Workshop on graphene and other 2D materials: A roadmap for Portugal
June 18-th, 2013, Escola de Ciências, Universidade do Minho

Time	WP	Presenter	Affiliation	Presentation title
9:00	Workshop Opening			Prof. António Cunha, Rector of Universidade do Minho Prof. Eduardo Maldonado, Coordenator of NCPs/FCT
9:15	Mar García Hernández		Graphene WP Leader	Graphene Flagship and Materials Domain
9:35	Eduardo Maldonado		FCT	ERA NET to support participation on national teams in Flagship Activities
9:45	Materials	Yuliy Bludov	UM	Surface plasmon-polaritons in graphene: a way to tunable excitation
10:10		Maria Conceição Paiva	UM	Synthesis of graphene nanoribbons from carbon nanotubes
10:35		Florinda Costa	UA	Synthesis of graphene and graphene hybrids by CVD and laser ablation techniques
11:00		Debate		
11:15	Coffee Break			
11:45	Health and Enviroment	João Pedro Alpuim	UM, INL	Chemical vapor deposition of graphene and device fabrication over large areas: towards THz modulators and biosensing applications
12:10		Paula Marques	UA	Interfacing graphene-based nanomaterials with health and environmental sciences
12:35		Fernanda Cássio	UM	Toxicology and environmental risks of nanomaterials
13:00		Debate		
13:15	Lunch			
14:15	Fundamental Science	Helder Crespo	UP	Nonlinear ultrafast optics in graphene: efficient broadband frequency conversion and its application to femtosecond pulse measurement
14:40		Joaquin Fernandez Rossier	INL	Spin Physics in Graphene (and other two dimensional crystals)
15:05		Eduardo Castro	IST-UTL	Silicene and MoS2: 2D electronic physics beyond graphene
15:30		Vitor Amaral	UA	Radioactive Ion Local Probing and Doping on Graphene
15:55		José Luis Martins	IST-UTL	Review of density functional methods applied to the electronic structure of graphite
16:20		Debate		
16:35	Coffee break			
17:05	Optoeletronics / Nanocomposites	Peter Shellenberg	UM	Optical and Spectroscopic properties of graphene
17:30		Manuel Franco	UM	Unzipping, stacking and folding
17:55		Konstantin Romanyuk	UA	Nanoscale study of V_2O_5-graphene composites via Scanning Probe Microscopy
18:20		Manoj Singh	UA	Production and Engineering of graphene for applications in Nanoelectronics
18:45		Debate		
19:00	Conclusions			

Yuliy Bludov

Surface plasmon-polaritons in graphene: a way to tunable excitation

It is shown, that unique property of graphene – an ability to control its doping (and conductivity) through the external electrostatic gating – opens a possibility to tune dynamically the dispersion properties of surface plasmon-polaritons in graphene and control their excitation both in the attenuated total reflection (ATR) and in periodical diffraction grating schemes. In particular, by adjusting the external gate voltage of ATR structure with graphene layer, it is possible to tune the reflectance of the incident electromagnetic wave from total absorption to total reflection, as well as the polarization of reflected wave. Also graphene layer deposited on substrate with periodically modulated thickness or dielectric constant demonstrates band-gap structure of the spectrum, where positions of gap edges (as well as the resonant frequencies of surface plasmon-polaritons, excited due to diffraction of external wave on such a periodic structure) can be effectively tuned by external gate voltage.

Helder Crespo

Nonlinear ultrafast optics in graphene: efficient broadband frequency conversion and its application to femtosecond pulse measurement

I. Introduction

Graphene, a single atomic layer of carbon atoms, is an extremely promising material for many applications owing to its unusual properties. Amongst them, it has been shown to possess an exceptionally high third-order nonlinear optical susceptibility, typically 10 8× larger than a normal insulator [1], which has motivated further investigation of its performance in various nonlinear optical processes. Achieving ultra-broadband third-harmonic generation (THG) at low intensities is currently a demanding task. One useful, widespread application of broadband THG is in femtosecond pulse characterization. The promise of graphene having an extremely broadband nonlinearity without macroscopic phase mismatch issues (since each layer is sub-nm thick) makes it highly attractive for ultrafast applications. Furthermore, its high nonlinearity should enable the characterization of low energy sources, such as high repetition rate femtosecond laser oscillators. The possibility of using a multilayer graphene film for enhancing the resulting signal [2] further adds to its interest as a practical nonlinear optical material.

In this work we demonstrate enhanced THG from multilayer graphene films compared with near-surface THG under loose focusing conditions and over a very large bandwidth in the deep-ultraviolet (DUV) spectral region [3]. Furthermore, we use this signal to make a complete measurement (amplitude and phase) of the pulses emitted by a few-cycle femtosecond laser oscillator using, for the first time, a dispersion-scan (d-scan) [3] setup based on THG and further compare these results to second-harmonic generation (SHG) d-scan [4]. Pulse characterization through dispersion-scan is based on the fact that when a pulse undergoes a nonlinear conversion process (e.g. SHG), the resulting spectral intensity has a well-defined dependence on the input spectral phase. This way, one only needs to measure the resulting spectrum for various different input spectral phases to be able to retrieve the initial spectral phase using an iterative algorithm. THG d-scan is desirable as an alternative to SHG d-scan due to the possibility of gating spectra over an octave in bandwidth without overlapping the nonlinear signal and the fundamental, as well as for its potential for the measurement of novel longer wavelength few-cycle mid-infrared lasers.

II. Experimental results

Broadband, 2.6 nanojoule pulses from a few-cycle laser oscillator (Femtolasers Rainbow CEP) were sent through a chirped mirror and glass wedge compressor and focused to intensities of the order of 100 GW/cm 2 in a nickel grown multilayer graphene sample transferred to an optical substrate (UV fused silica). The resulting broadband THG signal, extending from 230 to 305 nm, was spatially separated from the more intense fundamental using a double prism arrangement. The corresponding spectrum was then recorded with a calibrated spectrometer (Ocean Optics HR4000) as a function of dispersion by simply scanning the wedges of the compressor. This way we obtained a clear 2D THG d-scan trace with a high signal-to-noise ratio . This THG trace, like its SHG counterpart, contains enough information to fully retrieve the spectral phase of the pulses using the algorithm described in detail in [3], modified for the THG nonlinearity. An excellent agreement between pulses retrieved using the two techniques is observed. The retrieved pulse duration was 7.1 fs for a given optimum wedge insertion. (fig 1)

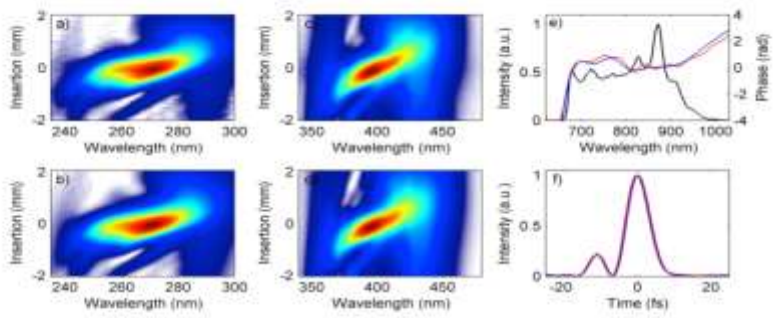


Fig. 1. Experimental Results: a) Measured THG d-scan in graphene. b) Retrieved THG d-scan. c) Measured SHG d-scan. d) Retrieved SHG d-scan. e) Black: spectral intensity. Red: Retrieved phase of shortest pulse, SHG-d-scan. Blue: Retrieved phase of shortest pulse, THG-d-scan. e) Measured fundamental spectrum and f) Temporal intensity corresponding to the spectrum and phases in Fig. 1e. Blue line: THG d-scan (7.1 fs FWHM). Red line: SHG d-scan (7.1 fs FWHM). The agreement between SHG d-scan and the new THG d-scan in graphene is excellent.

III. Conclusions

We report on efficient THG of few-cycle pulses over a broad bandwidth in the DUV (230-305 nm) from nickel-grown graphene multilayer samples that have been transferred to an optical substrate. We found that this signal is readily observable for nanojoule-level pulses even under loose focusing conditions (i.e.

not requiring short and unpractical focal lengths) and subsequently applied this process to broadband few-cycle pulse characterization using the dispersion-scan technique, with zero changes introduced in the previous setup. We have demonstrated, for the first time, pulse measurement and retrieval through THG d-scan and compared it to SHG d-scan, achieving excellent agreement. THG d-scan is a promising new technique for characterizing single-cycle and multi-octave-spanning pulses as well as few-cycle mid-IR laser sources.

Peter Shellenberg

Optical and Spectroscopic properties of graphene.

Early on after the discovery of graphene in 2004, the main interest of research was on its solid-state and electronic properties. However its optical and spectroscopic properties are increasingly catching attention. The experimental research conducted at the University of Minho focuses on these properties.

In the past years we have been developing different methods for the optical identification of graphene gained from natural graphite, that will be presented here. These methods are easy to utilize and may also serve to visualize patterned graphene structures. The first method is based on the microdroplet condensation technique, where the hydrophobicity difference between the substrate and the carbon sheets produce a clearly visible condensation pattern, that singles out the graphene flakes. The effect can be seen on a wide variety of substrates without the need for any specific surface modification or preparation. The contrast enhancement can also be observed in an optical transmission microscope, in which graphene flakes are notoriously difficult to see.
The second method is based on contrast enhancement by refractive index tuning. The graphene flake is immobilized on a transparent dielectric substrate, and by using a refractive index matching liquid the reflection from the substrate is greatly diminished, thereby enhancing the contrast of the monolayer or few-layer graphene. An estimation of the number of layers also becomes possible.

We are now in the process of investigating the distance dependence of the interaction of dye molecules immobilized by graphene by spectroscopic means. To this end, the fluorescence decay of the dye molecules is probed as a function of distance to the graphene. In another effort, the transient absorption of suspended graphene will be investigated.
We will also present possible future plans for research on optical and spectroscopic properties on graphene to be conducted at the Center of Physics at Uminho.

Pedro Alpuim

Chemical vapor deposition of graphene and device fabrication over large areas: towards THz modulators and biosensing applications

In this work mono and few-layers graphene are grown over large areas by chemical vapor deposition (CVD) using copper as a catalyst. Two types of Cu substrate are used for graphene growth: <002> preferentially oriented 15 μm Cu foil and <111> textured ~350 nm thin film Cu sputtered on oxidized Si wafers. The CVD process at 1000 °C is done in a cold wall reactor, which can accommodate up to 4" wafers. The transfer process is made using a temporary PMMA substrate that is spin-coated on the graphene layer. Two transfer techniques are employed, one involving dissolution of the Cu catalyst using $FeCl_3$, the other achieving the graphene/PMMA release from the Cu substrate by electrolysis in water. In the last case it is the hydrogen bubbling at the cathode – the Cu substrate covered with graphene – that promotes the release of the graphene/PMMA layer onto the solution, where it floats on the free surface with graphene facing down. The Cu substrate can then be re-used in a subsequent growth batch process. The structural quality of the graphene layers is accessed by Raman spectroscopy, SEM and AFM analysis. Optical or e-beam lithography are then used to pattern graphene top and bottom gate field effect transistors (GFET). Optical lithography is made compatible with graphene by using appropriate resists, solvents and process temperature. E-beam lithography using positive and negative tone resists is also used to fabricate smaller devices. The transfer characteristics of GFETs show a Dirac point shifted to > +50 V indicating highly unintentional p-type doping. Using $\mu_{FE} = \frac{L}{WC} X \frac{gm}{Vds}$ where g_m is transconductance, C is gate capacitance, L and W are channel length and width, respectively, and V_{ds} is source-drain voltage, gives field-effect mobility typically in the range 200-2000 $cm^2V^{-1}s^{-1}$. Channel length is in the range 250 nm < L < 250 μm and channel width, W = 10 μm. Devices with a periodic structure using two dielectric materials with enough contrast in their dielectric constants, and a transparent bottom gate are

under development to be operated as tunable modulators, polarizers or filters in the THz range of the electromagnetic spectrum, using the plasmonic effects that develop in a graphene layer placed in the interface between the incident medium and the periodic structure (grating). Based on such plasmonic devices, novel biosensors will be developed.

Paula Marques

Interfacing graphene-based nanomaterials with health and environmental sciences

This communication will specifically summarize the research advancements of our group in the field of graphene based nanocomposites for biomedical and environmental applications and the future perspectives in these areas. The bio-application opportunities lie in the unique attributes of graphene, i.e., its nano-scale structure that allows for bio-compatibility, the biofunctionalization of graphene for biological recognition, its mechanical, electronic and optical properties for bioimaging and external stimulus driven therapeutics, and its functionalities for tissue engineering.

Fernanda Cássio

Toxicology and environmental risks of nanomaterials

The ever-increasing production and use of nanomaterials increase the chance of their release to the environment, raising the question whether nanomaterials can pose a risk to living organisms. The potential harmful effects associated with the release of nanomaterials have been a cause of concern during the last few years, and this has driven a relevant amount of research to assess their toxicity and behavior in the environment. We will provide an overview of current knowledge regarding the impacts of metal-based nanomaterials (e.g. Ag and CuO) and carbon-based nanomaterials (e.g. carbon nanotubes, fullerene and graphene) to organisms by analyzing responses at different levels of biological organization, from communities to cellular targets. Particular attention will be given to aquatic ecosystems because they most likely will serve as terminal repository of nanomaterials.

Joaquin Fernandez

Spin Physics in Graphene (and other two dimensional crystals)

Summary: I will present an overview of the major scientific problems regarding spin physics in graphene. First, the origin of the unexpectedly short spin relaxation time. Second, the presence (or not) of ferromangetic order in the zigzag edges in graphene. Third, the peculiar consequences of the spin orbit coupling in graphene, which couple the spin and valley degrees of freedom. The latter point connect with the related emerging research fied of other two dimensional crystals, such as MoS2, which is attracting increasing attention.

Eduardo Castro

Silicene and MoS2: 2D electronic physics beyond grapheme

In this talk the electronic properties of the novel 2D materials silicene and the single layer of MoS2 will be discussed. Emphasis will be given to those properties that evade graphene physics, such as the possibility of a topologically non-trivial ground state in both silicene and MoS2 and also the possibility of a magnetic ground state in defected MoS2. Origin and robustness of these phases will be addressed.

Vitor Amaral

Radioactive Ion Local Probing and Doping on Graphene

Portuguese groups have established expertise of using exotic / unique local radioactive techniques with dedicated experimental infrastructures, which have been built along the years at ISOLDE-CERN. Today these methods are applied to modify (dope) and probe materials with the exceptional possibility to “see and feel” at the nanoscale. Hyperfine measurements of Electric Field Gradients and Magnetic Fields, using Perturbed Angular Correlations are currently applied to locally probe electron densities and the elements interactions on graphene, graphene-derivated structures and other surfaces, with extreme sensitivity (ppm doses of the probing atoms) and without interference of the probing method with the probed system. With about 1000 isotopes and more than 75 elements being currently delivered, the ISOLDE-CERN facility allows a large choice of case studies, of, e.g., add-atoms at the graphene surface. Complementing studies are undertaken with further techniques, like Raman and other optical spectroscopies. Modeling of properties using density functional ab-initio methods is used to support the theoretical interpretation of results (local coordination, polarization, density of states) and foster new studies directions. Some of the questions addressed are:
- Modification and charge screening effects of an impurity add-atom at graphene. Can hyperfine interactions probe how an atom is affected by the presence of a sea of 2D Dirac electrons with a linear dispersion? Does the renormalization change the cross-over conditions for quantum relativistic atomic collapse in a strong Coulomb from charges Z>170 to Z~1-2?
-Understanding of interactions, coordination binding energies, configurations and fields using add-atom probes at graphene, modified & functionalized surfaces and interfaces. This information is relevant to the nucleation of nano-structures. Examples are related to the growth of semiconductor nanostructures (e.g. CdS) aiming diverse devices, such as quantum dots.
-Investigating possibilities of electrical/optical/magnetic/strain tuning of properties (in device and sensor structures), performing isotopically selected studies of properties.
- prepare isotopically pure graphene layers or their modifications. Graphene synthesis or modification by ion implantation on substrates following carbon diffusion and recrystallization at the surface.

José Luis Martins

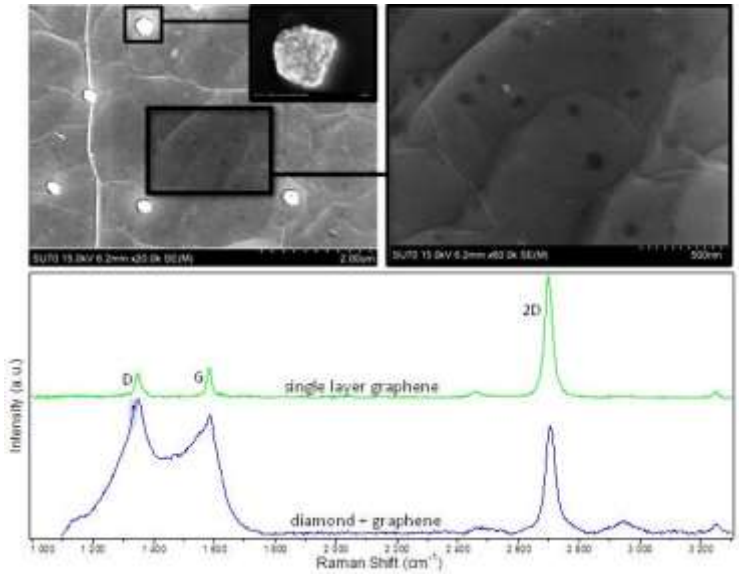
Review of density functional methods applied to the electronic structure of graphite

The electronic structure of graphite is well known from experiment and has been calculated long ago with many methods. The local density approximation of the density functional theory is a reference method, for graphite it predicts correctly its semi-metallic character, but fails in the prediction of the relative positions of the pi and sigma bands. This problem also occurs in C60 a graphitic material. Many other density functionals have been proposed to improve local density. The predictions of some of those functionals will be compared with experiment and the reference local density results

Florinda Costa

Synthesis of graphene and graphene hybrids by CVD and laser ablation techniques

Given the growing interest in graphene-based materials and the accumulated experience in producing carbon nanostructures, namely nanodiamond (NCD), carbon nanotubes (CNT) and more recently NCD/CNT hybrids, our group is now concentrating in the production of graphenes. During the last decade several projects were funded by FCT in carbon-based materials and currently three of them are still going on.
There are remarkable technological and scientific similarities in the synthesis of carbon nanostructures that can be potentiated by adapting the existing facilities to the growth of graphenes. That is the case of our CVD equipments: microwave plasma (MPCVD), hot filament (HFCVD) and thermal CVD. Moreover, a dedicated thermal CVD apparatus is being purchased along with a pulsed laser for ablation in liquids, both envisaging the synthesis of graphenes.
Graphene films were already obtained by HFCVD in nickel substrates while diamond/graphene hybrid materials were produced by MPCVD in standard copper substrates. SEM and Raman spectroscopy analysis confirmed unambiguously the presence of both allotropes after a few seconds of growth, as depicted in the figure below.



Maria Conceição Paiva

Synthesis of graphene nanoribbons from carbon nanotubes

The formation of graphene by exfoliation of carbon nanotubes (CNT) originates graphene nanoribbons (GNR) that are expected to present interesting properties, depending on their width and on their edge shape [1].
Recently, the formation of GNR was observed "in situ" by unzipping of carbon nanotubes under ultra-high vacuum scanning tunneling microscopy (UHV STM) [2]. The CNT under observation were functionalized by the 1,3-dipolar cycloaddition reaction [3], and the functionalization route seems to be responsible for the unzipping of the CNT under these conditions.
The present work describes the formation of GNR in solution by unzipping of functionalized CNT. The nanotubes were functionalized by the 1,3-dipolar cycloaddition reaction, binding pyrrolidine-type groups at the nanotube surface [3]. The GNR solutions produced presented the characteristic UV-visible spectra of graphene solutions. Raman spectroscopy confirmed the formation of nanoribbon bundles, as observed by transmission electron spectroscopy (TEM). Image analysis demonstrated that the nanoribbons formed regular stacks, with a large interlayer spacing of approximately 0.50 nm. Graphene layers and their intermolecular interactions were simulated with the MM3 force field [4]. The calculations lead to the conclusion that stacks of GNR containing one functional group in 50, 72 or 98 carbon atoms were characterized by interlayer distances of 0.51, 0.50 and 0.41 nm respectively, in agreement with the TEM observations.
Preliminary studies of the formation of layer-by-layer films by deposition of GNR, and other possible applications will be discussed.

Manuel Franco

Unzipping, stacking and folding

- We will talk mostly about unzipping of carbon nanotubes [1-2], something about the stacking of graphene [3] and very little about folding and curling of graphene [4].

Opening carbon nanotubes is a popular experimental route to produce GNRs [1]. We will present theoretical models we have applied to understand (unsuccessfully) the unzipping process as well as to the prediction of the structure and electronic properties of the unzipped materials [2]. We will also present our fast and very accurate, model for dispersion in quantum chemical periodic calculations [3] and discuss its performance on the *intermolecular* binding of graphite, few layers graphene and PAHS on graphene. Last but not least we will talk about classical models for the curling of graphene in solution [4] and *adsorbed* on incommensurate surfaces.

Konstantin Romanyuk

Nanoscale study of V_2O_5-graphene composites via Scanning Probe Microscopy

-Batteries are essential elements of mobile devices and various appliances. Conventional electrode materials are sufficient for personal mobile devices which do not require high power density and long life time, but still do not satisfy requirements for automotive and renewable energy applications. State-of-the-art metal-oxide electrodes possess high energy density and large capacity, but poor electrical conductivity, large volume change, and poor cycling stability [1]. Graphene is considered as one of the potentially attractive electrode materials for batteries due to its large active surface area, good chemical stability and structural flexibility, but a number of problems such as agglomeration and fast capacity degradation prohibit its wide use so far. Recent studies of graphene-metal oxide composites show that limitations of both metal oxide and graphene electrodes can be eliminated in composite materials [1]. There are several possible structural configurations combining metal oxides and graphene that are able to improve battery performance. In this work, we use Scanning Probe Microscopy (SPM) and its modification, Electrochemical Strain Microscopy (ESM) [2] to follow the microstructure and electrical properties of V_2O_5-graphene composite. Electrochemical hysteresis loops and relaxation curves are measured for a number of voltages on different interfacial structural elements. We detected strong influence of the interface state on electrochemical processes below the SPM tip.
The results are complemented with local conductivity, potential, and micromechanical studies. The results show the multilayered structures based on graphene can be useful for the battery development and SPM and ESM can bring about useful information of the battery functionality on the nanoscale.

Manoj Singh

Production and Engineering of graphene for applications in Nanoelectronics

The presentation will be focus on the development of new methodologies for producing highly pure graphene layers with tailored electronic properties that could be useful for technological applications in the field of nanoelectronics. In fact, graphene is a fundamental material for nanoengineering and nanomanipulation. By control modification of the graphene structure with foreign atoms could open new functional properties for designing graphene-based devices with dedicated properties.
In this context the present work dedicated on: (i) Large-area strictly monolayer graphene deposition by Hot-Filament Thermal CVD, (ii) controllable gas-phase doping of hetero atoms (nitrogen, hydrogen, boron…etc) by chemical vapor deposition (by using Radio-frequency and Microwave Plasma) technique, (iii) atomic-scale modification by Electron-beam Engineering by TEM, (iv) chemical functionalization of graphene by donor-acceptor organic molecules, (v) decoration of graphene with nobel metal particles and QDs.
The surface and electronic properties of the pristine and doped graphene is performed by state-of-the-art surface techniques for example high-resolution XPS, UPS, STM/STS, AFM and Raman as a previous step for the future development of graphene-based nanoelectronic devices.
In addition, we will also present the charge injection in few-layer graphene sheet by combining contact-mode atomic force microscopy (AFM) and scanning Kevin probe microscopy (SKPM).