

## Workshop on: **Two-Dimensional Materials: Probing the Limits of Physics and Engineering**

Madrid, June 22-23, 2016

### ABSTRACTS

**Wednesday, 22**

#### **Graphene and other 2D Materials**

**Pablo Jarillo-Herrero**

MIT.

Over the past decade, a revolution in materials science has taken place with the advent of atomically-thin layered materials. These materials exhibit unique physical properties, different from their bulk counterparts, as exemplified by graphene's ultra-relativistic electronic properties. Moreover, the possibility to stack different layered materials arbitrarily on top of each other to form what are known as van der Waals heterostructures, has paved the way for an even richer variety of electronic, optical, chemical and mechanical behaviors, which the physics, chemistry and engineering communities are just beginning to explore. In this talk I will describe my group's efforts in the area of quantum electronic transport and optoelectronics with van der Waals heterostructures, with examples ranging from the opening of a band gap in graphene to the thinnest photodetectors, solar cells, and LEDs based on transition metal dichalcogenides.

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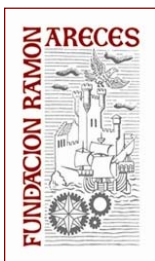
#### **Redefining Electronics: System-level Applications of 2D Materials**

**Tomás Palacios Gutiérrez**

MIT.

This talk will discuss some of the many applications of two dimensional (2D) materials in future electronic systems. These materials have tremendously diverse and unique properties. For example, graphene is a semimetal with extremely high electron and hole mobilities, hexagonal boron nitride forms an almost ideal insulator, while MoS<sub>2</sub> and other dichalcogenides push the limits on large area semiconductors. At the same time, the extreme thinness (3 or less atoms thick) of all these novel materials gives them great flexibility, optical transparency and an unsurpassed surface-to-volume ratio.

The growth of these materials over large areas has allowed their use in numerous applications. For example, the zero bandgap of graphene and its ambipolar conduction enables many new rf and mixed devices, including transistors with very high frequency performance, frequency multipliers, mixers, oscillators and digital modulators. At the same time, graphene has excellent properties for mid-infrared detectors, which can be easily integrated with conventional silicon chips to enhance their functionality at the end of Moore's law.



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In spite of the outstanding performance of graphene in many applications, digital electronics typically requires a semiconductor with a significant bandgap. Recently, the wide bandgap of MoS<sub>2</sub> in combination with advanced fabrication technology has enabled its use in memory cells, analog to digital converters and ring oscillators with orders of magnitude better performance than other materials being considered for large area applications. These and other examples will be reviewed to highlight the numerous new opportunities of 2D materials.

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### Graphene Optoelectronics

**Frank Koppens**

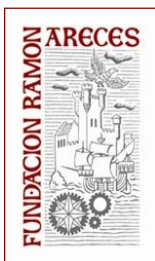
Instituto de Ciencias Fotónicas (ICFO).

The optoelectronic response of two-dimensional (2D) crystals, such as graphene and transition metal dichalcogenides (TMDs), is currently subject to intensive investigations. Owing to its gapless character, extraordinary nano-photonic properties and ultrafast carrier dynamics, graphene is a promising material for quantum nano-optoelectronics. Vertically assembling graphene with TMDs in so-called van der Waals heterostructures allows the creation of novel and versatile quantum and nano-optoelectronic devices that combine the complementary properties of their constituent materials.

Here we present a various new device capabilities, varying from quantum nano-photonic devices to ultra-fast and broadband electrical detectors. We applied femtosecond time-resolved photocurrent measurements on 2d material heterostructures, which reveals the charge dynamics across TMD and graphene layers directly in the time domain [2,3]. In addition, we apply for the first time infrared photocurrent nanoscopy to high-quality graphene devices [4]. Using this technique, we image the plasmon-voltage conversion in real space, where a single graphene sheet serves simultaneously as the plasmonic medium and detector [5,6]. In addition, nano-structured sandwiches of graphene with boron nitride have resulted in high quality plasmonic systems for infrared light [7].

#### *References:*

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F. H. L. Koppens et al. Nature Nanotechnol. 9, 780-793 (2014)
- [2] Picosecond photoresponse in van der Waals heterostructures  
M. Massicotte et al., Nature Nanotechnology 11 (2016)
- [3] Photo-thermionic effect in vertical graphene heterostructures. Mathieu Massicotte, Peter Schmidt, FabienViolla, Kenji Watanabe, Takashi Taniguchi, Klaas-Jan Tielrooij, Frank H.L. Koppens. arXiv: 1601.04196
- [4] Near-field photocurrent nanoscopy on bare and encapsulated graphene. A. Woessner, Nature Communications (2016).
- [5] Thermoelectric detection of propagating plasmons in graphene  
M.B. Lundberg et al., arXiv (2016) arXiv:1601.01977



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[6] Ultra-confined acoustic THz graphene plasmons revealed by photocurrent nanoscopy  
P. Alonso-González et al., arXiv (2016) arXiv:1601.0575.

[7] Highly confined low-loss plasmons in graphene–boron nitride heterostructures  
A. Woessner et al., Nature Materials, 14, 421-425 (2015)

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### Exotic 2D Materials

**Andrés Castellanos-Gómez**

IMDEA-Nanociencia.

In this talk I will review the recent progress on the application of atomically thin crystals different than graphene on optoelectronic devices. The current research of 2D semiconducting materials has already demonstrated the potential of this family of materials in optoelectronic applications [1-4]. Nonetheless, it has been almost limited to the study of molybdenum- and tungsten- based dichalcogenides (a very small fraction of the 2D semiconductors family). Single layer molybdenum and tungsten chalcogenides present large direct bandgaps ( $\sim 1.8$  eV).

Alternative 2D semiconducting materials with smaller direct bandgap would be excellent complements to the molybdenum and tungsten chalcogenides as they could be used for photodetection applications in the near infrared. Furthermore, for applications requiring a large optical absorption it would be desirable to find a family of semiconducting layered materials with direct bandgap even in their multilayer form.

Here I will summarize the recent results on the exploration of novel 2D semiconducting materials for optoelectronic applications: black phosphorus [5-7],  $\text{TiS}_3$  [8, 9].

### References

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- [2] Lopez-Sanchez, O., et al., Ultrasensitive photodetectors based on monolayer  $\text{MoS}_2$ , Nature Nanotech. (2013)
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- [4] Groenendijk D.J., et al., Photovoltaic and photothermoelectric effect in a doubly-gated  $\text{WSe}_2$  device, Nano Letters (2014)
- [5] Castellanos-Gomez, A., et al., Isolation and Characterization of few-layer black phosphorus. 2D Materials (2014)
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[9] Island J.O., et al., TiS<sub>3</sub> transistors with tailored morphology and electrical properties. Adv. Mater. (2015)

## Probing Graphene Physics at the Atomic Scale

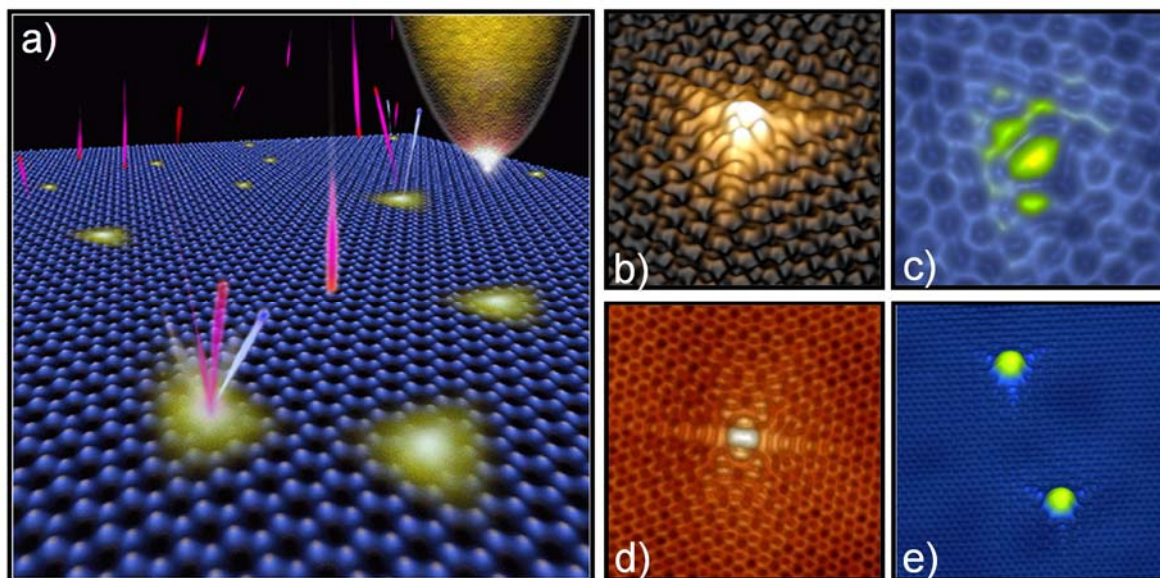
**Iván Brihuega**

Universidad Autónoma de Madrid (UAM).

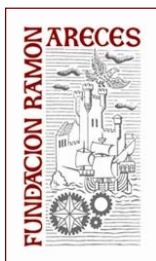
In 2004 graphene ceased being a theoretical chimera to become the object of desire of the scientific community. In just few years, numerous extraordinary properties have been demonstrated and many others are emerging as a result of the tremendous experimental and theoretical efforts devoted to this material. In this talk I will show how we use a scanning tunneling microscope to explore and manipulate graphene physics at an atomic level. I will mainly concentrate in two topics:

The investigation, at the atomic scale, of the impact that point defects like vacancies or atomic H have in the structural, electronic and magnetic properties of graphene layers grown on different substrates, where the pure bidimensionality of graphene gives to these atomic defects a critical role [1-3].

The study of the coupling of graphene with its local environment, which is absolutely critical to be able to integrate it in tomorrow's electronic devices [4-5].



(a) Art illustration of the generation and STM analysis of atomic point defects vacancies in graphene layers. (b-e) 4K STM data showing atomically resolved images of different kind of point defects in graphene layers grown on diverse substrates: (b) C vacancy on graphite, (c) C vacancy on graphene on Pt(111), (d) C divacancy, (e) H atoms on graphene.



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- [2] M. M. Ugeda, D. Fernández-Torre, I. Brihuega, P. Pou, A.J. Martínez-Galera, R. Pérez and J. M. Gómez-Rodríguez, *Phys. Rev. Lett* 107, 116803 (2011)
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### 3D Graphene for Energy Storage

**Fernando Calle**

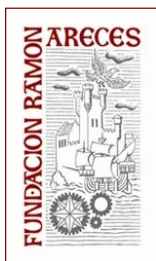
Universidad Politécnica de Madrid (UPM).

Graphene stands out by many different properties (electrical, optical, structural, mechanical, thermal, etc.), which combinations allow to improve device performance or enable new applications. Perhaps, energy storage by means of supercapacitors and batteries is the main short-term field in which graphene will be exploited.

Graphene can be prepared by several techniques. Chemical vapor deposition (CVD) using catalytic metal foils or films has demonstrated very good results for quality single or few-layer 2D graphene. Similarly, 3D graphene structures are grown by CVD on Cu or Ni metal foams or sponges, showing a high surface useful for supercapacitor electrodes. The graphene foam (GF) processing involves material growth, substrate removal and, eventually, functionalization. We are using plasma enhanced CVD to grow the graphene coating on a metal foam acting as a catalytic mesh. The coating thickness depends on the metal substrate and the growth conditions (gases ratio, growth time, etc.). A free-standing GF is obtained by wet etching the metal substrate. Finally, the GF may be functionalized by different techniques and materials (polymerisation, electrodeposition, sol-gel), either to modify the graphene properties and/or to provide robustness to the 3D structure.

In this work we will discuss several demonstrations of GF-based electrodes for supercapacitors, either by filling the GF with a hierarchical polymer nanostructure, or different oxides by electrodeposition or sol-gel. GFs can also be exploited to enhance the properties of batteries or other energy applications.

**Acknowledgement.** This work has been supported by Repsol (Inspire) and Ministerio de Economía y Competitividad (Project ENE2013-47904-C3-1).



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#### **Nanomechanical Systems**

**Adrian Bachtold**

ICFO.

When a graphene layer is suspended over a circular hole, the graphene vibrates as a music drum. However, the graphene drum has an extremely small mass, since the graphene is only one atom thick. Another difference is the quality factor  $Q$ , which becomes extremely large in graphene resonators at cryogenic temperature ( $Q$  above 1 million). Because of this combination of low mass and high quality factor, the motion is enormously sensitive to external forces, such as the radiation pressure of photons. Here, we couple the graphene resonator to a superconducting cavity via a radiation pressure-like force. We sideband cool the graphene motion to an average phonon occupation of 7.2 phonons, approaching the quantum ground-state. The superconducting cavity is also used as an efficient transducer of the graphene motion with a displacement sensitivity of  $1.3 \text{ fm/Hz}^{1/2}$ . In particular, it allows us to use the graphene resonator as a fantastic force sensor with a sensitivity of  $390 \text{ zN/Hz}^{1/2}$ , approaching the fundamental limit imposed by thermo-mechanical noise. The efficient transduction also allows us to probe the energy decay in atomically-thin mechanical resonators with an unprecedented accuracy. We find that energy decays in a way that has thus far never been observed nor predicted.

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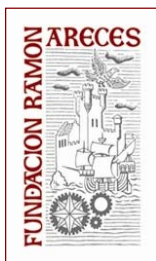
**Thursday, 23**

#### **Electron Transfer Chemistry in Graphene and 2D Electronic Materials: Fundamentals and Applications to Optoelectronics**

**Michael Strano**

MIT.

Our lab at MIT has been interested in how 2D electronic materials such as graphene can be utilized to advance new material concepts. Of particular interest to us has been how such materials participate in electron transfer chemistries as in the case of graphene spontaneously reacting with benzene diazonium salts, as well as electrochemical modification of 2D materials. This presentation will outline our work in applying and modifying electron transfer theory to extend to 2D materials, explicitly accounting for the electronic contributions due to the substrate. We show a stark difference in the rate of electron-transfer reactions with organic diazonium salts for monolayer graphene supported on a variety of substrates. Reactions proceed rapidly for graphene supported on  $\text{SiO}_2$  and sapphire, but negligibly on alkyl-terminated and hexagonal boron nitride (hBN) surfaces, as shown by Raman spectroscopy. We also develop a model of reactivity based on substrate-induced electron-hole puddles in graphene, and achieve spatial patterning of chemical reactions in graphene by patterning the substrate. Field-effect transistor (FET) devices composed of a  $\text{MoS}_2$ -graphene heterostructure can combine the advantages of



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high carrier mobility in graphene with the permanent band gap of MoS<sub>2</sub> for digital applications. We also investigate the electron transfer, photoluminescence, and gate-controlled carrier transport in such a heterostructure. We show that the junction is a Schottky barrier, whose height can be artificially controlled by gating or doping graphene. Atomically thin MoS<sub>2</sub> is of great interest for electronic and optoelectronic applications because of its unique two-dimensional (2D) quantum confinement, however, the scaling of optoelectronic properties of MoS<sub>2</sub> and its metallic junctions with layer number remains unaddressed. We utilize photocurrent spectral atomic force microscopy (PCS-AFM) to image the current and photocurrent generated between a biased PtIr tip and MoS<sub>2</sub> between  $n = 1$  to 10 layers. Dark current measurements in both forward and reverse bias reveal characteristic diode behavior well described by Fowler-Nordheim tunneling with a monolayer barrier energy of 0.605 eV and an effective barrier scaling linearly with layer number. Under illumination at 600 nm, the photocurrent response shows a marked decrease up to  $n = 4$  but increasing thereafter, which we describe using a model that accounts for the linear barrier increase at low  $n$ , but increased light absorption at larger layer number creating a minimum at  $n = 4$ . Comparative 2D Fourier analysis of physical height and photocurrent images shows high frequency spatial variations in substrate/MoS<sub>2</sub> contact that exceed the frequencies imposed by the ITO substrates. Lastly, we examine the chemical reactivity and stability of bilayer phosphorene and BP nanomaterials, showing that heterojunction stacks can passivate favorably for opto-electronic applications.

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### **Graphene Flexible Electronics for Functional Neural Interfaces**

**José Antonio Garrido**

Instituto Catalán de Nanociencia (ICN).

Graphene and graphene-based materials possess a rather exclusive set of physicochemical properties holding great potential for biomedical applications, in particular neural prostheses. In this presentation, I will provide an overview on fundamentals and applications of several graphene-based technologies and devices aiming at developing an efficient bidirectional communication with electrogenic cells and nerve tissue. To this end, I will discuss several device technologies based on graphene that are used to investigate the electrical activity in cell cultures and in acute experiments (nerve tissue slices); finally, we will disclose recent in vivo experiments in which flexible graphene devices are used to record brain activity. The results presented in this talk highlight the great potential of graphene technologies in neuroprosthetics.

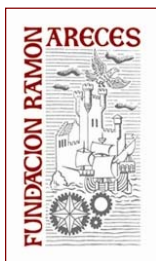
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### **Graphene Spintronics**

**Sergio Valenzuela**

ICN.

There is an intense research activity on the electronic transport properties of two dimensional materials given their unprecedented physical and chemical properties.



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Amongst these materials, graphene has attracted the attention of the spintronics community due to long spin lifetimes that stem from a small intrinsic spin-orbit coupling and the lack of hyperfine interaction with the most abundant carbon nuclei ( $^{12}\text{C}$ ). However, it can be argued that the most important quality is the tunability of its transport properties, which results into enhanced gate control and opens the door for subtle material engineering. Indeed, magnetism or large spin-orbit coupling could in principle be induced in graphene by proximity to suitable materials. After a presentation of basic concepts on spin transport, I will discuss current experimental and theoretical understanding of spin transport in graphene, including current challenges and new opportunities. I will then provide an outlook for potential applications, including the possibility of developing all-graphene spintronic devices.

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### **Graphene Membranes for Water Purification**

**Rohit Karnik**

MIT.

Nanoporous graphene has potential as an ideal ultrathin membrane for high-flux, high-selectivity, chemically-resistant membrane separations. I will discuss our work on understanding mass transport and developing membranes that employ nanoporous single-layer graphene as the selective layer. Through controlled nucleation of defects *via* ion bombardment and oxidative etching, sub-nanometer pores are created in the otherwise impermeable graphene placed on a porous support. The resulting membranes exhibit selectivity between ions and between salt and small molecules. We also present strategies for the design of defect-tolerant membranes using centimeter-scale areas of single-layer graphene, which allows for measurement of water flux and solute rejection during filtration by forward osmosis. The membrane can reject multivalent ions and small molecules, and exhibits a permeance that is consistent with theoretical predictions. We also demonstrate that these membranes exhibit high mechanical strength and are able to withstand applied pressures up to 100 bar. These studies illustrate the feasibility and potential of single-layer nanoporous graphene membranes for nanofiltration, water purification, and other applications.

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