J. Am. Chem. Soc.* **2007**, *129*, 13774-13775.
[4] V. León, M. Quintana, M. A. Herrero, J. L. G. Fierro, A. de la Hoz, M. Prato, E. Vázquez, *Chem. Commun,* **2011,** *47,* 10936-10938.

Hydrogen Peroxide Generation on a Pyridine-like Nitrogen-Palladium Doped Graphene surface

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We used density functional theory and molecular dynamics to study the interaction of two hydrogen molecules with a palladium atom anchored on a pyridine-like nitrogen defect on a graphene surface. The Quantum Espresso code [1] was used. We found that both molecules are adsorbed around the palladium atom, with adsorption energy 1.03 eV/H2. Then, we studied the interaction of two oxygen molecules with this system at atmospheric pressure and 300 K. Two hydrogen peroxide molecules are formed with adsorption energy 0.6eV/molecule. Then we increased the temperature to 800 K, and we found that the two hydrogen peroxide molecules remained bonded to the palladium atom.

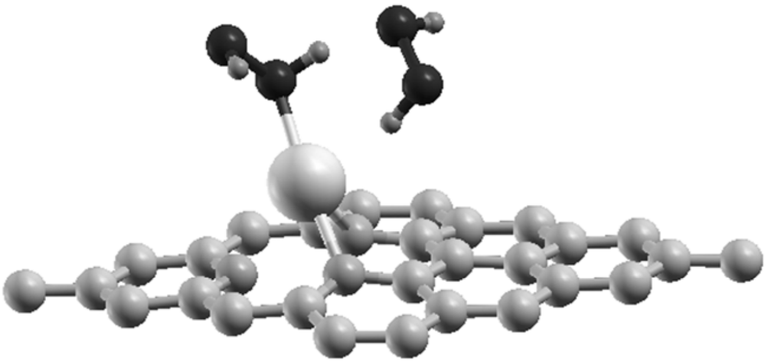

Figure 1: We show the system final configuration. We have two hydrogen peroxide molecules. One of them is bonded to the palladium atom anchored to the PNG.

[1] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, and R. M. Wentzcovitch, J. Phys.: Condens. Matter 21, 395502 (2009).

Interaction of Hydrogen and Oxygen Molecules with a Pyridine-like Nitrogen-platinum Doped Graphene Surface

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Using Density functional theory and molecular dynamics we studied the interaction of two hydrogen molecules around a platinum atom anchored on a pyridine-like nitrogen defect on a graphene surface. We found that only one molecule was adsorbed around the platinum atom and dissociated in this process. The adsorption energy was 2.6 eV. Then, the interaction of an oxygen molecule with this system is studied at atmospheric pressure and 300K. It is found that a water molecule is formed. This molecule remains physisorbed in this system. The remaining oxygen atom is bound to the platinum atom. We found that at 800 K, the hydrogen molecules are released, and the water molecule and the oxygen atom remain adsorbed. The Quantum Espresso code [1] was used.

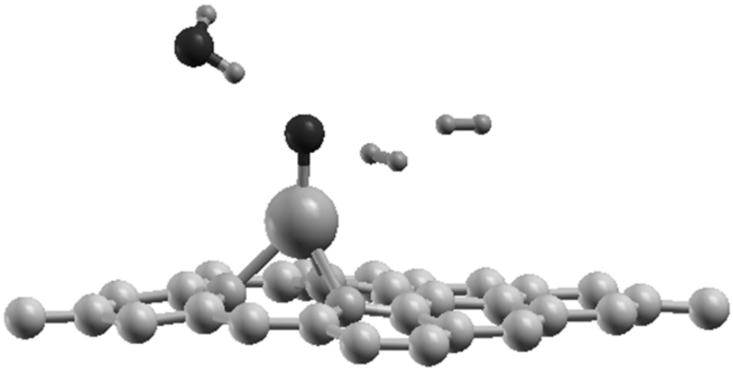

Figure 1: This is the system final configuration of. We have two hydrogen molecules, one oxygen atom bonded to the platinum atom anchored on the PNG, and one water molecule.

[1] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, and R. M. Wentzcovitch, J. Phys.: Condens. Matter 21, 395502 (2009).

Electronic and magnetic properties of nanographenes bonded to Cr_n and Co_n clusters

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We present Density Functional calculations of the electronic properties of small aggregates of two different transition metals, Cr_n and Co_n (n=1, 2, 4), interacting with small nanographenes with zigzag boundaries. We discuss the equilibrium geometries and the binding and formation energies, the electronic densities of states and the presence of different gaps for alpha and beta electrons, the structure of the edge orbitals which present p-d hybridization, the total magnetic moment of the combined systems, the distribution of the atomic magnetic moments and the charge and magnetic moment transfer between the metallic cluster and the nanographene. We pay special attention to the changes induced by the metallic clusters on the magnetic properties of the nanographene. In the case of Cr_n, we have considered two different triangular nanographenes (TNG) which present a net magnetic moment in their free ground state. For the Co_n aggregates we consider the interaction with a hexagonal nanographene (HNG) which has zero magnetic moment in its ground state.

The work was motivated by recent experiments on the interaction between Cr and Fe atoms with a free standing graphene structure [1].

Work supported by MICINN, Spain (Projects MAT2008-06483-C03-03 and MAT2011-22781). A. C. acknowledges the support of a grant ("Iniciación a la Investigación") of the University of Cantabria.

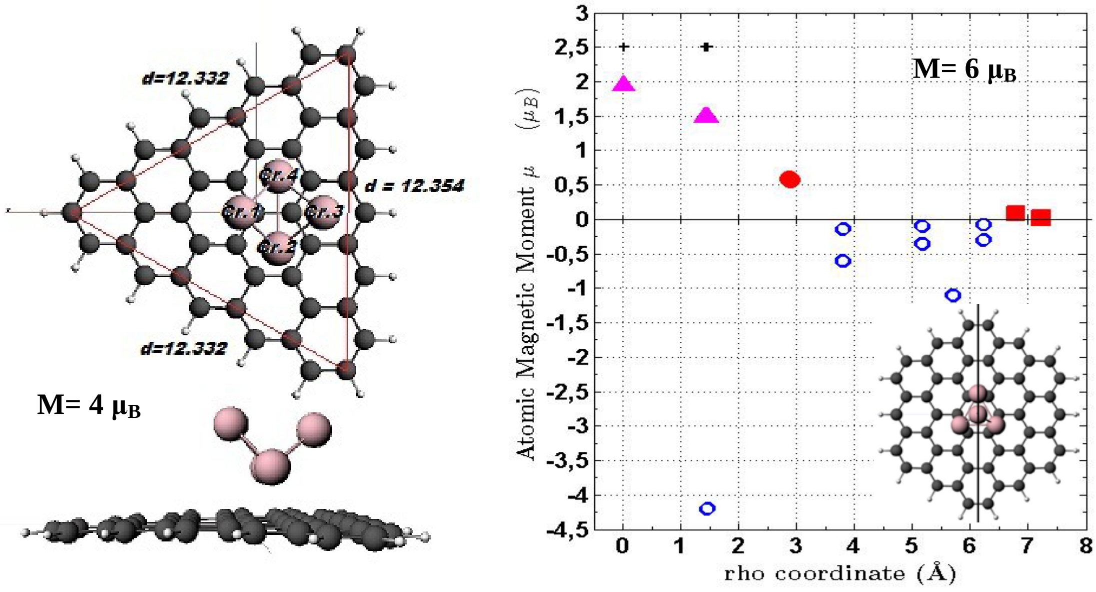

Figure 1: (Left) Equilibrium geometry for $Cr_4C_{46}H_{18}$(TNG) . The distances are in Å. (Right) Atomic magnetic moment for $Co_4C_{54}H_{18}$ (HNG) as a function of their distance to the centre of the HNG. Co (▲), C (●,○) and H(■). The values (+) are for Co in the free cluster. For C and H the values are multiplied by 100. In both figures M is the total magnetic moment.

[1] R. Zan, U. Bangert, Q. Ramasse, K. S. Novoselov, Nano Lett., **11** (2011),1087

Magnetic properties of Fe_2 and Fe_4 clusters adsorbed on a triangular nanographene

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Nanodevices that combine ferromagnetic materials with planar carbon nanostructures are being studied for their actual use in graphene-based nanoelectronics [1]. We present a theoretical study of the electronic and magnetic properties of small iron clusters adsorbed on a triangular carbon nanographene (TNG), using density functional theory (DFT). We use the ADF code [2] with the revPBE exchange-correlation functional. The atomic positions are optimized using a conjugate gradient method. The magnetic structure is analyzed using Mulliken atomic charges. The total magnetic moment is $M=(N_\alpha-N_\beta)\ \mu_B$, where N_α and N_β are the total numbers of majority and minority spin electrons.

The TNG has zigzag boundaries in which the dangling bonds are saturated with H atoms. The ground state of these finite TNGs presents a net magnetic moment which is mostly located at the zigzag boundaries [3]. In our case we obtain a net magnetic moment of $M=3\ \mu_B$ for the ground state of $C_{33}H_{15}$ TNG, as expected from the lattice population imbalance [3]. The isolated cluster Fe_4 has a distorted tetrahedral structure with a strong ferromagnetic coupling and total magnetic moment $M(Fe_4)=14\ \mu_B$. The dimer Fe_2 has $M(Fe_2)=6\ \mu_B$.

We have analyzed the interaction energy between the Fe_4 and the nanographene as a function of the distance between them for three different relative orientations, locating always the cluster over the center of the nanoflake. The most stable structure results when a triangular face of the iron cluster is parallel to the nanographene plane, with $M=13\ \mu_B$. Then we have considered two Fe_2 dimers located on opposite edges of the triangular structure and we have found that the most stable geometry corresponds to the two dimers vertically located on top of two of the outermost C atoms. We have analyzed two possibilities for the magnetic alignment of the dimers, resulting a lower energy for the parallel ($M_{FM}=15\ \mu_B$) than for the antiparallel structure ($M_{AFM}=1\ \mu_B$), with an energy difference $E_{AFM}-E_{FM}=29$ meV. The parallel structure has an energy $E_{FM}-E_0=1.94$ eV, higher than the ground state of the Fe_4-TNG system.

With respect to the Fe_4-TNG system, we have obtained a total reduction of 2.64 μ_B on the magnetic moment of the iron cluster, and an increment of 0.64 μ_B in the carbon structure. This increment is accumulated at the central hexagon of the TNG. The charge population analysis indicates a transfer from the iron aggregate to the carbon structure in the binding process (0.52 electrons in total). However, the changes on the magnetic moments are due mostly to the charge reorganization inside each subsystem and to a lower extent to the charge transfer. We obtain a large electronic gap for the alpha states and a negligible one for the minority spin.

Work supported by MICINN of Spain (Projects MAT2008-06483-C03-01 and -03, and MAT2011-22781), and by Junta de Castilla y León (Project VA158A11-2). P. V. acknowledges the support of a grant (“Iniciación a la Investigación”) of the University of Cantabria.

[1] R. Zan, U. Bangert, Q. Ramasse, K. S. Novoselov, Nano Lett., **11** (2011),1087; Y. Li, *et al.*, Applied Surface Science **257** (2011) *6059*; Y.-M. Lin, *et al.*, Science **332** (2011), 1294.
[2]C. Fonseca-Guerra, J.G. Snijders, G. te Velde, and E.J. Baerends, Theor. Chem. Acc. **99** (1998) 391.
[3] J. Fernández-Rossier, J. J. Palacios, Phys. Rev. Lett. **99** (2007), 177204.

Pulling graphyne out of the plane

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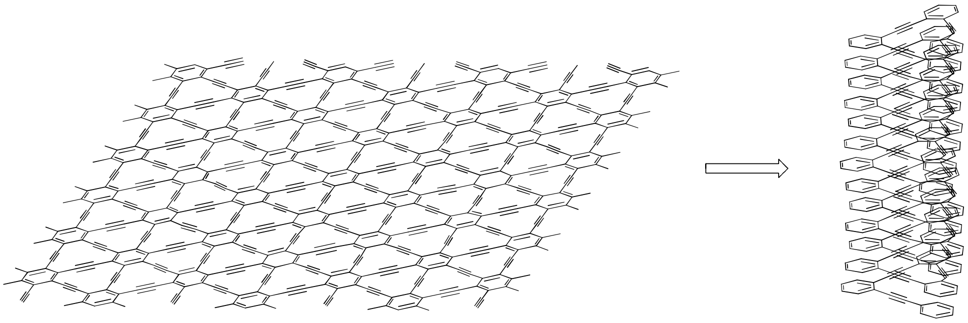
Graphene is the most famous 2D carbon allotrope. Nevertheless, graphene is not the only possible 2D periodic carbon-rich scaffold. Graphyne, graphdiyne and an infinite variety of conjugated backbones represent an active scope of research owing to their potential applications as optoelectronic materials.[1] The structural versatility of carbon atoms allow to go further and three-dimensional conductive arrays are also feasible. For example, graphyne basic structure can be transformed into a nanocoil. Carbon nanocoils (CNCs) [2] are carbon allotropes with tubular diameters down to 20 nm. They have been used to generate magnetic fields emulating the behaviour of a solenoid [3] and shown pseudoelastic properties allowing elongations up to 42%. [4] In a broad sense, [*n*]-helicenes and *o*-phenylenes can be considered CNCs but they have extremely rigid backbones in the axial direction and densely packed π-systems. Hence, the expected electron transport (ET) through the helical backbone could be hindered by ET through the π-stacked rings.[5] On the other hand, conformationally flexible *o*-phenylene-ethynylene oligomers (*o*-PEOs) can adopt helical arrangements by means of supramolecular/covalent interactions leading to the corresponding less tight graphyne-based CNCs. Here we present our ongoing efforts to broaden these carbon-based structures, mainly graphyne, into the third dimension and to study their specific properties.



[1] D. Malko, C. Neiss, F. Viñes, A. Görling, *Physical Review Letters*, 2012, **108**, 086804.
[2] N. Tang, W. Kuo, C. Jeng, L. Wang, K. Lin and Y. Du, *ACSNano* 2010, **2**, 781-788.
[3] K. Yamamoto, T. Hirayama, M. Kusunoki, S. Yang and S. Motojima, *Ultramicroscopy* 2006, **106**, 314-319.
[4] . Chen, S. Zhang, D. A. Dikin, W. Ding, R. S. Ruoff, L. Pan and Y. Nakayama, *Nanolett.* 2003, **3**, 1299-1304.
[5] E. Ohta, H. Sato, S. Ando, A. Kosaka, T. Fukushima, D. Hashizume, M. Yamasaki, K. Hasewaga, A. Muraoka, H. Ushiyama, K. Yamashita and T. Aida, *Nature Chem.* 2011, **3**, 68-74.

Graphene nanoribbon functionalization for electronic applications

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Graphene nanoribbons (GNRs) have come into the picture as promising candidates for the design of electronic devices, due to their finite width and distinct electron confinement, opening a band gap in a useful range for electronic and solar cell application. According to previous studies, armchair GNRs below 3 nm in width present band gaps that fall in the same range of the current worldwide-used semiconductors materials, while zigzag GNRs have shown to present a band gap close to zero. Furthermore, a periodicity in the band gap of armchair GNRs exists as the width of the GNR increases, which makes the band gap strongly dependent on the width.[1] Thus, a proper characterization of GNRs is crucial to predict their electronic properties.

In this work, a thorough analysis concerning the effect of chemical functionalization on the band gap is performed for both zigzag and armchair GNRs. The periodicity in the band gap values for armchair GNRs is explained by analyzing the aromaticity within the framework of Clar's Sextet Theory.[2] The aromaticity distribution obtained resembles the patterns already described for CNTs,[3,4,5] and it is shown that length is in CNTs what width is in GNRs, which finally ends up in a similar electron confinement and an equal aromaticity distribution.[2]

Fluorine, Oxygen and Hydrogen edge functionalization are considered in order to control both the aromaticity patterns and the band gap values. Even more, a way to open a band gap on zigzag GNRs by selective edge functionalization is shown. It demonstrates that rational tuning of the band gap can be performed, allowing the application of GNRs in semiconducting devices.

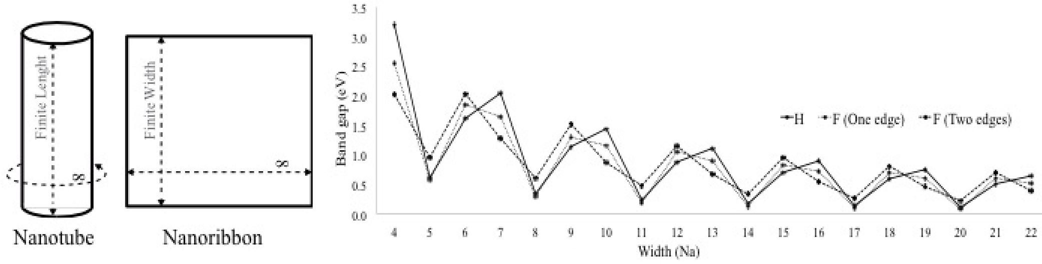

Figure 1: Schematic representation of the similar electronic confinement in CNTs and GNRs (left). Band gap tuning by fluorine functionalization (right).

[1] Barone, V.; Hod, O.; Scuseria, G. E. *Nano Lett.* 6, 2748 (2006)
[2] Martin-Martinez, F.J.; Fias. S.; Van Lier, G.; De Proft, F.; Geerlings, P. *Chem. Eur. J.* 18, 6183 (2012) (+ Cover)
[3] Matsuo, Y.; Tahara, K.; Nakamura, E. *Org. Lett.* 5, 3181 (2003)
[4] Martin-Martinez, F.J.; Melchor, S.; Dobado J.A. *Org. Lett.* 10, 1991 (2008)
[5] Martin-Martinez, F.J.; Melchor, S.; Dobado J.A. *PCCP* 13, 12844 (2011)

NanoLEDs with graphene electrode

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Nitride nanocolumns (III-N NCs) are the subject of intense research since the past decade because of their unique properties and potential electronic and optoelectronic applications. NCs are usually grown on Si(111), Si (100), SiC, and sapphire substrates by a self-assembly process using plasma-assisted molecular beam epitaxy [1-3]. NCs are excellent candidates to develop arrays of highly efficient nanolight-emitters in the infrared-visible-ultraviolet range.

Normally, the transparent conducting electrode used for the light emitting diodes (LEDs) is the indium tin oxide (ITO), but this material has a high cost and is instable in the presence of acids or bases and has poor transparency in the blue and near-infrared light ranges [4]. Furthermore the need for a substitute for ITO is ever increasing due to the limited availability of indium on earth [5]. Graphene is the ideal candidate in order to replace the ITO due to its excellent electrical, optical and mechanical properties.

In this work, we propose the use of a graphene layer as a transparent electrode for the fabrication of GaN nanoLEDs. The higher electrical conductivity of the graphene electrode and its flexibility makes it the best material for contacting all the nanocolumns.

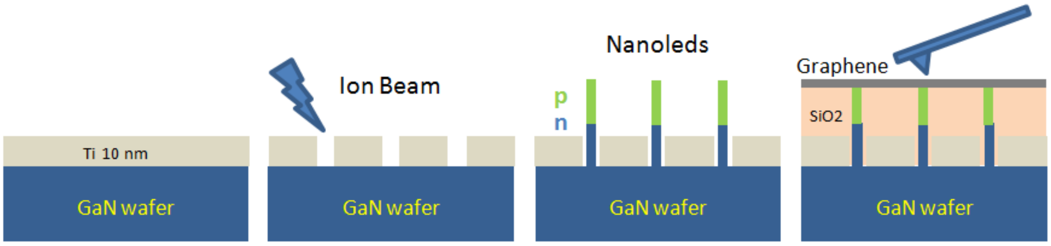

Figure 1: Fabrication scheme of the GaN nanoLEDs.

[1] M. Yoshizawa, A. Kikuchi, M. Mori, N. Fujita, K. Kishino, *Jpn. J. Appl. Phys.* **36** (1997) L459.
[2] M. A. Sanchez-Garcia, E. Calleja, E. Monroy, F. J. Sanchez, F. Calle, E. Muñoz , R. Beresford, *J. Cryst. Growth* **183** (1998) 23.
[3] L. Cerrutti, J. Ristic, S. Fernandez-Garrido, E. Calleja, A. Trampert, K. H. Ploog, S. Lazic, J. M. Calleja, *Appl. Phys. Lett.* **88** (2006) 213114.
[4] G. Jo, M. Choe, C. Y. Cho, J. H. Kim, W. Park, S. Lee, W. K. Hong, T. W. Kim, S. J. Park, B. H. Hong, Y. H. Kahng, T. Lee, *Nanotechnology* **21** (2010) 175201.
[5] H. Park, J. A. Rowehl, K. K. Kim, V. Bulovic, J. Kong, *Nanotechnology* **21** (2010) 505204.

Charge transfer in graphene flakes covered with metals probed by Raman spectroscopy

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In order to build graphene-based devices, it is necessary to know how graphene is going to behave when different metals are deposited on it. Mainly, the difference in work function between graphene and the metal would cause a transfer of electrons which is expected to be from the material of lower work function to the higher one. The doping implies a change on the electron-phonon interaction and the most effective method to detect this change is by means of Raman spectroscopy [1], [2]. Sometimes, the change observed is opposite to what would be expected in terms of work function differences, which means that other phenomena, mainly stress, must explain this anomalous change.

In this study, 3nm of diverse metals were evaporated by electron beam evaporation over graphene flakes, previously grown by mechanical exfoliation on 285nm of SiO_2 substrate. The Raman spectra of all the metals except that of cobalt show a similar behaviour. On the cobalt-graphene spectrum, two new peaks appear at ~1130cm^{-1} and ~1520cm^{-1} which do not correspond to uniaxial strain but maybe to more intrinsic cobalt-graphene bonding properties, definitely different from the ones of the other metals studied.

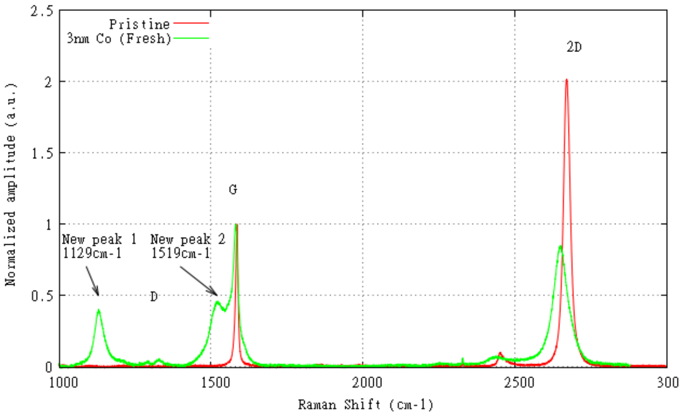

Figure. 1: Raman spectrum of a cobalt-graphene sample (normalized to the G peak intensity after background removal).

[1] A. Jorio, M. Dresselhaus, R. Saito, G.F. Dresselhaus. *Raman Spectroscopy in Graphene Related Systems.* Wiley-Vch.

[2] A. Ferrari. *Raman spectroscopy of graphene and graphite: Disorder, electron-phonon coupling, doping and nonadiabatic effects.* Solid State Communications 143 (2007) 47- 57

Elastic Properties of Epitaxial Graphene from angle-resolved vibrational experiments on phonon dispersion

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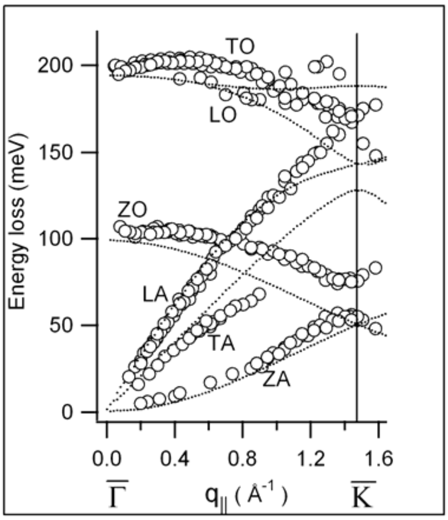
Ultra perfect graphene monolayers can be epitaxially grown on many single crystal metal surfaces under Ultra High Vacuum conditions [1]. These graphene layers are spontaneously nanostructured forming a periodic array of nanoripples caused by the difference in lattice parameter between graphene and the different substrates. The periodicity of the ripples is 2-3 nm depending on the metal substrate. The elastic properties of epitaxial graphene have been estimated by the analysis of the phonon dispersion measured by using angle-resolved energy loss spectroscopy [2]. The sound velocities for longitudinal and transverse acoustic waves have been extracted by the phonon dispersion curves, together with the interatomic force constants. The elastic properties of a macroscopical graphene sample grown on Pt(111) showed values similar to the theoretical strength for free-standing graphene. In particular, we found a Poisson's ratio of 0.19 and a Young's modulus of 342 N/m [4] Our results indicate that the excellent crystalline quality of graphene grown on metal substrates leads to macroscopic samples with high tensile strength and bending flexibility. This opens the possibility to use graphene for electromechanical devices and for carbon-fiber reinforcements, in spite of its hitherto difficult application in technology due to the presence of defects and grain boundaries in suspended graphene membranes.

[1] R. Miranda and A.L. Vázquez de Parga, Nature Nanotechnology 4, 549 (2009)
[2] A. Politano at al. Phys. Rev. B 84, 033401 **(**2011).
[3] A. Politano at al, to be published



Dispersion relation for phonons obtained from High Resolution Electron Loss Spectroscopy data recorded on epitaxial graphene grown on Pt(111).

A evaluation of quality of few-layer graphenes synthesized by plasma

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In recents years, graphene has become a novel material with many potential applications in electronic, as supercapacitors[1]; or a chemical synthesis, a chemical routes derived of graphene oxide[2]. For the development of these applications, an important point to consider is the quality of graphene materials, Raman spectrocopy being the most widely used technique for the evaluation of the quality[3].

We synthesized graphene layers by plasma using n-hexane as the starting hydrocarbon material. To form the plasma, argon was introduced to the reactor and a auxiliary gas (H_2, N_2, air,etc.) to study the quality of nano-graphene synthesized by this novel route.

The reactor and the method of synthesis are protected by patent.

The Raman spectra (figure 1) and TEM images (figure 2) demonstrate the nature of the species synthesized.

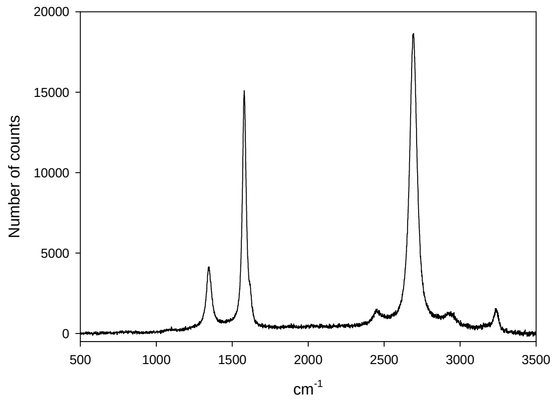

Figure 1: Raman spectra of a few-layer graphene

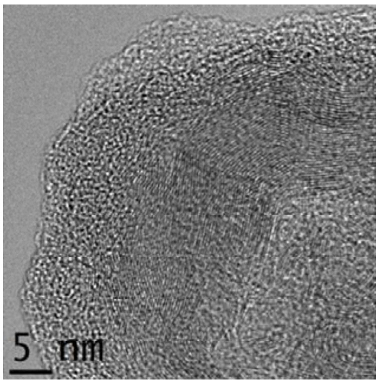

Figure 2: TEM image of a few-layer graphene

[1]Vivekchand S.R.C, Rout C.S, Subrahmanyam K.S, Govindaraj A, Rao C.N.R *Graphene-based electrochemical supercapacitors,* Journal of Chemical Sciences 120 (2008) 9-13.
[2]Dreyer D.R, Park S, Bielawski C.W, Ruoff R.S, *The chemistry of graphene oxide,* Chemical Society Reviews 39 (2010) 228-240.
[3]Ferrari A.C, Meyer J.C, Scardaci V, Casiraghi C, Lazzeri M, Mauri F, Piscanec S, Jiang D, Novoselov K.S, Roth S, Geim A.K. *Raman spectrum of graphene and graphene layers,* Physical Review Letters 97 (2006) Article number 187401.

ELECTROMAGNETIC DEVICES BASED ON GRAPHENE AND CARBON NANOTUBES: A NUMERICAL APPROACH

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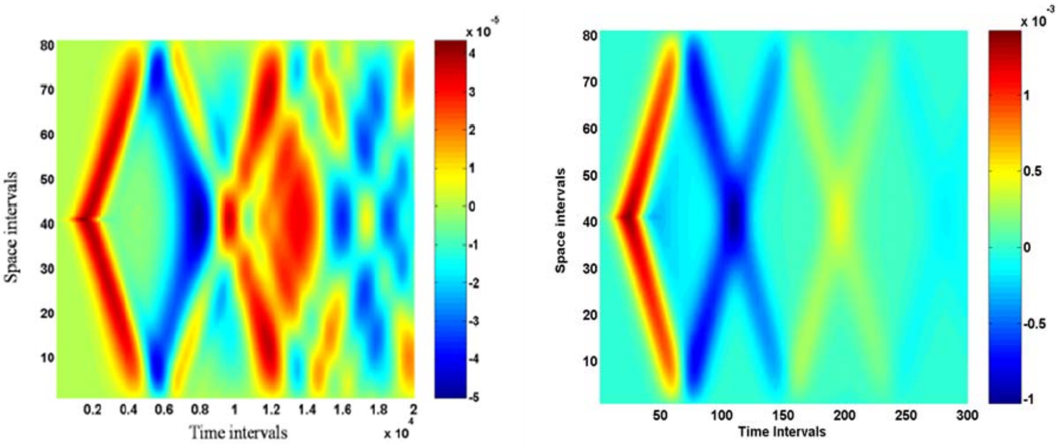
In this communication, we summarize the recent contributions developed in the Electromagnetics Group of the University of Granada for the numerical modeling of the electrodynamics of graphene and carbon nanotubes structures. Still in an early stage of research, the understanding of the possibilities offered by those structures to applied electromagnetic devices remains an open issue. Some topics, as the radiation and scattering of electromagnetic waves or the surface electromagnetic waves propagation in those structures, will be reviewed through numerical simulations of the time-domain Maxwell's equations, which provide a physical insight of the electrodynamics phenomena involved. Additionally, some thoughts about the key and unsolved issues from an engineering point of view, as well as comparisons with other existing technologies and devices will be discussed.



(a) (b)

Figure 1: Comparison of time-domain surface currents (amps) for: a) an armchair carbon nanotube dipole of 3 µm length and 13.56 nm radius, and b) silver metallic nanowire dipole of 0.2 mm length and 100 nm radius.

[1] M. F. Pantoja, D. H. Werner, P. L. Werner, A. R. Bretones, *TDIE modeling of carbon nanotube dipoles at microwave and terahertz bands*, (IEEE Antennas and Wireless Propagation Letters, 2010)
[2] M. F. Pantoja, M. G. Bray, D. H. Werner, P. L. Werner, and A. R. Bretones, *A computationally efficient method for simulating metal-nanowire dipole antennas at infrared and longer visible wavelengths*, (IEEE Transactions on Nanotechnology, 2012)
[3] A. Vakil, N. Engheta, *Transformation Optics Using Graphene*, (Science, 2011)

Reduced graphene oxide-mesoporous silica nanoparticle composites

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Reduced graphene oxide-mesoporous silica nanoparticle (RGO-MSN) composite sheets have been prepared by selective growth of MSNs a few tens of nanometers in diameter onto graphene oxide. The synthesis procedure was based on cationic surfactant templating of the nanoparticles followed by a heat treatment step to thermally reduce the graphene oxide sheets and remove the surfactant from the silica mesopores [1]. The MSNs could be produced with varying densities on the RGO support, from isolated objects (Fig. 1a) to close-packed monolayers that uniformly covered both sides of the sheet (Fig. 1b), with internal mesopores ~3.7-4.0 nm wide. The experimental conditions that allowed the generation of the MSNs selectively on the RGO sheets have also been investigated and discussed [2].

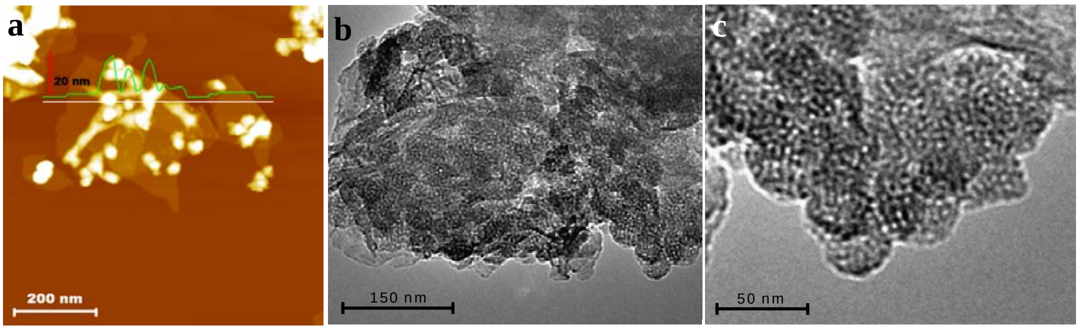

Figure 1: (a) Atomic force microscopy image of isolated MSNs grown onto RGO sheets. (b) Transmission electron microscopy (TEM) image of a close-packed monolayer of MSNs covering both sides of a sheet. (c) TEM image showing the mesoporous structure of individual MSNs.

[1] S. Yang, X. Feng, L. Wang, K. Tang, J. Maier, K. Müllen, Angew. Chem. Int. Ed. 49 (2010), 4795-4799.

[2] L. Guardia, F. Suárez-García, J.I. Paredes, P. Solís-Fernández, R. Rozada, M.J. Fernández-Merino, A. Martínez-Alonso, J.M.D. Tascón, Microporous Mesoporous Mater 160 (2012), 18-24.

Promoting processes in aqueous graphene oxide dispersions with UV light: graphene oxide reduction, formation of hybrids with metal nanoparticles and dye degradation

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The production of well-dispersed, stand-alone graphene sheets by UV-assisted photoreduction of aqueous graphene oxide suspensions has been accomplished without the need of any photocatalysts or reducing agents (Fig. 1a and 1b). Reduction of the graphene oxide sheets is believed to occur as a result of local photothermal processes induced by intense UV irradiation (~1 W cm^{-2} at the surface of the dispersion). This UV-based approach allows carrying out additional processes in aqueous medium, including the synthesis of metal nanoparticles on the graphene sheets (Fig. 1c and d for a graphene-gold nanoparticle hybrid), or the degradation of a dye molecule (rhodamine B), the latter performed in the presence of only graphene oxide. Some potential applications of the graphene-gold nanoparticle hybrids synthesized by UV irradiation have also been explored, including their use as surface enhanced Raman scattering substrates (Fig. 1d) or as catalysts (Fig. 1f).

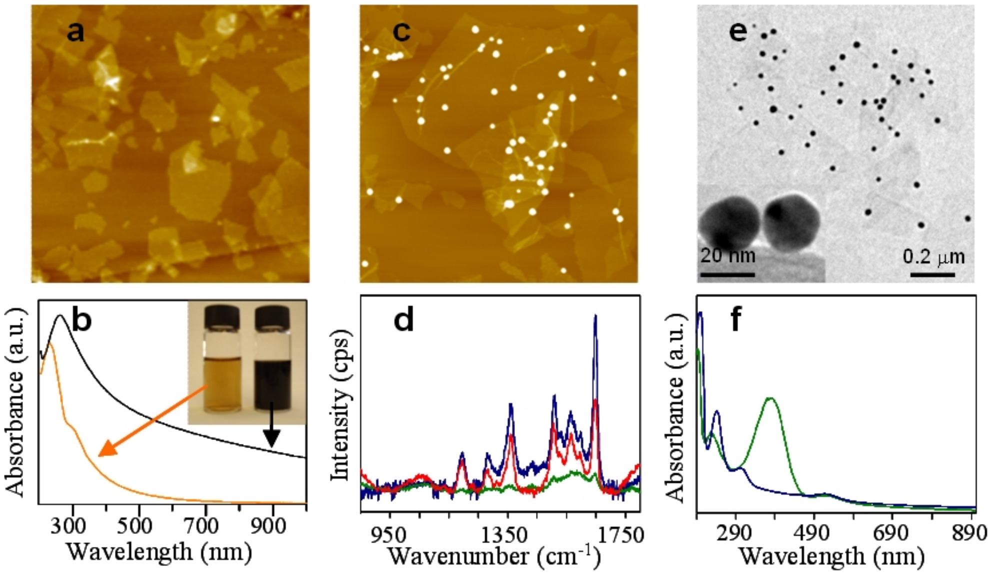

Figure 1: (a) Atomic force microscopy (AFM) image of photoreduced graphene oxide sheets. (b) UV–vis spectra of as-prepared (orange) and UV-irradiated (black) graphene oxide dispersions. Inset: pictures of both dispersions. (c) AFM image of graphene–gold nanoparticle hybrids prepared by UV irradiation of mixed graphene oxide/$HAuCl_4$ solutions. (d) Raman spectra of rhodamine B deposited onto SiO_2/Si (green) and SiO_2/Si covered with only gold nanoparticles (red) or with graphene–gold nanoparticle hybrid (blue). (e) Transmission electron microscopy image of graphene-gold nanoparticle hybrid. Inset: detail of individual nanoparticles. (f) UV–vis spectra of *p*-nitroaniline in an aqueous graphene–gold nanoparticle dispersion before (green) and after (blue) reduction with $NaBH_4$.

Mechanical properties of a novel graphene /ultra high molecular weight polyethylene composites. Effect of gamma irradiation

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Ultra high molecular weight polyethylene (UHMWPE) is a thermoplastic polymer widely used in industry components and in total hip and knee replacements, due to their mechanical properties and excellent biocompatibility. Carbon fiber reinforced UHMWPE was an attempt to obtain better mechanical and tribological performances of UHMWPE in bearing prostheses [1]. Recently, composites of multi-wall carbon nanotubes have been reported with promising mechanical properties and scavenger effect for the free radical generated by gamma irradiation [2]. This is the mainly used method for crosslinking this semicrystalline polymer and obtaining a higher wear resistance behaviour. The intrinsic mechanical properties of graphene has allowed that new composite materials emerge in order to obtain new materials with better stiffness, toughness and fatigue behavior.

In the present work, novel graphene/UHMWPE composites were prepared using a ball milling process and subsequent compression moulding. Raw UHMWPE, 0.5 % wt graphene /UHMWPE composite and both materials irradiated at 90 kGy gamma doses were studied by uniaxial tensile test in order to assess the influence of the graphene reinforcement, and the interaction between the graphene and the radical free generated by the irradiation in the polymeric matrix.

The results point out increases in the elastic secant modulus and yield stress close to 10 % when the UHMWPE is reinforced with 0.5 % wt of graphene. However, the work of fracture undergoes an appreciable reduction due probably to the presence of graphene aggregates which introduce stress concentrator effects. The influence of gamma irradiation in both compounds is positive respect to the stiffness and negative to the toughness. It points out the absence of favourable interactions between graphene and the host matrix. Differential scanning calorimetry (DSC) and dynamic mechanical-thermal analysis (DMTA) were also performed to evaluate the influence of the graphene and the gamma irradiation in the molecular dynamics of this new composite.

[1] Farling G, inventor; Zimmer Inc., assignee. Human body implant of graphitic carbon fiber reinforced UHMWPE. United States Patent No. 4, 055,862; 1977

[2] Martínez-Morlanes MJ, Castell P, Alonso P.J., Martinez MT, Puértolas JA. Carbon 50 (2012):2442-2452.

From hybrid multifunctional multilayers towards monolayer systems

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Owing to the manifold of attractive properties that are intrinsic to molecules (lightness, biocompatibility and easy processability for instance), molecule-based materials are nowadays a key area within materials science. Molecular building blocks provide a wide range of functionalities that may be combined at will. This sets the basis of the hybrid multifunctional materials. A more recent alternative for the synthesis of multifunctional materials takes advantage of the combination of molecular components with solid-state inorganic structures. This new strategy paves the way for obtaining hybrid systems that combine the robustness of an inorganic host with the versatility of molecular building blocks. So far, the method has opened the door for the combination of what are considered to be two antagonistic states of matter in a multilayer system: ferromagnetism and superconductivity as shown in [1]. This technique relies on the facile exfoliation of the layered inorganic solid-state counterpart, which is built from the stacking of neutral weakly-interacting 2D layers. One may therefore easily envision the isolation of individual crystalline sheets of the inorganic host as firstly reported by Novoselov *et al.* at [2]. Either mechanically or via wet chemistry methods, monolayers may be conveniently deposited on a wide variety of surfaces. It is the starting point of an all-new strategy for the synthesis of multifunctional multilayers and for their application in potentially sensing devices.

Herein we report the exfoliation and characterization of variable thickness bidimensional flakes of dichalcogenide functional materials. Scanning Probe Microscopies have been extensively used to map and even to manipulate the chemical nature of such surfaces.

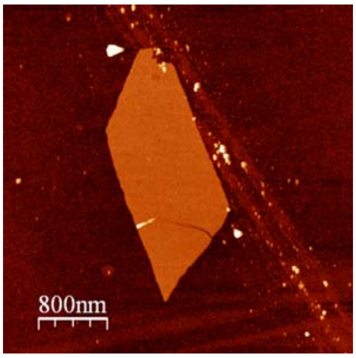

Figure 1: 4 µm x 4 µm AFM image of one monolayer of TaS_2 on a Si (100) surface.

[1] E. Coronado, C. Martí-Gastaldo, E. Navarro-Moratalla, A. Ribera, S. Blundell, P. Baker, *Nature Chem*, *2*, 1031–1036 (2010)
[2] K. S. Novoselov, D. Jiang, F. Schedin, T. J. Booth, V. V. Khotkevich, S. V. Morozov, and A. K. Geim, *Proc. Natl. Acad. Sci. USA* 102, 10451–10453 (2005)

Study of the process parameters on the CCVD growth of graphene on Cu foil

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Graphene, a two dimensional mono-layer of sp^2 bonded carbon atoms, has been the focus of much research because of its unique and desirable properties [1].

Graphene was grown using via ambient pressure methane Catalytic Chemical Vapour Deposition (CCVD), that is considered as one of the most promising synthesis technique, thanks to its capability of producing large area deposition [2]. Here, we present CCVD on 25 µm thick copper foil, to fabricate few-layer graphene films. We investigated, in chemical regime, the effects of growth parameters such as Cu foil crystallographic orientation, reaction time, methane and hydrogen concentrations, feed composition, in presence of on-line analyzers able to monitor the concentration of the exhaust stream form the reactor, on graphene characteristics. The pyrolysis was carried out in a laboratory apparatus consisting of a continuous flow vertical arranged micro-reactor, fed by methane, nitrogen and hydrogen. Mass flow controllers (M.F.C.) were used, in order to assure constant flow rate.

Graphene was characterized using micro-Raman spectroscopy and X-ray diffraction (see Figure 1), Scanning (SEM) and Transmission (TEM) Electron Microscopy.

A set of experiments have been conducted on Cu foils by varying: methane and hydrogen concentrations in feed, reaction time and the cooling rate. After synthesis graphene was transferred on a suitable substrate: first of all gluing on the carbon layer a thermal release tape by applying soft pressure; followed by an etching to remove the Cu foil; and finally transferring the few layers graphene film on glass applying uniform pressure at 80°C.

In conclusion, we have successfully synthesized few layers graphene film on polycrystalline Cu foil using via ambient pressure CCVD that was successfully transferred on glass substrate.

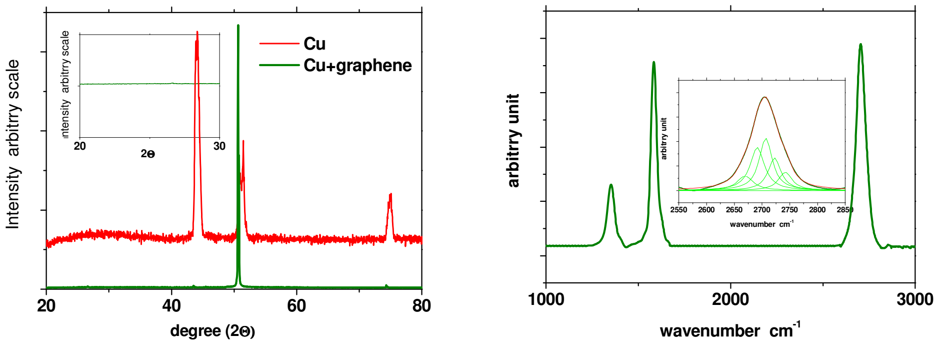

Fig. 1: X-ray diffraction pattern of Cu and Graphene on Cu. Raman spectrum of graphene on Cu foil.

[1] A. K. Geim, K. S. Novoselov, Nature Materials, (2007)

[2] A. Reina, S. Thiele, X. Jia, S. Bhaviripudi, M.S. Dresselhaus, J.A. Schaefer, J. Kong, Nano Research, (2009)

Giant Magnetoresistance with Temperature-dependent Crossover in $FeNi_3$-graphene Nanocomposites

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A low-temperature route for the synthesis of $FeNi_3$-graphene nanocomposites is described. The soft chemical approach here employed involves the thermal decomposition of a hybrid Layered Double Hydroxide (LDH) precursor, a sebacate-intercalated NiFe-LDH.[1] The as-synthesized nanocomposites consist on ferromagnetic $FeNi_3$ nanoparticles embedded in a few-layers graphene matrix, whose conductivity can be tuned with temperature, thus offering the possibility of modulate the MR behavior. A dramatic temperature-dependent crossover from positive room-temperature Giant Magnetoresistance (GMR) to negative Low-field Tunneling Magnetoresistance (LFTMR) below 50 K is observed in these nanocomposites. Moreover, two clearly different behaviors have been discovered, being the temperature barrier ca. 50 K. The low-temperature behavior is particularly sensitive to low magnetic fields.

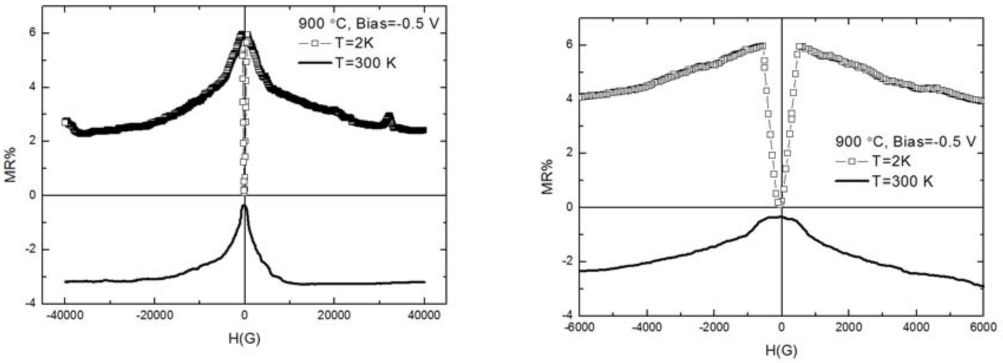

Figure 1: *left*, magneto-resistance for $FeNi_3$-graphene nanocomposite synthesized at 900 ºC, and *right*, zoom in of the low magnetic field range.

Our GMR granular nanocomposites can operate at room temperature or low fields in contrast to multilayered GMR materials, where a high magnetic field is required to saturate the MR, suggesting promising applications as GMR sensors.[2] This work represents a straightforward methodology based on chemical synthesis for the preparation of magnetoresistance materials. The synthetic method described here should be easily expanded to the preparation of different materials composed of magnetic nanoparticles in intimate contact with graphene, just by changing the nature of the LDH precursor.

[1] Gonzalo Abellán, Eugenio Coronado, Carlos Martí-Gastaldo, Antonio Ribera, Juan F. Sánchez-Royo, *Chemical Science*, (**2012**), *3*, 1481.
[2] Gonzalo Abellán, Eugenio Coronado, Helena Prima-García, *to be Submitted*.

Effect of gamma-irradiation on graphene obtained from different sources

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The effect of gamma irradiation on two different graphene materials was evaluated. The materials were obtained by two different strategies: the first method was based on the reduction of graphene oxide [1] and the second method was based on the unzipping by chemical oxidation of multiwalled carbon nanotubes (MWCNTs) obtained by the arc discharge method [2]. The materials obtained with these two strategies was afterwards gamma irradiated at different doses (60, 90 and 150 kGy) to evaluate their effect on the properties of graphene. The material was completely characterized by X-Ray Photoelectron Spectroscopy (XPS), Raman Spectroscopy The XPS data showed that the gamma irradiation reduced the oxygen content in both graphene materials, and the restoration of the sp^2 structure was noticeable at the highest irradiation dosages. Raman spectroscopy indicated that the G band intensity increased in the irradiated samples due to a graphitization effect resulting from reorganization on the sp^2 structure on the graphene surface previously observed in MWCNTs [3]. The two different graphene based materials showed similar tendencies after gamma irradiation by XPS and Raman spectroscopy. Electron Spin Resonance (ESR) data were also carried out in all the studied material and further analysed.

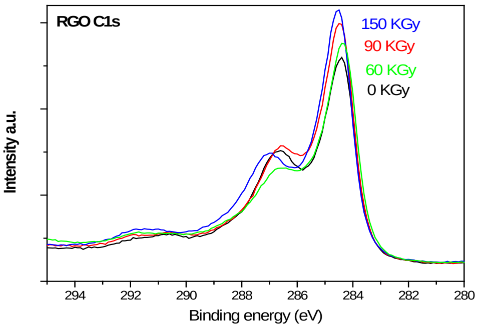

Figure 1: C1s región of the XPS spectra of the gamma irradiated RGO

[1] C. Vallés, J.D. Nuñez, A.M. Benito, W.K. Maser, *Carbon* 50 (2012), 835
[2] A.L. Higginbotham, D.V. Kosynkin, A. Sinitskii, Z. Sun, J.M. Tour, ACS Nano, 4 (2010) 2059-2069.
[3] P. Castell, M.J. Martinez-Morlanes, P.J. Alonso, V. Martinez-Nogues, M. T. Martinez, J. A. Puertolas *J. Biomedical Materials Research B* Under revision 2012

Spectroscopic properties of oxidized and thiolated graphene quantum dots: A comparative study

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In recent years, the optical properties of carbon nanostructures (carbon nanotubes, carbon dots, nanographene, nanodiamond etc.) were deeply investigated by the scientific community [1-3]. Potential applications of these nanostructures in nanoelectronics, photonics and bio-imaging pushed the attention of the researchers towards the synthesis of new highly fluorescent carbon-based nanoparticles. Moreover the possibility to functionalize the carbon surface via covalent bonding with different molecules allows the synthesis of carbon nanostructures with a controlled solubility in different solvents.

Herein, we report a new method for the high yield isolation of strongly photoluminescent GQDs from oxidized carbon nanotubes (CNTs). Fluorescent nano-graphene quantum dots (GQD) have been isolated from oxidized carbon nanotube suspension with the aid of cysteamine molecules. The oxidized GQD (ox-GQD) were converted to thiol-functionalized GQDs (thio-GQD) in presence of a coupling agent.

The GQD were chemically characterized by means of X-ray photoelectron spectroscopy, while their dimensions were analyzed by atomic force microscopy analysis. The obtained GQD posses a lateral size of around 4-5 nm and an average height around 1.2 nm (associated to a bi or tri-layered graphene structure). The photoluminescence properties of oxidized and thiolated GQDs were investigated trough fluorescence spectroscopy. Both samples possess a good photoluminescence quantum yields ranging from the 3.2% for ox-GQD in water to 10.3% for thio-GQD in dimethylformamide (DMF).

The optical characteristics of these materials make then an excellent candidate for numerous applications in photonics, optoelectronics and bio-imaging. In addition, due to their intense luminescence and their high solubility in polar solvents like dimethylformamide and ethanol, thio-GQD can be of significant interest for applications such as phosphor in UV based light emitting diodes.

References

[1] L. Cao, X. Wang, M. J. Meziani, F. Lu, H. Wang, P. G. Luo, Y. Lin, B. A. Harruff, L. M. Veca, D. Murray, S. Y. Xie, Y. P. Sun *J. Am. Chem. Soc.* 129, (2007), 11318.

[2] S. T. Yang, X. Wang, H. Wang, F. Lu, P. G. Luo, L. Cao, M. J. Meziani, J. H. Liu, Y. Liu, M. Chen, Y. Huang and Y.-P. Sun *J. Phys. Chem.* C 113, (2009), 18110.

[3] X. Wang, L. Cao, F. Lu, M. J. Meziani, H. Li, G. Qi, B. Zhou, B. A. Harruff, F. Kermarrec Y. P. Sun *Chem. Commun.* (2009), 3774.

A perfect mirror for neutral atomic and molecular beams made from epitaxial graphene

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Although the discovery of electron diffraction by Davisson and Thompson in the 30´s was quickly followed by the development of Electron Microscopy by Ruska, the observation of He atom diffraction by Stern has not led to the development of He Atom Microscopy. This is due to the difficulty in accelerating or bending beams of neutral atoms, and, in general, in producing optic elements for atoms of meV energy. The only possible solution envisaged is based on curved mirrors that can focus a beam of neutral He atoms. The specular reflectivity of these mirrors has to be as large as possible [1]. The required perfection of the surface of the mirror (perfect on the atomic scale over several mm), however, has precluded this achievement so far, with maximum intensities being of the order of 1% of the He specular beam [2]

We report here that a single monolayer of graphene grown on Ru(0001) thin films deposited in turn on c-axis sapphire, shows an extrordinary high specular reflectivity for He and H_2 beams (23% and 7% of the incident beam, respectively) [3]. The quality of the angular distribution exceeds the one obtained from graphene/Ru(0001) single crystals [3]. The Debye temperature of the gr/Ru(0001) system is 1045 K [3] and the graphene mirror is thermally stable up to 1150 K and ambient resistent. This represents a significant step toward high-reflectivity curved mirrors for He atom microscopy

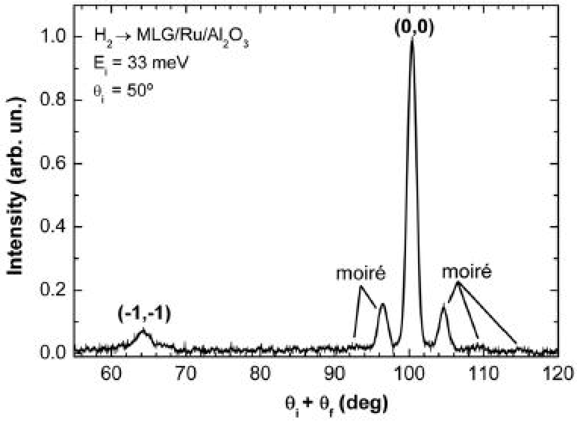

Figure 1: He reflectivity as a function of the scattering angle for a monolayer of graphene deposited on a 50 nm thick film of Ru(0001)/Al(0001)

[1] D. Barredo et al. Adv. Mater. **20**, 3492 (2008)
[2] D. Barredo et al. Appl. Phys. Lett. **96,** 081901 (2010)
[3] E. Sutter et al. Appl. Phys. Lett. **96,** 081901 (2012)
[4] A. Politano et al. Phys. Rev. B, **84**, 035450 **(**2011**)**

Intercalation of Pb underneath graphene on Ir(111)

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Graphene supported on metallic substrates is a widely studied subject, among other things because of the interesting moiré patterns arising from the lattice mismatch between graphene and the metal. However, interaction with the metal often leads to the supression of many interesting effects, like the inter-valley scattering between neighbouring Dirac cones of the surface Brillouin zone (SBZ) vertices, present in the case of non-metallic substrates [1]. A possible way to decouple graphene from the metallic substrates is the intercalation of an atomic layer of a different element between them, and indeed it has been recently shown that graphene on Si/Ru(0001) do present inter-valley scattering [2].

Here we study the graphene/Pb/Ir(111) system and show that, under the explored growth conditions, Pb enters through graphene-free patches and intercalates between graphene and iridium with a thickness limited to 1 ML. Our STM measurements indicate that in the Pb intercalated areas graphene preserves it's atomic and moiré periodicities, while signatures of the inter-valley scattering appear. Therefore this system could allow to study the interaction of the Dirac states with the superperiodicity imposed in the potential by the moiré pattern.

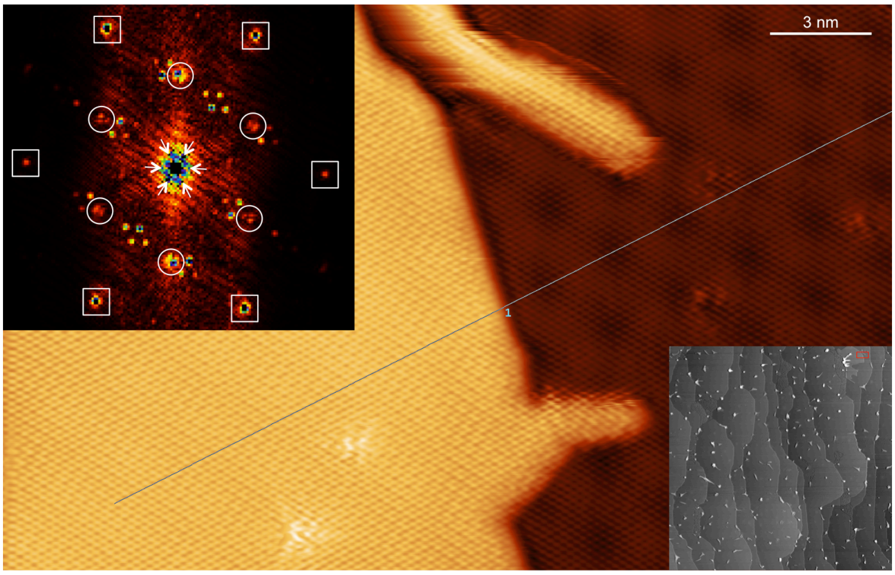

Figure 1: STM image acquired on graphene/Ir(111) with (left) and without (right) an intercalated Pb monolayer, recorded at -5 mV bias and 2.5 nA. Right inset: Larger scale image containing the corresponding area (red rectangle). Left inset: FFT map of the Pb part, where the squares circles and arrows mark the spots of graphene, its surface Brillouin zone vertices, and the spots of the moiré pattern respectively.

[1] G.M. Rutter et al, *Science* **317**, 219 (2007).
[2] J. Mao et al, *APL* **100**, 093101 (2012).

Formation of a spatially extended intermolecular band for TCNQ molecules on graphene/Ru(0001) measure by means of Scanning Tunneling Spectroscopy and DFT calculations

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The adsorption of molecules on graphene is attracting a great deal of attention for several reasons. First, appropriate molecular doping can be used to tailor the electronic properties of graphene, engineer its band gap or add magnetic functionalities. Another reason is the intrinsic interest in developing a chemistry of graphene, in analogy to the established chemistry of fullerenes and carbon nanotubes and, finally, because the graphene monolayer could efficiently isolate the molecules from the strongly interacting metallic substrates [1,2] and, accordingly, it could be used as an ideal playground to explore the mutual interaction between organic molecules in two dimensions.

Graphene on Ru(0001) presents a moiré pattern with a periodic chemical interaction between carbon atoms and the ruthenium, leading to a modulation in the electronic structure and surface potential [3,4]. In this communication, we show that early stages of 7,7',8,8'-tetracyano-*p*-quinodimethane (TCNQ) molecules growth on graphene on Ru(0001) occur in the lower areas of the moiré, where the surface potential is smaller, and the ordering is dominated by intermolecular attractive interactions which results in the formation of a compact monolayer.

Our scanning tunneling spectroscopy (STS) measurements and accurate Density Functional Theory (DFT) calculations show that molecules are negative charge due to a charge transfer from the substrate to the TCNQ molecules. The energy position and spatial distribution of the molecular frontier orbitals for a single molecule are measured by STS maps at 4.6 K in ultra high vacuum. When the molecular coverage is increased the molecules begin to form chains that finally cover completely the graphene surface. STM images show the formation of a tube like structures connecting the TCNQ molecules at the energies corresponding to the frontier molecular orbitals. The DFT calculations determine that the additional electrons transferred from graphene into the TCNQ molecules occupy the delocalized, spatially extended bands.

[1] S. Barja, M. Garnica, J.J. Hinarejos, A.L. Vázquez de Parga, N. Martín and R. Miranda. *Chem. Comm.* 46, 8198 (2010).
[2] J. Mao, H. Zhang, Y. Jiang, Y. Pan, M. Gao, W. Xiao, and H.-J. Gao. J. *Am. Chem. M. Soc.* 131, 14136 (2009).
[3] A. L. Vázquez de Parga, F. Calleja, B. Borca, M.C.G. Passeggi, J.J. Hinarejos, F. Guinea and R. Miranda, *Phys. Rev. Lett.* 100, 056807 (2008).
[4] B. Borca et al, *Phys. Rev. Lett.* 105, 036804 (2010).

Synthesis of chiral alcohols: A comparison between microorganism- and ruthenium-catalyzed reactions

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Key words: hydroxyesters, enantioselective reduction, *saccharomyces cerevisiae*

Nowadays a major concern for chemists is the design of new, low-cost and highly sustainable methodologies following green chemistry principles.[1] The use of water as solvent allows one to fulfill most of these requirements and catalysis in water represents a major area.[2] In this area we have studied catalysts for ATH reduction of ketones in water and reported on ruthenium-based catalysts which are reusable both with the same substrate or changing the ketone for each reduction without a loss of enantioselectivity.[3] Furthermore a variety of ligands were compared in multi-substrate one-pot reductions in order to optimize the catalyst.[4] We selected three ligands as the most enantioselective ligands for ruthenium-catalyzed reductions of aromatic ketones in water. Biocatalyses are alternative methods to perform reactions under mild conditions with high enantioselectivities and have been widely employed for the preparation of chiral alcohols. In order to compare both the activities and the enantioselectivities of *S. cerevisiae* as a biocatalyst and of ruthenium complexes for the reduction of ketoesters in water, we selected a variety of substrates. As a general trend the reduction of the various α and β-ketoesters catalyzed by *S. cerevisae* gave higher enantiomeric excesses than ruthenium complexes. However, ruthenium complexes afforded interesting asymmetric inductions (>70% ee) in some cases. As expected reductions of aromatic α - and β –ketoesters were more enantioselective than the corresponding aliphaticmolecules. Interestingly, for several substrates both enantiomers of the hydroxyesters have been obtained according either to the catalytic method or to the structure of the ligand. The work-up is very simple for both procedures with an easy separation of the product from the catalyst. The results obtained show that both procedures made it possible to carry out a certain number of key reactions, in the most effective way and most selective possible, under conditions of green chemistry.

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[1] a) B. M. Trost, *Science* **1991**, 1471 – 1477; *Angew. Chem. Int. Ed*. **1995**, 107, 285 – 307.

[2] a).S. Kobayashi, S. C. Ogawa, *Chem. Eur. J.* **2006**, 12, 5954 – 5960; b) C.-J. Li, *Acc.Chem. Res*. **2002**, 35, 533 – 538; c) T. Dwars, G. Oehme, *Adv. Synth. Catal*. **2002**, 344, 239 – 260.

[3] Zeror, S.; Collin, J.; Fiaud, J.-C.; Aribi-Zouioueche, L. *J. Mol. Catal. A* **2006**, 256, 85–89.

[4] Zeror, S.; Collin, J.; Fiaud, J.-C.; Aribi-Zouioueche, L. *Adv. Synth. Catal*. **2008**, 350, 197–204.

Author Index

GRANADA'12

Mosaics in the Alhambra: p6 symmetry group

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