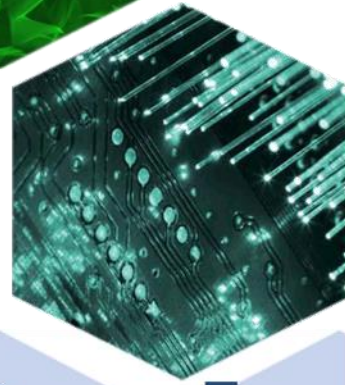
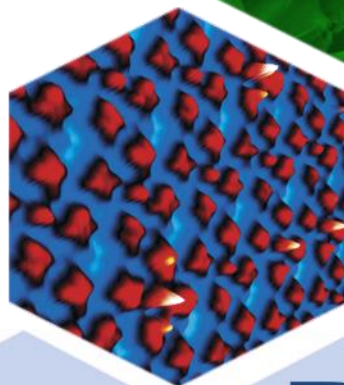
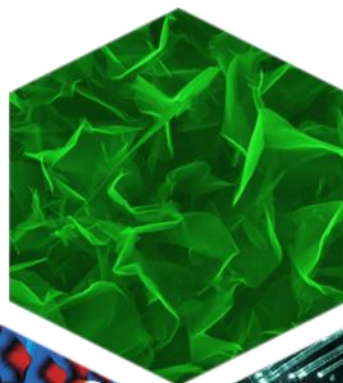


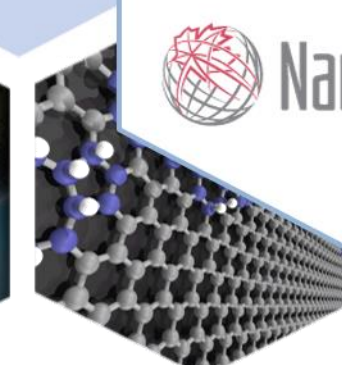
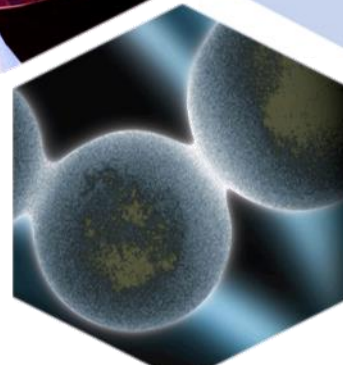
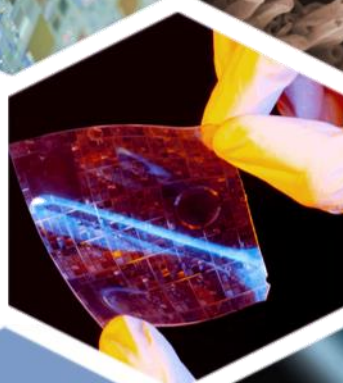
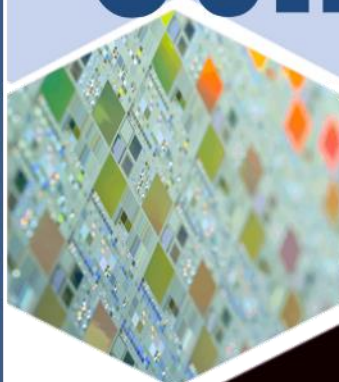
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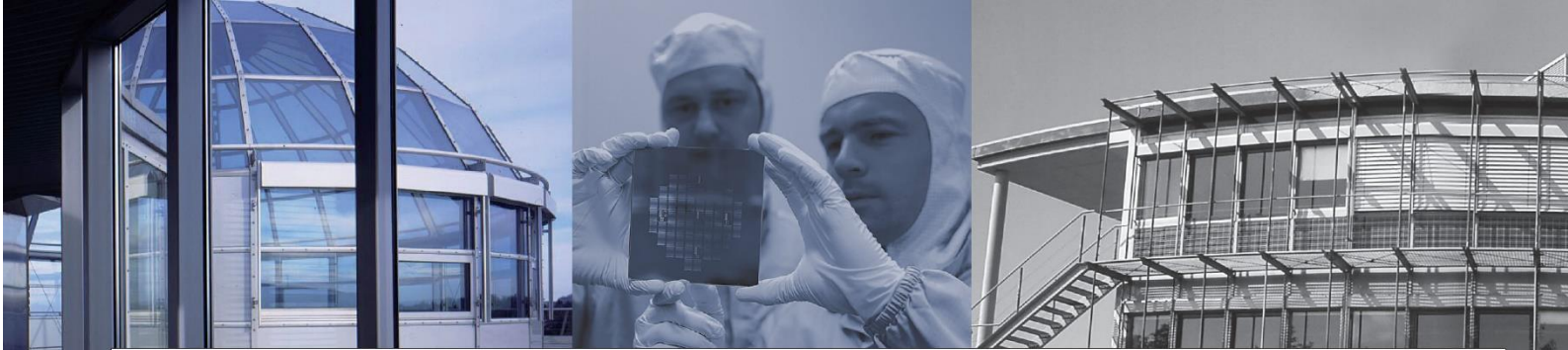
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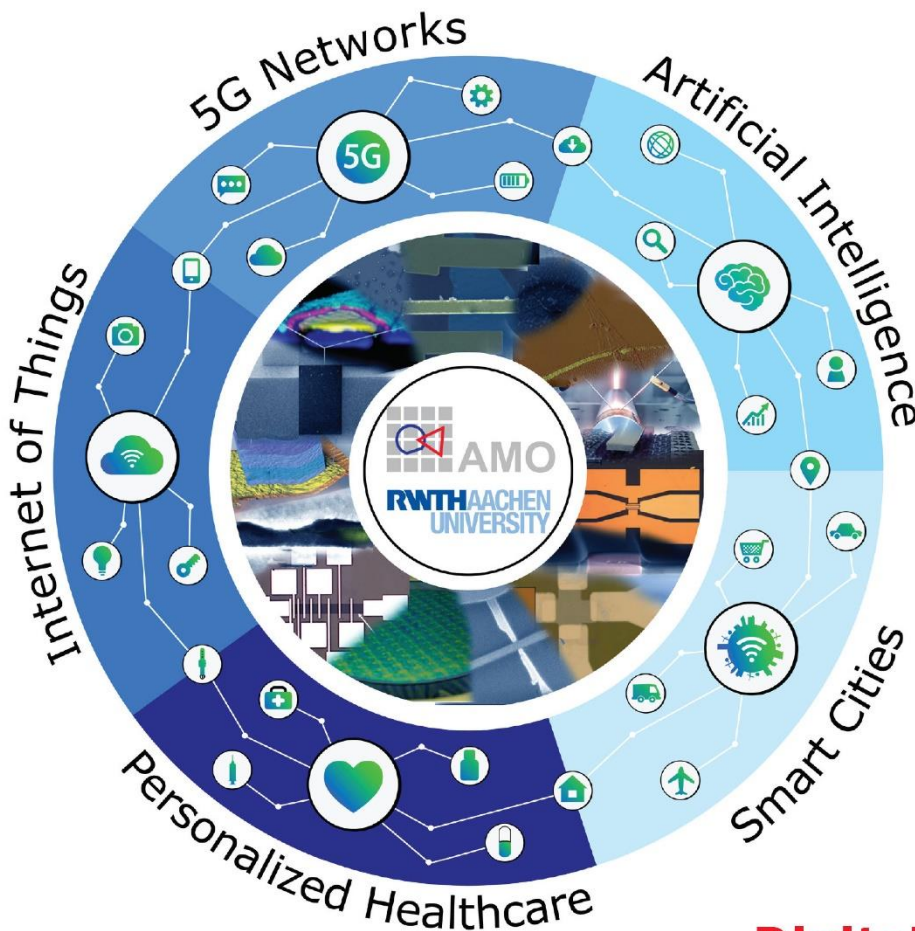
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Flat Bands and Correlated Electronic States in Two Dimensional Atomic Crystals

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Abstract (Arial 11)

Stacking two-dimensional atomic crystals or exposing them to periodic potentials, can radically change their electronic properties. In particular, it is possible to engineer conditions leading to the creation of essentially “flat” energy bands, where the quenched kinetic energy facilitates the emergence of correlated electronic states, including superconductivity, Mott insulators or ferromagnetism. This talk will highlight two examples where the electronic ground state and Fermi surface topology depend sensitively on the filling of the flat bands: twisted graphene bilayers that develop a flat band at a “magic” twist-angle [1,2], and buckled graphene layers in which a strain-induced periodically modulated pseudo-magnetic field creates a post-graphene material with flat electronic bands [3].

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FIGURES

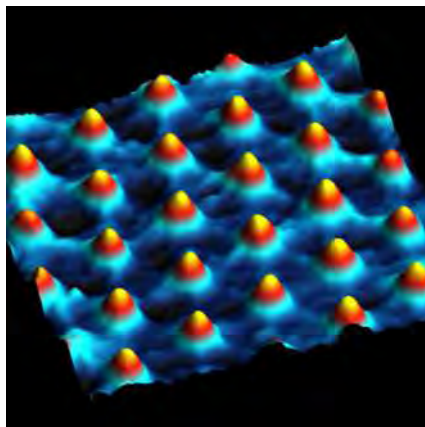


Figure 1: Stiff membranes under compressive stress can relax their stored energy by undergoing a buckling transition from an initially flat geometry to a periodic structure of out of plane dimples. In graphene, these out of plane distortions mimic the effect of very large magnetic fields, which are unattainable with today's magnet technologies, leading to dramatic changes in the material's electronic properties. The image shows the topography of the buckling structure obtained with scanning tunnelling microscopy.

Large-scale production of 2D crystals for energy applications

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Abstract

The development of industrial-scale, reliable, inexpensive production processes of graphene and related two-dimensional materials (GRMs)[1,2] is a key requirement for their widespread use in several application areas,[1-6] providing a balance between ease of fabrication and final product quality.

In particular, in the energy sector, the production of GRMs in liquid phase [2,6] represents a simple and cost-effective pathway towards the development of GRMs-based energy devices, presenting huge integration flexibility compared to other production methods. Here, I will first present our strategy to produce GRMs on large scale by wet-jet milling [7] of their bulk counterpart and then an overview of their applications for energy conversion and storage devices. [3,8-18]

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2D material inks: from printed devices to polymorph's selectivity

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Solution processing of 2D materials [1] allows simple and low-cost techniques, such as ink-jet printing, to be used for fabrication of heterostructure-based devices of arbitrary complexity. However, the success of this technology is determined by the nature and quality of the inks used.

In my group we have developed highly concentrated, defect-free, printable and water-based 2D crystal formulations, designed to provide optimal film formation for multi-stack fabrication [2]. I will give examples of all-inkjet printed heterostructures, such as large area arrays of photosensors on plastic [2], programmable logic memory devices [2], capacitors [3] and transistors on paper [3,4]. Furthermore, inkjet printing can be easily combined with materials produced by chemical vapor deposition, allowing simple and quick fabrication of complex circuits on paper, such as high-gain inverters, logic gates, and current mirrors [5].

If time allows, I will show that the ability to tune the surface properties of solution-processed graphene allows for polymorph selectivity in templated crystallization of glycine molecules [6].

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Chemically Tailored 2D Materials for Electronic and Energy Technologies

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Layered two-dimensional (2D) materials interact primarily via van der Waals bonding, which has created new opportunities for heterostructures that are not constrained by epitaxial growth. However, it is important to acknowledge that van der Waals interactions are not limited to interplanar interactions in 2D materials. In principle, any passivated, dangling bond-free surface interacts with another via non-covalent forces. Consequently, layered 2D materials can be integrated with a diverse range of other materials, including those of different dimensionality, to form mixed-dimensional van der Waals heterostructures [1]. Furthermore, chemical functionalization provides additional opportunities for tailoring the properties of 2D materials [2] and the degree of coupling across heterointerfaces [3]. In order to efficiently explore the vast phase space for mixed-dimensional heterostructures, our laboratory employs solution-based additive assembly. In particular, constituent nanomaterials (e.g., carbon nanotubes, graphene, transition metal dichalcogenides, black phosphorus, boron nitride, and indium selenide) are isolated in solution, and then deposited into thin films with scalable additive manufacturing methods (e.g., inkjet, gravure, and screen printing) [4]. By achieving high levels of nanomaterial monodispersity and printing fidelity, a variety of electronic and energy applications can be enhanced including photodetectors, optical emitters, supercapacitors, and batteries [5-7]. Furthermore, by integrating multiple nanomaterials into heterostructures, unprecedented device function can be realized including anti-ambipolar transistors, gate-tunable Gaussian heterojunction transistors, and neuromorphic memtransistors [8-10]. In addition to technological implications for electronic and energy technologies, this talk will explore several fundamental issues including band alignment, doping, trap states, and charge/energy transfer across van der Waals heterointerfaces.

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Bilayer Graphene as a Model Hydrodynamic Semiconductor

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Hydrodynamic electronic transport occurs when carrier-carrier collisions constitute the dominant scattering mechanism. This regime has attracted intense recent interest with its discovery in two dimensional materials, for which interactions are intrinsically strong and disorder plays a minimal role. Here we show that bilayer graphene is a model hydrodynamic semiconductor, in which carrier-carrier collisions play a dominant role over a wide range of temperature and carrier density. Remarkably, a simple model captures the complex interplay between carrier-carrier scattering and conventional dissipative scattering. This model, depicted in Figure 1 below, consists of a universal Coulomb drag contribution that dominates at charge neutrality and decays with increasing density, and a non-universal dissipative contribution corresponding to collective motion of the electron-hole plasma. We compare this model to electrical transport measurements of ultraclean bilayer graphene encapsulated within hBN, with dual gates providing independent control over carrier density and bandgap. At charge neutrality, these samples show electron-hole limited conductivity over a wide temperature range (Fig. 2a). A single set of fit parameters provides quantitative agreement with experiments at all densities, temperatures, and gaps measured, allowing for separate extraction of the electron-hole and dissipative contributions (Fig. 2b). Our work provides an intuitive understanding for electron-hole limited transport in a semiconductor across a wide range of parameters and provides a unique link between semiconductor physics and the emerging field of viscous electronics.

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FIGURES

$\mathbf{u}_h - \mathbf{u}$ $\mathbf{u}_e - \mathbf{u}$

$\mathbf{j}_e = -n_e e (\mathbf{u}_e - \bar{\mathbf{u}})$

$\mathbf{j}_h = n_h e (\mathbf{u}_h - \bar{\mathbf{u}})$

$\sigma = \frac{4n_e n_h}{n_e + n_h} \frac{e^2 \tau_0}{m^*} \approx \sigma_0 \exp \left[-\frac{1}{3} \left(\frac{\mu}{k_B T} \right)^2 \right]$

\mathbf{u}

$\mathbf{j} = (n_h - n_e) e \bar{\mathbf{u}}$

$\sigma = \frac{(n_h - n_e)^2}{n_e + n_h} \frac{e^2 \tau_{dis}}{m^*}$

Figure 1: Schematic of Coulomb drag and center-of-mass contributions to hydrodynamic conductivity.

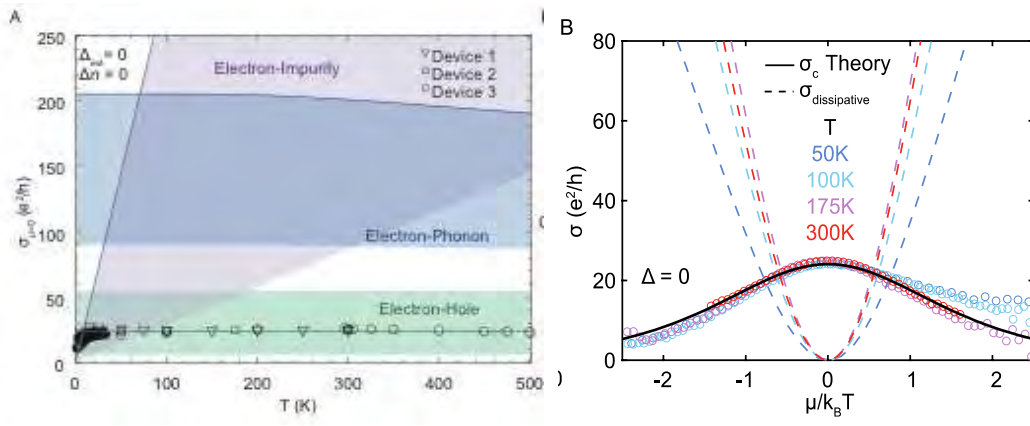


Figure 2: (A) Measured conductivity of bilayer graphene at charge neutrality, with predicted contributions from impurity, phonon, and electron-hole scattering. (B) Extraction of the universal Coulomb drag and non-universal dissipative terms.

Unusual quasiparticle pairing in stacked atomic layers

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Interactions between particles in quantum many-body systems can lead to collective behavior. In a condensed matter system consisting of weakly interacting particles, a propagating particle interacting with its surroundings can be viewed as a 'dressed' quasiparticle with renormalized mass and other dynamic properties. Heterogeneous interfaces between two dissimilar materials are an essential building block for modern semiconductor devices. The 2-dimensional (2D) van der Waals (vdW) materials and their heterostructures provide a new opportunity to produce atomically sharp interfaces in the ultimate quantum limit for the electronic and optoelectronic processes. In this talk, we will discuss several research efforts to realize unusual quasiparticle pairing mesoscopic devices based on stacked vdW interfaces between 2-dimensional materials. The topics include semiconducting exciton condensations, paired composite fermions, spin-polarized cooper pairs and non-abelian anions in induced superconductivity in quantum Hall edge states.

Transparent image sensor for eye-tracking and nanophotonic infrared photodetectors

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Integrating and manipulating the nano-optoelectronic properties of Van der Waals heterostructures can enable unprecedented platforms for photodetection, sensing and modulation. Many of the realized devices have already demonstrated competitive performances and proof-of-concept integration with Si-CMOS technologies has been demonstrated [1,2]. But many challenges remain, and there is still a clear need for competing photodetectors for the full spectral range from short-wave infrared, infrared and terahertz.

In this talk, we present

- 1) the first transparent camera, applied as an eye-tracking device
- 2) demonstrate several new photodetection concepts for infrared light.

Image sensors hold a pivotal role in society in their ability to digitize visual scenes. Currently, all commercial image sensors and therefore cameras are opaque. We present the first transparent camera based on an array of graphene photodetectors. These transparent image sensors can have a far-reaching impact on human-computer interfaces, smart displays, and eye-tracking for augmented and virtual reality. The operation of these devices presents a fundamental shift in how we think about image sensor, as these devices can be hidden in plain sight.

In the second part of the talk, we present several new photodetection concepts for infrared light [3]. The first is a novel approach for highly responsive graphene-based photodetectors with orders of magnitude lower dark current levels, exploiting a metal-insulator-graphene diode structure [4]. This detector takes advantage of the low density of states of graphene near the neutrality point, giving rise to a novel type of gain mechanism. We also present an infrared photodetector based on a plasmonic antenna coupled to hyperbolic phonon-polaritons in hexagonal-BN to highly concentrate midinfrared light into a graphene pn-junction [4]. This novel approach explicitly benefits from the extraordinary nanophotonic properties of 2D materials and yields remarkable device performance featuring room temperature high sensitivity, hence achieving a combination currently not present in the state-of-the-art graphene and commercial mid-infrared detectors.

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FIGURES

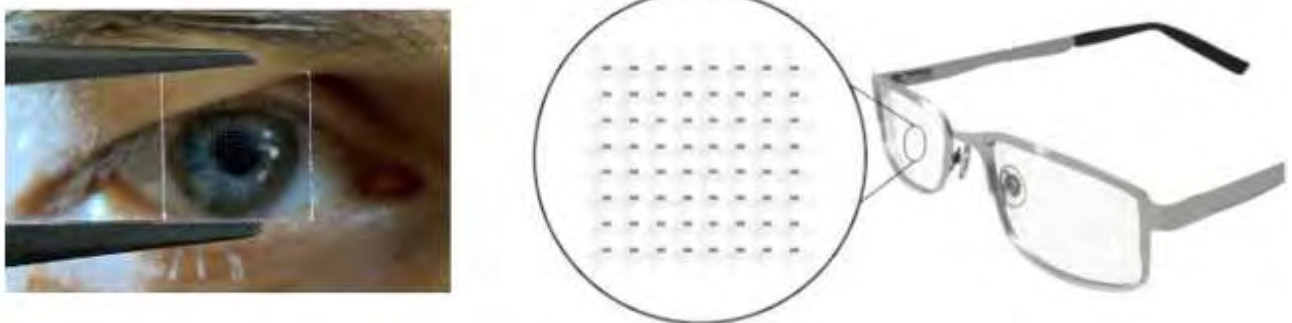


Figure 1: Left: transparent image sensor based on an array of graphene photodetectors. Right: eye-track device

2D Materials for Artificial Intelligence Systems - Eyes, Ears, Nose and Brain?

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Artificial Intelligence (AI) is going to revolutionize all aspects of life, from autonomous vehicles, industrial production and healthcare to environmental monitoring. Conventional computer hardware can deliver the performance required to run specific AI software, but only at the cost of severe energy consumption due to the so called von Neumann-bottleneck – the separation of memory and logic. This is particularly problematic in mobile systems, like vehicles or sensor networks, where the energy supply is limited, while sensor data is processed and analyzed through AI. Two-dimensional (2D) materials offer superior performance for many sensory tasks at the device level, such as photodetection, microphones or gas sensors, and should thus be considered as sensory inputs to AI systems. Several such sensor options that outperform existing technologies will be discussed in the talk. In addition, many applications for future AI will also require energy efficient hardware for data processing, which may come in the form of memristive circuit elements. 2D materials are heavily investigated regarding their memristive behavior, and there are several concepts with different underlying physics. I will discuss one option of molybdenum disulfide memristors that utilizes ion transport in van der Waals gaps to achieve plasticity.

Canted Topological Spin Transport in Low-symmetry Quantum Materials

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In this talk, I will present theoretical spin transport features in MoTe_2 and WTe_2 -based materials which have recently been the subject of great attention within the broad context of Quantum Materials [1]. By focusing on the monolayer limit, using DFT-derived tight-binding models and using both efficient bulk and multi-terminal formalisms and techniques [2,3], I will first discuss the emergence of new forms of *intrinsic spin Hall effect (SHE)* that produce large and robust in-plane spin polarizations. Quantum transport calculations on realistic device geometries with disorder demonstrate large charge-to-spin interconversion efficiency with gate tunable spin Hall angle as large as $\theta_{xy} \approx 80\%$, and SHE figure of merit $\lambda_s \theta_{xy} \sim 8\text{-}10$ nm, largely superior to any known SHE material [4]. Besides, I will present our theoretical prediction of an *unconventional canted quantum spin Hall phase* in the monolayer T_d - WTe_2 , which exhibits hitherto unknown features in other topological materials [5]. The low-symmetry of the structure induces a canted spin texture in the yz plane, dictating the spin polarization of topologically protected boundary states. Additionally, the spin Hall conductivity gets quantized ($2e^2/h$) with a spin quantization axis parallel to the canting direction. Our theoretical predictions for the canted QSHE findings have just been confirmed experimentally [6].

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FIGURES

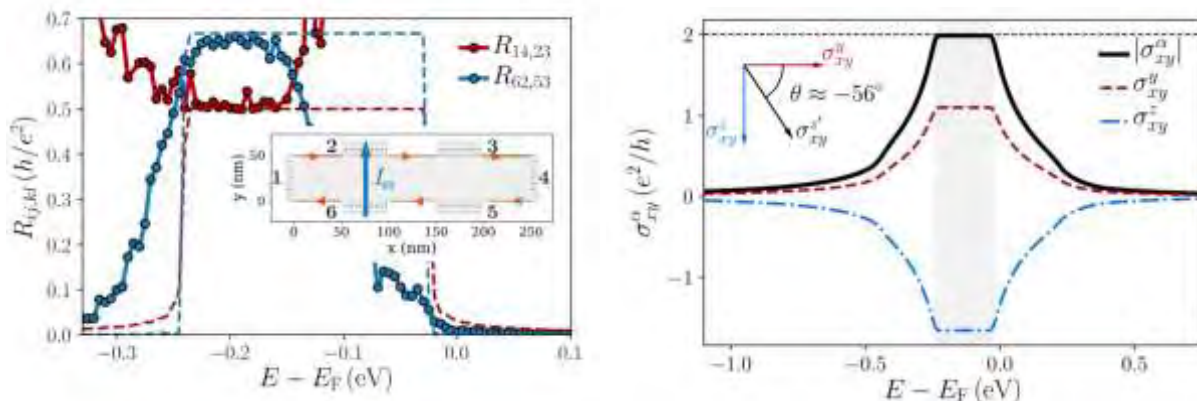


Figure 1: Right: Multiple components of the spin Hall conductivities computed for monolayer WTe_2
Left: Nonlocal resistances (6-terminals device), evidencing topological edge transport quantization

Structure Engineered Graphene Quantum Dots for Advanced Planar Micro-Supercapacitors

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The fabrication of micro-supercapacitors is essential for future microelectronics and flexible devices. But the relative low energy density has significantly impeded its wider applications. We have reported a micro-supercapacitors constructed with capacitor-type N-GQDs as negative electrode and battery-type MoS₂-QDs as positive electrode display outstanding electrochemical performance compared to other reported micro-supercapacitors, including a high energy density, an excellent rate capability, a fast frequency response capability, and a long-term cycling stability. The study presented here provides a new insight for the construction of high-performance MSCs, and, more importantly, offers a new reference in designing other high-performance energy storage devices based on 2D materials QDs.

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FIGURES

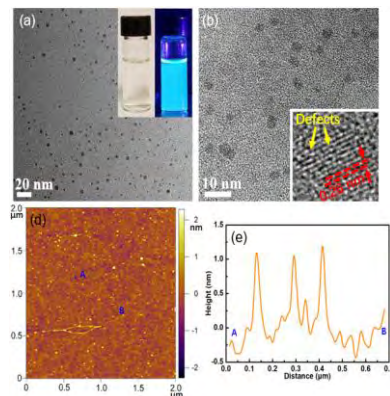


Figure 1: TEM and AFM characterizations of graphene quantum dots.

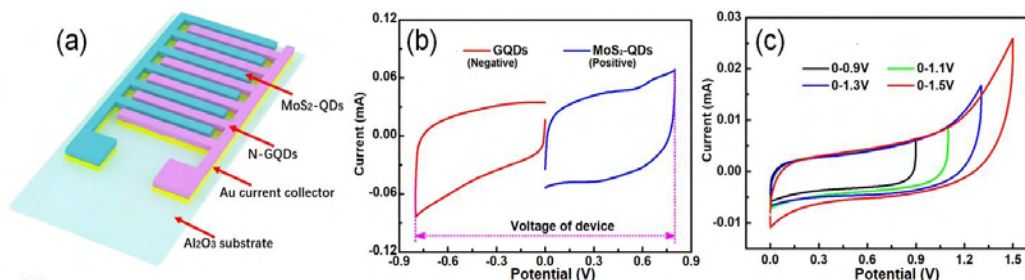
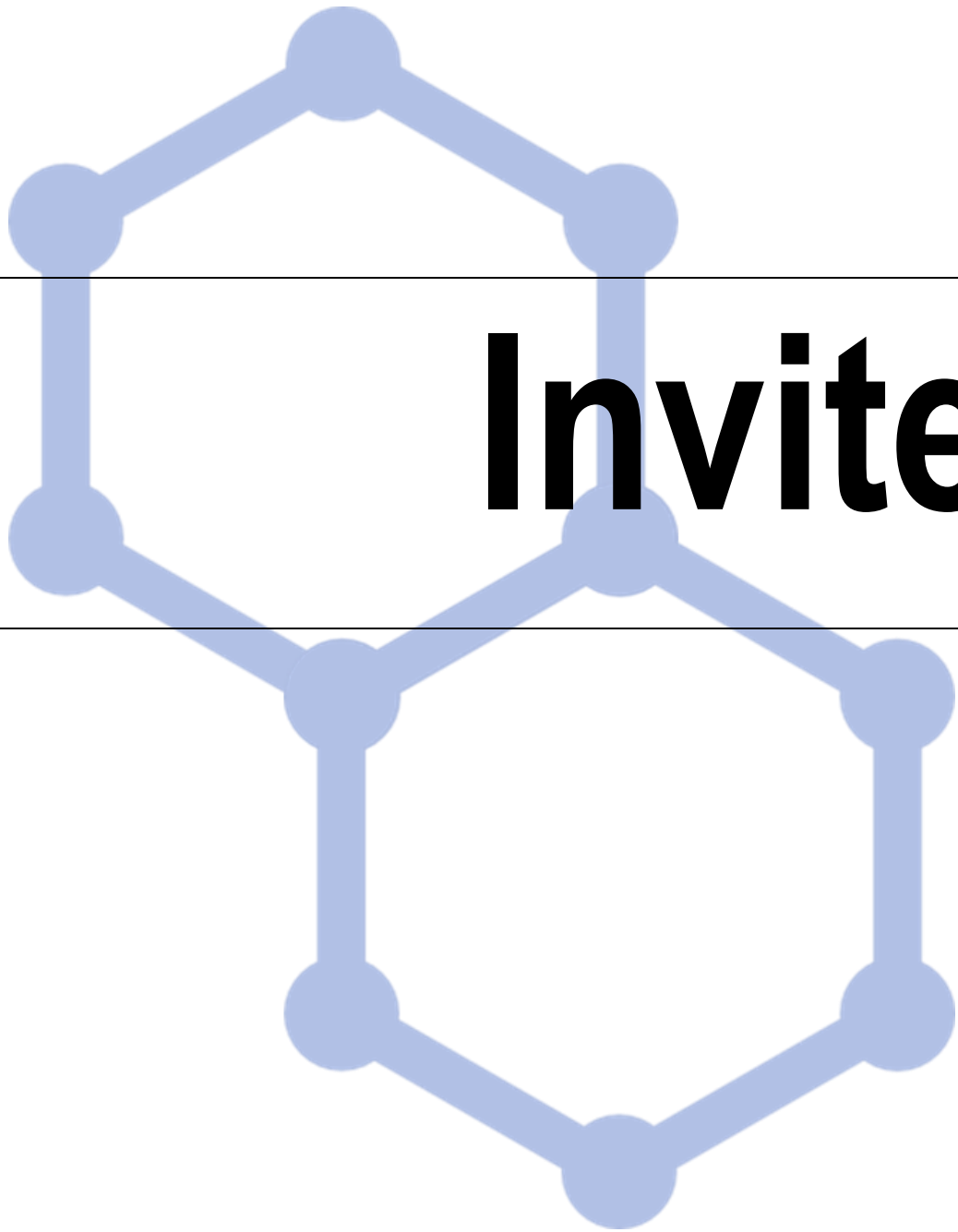


Figure 2: Illustration of asymmetric micro-supercapacitor and its performance.



Invited

Graphene aerogels: from self-assembly to applications

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Graphene aerogels have been proposed for applications in fields as varied as environmental remediation, Li-ion batteries, and bone tissue engineering. All these applications have different requirements in terms of mechanical properties, pore size, connectivity, and interfaces with the exterior environment. In this talk we will explore how we can tune the properties of reduced graphene oxide gels made by hydrothermal reduction of graphene oxide suspensions by controlling how graphene oxide flakes self-assemble during the process, and show few examples of applications of the resulting gels.

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Graphene-Perovskite photovoltaics: from lab cells to panels

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Abstract

Two-dimensional (2D) material such as graphene and related materials have been recently considered for photovoltaic applications. In particular, halide perovskite and 2D materials, including 2D perovskites, can be combined to enhance efficiency and stability of solar cells. In this talk I will present the progresses made in the use of Graphene and other related 2D materials (GRM) such as MoS₂ and MXenes to improve the performance and the stability of perovskite solar cells. The use of 2D materials allowed us to reach more than 26% efficiency in a tandem graphene-perovskite/silicon cell and permitted to realize a solar farm with 0.5 sqm panels obtained with single junction graphene-perovskite sub-modules with efficiency up to 16% (on a substrate area of more than 100cm²) and panel efficiency exceeding 10%. With a thorough multiscale experimental investigation, we point out that GRM can tune interfaces properties, reduce ion migration and modify the work-function of the perovskite absorber and charge transporting layers, all aspects that directly impact on the final efficiency and the stability under accelerated stress tests.

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High-temperature topological superconductivity in twisted double layer copper oxides

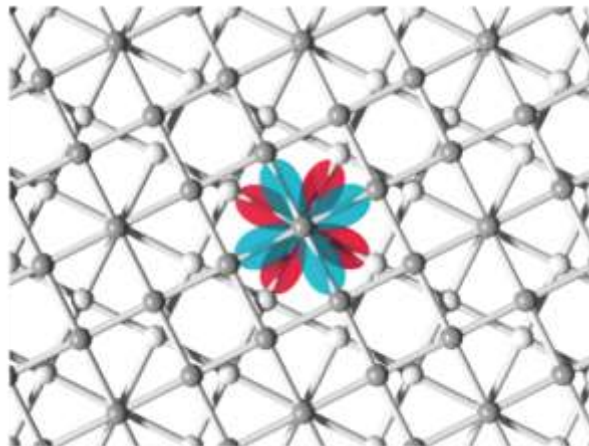
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Abstract:

A great variety of novel phenomena occur when two-dimensional materials, such as graphene or transition metal dichalcogenides, are assembled into bilayers with a twist between individual layers. As a new application of this paradigm, we consider structures composed of two monolayer-thin *d*-wave superconductors with a twist angle θ that can be realized by mechanically exfoliating van der Waals-bonded high- T_c copper oxide materials, such as $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$. On the basis of symmetry arguments and detailed microscopic modelling, we predict that for a range of twist angles in the vicinity of 45° , such bilayers form a robust, fully gapped topological phase with spontaneously broken time-reversal symmetry and protected chiral Majorana edge modes. When $\theta \approx 45^\circ$, the topological phase sets in at temperatures close to the bulk $T_c \approx 90$ K, thus furnishing a long sought realization of a true high-temperature topological superconductor.

REFERENCES



FIGURES

Figure 1: Schematic view of two copper-oxygen square lattices with twist angle close to 45° .

Atomic scale electronics and photonics (AtomEP) with quantum dots in 2D materials

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Shrinking electronic circuits down to nanometer scale may enable atomic scale electronics and photonics powering quantum processors and nanoscale robots. We describe here recent theoretical and experimental work aiming at design of atomically precise nanostructures in graphene and transition metal dichalcogenites (TMDCs) capable of realizing the three functionalities of a quantum circuit: electronics, photonics and spintronics. The design tools include combination of materials, number of atomic layers, lateral size, shape, type of edge, sublattice symmetry, topology and carrier density in graphene and TMDC quantum dots. In graphene, sublattice engineering allows design of magnetic moments tunable with voltage and light and size engineering leads to optical gaps from THz to UV[1-4]. Electrostatically defined quantum dots bypass the need to control the edges of finite structures. We describe the role of gates, K and Q valleys, SO, topology, number of electrons and electron-electron interactions on the electronic properties of electrostatically gated quantum dots in bilayer graphene and MoS₂ [5-7]. The existence of valley polarized broken symmetry many-body states will be discussed.

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Visualizing 2D materials at the atomic scale

Adina Luican-Mayer

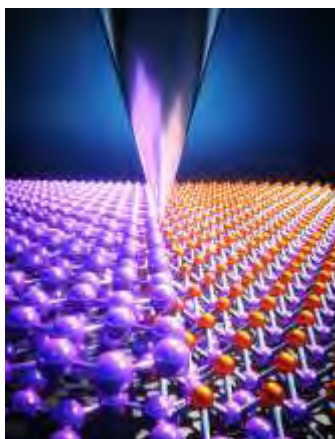
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Understanding and controlling the properties of 2D materials to our advantage can be contemplated with the development of experimental tools to probe and manipulate electrons and their interactions at the atomic scale. In this talk, I will present scanning tunnelling microscopy and spectroscopy experiments aimed at: elucidating the nature of atomic-scale defects in 2D materials [1], visualizing moiré patterns between crystals with different symmetries [2] and imaging surface and edge states in a magnetic topological system. Moreover, I will discuss how we leverage our expertise in probing and engineering electronic states at surfaces of 2D materials to further the development of graphene-based gas sensors [3] and gated quantum dot circuits based on 2D semiconductors [4].

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Graphene-based materials in sensors and biosensors

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Abstract

A general overview on the graphene-related materials (GRM) such as graphene oxide (GO) and graphene quantum dots (GQDs) with interest in (bio)sensors application will be given. We take advantages of GRMs characteristics to design and fabricate innovative cost-efficient (bio)sensing platforms and even smart devices such as nano/micromotors for a myriad of applications. Both optical and electrical properties of GRMs are exploited. For optical-based platforms we explore phenomena such as quenching of the fluorescence induced by GO or photoluminescence of GQDs that can easily operate in synergy with various other nanomaterials opening the way to several unprecedented biosensing strategies. For electrical-based platforms we take advantages of electrical properties of GRM including laser scribed ones patterned onto paper/plastic while building electrical/electrochemical sensing device and unique, simple nanomotors. Taking advantage of GRMs we are developing simple, sensitive, selective and rapid biosensing platforms that include: a) GO – based microarray & laterals flow technologies taking advantages of high quenching efficiency of GO. A “turn ON by a pathogen” device will be shown as a highly sensitive detection system using plastics or paper/nanopaper substrates; b) GQDs–based sensors for contaminants detection based on the use of multifunctional composite materials that enable rapid, simple and sensitive platforms in connection to smartphone; c) electroluminescent-based approaches d) A water activated GO transfer technology using wax printed membranes for fast patterning of sensors as well as for a cost-efficient nanomotor building technology for several applications. This work is supported by EU (Graphene Flagship), CERCA Programme / Generalitat de Catalunya. The ICN2 is supported by the Severo Ochoa Centres of Excellence programme, funded by the Spanish Research Agency (AEI, grant no. SEV-2017-0706).

Commercializing Graphene for Everyday Use: The Critical Role of Regulation

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Abstract

The historical challenge for the commercialization of graphene has always been about how to produce it at large volume and at low cost. The graphene players fascinated by its unique performance often forget that the industrial adoption of graphene, like any other new nanomaterial, can never happen if the material is not regulated. The regulatory agencies require very specific toxicological study reports (in accordance to OECD guidelines) to be able to regulate the material. Such studies could cost millions of dollars and impede many graphene producers from fully engaging in the exhausting regulatory activities. In 2020, NanoXplore Inc. completed five major studies on acute inhalation, dermal sensitization, dermal irritation, in-vitro gene toxicity and in-vivo gene toxicity on a few-layer graphene in accordance with OECD 436, 406, 404, 473 and 474-489, respectively [1]. The results revealed much lower health risk than what were usually anticipated for graphene.

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Hybrid Molecule/2D Material van der Waals Heterostructures

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The rise of graphene and related 2D materials makes it possible to form heterostructures held together by weak interplanar van der Waals (vdW) interactions. The interactions of such 2D layers with adventitious contaminants is able to exert a strong effect on its major electronic characteristics [1]. However, the controlled incorporation of ordered organic molecules within these systems holds an immense potential. Whilst nature offers a finite number of 2D materials, an almost unlimited variety of molecules can be designed and synthesized with predictable functionalities [2-3]. The possibilities offered by systems in which continuous molecular layers are interfaced with inorganic 2D materials to form hybrid organic/inorganic van der Waals heterostructures are emphasized. Similar to their inorganic counterpart, the hybrid structures have been exploited to put forward novel device architectures. Moreover, specific molecular groups can be employed to modify intrinsic properties and confer new capabilities to 2D materials. During my talk, I will give a brief overview of how molecular self-assembly at the surface of 2D materials can be mastered to achieve precise control over position and density of (molecular) functional groups, paving the way for a new class of hybrid functional. In particular, within such vdW heterostructures, currently assembled by mechanical superposition of different layers, periodic potentials naturally occur at the interface between the 2D materials. These potentials significantly modify the electronic structure of the individual 2D components within the stack and their alignment, thus offering the possibility to build up hybrid and novel materials with unique properties. Furthermore, I will also show how dynamic light-switchable supramolecular lattices can be created on graphene thus imparting novel functionalities to the pristine material.

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FIGURES

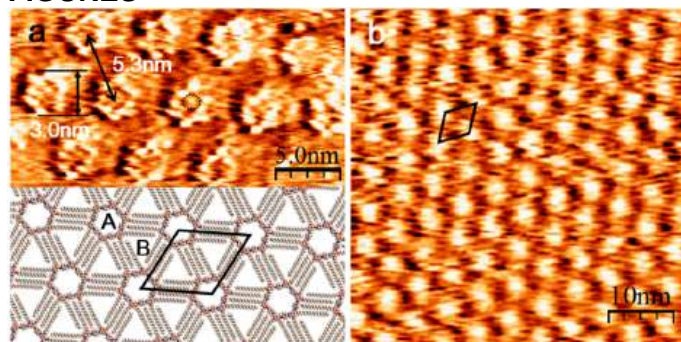


Figure 1: Various molecules on a graphene surface forming different patterns that result in different electronics properties

Development of International Measurement Standards

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Companies cannot efficiently develop new applications in the many technological areas where graphene is predicted to be disruptive, as they do not know the properties of the material supplied to them. Thus, there is a need for reliable, accurate and precise measurements for material testing, which are standardised across the industry and therefore allow end-users to be able to compare commercially-available materials from around the world.

The current state of international measurement standards covering the material properties of the graphene family will be detailed, including the ISO/IEC standard "TS 21356-1 Structural characterization of graphene: Graphene from powders and dispersions". Based on the NPL Good Practice Guide [1] that was developed in collaboration with the University of Manchester, this standard details the techniques and decision making process of characterising the percentage of 'graphene' or 'few-layer graphene', as defined by ISO [2], in materials sold globally. Importantly, the sample preparation, measurement protocols and data analysis are all described, to enable more reproducible comparisons. The development of the understanding of one of the techniques included in the standard, the Brunauer-Emmett-Teller (BET) method will also be reported.

A key part of developing international measurement standards is the validation of protocols through international interlaboratory comparisons. As an example, the initial results of a VAMAS interlaboratory study, TWA 41 Project 1, on Raman spectroscopy of chemical vapour deposition (CVD) grown graphene will be reported. This project will directly support the development of the ISO/IEC standard "PWI 21356-2 – Structural Characterisation of CVD-grown Graphene". This interlaboratory study gathered data from 14 participants across academia, industry (including instrument manufacturers) and National laboratories, revealing key metrology issues that must be considered.

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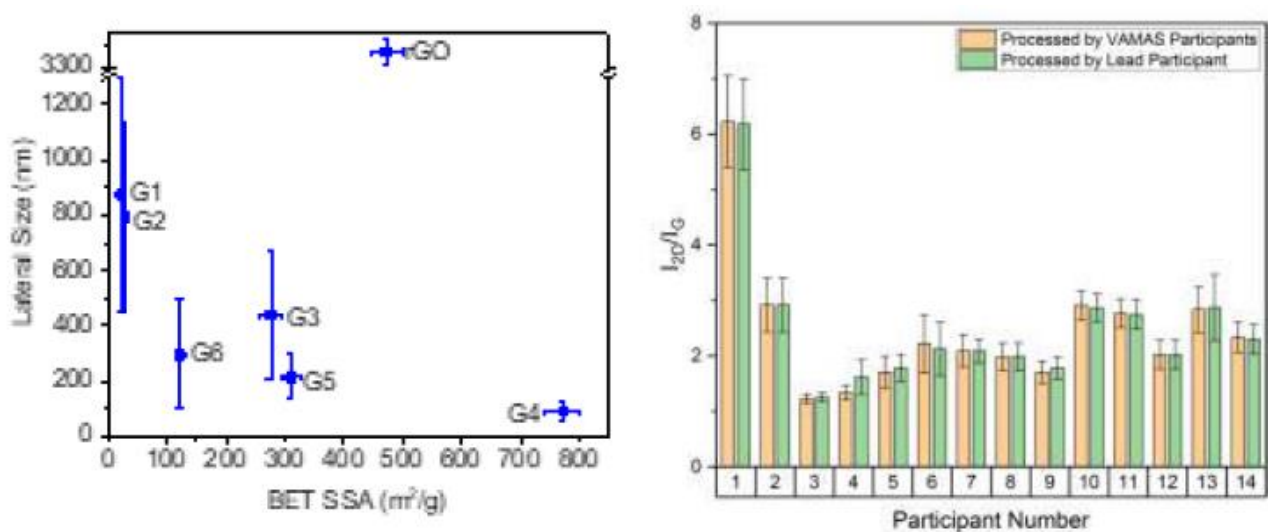


Figure 1: (Left) SEM lateral size of flakes from commercial powders vs the BET specific surface area (SSA). (Right) I_{2D}/I_G Raman peak intensity ratios of CVD-grown graphene reported in an international comparison. Differences in peak intensity ratios due to the data analysis being performed by the individual (green) and lead (orange) participants are also shown.

Precision ion sensitive transistors enabled by wafer scale graphene

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Abstract

Accurate, real-time measurement of ion concentration is of broad importance to the management of fresh water resources, effective waste water treatment, and industrial process control. I will present recent work on large-area graphene based ion sensitive field effect transistors (ISFETs), employing metal oxide layers or ionophore based membranes and wafer scale graphene processing methods [1-4]. Large-area graphene ISFETs benefit from the combination of high mobility charge transport ($\mu = 5000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), reduced low-frequency noise with increasing transistor channel area ($K = f \langle \Delta V^2 \rangle / V_0^2 = 5 \times 10^{-13}$ for a 5 mm x 5 mm device), and facile integration with ion sensitive layers (for example, sensitive to H^+ , K^+ , Na^+ , NH_4^+ , Cl^- , NO_3^- , HPO_4^{2-} and SO_4^{2-}). The combination of Nernstian limited sensitivity with low $1/f$ noise enables concentration resolution of $r \sim 0.003 \log \text{ M}$. The stability and resolution of graphene ISFETs allows simultaneous, real-time measurement of multiple analytes through the application of Nikolskii-Eisenmann analysis to an array of graphene ISFETs, improving selectivity over that achievable with a single ISFET. I will conclude with a discussion of challenges and prospects for future development of graphene ISFETs for water quality monitoring applications.

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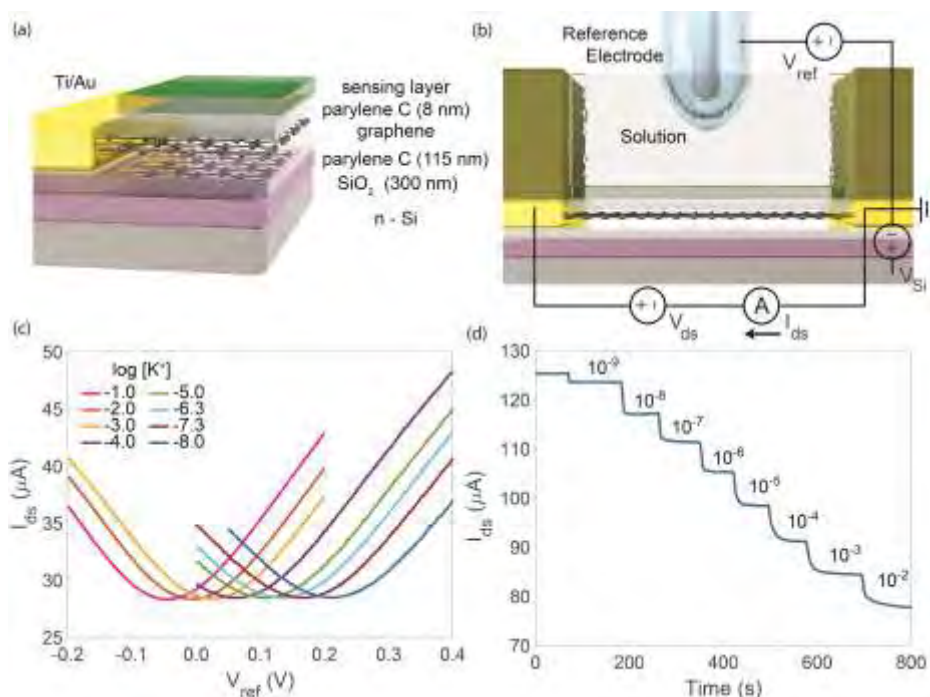


Fig. 1. (a) Schematic of a graphene ISFET encapsulated with parylene and a sensing layer on a SiO_2/Si substrate. (b) Electrical schematic for measuring the current through the graphene channel I_{ds} for different electrolytic solutions, with bias V_{ds} , and reference electrode V_{ref} (c) The measured channel current, I_{ds} , versus V_{ref} , for a representative K^+ -sensitive graphene ISFET. (d) Continuous real-time measurement of I_{ds} of a K^+ -sensitive graphene ISFET while increasing K^+ molar concentration in decade steps.

ZEN Graphene Solutions Response to COVID-19

Antiviral Coatings and Viral Detection

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Summary

ZEN Graphene Solutions is a Canadian company with a mission to produce consistent, high-quality graphene products at industrial scale and make graphene easy to use in industrial processes and technology through a variety of solutions (masterbatch, master alloys, inks, and dispersions) produced economically with environmentally and socially responsible principles.

In April, the response to COVID-19 closed the research facilities of ZEN's collaborators including universities and industrial partners. ZEN refocused their resources to pursue possible graphene solutions that could contribute towards the fight against COVID-19. Three potential areas have shown promise and results will be featured in the presentations.

1. ZEN Graphene Solutions developed an antiviral coating that has been proven to be over 99% effective to inactivate the SARS-CoV-2 virus and is suitable to be incorporated into masks and filter technology. The coating features the symbiotic activity of graphene oxide and metallic nanoparticles (see Fig. 1).
2. ZEN Graphene is supporting Dr. Ménard from the University of Ottawa to develop a coating with an anti-pathogen mechanism of graphene based on the atomic-scale edges of graphene that effectively act as nano-razors piercing the cellular membrane and, hence inactivating viruses as well as other types of pathogens such as bacteria and fungi (see Fig.2).
3. ZEN Graphene is in collaboration with researchers at the University of Ottawa and McMaster University to develop a graphene-based rapid COVID-19 paper sensor that utilizes aptamer technology which is a synthetic single-stranded DNA. Each aptamer has a unique shape that has a specific molecular recognition (bonding).

FIGURES

Figure 1: ECS imagery of coated mask material showing carbon and oxygen content of Graphene Oxide on mask

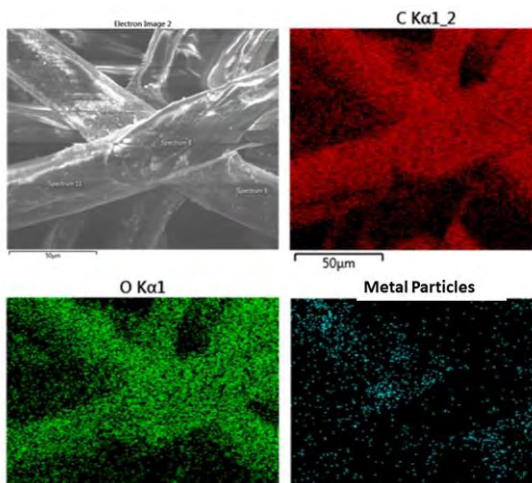
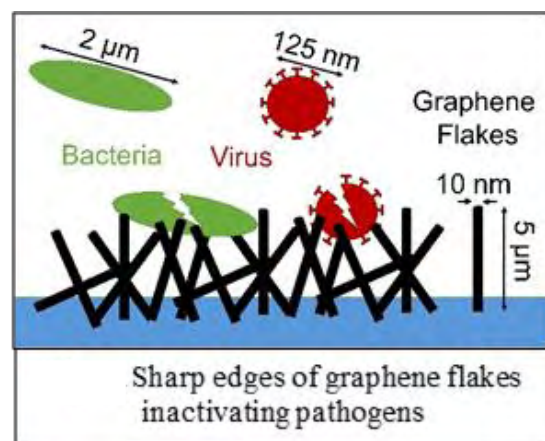


Figure 2: Graphene acting as nano-scissors



Graphene Integration in the Electronic Industry

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Abstract

The most straightforward and economically viable way to introduce a new advanced material into the market is by integrating it into an existing industry, however, this integration comes with many challenges. Graphene devices such as sensors [1,2] and biosensors to aid in the current pandemic situation and photodetectors for future data communication and night vision camera applications are getting closer to the market and thus many aspects need to be taken into consideration. Such as the industrial growth, transfer and device fabrication of graphene at relevant throughputs and wafer scales, Figure 1. In addition, the existing electronics industry will impose certain restrictions like the need to meet strict metal contamination levels. However, the straightforward integration of graphene with off the shelf CMOS technology [3] is a clear demonstration that things are moving in the right direction. During this talk I will try to cover how to overcome some of those challenges in order to move graphene closer to the industrial market.

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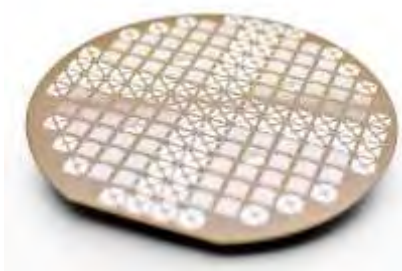
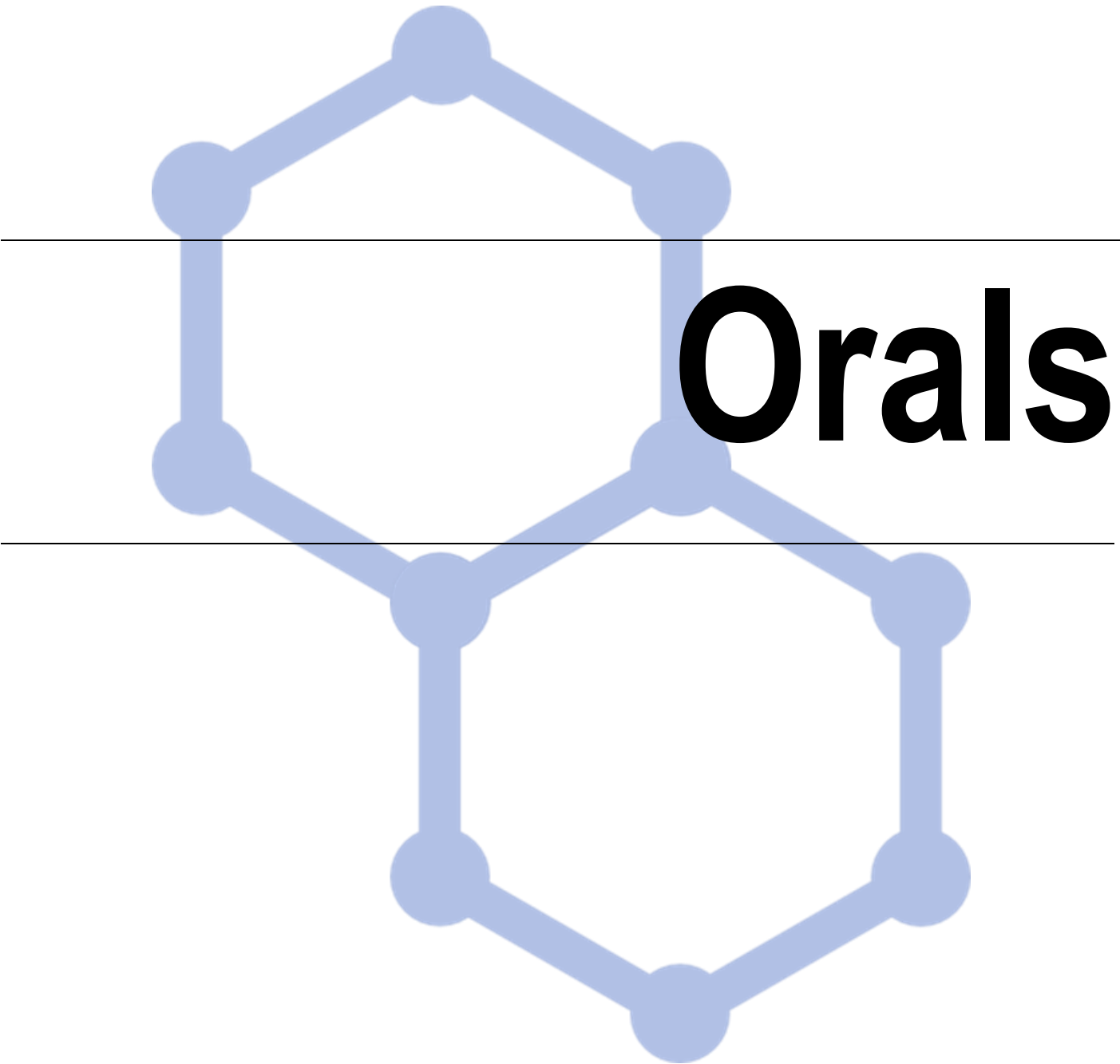


Figure 1: Graphene field effect transistors (GFETs) at wafer scale.



Layer Dependant Mechanical Properties of Graphene

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The impressive mechanical properties, including the elastic modulus, toughness, and lubrication properties of graphene has resulted in a significant interest in understanding their origins and limitations. For example, graphene has been shown to be one of the stiffest materials known, having an in-plane stiffness of 1 TPa [1]. Several studies have shown that many of these properties are dependent on the substrate supporting graphene and/or how many layers of graphene cover the substrate. For example, the friction properties have been observed to be layer dependent, with the mechanism of layer dependent friction being attributed to variations in the out-of-plane bending stiffness of graphene varying with its thickness [2-4]. While this friction mechanism has been often used, there have been little experimental work supporting the theoretical claims of layer-dependent out-of-plane stiffness. Here we conduct a rigorous set of experiments using ultra-high vacuum atomic force microscopy (AFM) to investigate these layer-dependent mechanical properties of graphene. Specifically, contact resonance AFM was conducted with Si tip on graphene of varying layers supported by a silicon substrate. Variations in the obtained contact resonance indicate changes in the elastic modulus in out-of-plane bending that shows a linear decrease in the elastic modulus with the number of layers of graphene. More specifically, an elastic modulus of 0.97 ± 0.001 TPa was measured for one layer graphene and observed decrease of 4.95% is observed with each additional layer of graphene up to 4 layers. These findings provide a substantial evidence for the frictional behaviour of graphene as well as enriching the knowledge about its layer dependant stiffness on top of simulation studies.

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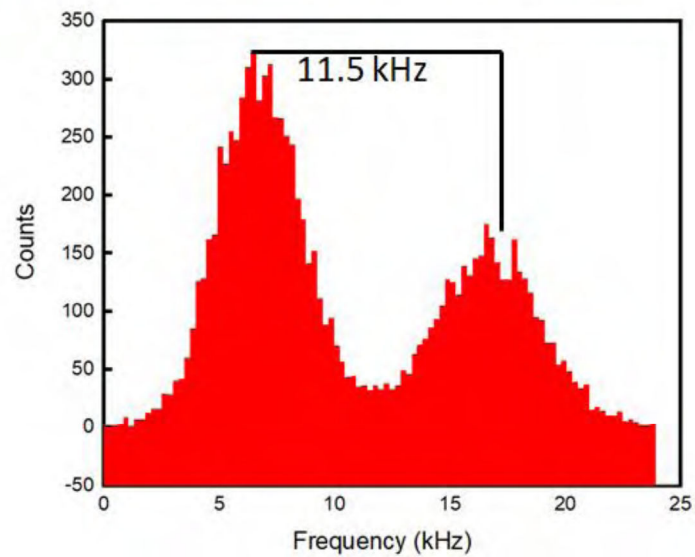
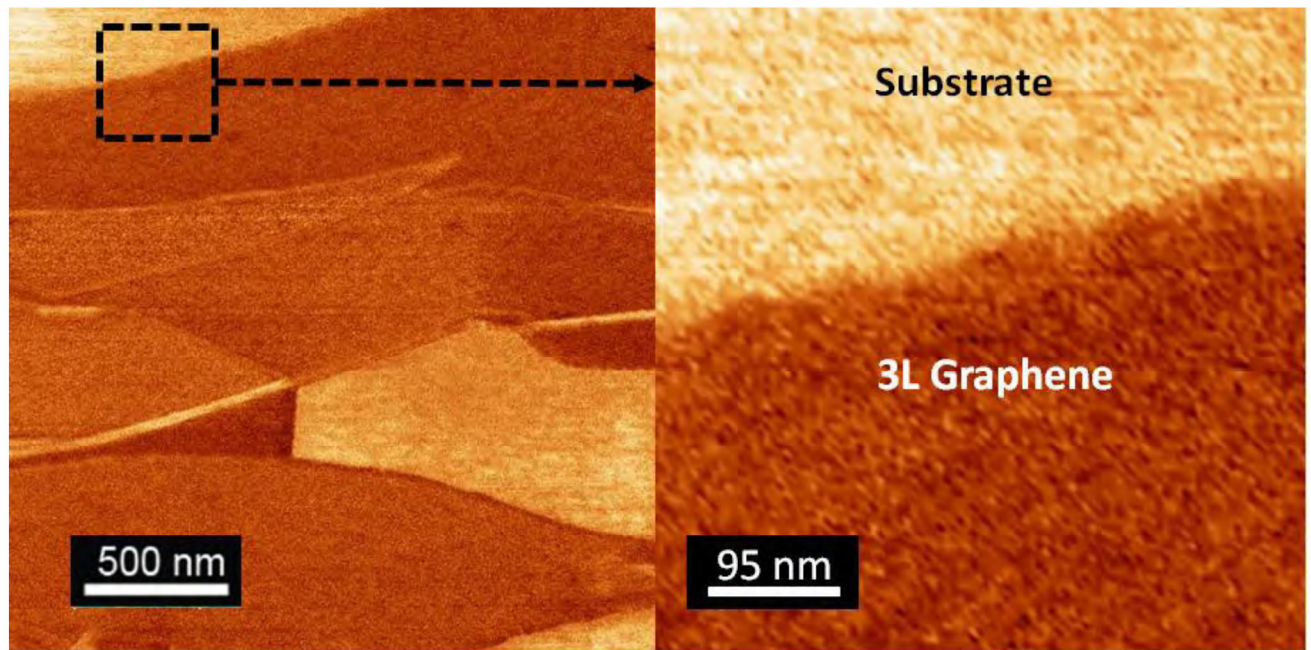


Figure 1: The histogram of the contact resonance frequency indicates a variation of about 12 kHz with addition of three layers graphene.

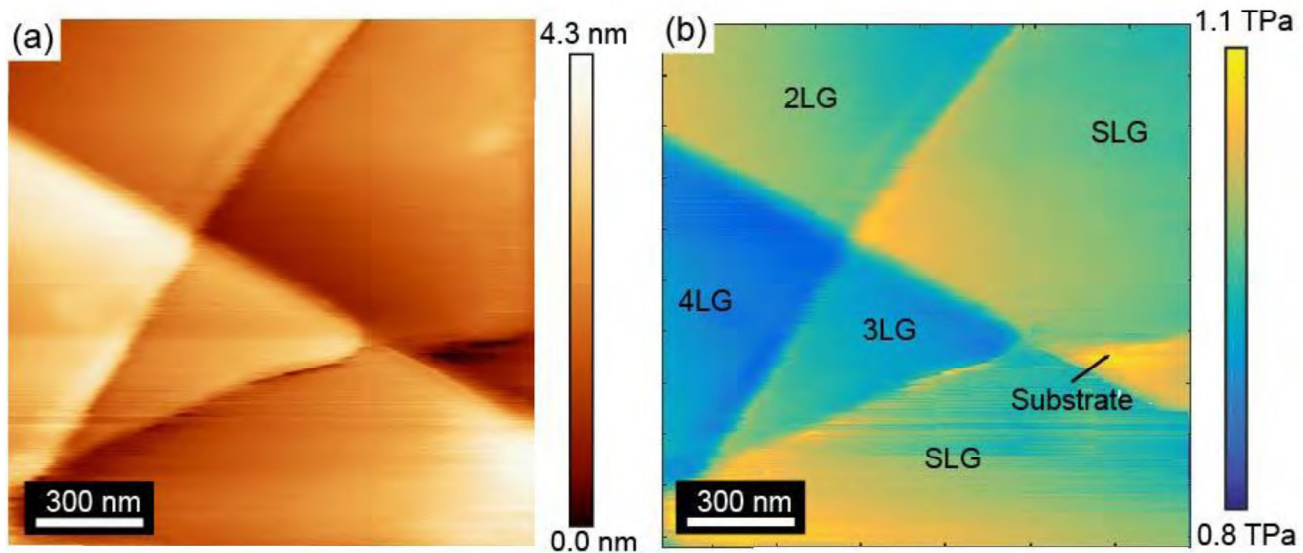


Figure 2: Topography of graphene area contains different graphene layers obtained by NC-cantilever. (b) Calculated elastic map through the CR experiments data.

Valley Polarization in WS₂/Graphene Heterostructures

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Understanding valley polarization is vital for transferring data in next-generation electronics. Due to spin-orbit coupling, WS₂ is a promising material for valleytronic devices. Here we address the behavior of valley polarization in different WS₂ heterostructures. The results indicate that unlike interaction in WS₂ encapsulated with hBN, the interaction between WS₂ and graphene has an intense impact on the temperature dependence depolarization. Furthermore, intervalley scattering rates under resonant and non-resonant excitation energy are crucial parameters to see the temperature dependence by considering that Fröhlich coupling is calculated. The results show that the scattering rate is almost independent of temperature due to large phonon energy. The results suggest that the major contribution of valley depolarization merges from the change in the radiative lifetime.

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FIGURES

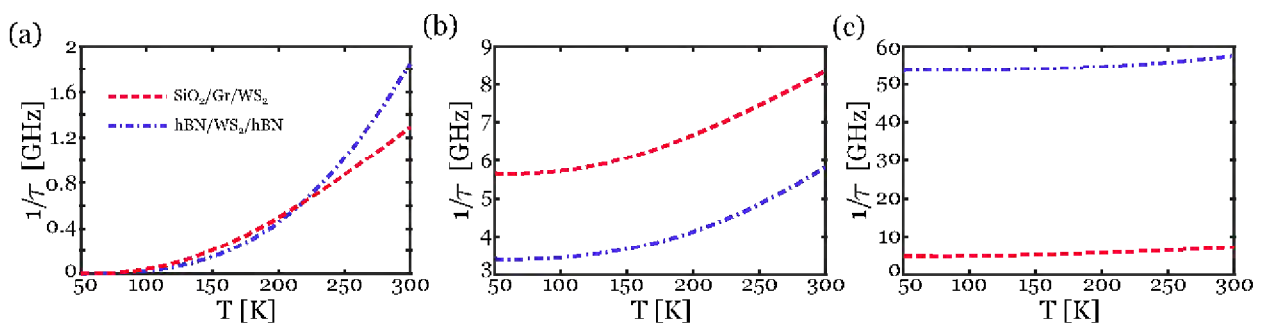


Figure 1: Inter-valley scattering rates of electrons in WS₂ heterostructures. (a) on resonance excitation conditions, (b) 55 meV above resonance excitation, and (c) 200 meV above resonance excitation.

Controlled growth of vertical MoS₂ flakes to in-plane MoS₂ and their utilizations in photodetectors

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Abstract (Arial 11)

Here, we proposed controlled growth of vertical MoS₂ flakes from in-plane MoS₂ by our modified chemical vapor deposition (CVD) technique. We synthesized in-plane MoS₂, vertical MoS₂ and pyramid MoS₂ flakes from CVD. Detailed structural, optical and morphological characterizations were performed. The initial in-plane MoS₂ flakes worked as the seeding platform for the growth of vertical MoS₂. We systematically played with the gas flow rate to grow these unique structures.

Further, we utilized the unique vertical MoS₂ structures in fabricating broadband photodetectors. We formed the heterojunction of p-type earth abundant 3D Cu₂ZnSnS₄(CZTS) and n-type 2D-layered MoS₂ to develop photodetector. Detailed photoelectron spectroscopy performed, not just to inspect the chemical bonding at the interface, but also to uncover the electronic interaction at the interface in terms of band alignment. Taking a step further, photoluminescence (PL) measurements were carried out as a curiosity to investigate any significant change in the PL signal while going from MoS₂ side towards the CZTS/MoS₂ interface.

As a proof of concept, a self-driven CZTS/MoS₂ heterojunction broadband photodetector was constructed exhibiting pronounced photovoltaic features with high responsivity 141 mA/W, outstanding photo switching capability ($I_{on}/I_{off} = 112$) and fast response ($\tau_r/\tau_d = 81/79$ ms). The responsivity was further enhanced to 79 A/W at moderate bias (@ 6V). Additionally, the device showed exceptional stability after 1500 hours of operation. This work intends to trigger the research on 3D/2D for high performing optoelectronic devices based on CZTS/MoS₂ heterojunctions.

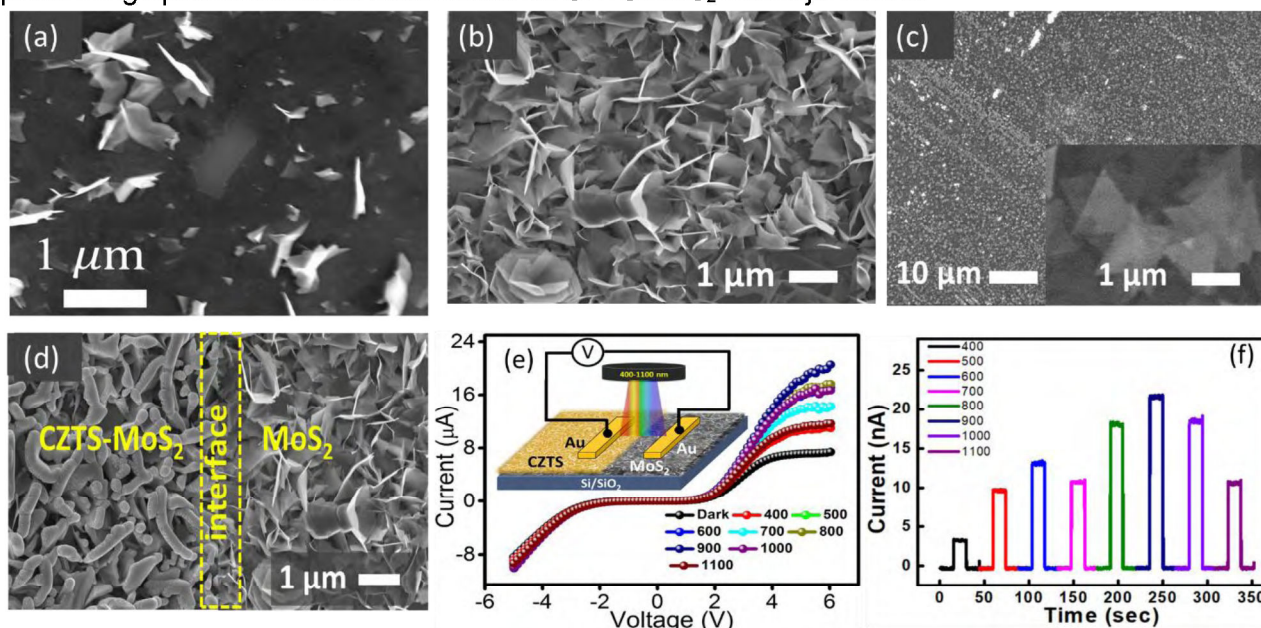


Figure: FESEM image of (a) mixed MoS₂ flakes (b) Vertical MoS₂ (c) Pyramid MoS₂ flakes (d) FESEM image of area showing the interface between CZTS and MoS₂. (e) CZTS/MoS₂ p-n junction PD, in dark and under illumination with different wavelengths, (wavelengths in nm scale). (f) Transient photoresponse measurements of CZTS/MoS₂ PD at different wavelengths ranging from 400 to 1100 nm in self-powered mode (0V bias).

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Enabling predictive capabilities for the polaritonic response of the biaxial van der Waals crystal α -MoO₃

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Highly anisotropic crystals have recently attracted considerable attention because of their ability to support polaritons with a variety of unique properties, such as hyperbolic dispersion, negative phase velocity, or extreme confinement. Particularly, the biaxial van der Waals semiconductor α -phase molybdenum trioxide (α -MoO₃) has recently received substantial attention due to its ability to support in-plane hyperbolic phonon polaritons (PhPs) —infrared (IR) light coupled to lattice vibrations in polar materials—, offering an unprecedented platform for controlling the flow of energy at the nanoscale [1,2]. Yet, to accurately predict the IR response of α -MoO₃ and thus to enable predictive capabilities for the extraordinary optical response of this material, it is imperative to develop both an accurate IR dielectric function model for α -MoO₃ and a theoretical study on electromagnetic modes in biaxial crystal slabs.

Here [3], we derive the dispersion relation of electromagnetic modes in biaxial slabs surrounded by semi-infinite isotropic dielectric half-spaces with arbitrary dielectric permittivities. Apart from a general dispersion relation, we provide very simple analytical expressions in typical experiments in nano-optics: the limits of short polaritonic wavelength and/or very thin slabs, allowing for an in-depth analysis of anisotropic polaritons in novel biaxial van der Waals materials.

Moreover, we report the accurate IR dielectric function of α -MoO₃ [4] by modelling polarized IR reflectance spectra acquired on a single thick flake of this material. Unique to our work, the far-field model is refined by contrasting the experimental dispersion and damping of PhPs extracted by near-field polariton interferometry using scattering-type scanning nearfield optical microscopy (s-SNOM) on thin flakes of α -MoO₃, with analytical [3] and transfer-matrix calculations, as well as full-wave simulations (Fig. 1). Through these correlative efforts, exceptional quantitative agreement is attained to both far- and near-field properties for multiple flakes, thus providing strong verification of the accuracy of our model, while offering a novel approach to extracting dielectric functions of nanomaterials, usually too small or inhomogeneous for establishing accurate models only from standard far-field methods. In addition, by employing density functional theory (DFT), we provide insights into the various vibrational states dictating our dielectric function model and the intriguing optical properties of α -MoO₃.

Our findings will enable the interpretation of experimental far- and near-field data, as well as an efficient design of nanostructures supporting such highly anisotropic polaritons supported by α -MoO₃.

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Graphene field effect transistors for detection of volatile organic compounds and simulants of chemical warfare agents

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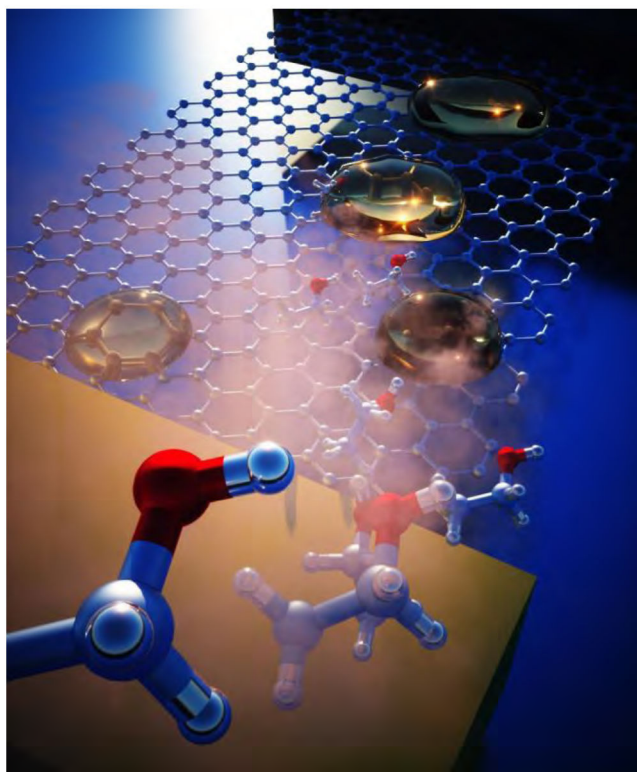
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Graphene is a strong candidate for the development of new gas sensing technologies due to its high surface-to-volume ratio, mechanical strength and flexibility, large conductivity, and low electrical noise. Yet control over material growth and understanding of how material imperfections affect the performance of devices are challenges that hamper the development of applications.^{2,3} Here we report our results using graphene field effect transistors based on CVD graphene as gas sensors. Specifically, we monitor the response of graphene chemiresistors while exposed to both the volatile organic compound ethanol and dimethyl methyl phosphonate (DMMP), a nerve agent simulant. On the fabrication side, we report that generally thermal surface treatments after the devices are fabricated lead to improved sensitivity and reduced device-to-device variation. Using such methods, we can detect DMMP vapours at ppb concentration. Supported by theoretical simulations, we discuss our understanding of the mechanisms underlying the sensor's response as well as next steps towards optimizing the graphene sensor's performance.

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Exceptional properties of Disordered materials for novel applications

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The fabrication and characterization of disordered materials has recently witnessed an outstanding progress leading to materials with unprecedented properties. In particular, the possibility to synthesize wafer-scale two-dimensional amorphous carbon monolayers, structurally dominated by sp² hybridization, has been demonstrated. This achievement has initiated a new platform of low-dimensional materials allowing to explore alternative forms of membranes with enhanced chemical reactivity which could be employed for coating [1,2].

The excellent physical properties of the mentioned materials derive from the nature and degree of their disorder which, controlled at the fabrication level, represents the key ingredient to tune their physical/chemical properties for specific target applications. In this respect, new fabrication strategies to modify the degree of disorder and a systematic theoretical characterization of the impact of the material structural quality on the ultimate performance is urgent. Even more importantly, the search for new disordered materials for novel applications appears as an extremely promising way.

In this talk we present a systematic analysis of the structural and vibrational properties of amorphous carbon monolayers as a function of the structural quality of the material, showing how disorder results in a tunable thermal conductivity varying by more than one order of magnitude [3]. Finally, we present the results of the newly demonstrated synthesis of a thin film of amorphous Boron Nitride showing extremely low dielectric characteristics: high breakdown voltage and likely superior metal barrier properties [4]. The fabricated material aims at replacing current interconnect insulators in the next-generation of electronic circuits. We discuss the experimental setup and present the results of our calculations which have contributed to the understanding of the structural morphology of the amorphous material as well as explaining the superior dielectric performances.

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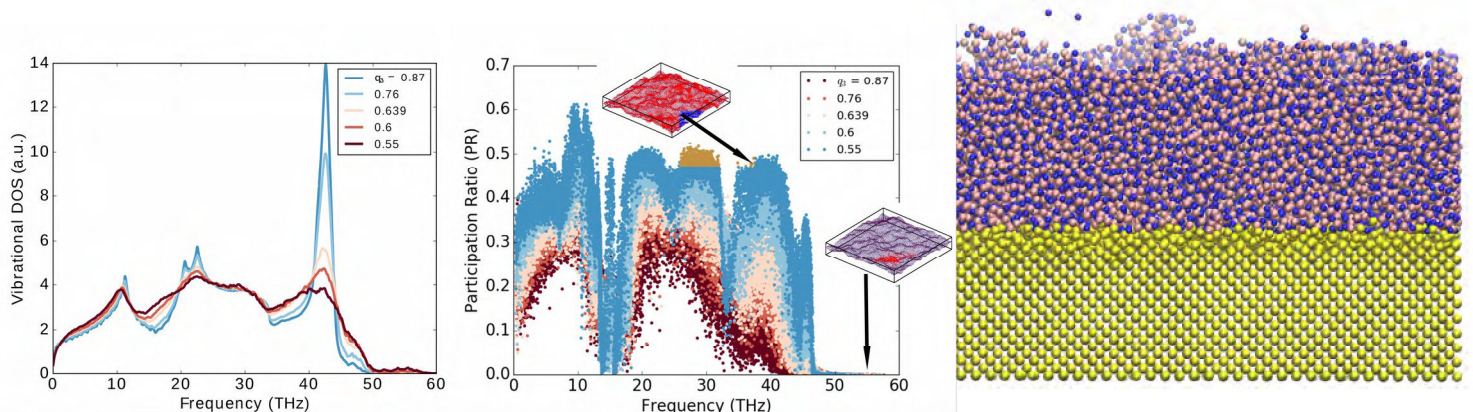


Figure 1: (Left) Vibrational DOS of Amorphous Graphene for different degrees of amorphousness. (Right) Participation Ratio of the samples and atomic displacements (insets)

Figure 2. Atomistic sample of Amorphous Boron Nitride.

2D Layered Metal Monochalcogenides for Photoelectrochemical (PEC)-Type Photodetectors and Water Splitting Applications

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Aqueous-based photoelectrochemical (PEC) devices, such as self-powered photodetectors and water splitting cells, represent powerful tools to convert the electromagnetic radiation into chemical fuels and electricity.[1] To achieve efficient PEC systems, it is mandatory to develop photocatalytic materials that efficiently absorb light in the desired spectral range (UV/visible for energy conversion systems), creating free charge carriers with suitable energies to carry out the oxidation-reduction (redox) reactions before they recombine.[2] In order to progress in these tasks, two-dimensional (2D) materials, including either single- and few-layer flake forms, are attracting huge interest as potential advanced photo(electro)catalysts.[3] Recently, 2D group-IIIA and group-IVA metal monochalcogenides (MCs), with chemical formula MX (M = Al, Ga, In, Tl and M = Si, Ge, Sn, Pb respectively; X = S, Se, Te), have been theoretically predicted to be low-cost and environmentally friendly water splitting photocatalysts. Among them, layered germanium selenide (GeSe) and indium selenide (InSe), are promising material candidates for optoelectronic devices due to their tuneable electronic structure, strong visible-light absorbance, photoresponse and environmental stability. However, the evaluation of their photo(electro)catalytic properties was still incomplete until last years, pointing out the need of experimental trials and validation. Here, we report the first experimental characterization of the PEC water splitting activity of single-/few-layer flakes of GeSe and InSe produced in inks form by scalable liquid-phase exfoliation (LPE) approach in non-toxic solvent (*i.e.*, 2-propanol).[4] The PEC behaviour of MCs-based photoelectrodes, obtained by spray coating approach,[5] were evaluated in different aqueous media, ranging from acidic to alkaline solutions and under different illumination wavelengths in the visible spectral range, namely 455, 505 and 625 nm. The obtained performances (responsivity and external quantum efficiency -EQE- up to 0.32 A/W and 86.3%) are superior to those of several self-powered and low-voltage solution-processed photodetectors, approaching the ones of their commercial UV-Vis counterparts. Finally, we demonstrate the use of MCs-based photoelectrodes as photoanodes or photocathodes for water splitting reactions under simulated sunlight, inspiring the use of 2D MCs in innovative PEC systems.

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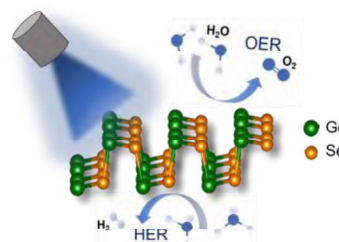
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FIGURE

Figure 1: Schematic processes of photoelectrochemical water splitting on transition metal monochalcogenide nanoflakes.



This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement GrapheneCore3 - 881603

Orbital Hall insulating phase in transition metal dichalcogenide monolayers

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The orbital-Hall effect (OHE), in resemblance to the spin-Hall effect (SHE), refers to the creation of a transverse flow of orbital angular momentum (OAM) that is induced by a longitudinally applied electric field [1]. It has been explored mostly in three-dimensional metallic systems, where it can be quite strong [2]. However, recent theoretical results have predicted the existence of OHE in 2D insulating systems, suggesting that this effect could possibly be found in other elements of this class of systems [3]. Differently from the SHE, the OHE does not rely on strong spin-orbit coupling (SOC) [2],[4]. It can be linked to orbital textures in reciprocal space, where the OAM and the carrier momentum are locked (similar to the locking between the spin and carrier momentum observed due to the Rashba-Edelstein effect), which are present in a diverse pool of materials [4].

We showed that the 2H transition metal dichalcogenide (TMD) monolayers, such as MoS₂ and WSe₂, are orbital-Hall insulators. They exhibit large orbital-Hall conductivity plateaux within their semiconducting gaps, where the spin-Hall conductivity vanishes. Our results open the possibility of using TMDs for orbital-current injection and orbital torque transfer that surpass their spin-counterparts in spin-orbitronic devices. The orbital-Hall effect in TMD occurs even in the absence of spin-orbit coupling. It can be linked to exotic momentum-space Dresselhaus-like orbital textures, analogous to the spin-momentum locking in two-dimensional Dirac fermions that arise from a combination of the orbital attributes and lattice symmetry.

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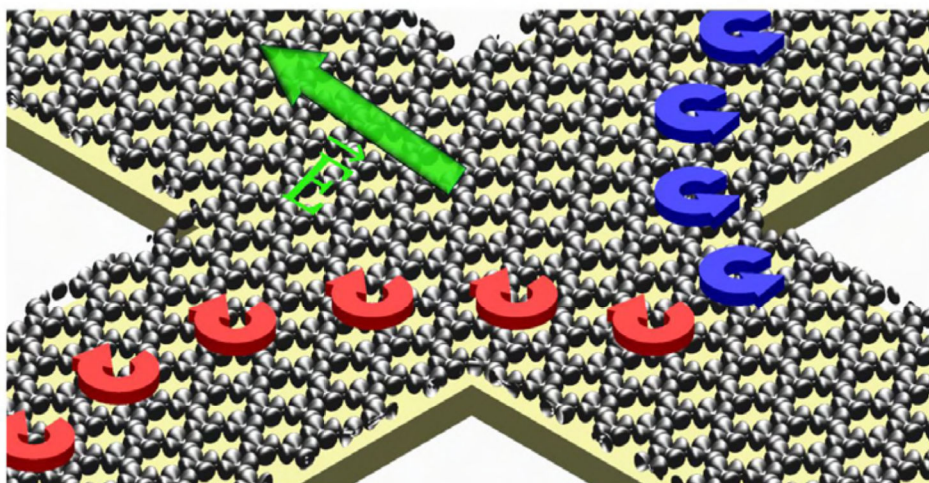


Figure 1: Schematic representation of the orbital-Hall effect in a Hall bar.

Graphene oxide, reduced graphene oxide and composite scaffolds for bone tissue engineering with hierarchical pore size distributions via a dual-templating strategy

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Scaffolds for bone tissue engineering (BTE) are three-dimensional (3D) porous matrices that provide the necessary sites for cell adhesion and proliferation, where the architecture plays an important role. Ideally, BTE scaffolds should have an interconnected network of both large (>100 μm) and small pores to facilitate the infiltration of cells and the diffusion of growth factors and nutrients¹. Scaffolds for BTE should also enhance osteogenic differentiation to improve bone regeneration. Graphene oxide (GO) and reduced graphene oxide (rGO) can promote osteogenic differentiation of mesenchymal stem cells (MSCs) because they can provide biophysical cues and adsorb biological factors². However, due to the lack of effective fabrication strategy, it remains a challenge to develop GO and GO composite scaffolds with a hierarchical architecture aiming for BTE. In this study, we developed a dual-templating method that produces GO scaffolds with interconnected hierarchical porosity: upon freezing and drying GO-based high internal phase emulsions, large pores were templated by the oil droplets, and small pores by ice crystals formed in the water phase, whose size can be controlled by the freezing temperature. We also obtained GO emulsions composited with polyacrylic acid (PAA), hydroxyapatite (HA), and elastin from bovine neck ligament. From the emulsions, we obtained GO composite scaffolds with hierarchical architectures. Furthermore, through the thermal reduction of GO scaffolds, we also fabricated rGO scaffolds with different reduction degrees that maintained the mother scaffolds' structure. We studied the formation of emulsions and the structural and chemical properties of scaffolds through optical microscopy, scanning electron microscopy (SEM), synchrotron-based X-ray phase contrast imaging (PCI), X-ray photoelectron spectroscopy, and attenuated total reflectance Fourier transform infrared spectroscopy. We seeded mouse bone marrow MSCs on GO scaffolds and analyzed the cells after 7 days of incubation using SEM and confocal microscopy to study cell morphology, attachment, and infiltration in the scaffolds. The resulting GO scaffolds were excellent substrates for MSC growth and penetration — an unprecedented result since previous fabrication methods did not produce GO scaffolds with suitable pore size for BTE. This method also enabled, for the first time, the synthesis of complex hierarchical architectures in GO, rGO, and GO composite scaffolds, through a single, versatile strategy.

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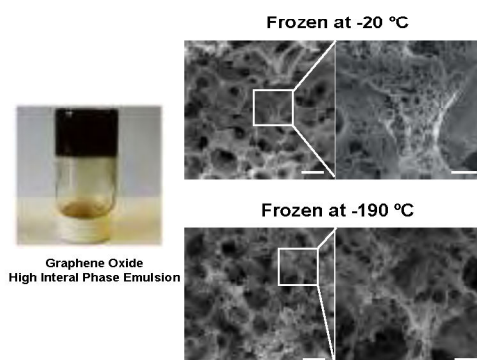


Figure 1: Photo of graphene oxide high internal phase emulsion in a glass vial, SEM images of hierarchical porous scaffolds obtained by emulsion and ice dual-templating frozen at different temperature.

Electrically driven photon emission from individual atomic defects on monolayer tungsten disulfide

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Atomistic point defects, such as NV centers in diamond and point defects in silicon carbide, are a powerful platform for creating next-generation solid state quantum emitters. In particular, the use of two dimensional (2D) materials is of interest due to their high photon extraction efficiency, synthetic flexibility, and tunability through gating and substrate engineering. Recently, single photon emitters have been observed in hBN as well as semiconducting transition metal dichalcogenides (TMDs), however the atomic scale origin of the emission is still actively debated. Furthermore, the ability to create identical emitters with the required spatial precision and specificity is currently lacking. These challenges prevent the systematic development and deployment of quantum emitters in 2D materials.

Here we use scanning tunneling microscopy light emission (STM-L), scanning tunneling spectroscopy (STS), and noncontact atomic force microscopy (ncAFM) to correlate photon emission with the atomic and electronic structure of individual defects in monolayer WS₂. [1,2] With a gold coated STM tip, we observe single photon emission from intrinsic tungsten substitutes and deliberately created sulfur vacancies by tip induced electroluminescence. We are able to tune photon emission by the applied bias and map photon emission with atomic resolution. There is a correlation between the bias onset for photon emission and the energy of the lowest unoccupied in gap states observed in STS. In addition, the photon maps closely resemble the in gap defect atomic orbital resonances. This indicates that the luminescence arises from the inelastic tunneling of the electrons from the continuum of tip states into the in-gap defect states. Inelastic charge-carrier injection into localized defect states of 2D materials thus provides a powerful platform for electrically driven, broadly tunable, atomic-scale single-photon generation.

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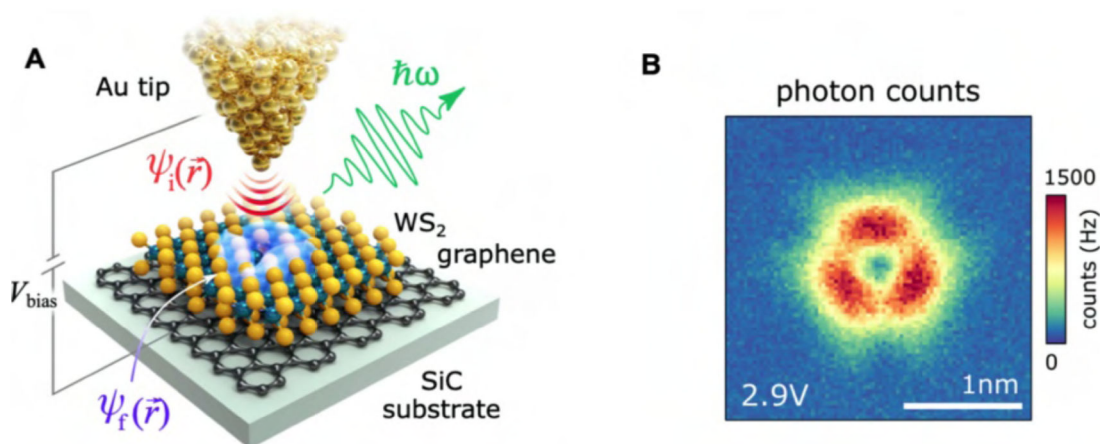


Figure 1: A. Scheme of experimental configuration. B. Spectrally integrated photon map of a sulfur vacancy defect.

Printing and Patterning of Conductive Graphenic Nanomaterial-Polymer Composites

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Advances in both manufacturing techniques and materials are leading to the development of a new class of flexible, inexpensive and light-weight electronic devices, with applications in areas which include antennas for supply-chain monitoring, wearable electronics, and distributed sensors for internet-of-things. Graphenic nanomaterials are attractive in this field based on two main properties: (1) they are electrically conductive, and (2) they can be processed and patterned outside of a traditional cleanroom using techniques such as casting and printing. While layers of materials such as graphene and reduced graphene oxide (rGO) can be printed directly to form conductive traces, these layers tend to be brittle and lack stability in varying environments (e.g. undergoing a change in conductivity as the humidity varies).

The focus of our work is to engineer graphenic-nanomaterial polymer composites that can be patterned from solution using 2D or 3D printing. When conducting particle fillers (such as graphene nanomaterials) are introduced into a matrix of insulating polymer, a conductive composite material may be achieved, even at a relatively low concentration of conductive filler. Judicious selection of a polymer matrix and conductive material can allow materials with tailored properties to be achieved. In the first part of the presentation I will describe our work engineering conductive composites from rGO and polyhydroxybutyrate, a hydrophobic, biocompatible polymer with high thermal stability and solvent-resistance [1]. In the second part of the presentation I will show how these materials can be patterned using solvent-casting and 3D printing to implement temperature responsive sensors which are highly selective to only the desired stimulus [2]. Finally, I will outline some challenges and opportunities for applying graphenic composite in 2D and 3D printing.

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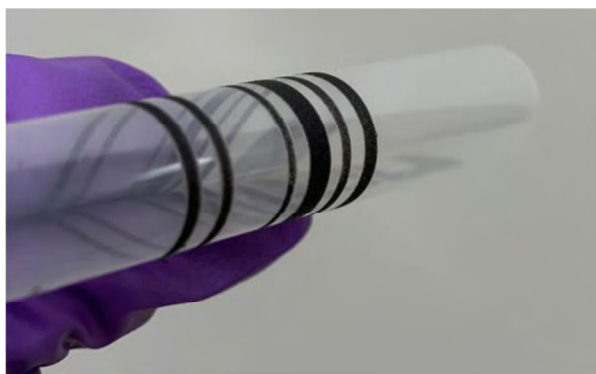


Figure 1: 2D rGO-PHB lines printed on a flexible substrate, shown here deformed (post-printing) into a cylindrical shape

Tuning the doping of epitaxial graphene on a conventional semiconductor via substrate surface reconstruction

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Investigating the interfacial properties of graphene with traditional semiconductors is crucial to developing of novel electronics [1]. In this framework, Graphene/Ge(110) has received a great deal of attention recently, especially over the last couple of years [2–4]. However, a detailed picture of the structural and electronic properties of this interesting system is today still unavailable. Here, combining scanning tunneling microscopy (STM) and angle-resolved photoemission spectroscopy (ARPES) experiments (Figure 1) with density functional theory (DFT) simulations, we unveil the interfacial properties of Graphene/Ge(110). In more details, we show that temperature-triggered structural changes at the interface strongly modify graphene's doping level. After growing graphene by chemical vapor deposition (CVD), the Ge surface results in being passivated by hydrogen that was present in the growth atmosphere (phase α) [3]. ARPES results show that at this stage graphene is p-doped. The sample is then annealed in vacuum, at a temperature above 350 °C, leading to desorption of hydrogen and subsequent reconstruction of the Ge surface into the (6x2) phase (phase β). Here, we find from ARPES data that graphene is interacting more weakly with the Ge substrate, and is now close to an undoped state. Upon higher-temperature annealing, the Ge surface further modifies (phase γ) [4]. Our ARPES data reveals a stronger interaction between graphene and Ge, and graphene results now in being n-doped. To gain more insights into this fascinating system, we successfully simulate the cases of as-grown and high-temperature annealed samples. Interestingly, when simulating the sample after high temperature annealing, we observe that locally some of the Ge atoms in the surface rearrange, thus creating a certain degree of disorder. Such disorder, in addition to many thermally induced vacancies, is indeed confirmed by STM investigation.

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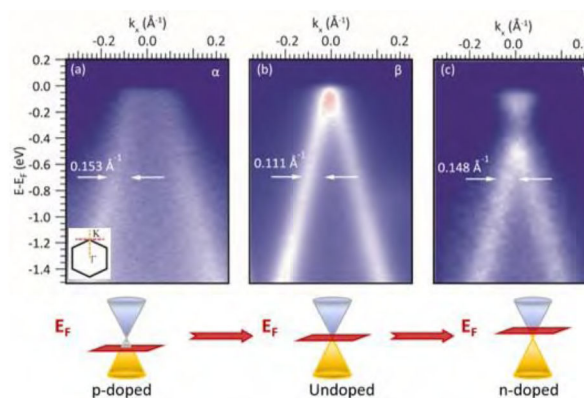


Figure 1: Photoemission intensity of the graphene/Ge(110) system in (a) phase α , (b) phase β , and (c) phase γ . The spectra were acquired along the direction orthogonal to the Γ K direction in the Brillouin zone, as schematically shown in the inset in panel (a). Bottom row: sketch highlighting the graphene doping level in the three phases.

Holography and Graphene

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Abstract (Oral contribution)

We present a 1+2 dimensional model holographically realized as the boundary theory of a four-dimensional gravity model for negative-curvature, Anti de Sitter spacetime. The appropriate boundary conditions chosen for the four-dimensional fields lead to an effective model for massive fermions living on a curved, graphene-like background [1].

In particular, the unconventional supersymmetry present in the boundary theory allows to introduce suitable internal degrees of freedom, which can provide an application of the model to the description of the charge carrier properties of graphene-like 2D materials at Dirac points \mathbf{K} and \mathbf{K}' . In this picture, the two valleys can be shown to correspond to the two independent sectors of the boundary description, connected by a parity transformation. The fermion masses entering the corresponding Dirac equations depend on the torsion parameters of the substrate in the three-dimensional model: the parity-even and odd components of the corresponding masses can then be identified with Semenoff and Haldane-type mass contributions, respectively [2,3].

The application of the derived model to the effective description of the electronic properties of graphene-like 2D materials provides a top-down approach to the study of the phenomenology of this physical system, as the effective three-dimensional theory, derived at the boundary and defining a Dirac fermion living in 1+2 dimensions, originates from a well-defined effective supergravity in the bulk.

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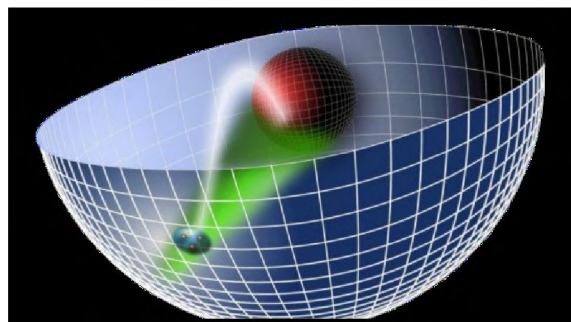


Figure 1: Holographic correspondence

NanoFrazor – A Versatile Nanopatterning Tool for 2D materials

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NanoFrazor (thermal scanning probe) lithography has recently entered the market as the first true alternative to electron beam lithography (EBL) [1]. It uses a heatable tip that can pattern and simultaneously inspect nanostructures. NanoFrazor can pattern very high-resolution (< 10 nm half-pitch) nanostructures by locally evaporating resist materials. The structures are inspected by the cold tip before or during with the patterning, enabling stitching and markerless overlay with sub-5 nm accuracy [2]. This technique is compatible with all standard pattern transfer processes [3,4].

To study the properties of 2D materials, one often needs to shape them (e.g. into nanoribbons, Hall bars etc), to contact them or to modify them mechanically or chemically. Predominant fabrication process (EBL followed by etching or lift-off of metal) has a limited resolution due to proximity effects; it may require complex overlay procedures; and it often yields poor quality non-ohmic contacts [6]. We show that NanoFrazor lithography can be used to shape the flakes with high precision (Figure 1a-b) [7-8]; to make high-quality contacts on 2D materials (Figure 1c) [5]; to induce precisely controlled local strain (Figures 1d-e) [9]; and to locally define the doping through absorption of charged defects from controlled environment (Figure 1f) [10]. NanoFrazor also has an integrated direct laser sublimation module for rapid patterning of coarse features, e.g. contact pads [11].

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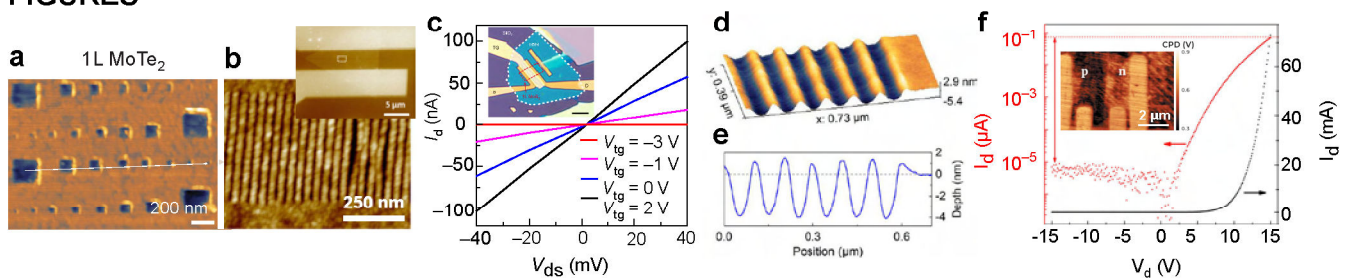


Figure 1: Versatile devices fabricated using t-SPL (a) AFM topography of nanosquare arrays in 1L MoTe₂ obtained by thermomechanical nanocutting. Feature sizes in the range from 20 to 200 nm along the line [8]. **(b)** AFM image of 18-nm half-pitch 1L MoS₂ nanoribbon array patterned by t-SPL and reactive ion etching. Inset shows the position and orientation of the nanoribbons array [7]. **(c)** Small-voltage I_d (V_{ds}) curves at different top-gate voltages show ohmic behaviour of the contacts patterned by t-SPL. Inset: Optical image of the 1L MoS₂ FET fabricated on the h-BN dielectric, for which the IV curves are shown. Scale bar 5 μ m [5]. **(d)** Three-dimensional AFM topography of nanoripples written into 1L MoS₂ and **(e)** Depth profile of the nanoripples. The nanoindentation depth is around 4 nm and the pileup height is around 1.5 nm. Strain up to 10 % resulting in tuning the bandgap to 180 meV was obtained [9] **(f)** Output curve of a lateral p-n junction in logarithmic (red) and linear scale (black), measured at the optimal back gating of -32 V. A rectification ratio $>10^4$ has been achieved. Inset: a KPFM image of a FET channel after the formation of the lateral p-n junction. p-n junction defined by localized dopant absorption via thermochemical SPL [10].

Large Scale Production and Industrialization of Graphene Oxide

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Graphene oxide (GO) has been studied and tested for diverse applications for several years. Now, these years of work are taking GO from the laboratory to the industry. Up-coming applications comprise such diverse fields as energy storage, membrane design, corrosion protection, water remediation, composites and coating of certain electronic components. As a result, reliable production is required to cover the demand of high-quality GO in the market.

Abalonyx has worked with GO production and development of GO derivatives for 12 years. We have developed a scalable, safe and cost-effective process, and current production capacity is 1 kg/batch, but we now see increased demand and need for scale-up. Thus, we are now installing a new 3 kg/batch reactor and have ready plans for 6kg/batch in a fully automated production facility, see Figure 1. Also, we are registering for REACH to be ready to produce up to 10 tons/year. Our ambition is to become Europe's largest certified supplier of graphene oxide by offering high-quality and reproducible materials, competitive prices and ability to supply industrial end-users.

In response to special needs from customers we have developed a range of derivative products including deacidified and basic GO, partly and fully reduced graphene oxide (rGO), rGO, nitrogen doped GO and rGO, films, aerogels and pillared GO and rGO. In addition, we have been working extensively in quality control and HSE-issues as we are aware these aspects are fundamental to industrial end-users for the eventual successful commercialization of a product.

One of the most promising applications we are working on is in collaboration with our Canadian partner, ORA Graphene Audio. ORA is developing the (GQ™) membranes that have been already tested and are under test production now. Membranes made with Abalonyx' GO show superior Young's modulus, damping and lower density, to conventional acoustic diaphragm materials. As a result, the performance of these membrane in loudspeakers show a 50% improvement in frequency response, up to 70% increase in battery life and 25% improvement in power handling over the current state-of-the-art technology.

FIGURES

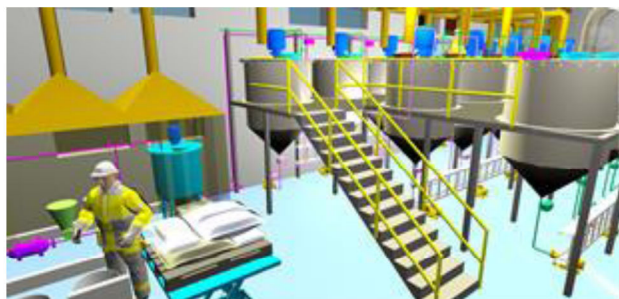


Figure 1: 3-D model for 6 kg/batch production of graphene oxide at Abalonyx's production site.

2N-rule: Searching topological phases and robust edge modes in carbon nanotubes

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Carbon nanotubes (CNTs) can be generally classified to two phases, metal or insulator, depending on their tube indexes. So far, the insulating CNTs are considered identical apart for some quantitative gap difference. However, here we show that the insulating phases may be topologically non-equivalent. We theoretically report an explicit and robust scheme, 2N-rule, for systematically searching topological phases in CNTs of all diameters. By investigating the topological Zak phase based on both analytical model and first-principles approaches, such a 2N-rule of insulating CNT($n,0$) is generally established: when $n = 2N$ where N is an integer, it is a topological insulator; otherwise, it is a normal insulator. For finite-length topological CNTs, topologically protected quantum modes naturally occur at the tube ends, which hold significant robustness against external environment perturbations, taking advantage over fragile edge states in conventional systems.

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FIGURES

CNT($n,0$)	...	7	8	9	10	11	12	13	14	15	16	17	...
Phase	...	NI	TI	M	TI	NI	M	NI	TI	M	TI	NI	...

Figure 1: Complete phase table of CNT($n,0$). Green, red, and blue regions denote the metal (M), topological insulator (TI), and normal insulator (NI), respectively

Three-Terminal Suspended Graphene Energy Efficient Switches

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For the last 70 years, solid-state technology has evolved immensely to reflect our dependence on faster, more dependable and more energy efficient systems. Modern electronic hardware still contributes significantly to our energy consumption. In 2018, approximately 200TWh of electricity was consumed by the servers and storage systems of data centres worldwide, and that figure is expected to rise up to 40,000 by 2030 [1]. The average energy consumed per solid-state transistor per clock-cycle in a circuit is $E \propto CV^2$, where C is the average capacitance dominated by metallic connections and $V \sim 1V$ is the operating voltage [2]. Finding an alternative to conventional transistor technology to reduce the dissipated energy is crucial. Electromechanical switches could reduce the operating voltage, while maintaining high on/off current ratios, thereby reducing energy consumption while retaining competitive operating speeds and relatively small sizes. Our goal is to develop a three-terminal electromechanical switch using a suspended graphene structure that can operate below 1V. Graphene is the strongest known material with a Young's modulus of $Y \sim 1TPa$, however its elastic stiffness $E \propto Yt$ is low compared to other materials due to its atomic thickness $t = 0.34$ nm. Theoretical simulations show that suspended graphene switches can be operated with voltages much lower than 1V by optimizing device geometry [3,4,5]. We can establish optimal designs in order to fabricate devices with operating voltages around 100 mV using state-of-the-art cleanroom equipment, scanning electron microscopy (SEM), electronic transport measurements and actuation tests. We will present our experimental work towards realizing suspended graphene NEMS switches combining large area CVD graphene and simple silicon / silicon oxide processing methods.

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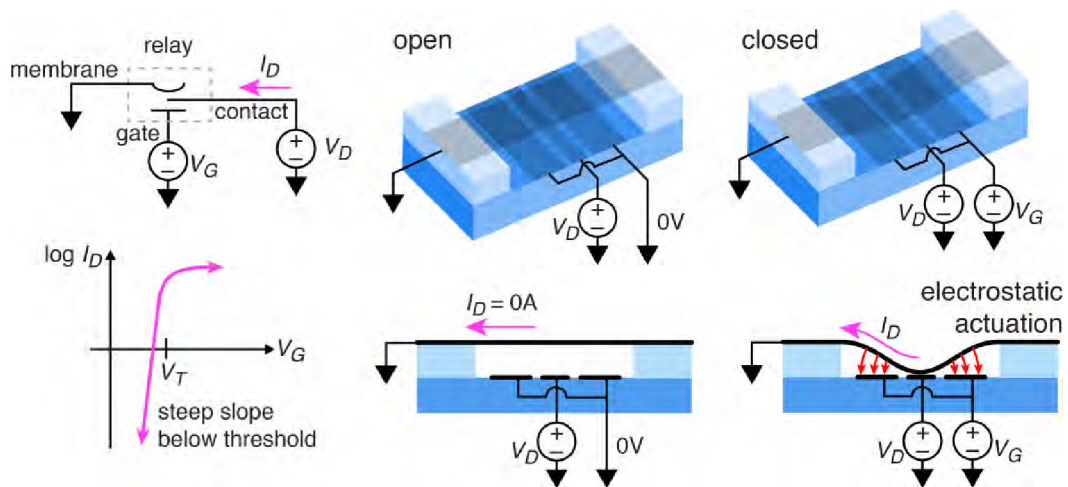


Figure 1: The proposed graphene nanomechanical switch, where the three terminals consist of a suspended graphene membrane, a bottom contact strip, and a split gate. A low-threshold voltage V_T , and steep slope in $\log I_D$ versus V_G below threshold can enable low-voltage operation.

Characterization of Few-Layer Graphene Aerosols by Laser-Induced Incandescence

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The numerous possible applications of few-layer graphene (FLG) create a demand for large-scale synthesis for this material. One of the promising routes is the gas-phase synthesis of FLG aerosols that is capable of producing large amounts of high-quality material [1]. Optimizing the gas-phase synthesis requires a detailed understanding of the graphene formation kinetics, which in turn demands diagnostics for characterizing FLG aerosols *in situ*. Laser-induced incandescence (LII), a laser-based nanoparticle characterization technique, is ideal for this purpose, due to its high temporal and spatial resolution, and the fact that it requires optical but not physical access to the aerosol. LII involves heating nanoparticles with a short laser pulse to incandescent temperatures and detecting the spectral incandescence from the particles while they cool down to the ambient temperature. Various aerosol properties can be inferred through the analysis of the detected incandescence signals.

In this work, FLG powder was formed via a gas-phase microwave-plasma synthesis route using vaporized ethanol as a precursor. *Ex situ* analysis showed that the powder consisted of highly structured few-layer graphene flakes without contamination. FLG sample was dispersed in ethanol, nebulized with a pneumatic nebulizer, and investigated by LII.

We show that LII can be used to measure FLG aerosol concentration *in situ*, monitor the particle surface area, and differentiate FLG from soot particles that may also form during the synthesis process [2].

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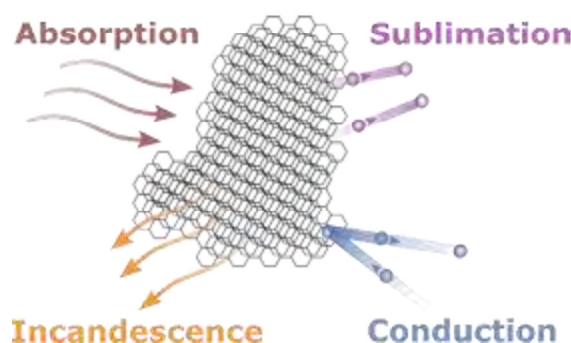


Figure 1: Heat and mass transfer processes underlying laser-induced incandescence on a few-layer graphene.

Metallic 2D crystals for bifunctional, pH-universal electrocatalysts for water splitting reactions

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ABSTRACT:

The design of efficient electrocatalysts for water splitting reactions is crucial to unlock the “Hydrogen economy”, *i.e.*, the vision of using molecular hydrogen (H₂) as carbon-free fuels produced by renewable energy sources.[1] Unfortunately, the costs and the scarcity of their most effective catalysts, *e.g.*, Pt-group elements for hydrogen evolution reactions (HER) at the cathode, and RuO₂/IrO₂ for oxygen evolution reactions (OER) at the anode, hinder massive commercial electrolyzers. Therefore, it is mandatory to search for alternative non-precious catalysts, or at least to reduce the content of precious metals, with the goal to maintain state-of-the-art electrochemical performances.[2] Recently, two-dimensional (2D) transition metal dichalcogenides (TMDs) have been investigated as catalytic models to perform the HER.[3] In particular, the catalytic activity of the most established TMDs (*i.e.*, group-6 TMDs, such as MoS₂ and WS₂) originates from unsaturated edges of semiconducting (2H) phase and metallic (1T) phase.[4] However, both the basal plane inertness in their natural phase and the susceptibility of the electronic structure of their catalytic sites to electrolytic media, result in insufficient specific catalytic performances (*e.g.*, catalytic activities normalized to catalyst mass). Contrary to group-6 TMDs, metallic group-5 TMDs (*e.g.*, TaS₂, NbS₂ and VSe₂) have been predicted to display both edges and basal planes as the catalytic sites in their natural phases. In our work, we produce 2D group-5 TMD through scalable liquid-phase exfoliation of the bulk crystals, to be used as efficient bifunctional catalyst for HER and OER, either in acidic or alkaline media.[5,6,7] To fully exploit the potential of such electrocatalysts, we nanoengineer their structural properties by means of: 1) thermal treatments in reactive atmosphere, 2) chemical treatments with lithium salts and 3) liquid-phase microwave treatments. The reactivity of group-5 TMDs is also used to drive their topochemical transformation in non-layered (but 2D) metallic oxides (*e.g.*, room temperature-stable rutile VO₂), which also act as effective electrocatalysts. The hybridization of group-5 TMDs is used as universal strategy to tune the Gibbs free energy of the adsorbed atomic hydrogen onto the surface of heterogeneous electrodes to the optimal thermo-neutral value. Beyond to reach catalytic activities approaching to the state-of-the-art for both HER and OER, we shed light on the phase, morphological and chemical changes of the materials during their electrochemical operations. Our results provide fundamental understandings for the development of efficient and viable electrocatalysts based on metallic 2D TMDs.

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This project has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement GrapheneCore3 – 881603.

Spin-Orbit Torque in van der Waals Heterostructures of Magnetic Two-Dimensional Materials

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The bilayer heterostructures composed of an ultrathin ferromagnetic metal (FM) and a nonmagnetic material hosting strong spin-orbit coupling (SOC) are a principal resource for spin-orbit torque (SOT) [1] and spin-to-charge conversion [2] effects in next generation spintronics. The key to understand these effect is current-driven nonequilibrium spin density [3]. For example, it generates SOT when it is noncollinear to the direction of local magnetization and it can arise due to variety of microscopic mechanisms, including the spin Hall effect, spin-orbit proximity effect and different interfacial scattering mechanisms. The recently discovered two-dimensional (2D) magnetic materials [4] offer new avenue for highly efficient and gate- or disorder-tunable SOT in van der Waals (vdW) heterostructures composed of few monolayers of atomically thin materials where the spin Hall effect from the bulk is absent. Using first-principles quantum transport calculations, which combine nonequilibrium Green functions with noncollinear density functional theory [1], we predicted [5] that injecting unpolarized charge current parallel to the interface of bilayer-CrI₃/monolayer-TaSe₂ vdW heterostructure will induce SOT-driven dynamics of magnetization on the first monolayer of CrI₃ that is in direct contact with metallic transition metal dichalcogenide (TMD) TaSe₂. By combining calculated complex angular dependence of SOT with the Landau-Lifshitz-Gilbert equation for classical dynamics of magnetization, we find that this can reverse the direction of magnetization on the first monolayer to become parallel to that of the second monolayer, thereby converting bilayer CrI₃ from antiferromagnet to ferromagnet which can be detected by passing vertical current and is of potentially great interest to magnetic memory applications since it does not require any external magnetic field. We explain the mechanism of such *current-driven nonequilibrium phase transition* by showing that first monolayer of CrI₃ becomes conducting due to doping by evanescent wavefunctions injected by metallic TaSe₂, while concurrently acquiring strong SOC via this proximity effect. Another vdW heterostructure exhibiting SOT is *doubly proximitized* graphene, which is neither magnetic nor hosts SOC in its isolated form, but proximity induced magnetic moments will exhibit SOT in Cr₂Ge₂Te₆/graphene/WS₂ vdW heterostructure which can be tuned by two orders of magnitude via the gate voltage [6].

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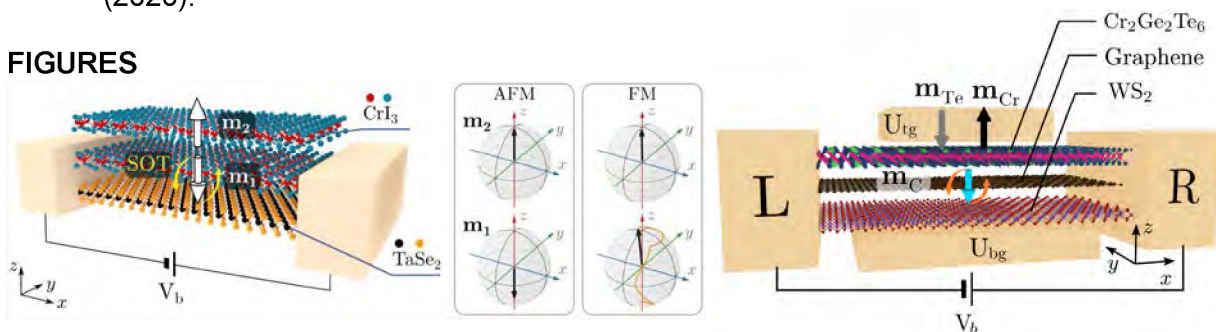


Figure 1: Spin-orbit-torque-operated van der Waals heterostructures from Ref. [5] (left panel) and Ref. [6] (right panel).

Optically enhanced gas sensing performance of graphene field effect transistors

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Graphene field effect transistors (GFETs) have an enormous potential for the development of next-generation gas sensors, but more efforts are required to improve their sensitivity and selectivity. In this talk we discuss UV illumination as a promising method to enhance the performance of GFETs for the detection and recognition of analytes such as ethanol, water vapor and dimethyl methylphosphonate (DMMP), a molecule with structural similarities to nerve agents such as sarin. We show that illuminating the devices in operando with a UV LED (365 nm) results in both improved sensitivity and selectivity. By monitoring the sensing response of the GFETs as a function of gate voltage, we directly demonstrate that a shift in the Dirac point due to the optical doping is associated with the increased sensitivity. Moreover, we discuss how the substrate and fabrication residues on the surface of the graphene sensors can play a role in modifying the sensing performance.

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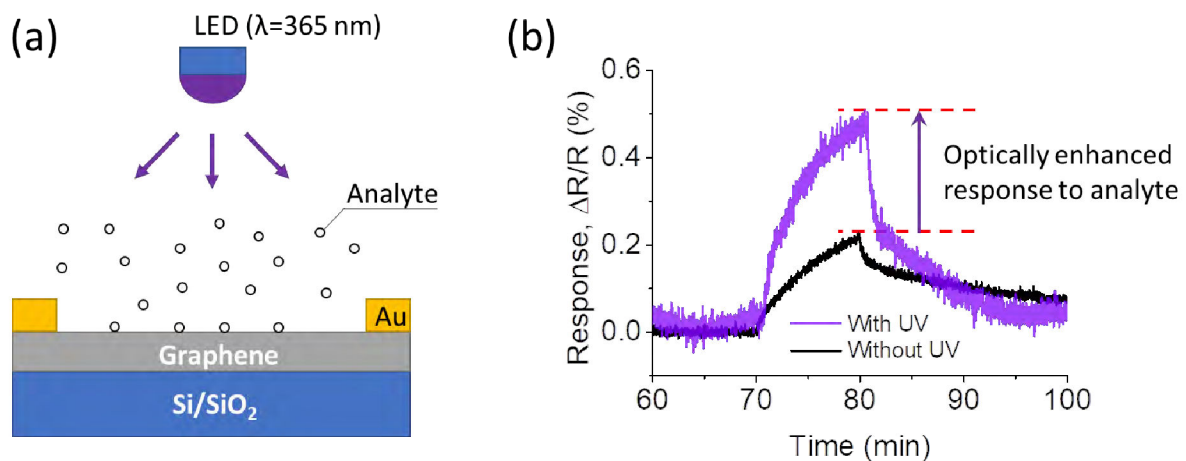


Figure 1: (a) Schematics of optically enhanced gas sensing of GFET and (b) its improved sensing response under UV.

Variable angle spectroscopic ellipsometry investigation of turbostratic CVD-grown bilayer and trilayer graphene

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We report a Variable Angle Spectroscopic Ellipsometry (VASE) characterization of the surface of CVD-grown bilayer and trilayer graphene produced by multiple transfer on SiO₂/Si and polyethylene terephthalate (PET) substrates. The study of the optical properties of single- and few-layer graphene on PET could be useful in the light of novel graphene-based flexible and stretchable electronics applications. The absorption peak due to resonant excitons has been found at 4.4 eV on bilayer graphene on SiO₂/Si. Moreover, an absorption peak at 3 eV for SiO₂/Si samples, which has not been revealed in previous studies, is discussed for the first time.

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Graphene-based cement-composite

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Abstract

Nowadays, concrete is a broadly exploited material worldwide, with consumption exceeding thirty billion tons per year and with continued demand growth.[1] The cement production processes have a significant impact on the environment due to considerable CO₂ emissions (*i.e.* 900 kg for every 1000 kg of cement). [2] To solve this environmental problem is necessary to diminish the cement degradation over time, resulting in a reduction of the demand, and thus a reduction in CO₂ emissions. The use of nano additives (*e.g.*, SiO₂ or CaCO₃ nanoparticles) can aid to increase the durability of cement conglomerates.[3] Moreover, nanoparticles can improve additional properties or functions of the cement composites, *e.g.*, self-sensing properties, photocatalytic or electrothermal [4], thus transforming the traditional concrete into a so-called “smart concrete”. Graphene stands out among the wide variety of carbon-based nano additives that could revolutionise the cement composites sector. Nevertheless, the production at a large scale of graphene is still a bottleneck, preventing the commercialisation of the desired smart concretes. [5,6]

In this regard, we used the high-pressure homogenisers (HPH) for the production of multi-layer and few-layers graphene at semi-industrial rates, *i.e.* kg per day (Fig 1a).[7] The high production rate of graphene offered by HPHs enables us for testing innovative graphene-based cement composites (Fig 1b). The few-layer graphene-based mortars produced shown an improvement of ~25% for both the flexural and compressive strength compared to a standard cement mortar.

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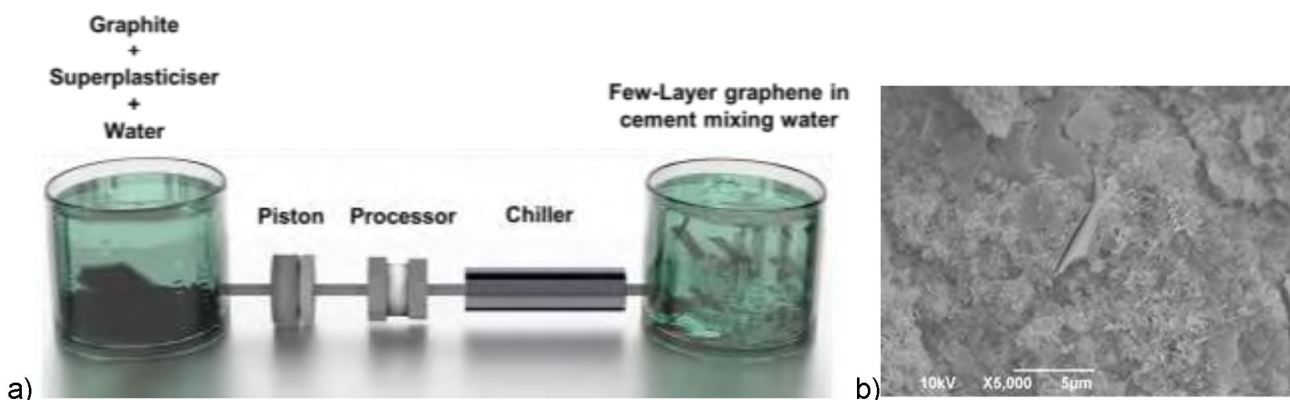


Figure 1: Schematic representation of the production process of FLG using the WJM (a); SEM Image of a graphene flake in the mortar microstructure (b).

Thin-Suspended 2D Heterostructures: Facile, Versatile and Deterministic Transfer Assembly

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We report a deterministic 2D material (2DM) transfer method to assemble any-stacking-order heterostructures incorporating suspended ultra-thin 2D materials, such as monolayer graphene (MLG) and bilayer graphene (BLG). The transfer procedure uses a nitrocellulose micro-stamp which improves the imaging and alignment of 2DMs during the process, can dry pick-up naked crystals (graphene, MoS₂, and hBN) directly from a SiO₂ substrate, and precisely transfer them on substrates or trenches. Optical and Raman data show that no significant defect is introduced upon transfer, even in suspended MLG and BLG. The areas transferred range up to 600 μm² on substrate. High-yield transfer of suspended ultra-thin 2DM does not require critical point drying for areas up to 15 μm² and suspension heights down to 160 nm. To demonstrate the method's capabilities, we assembled on-substrate and suspended optical cavities tuning BLG's Raman scattering intensity (proportional to light absorption) by factors of 19 and 4, respectively. This versatile and facile fabrication of heterostructures incorporating suspended 2DMs is likely to accelerate research in twistrionics, straintrionics, and nano-opto-electro-mechanical systems (NOEMS).

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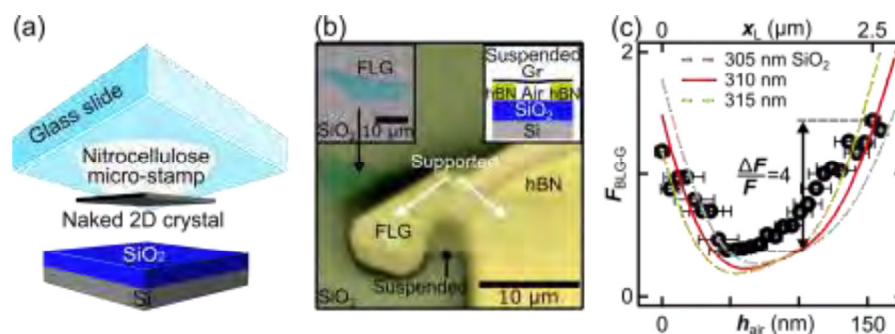


Figure: 2DM Deterministic transfer based on nitrocellulose micro-stamp. (a) Schematics of transfer method. (b) Top-view optical image of a thin-suspended-graphene/Air/SiO₂/Si heterostructure. Inset: Left, optical image of graphene crystal before transfer. Right, structure geometry. (c) Tuning Raman scattering intensity (Raman factor, F_{BLG}) as a function of varying air-spacer thickness (h_{air}).

Integrating Graphene Nanoribbons on CMOS-compatible Platforms for Semiconductor Electronics

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Abstract

Graphene nanoribbons are quasi-1D strips of graphene that are tunable semiconductors and can exhibit excellent electron mobility and velocity, high current carrying capacity, thermal conductivity, and mechanical strength. Field effect transistors made of sub-10 nm wide GNRs with smooth, armchair edges can achieve higher drive current than silicon-MOSFETs and suppress short channel effects due to ultra-thin geometry. However, practical realization of commercial GNR-based technologies requires scalable, deterministic placement of GNRs on CMOS-compatible platforms. In this presentation, I will showcase some of our group's recent scientific breakthroughs towards exploiting chemical vapor deposition (CVD) – a process widely used in the industry – to achieve bottom-up synthesis of sub-10 nm wide armchair graphene nanoribbons, with smooth edges on Ge/Si(001). (1-3) By initiating the CVD growth from deterministically placed graphene nanoseeds, we have been able to precisely control the dimensions, placement and orientations of these nanoribbons and create densely aligned mesoscale assemblies of nanoribbons and nanoribbon-meshes, making it a versatile technique for large-scale production of nanoribbons for future semiconductor electronics. (4, 5)

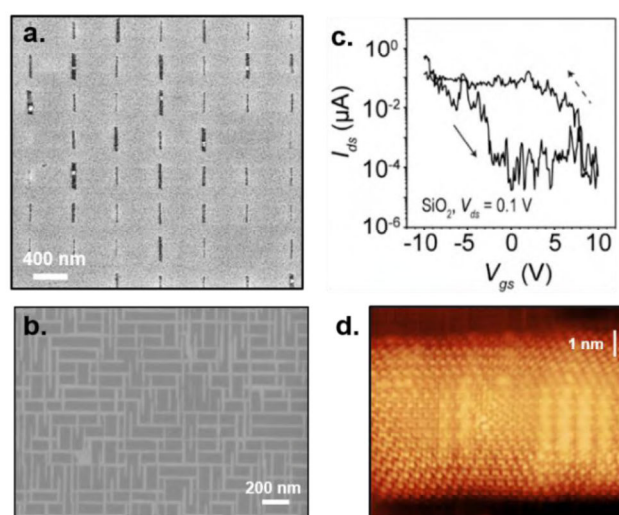


Figure 1: (a) Aligned array of CVD-synthesized graphene nanoribbons on Ge(001). (b) Bottom-up synthesized graphene nanomesh on Ge(001). (c) Transfer characteristics of a single nanoribbon FET showing an on/off conductance modulation of 2×10^4 . (d) Atomically resolved scanning tunneling topographic image of CVD-synthesized nanoribbon, showing smooth, armchair edges.

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Exfoliated Silicate Nanosheets as Novel Near-Infrared Fluorophores for (Bio)Photonics

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Imaging of complex (biological) samples in the near-infrared (NIR) range of the spectrum is beneficial due to reduced light scattering, absorption, phototoxicity and autofluorescence. However, there are only few near-infrared fluorescent materials known and suitable for biomedical applications. Here, we use layered silicates that emit NIR fluorescence ($\lambda_{exc} \approx 550\text{-}650\text{ nm}$, $\lambda_{emi} \approx 920\text{-}950\text{ nm}$) with a long excited state lifetime ($\tau \approx 10\text{-}100\ \mu\text{s}$): Egyptian Blue ($\text{CaCuSi}_4\text{O}_{10}$, EB), Han Blue ($\text{BaCuSi}_4\text{O}_{10}$, HB) and Han Purple ($\text{BaCuSi}_2\text{O}_6$, HP). Via a mixed approach consisting of milling, tip sonication and centrifugation steps, we exfoliate these silicates into nanosheets (NS) with lateral sizes and thicknesses down to few tenths of nm. The intense NIR fluorescence emission is retained, enabling the employment of these NS as NIR labelling agents. So far, most of our efforts have focused on EB-NS [1], which, compared to standard fluorophores, show no bleaching while displaying outstanding fluorescence intensity. Furthermore, we demonstrated the high potential of EB-NS as NIR fluorophore for bioimaging by *in vivo* single-particle tracking and microrheology measurements in developing Drosophila embryos. Additionally, we have shown that EB-NS can be successfully detected in plants by means of a low cost stand-off detection setup, despite strong plant background fluorescence. EB-NS, HB-NS and HP-NS are also bright enough to be imaged through several cm of tissue phantoms. Additionally, we demonstrate fluorescence lifetime imaging of all the mentioned NS on the microscopic and macroscopic level [2]. In summary, we present a new route to NIR fluorescent nanosheets that promise high potential as novel NIR fluorophores for bioimaging and photonics.

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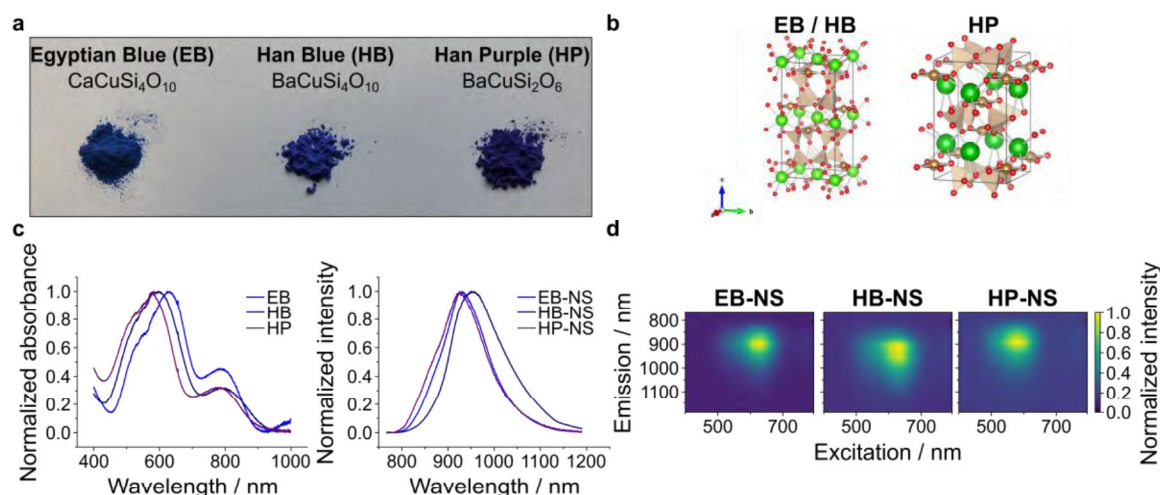


Figure 1: Egyptian Blue (EB), Han Blue (HB) and Han Purple (HP): a family of NIR fluorophores [1]. **a** Picture of bulk, pristine powders of EB, HB and HP. **b** Crystal structures of the three pigments: Si is shown in its typical tetrahedral geometry, Ca (Ba for HB and HP) is depicted as green, Cu as bronze, and O as red spheres. **c** Normalized absorption (reflection) of bulk EB, HB and HP powders, next to 1D fluorescence spectra of EB, HB and HP nanosheets (NS). **d** Normalized 2D excitation-emission spectra of EB-NS, HB-NS and HP-NS.

Design of Graphene-Based Nanomaterials for Energy and Environmental Applications

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Abstract

Graphene-based materials are poised to revolutionize the energy and environmental sectors due to their versatile nature, unique properties, and tunability, which make them strong candidates for a myriad of energy storage and environmental remediation applications. The doping and functionalization of graphene-based materials can also modify their electronic properties to enhance the utility of electrochemistry. Here, we present four different graphene-based nanomaterials: graphene oxide (GO), fluorine-doped graphene oxide (F-GO), interconnected reduced graphene oxide (ICrGO) and nitrogen-doped interconnected reduced graphene oxide (N-ICrGO) [1-5]. All were synthesized from high-purity graphite produced from the Albany graphite deposit, which is owned and currently under development by ZEN Graphene Solutions Ltd. GO and F-GO have a two-dimensional sheet morphology whereas ICrGO and N-ICrGO exhibit a three-dimensional interconnected morphology. The fabricated GO showed efficient dye adsorption properties due to the abundance of the C=O and O-H functional groups. The synthesized F-GO exhibited high-performance for the simultaneous determination of ultra-low concentrations of multiple heavy metal ions such as Cd, Pb, Cu, and Hg. The novel ICrGO possessed a large specific capacitance for energy storage, while the N-ICrGO exhibited high catalytic activity for the oxygen reduction reaction. The effect of the morphology, modification and functionalization of these graphene-based nanomaterials on the environmental, sensing and energy applications are discussed.

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FIGURES

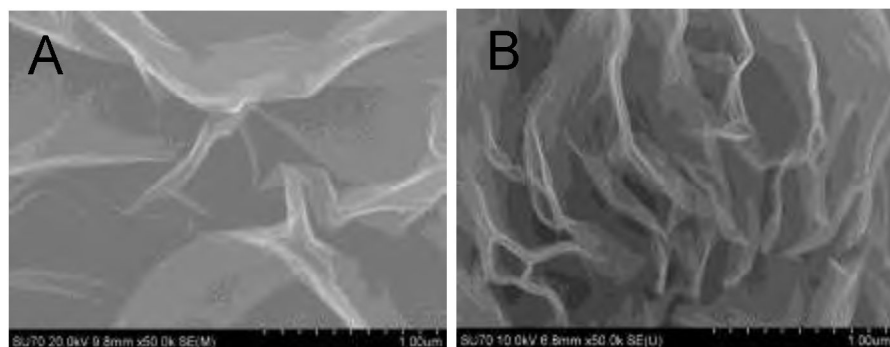


Figure 1: Scanning electron microscopic images of (A) F-GO and (B) N-ICrGO.

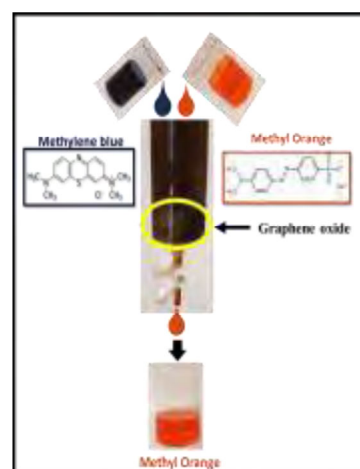


Figure 2: Schematic diagram of the use of GO for separation of different dyes.

Exciton g-factors of van der Waals heterostructures from first principles calculations

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External fields are a powerful tool to probe optical excitations in a material. The linear energy shift of an excitation in a magnetic field is quantified by its effective g-factor. Here we show how exciton g-factors and their sign can be determined by converged first principles calculations. We apply the method to monolayer excitons in semiconducting transition metal dichalcogenides and to interlayer excitons in MoSe₂/WSe₂ heterobilayers and obtain good agreement with recent experimental data. The precision of our method allows to assign measured g-factors of optical peaks to specific transitions in the band structure and also to specific regions of the samples. This revealed the nature of various, previously measured interlayer exciton peaks. We further show that, due to specific optical selection rules, g-factors in van der Waals heterostructures are strongly spin and stacking-dependent. The presented approach can potentially be applied to a wide variety of semiconductors. [1]

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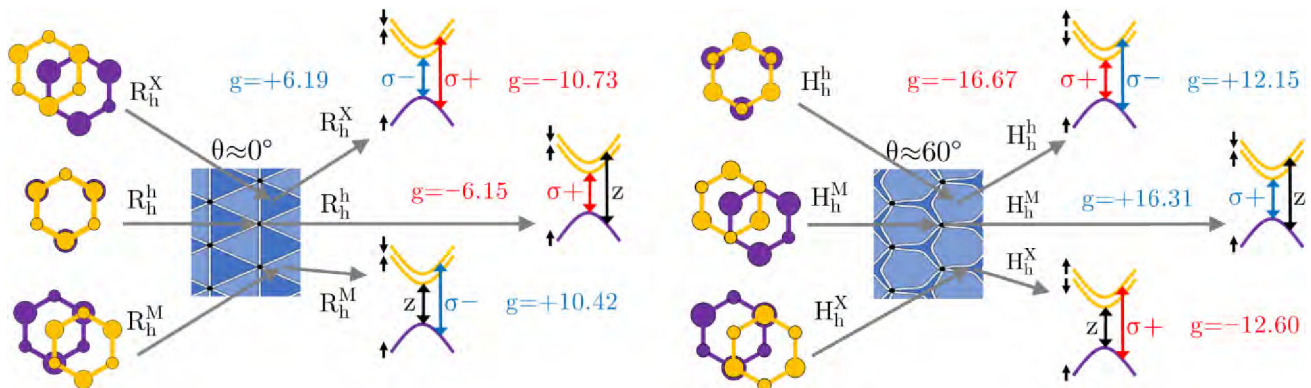


Figure 1: Exciton g-factors for high-symmetry stacking configurations in 0° and 60° MoSe₂/WSe₂ heterobilayer

Self-assembled Polydiacetylenes on Nanographene for Construction of Hybrid Sensing Materials

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Abstract

Polydiacetylenes (PDA) are a class of chromic polymers used extensively in sensing applications. These polymers are ideal for sensing applications because they have an easily monitored blue to red phase-transition that can be induced by heat, pH, organic solvents or pressure.¹ The monomer readily self assembles on surfaces, interacts with polymers, and forms micelles in solution.² Unfortunately, the precise alignment of the monomers required for polymerization leads to inhomogeneity and incomplete polymerization in cast films and hybrids.³ Understanding how these monomers assemble on specific substrates and in films is important as PDAs have potential applications in nonlinear optics, photo-detectors and biological sensing devices.⁴ In this work we have fabricated composites of nanographene (nG) and poly(10,12-pentacosadiynoic acid (pPCDA) a thermochromic polydiacetylene. Experiments measuring the reversible blue to red phase change temperature range of these hybrids have been completed up to 135 °C. The chromic reversibility of the composite is maintained at temperatures from 65 - 135 °C. Scanning Transmission X-ray Microscopy (STXM) using synchrotron radiation was used for mapping these hybrid systems which provided local information of bonding environments and elemental mapping of significant regions in the pPCDA-NG hybrid. Resonant Raman spectroscopy was used in this study to determine the phase of the polymer while assembled on the graphitic substrate. This study addresses the difficulties in the construction and characterization of self assembled nanocomposites and contributes solutions that are applicable to a broad range of systems.

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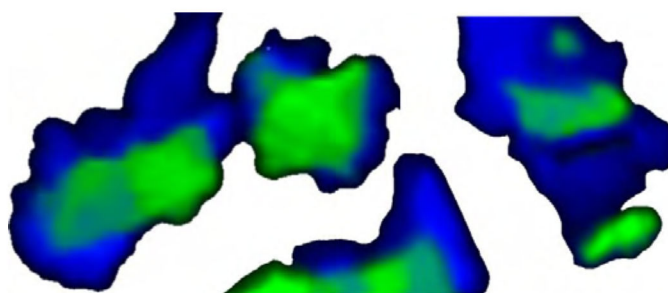


Figure 1: Scanning transmission X-ray microscopy images of hybrids showing areas of nanographite (green) and polydiacetylene (blue).

Group-III layered Semiconductors (GaSe and GaS) for Photoelectrochemical (PEC)-type Photodetectors

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Layered semiconductors of group-III have attracted considerable attentions thanks to their distinctive optoelectronic and anisotropic structural properties[1]. Currently, two-dimensional (2D) gallium selenide (GaSe) and gallium sulphide (GaS) have been emerging as a promising candidate for the realization of PEC-type photodetectors[2]. A requirement for large-scale applications is the development of low-cost, reliable industrial production processes[3],[4]. In this context, liquid-phase exfoliation (LPE) methods can provide scalable production of 2D materials in form of liquid dispersion, enabling their processing in thin film through low-cost and industrially relevant deposition techniques[5]. In this study, we report the first experimental characterization of the PEC properties of single-/few-layer flakes of GaSe and GaS produced in form inks by LPE approach in green solvents (2-propanol), which has been reported to be effective for exfoliating others monochalcogenides[6]. The as-produced inks were deposited through printing techniques, *i.e.*, spray coating, to obtain solution processed self-powered PEC-type photodetectors. The PEC behaviour of GaSe-/GaS-based photoelectrodes were evaluated in different aqueous media, ranging from acidic to alkaline solutions: 0.5 M H₂SO₄ (pH 0.3), 1 M Na₂SO₄ (pH 6), 1 M KCl (pH 6.5), 1 M KOH (pH 14) under different illumination wavelengths in the UV/visible spectral range, namely 275, 455, 505 and 625 nm. GaSe photoelectrodes show a responsivity of 0.16 A W⁻¹ upon 455 nm illumination at a light intensity of 63.5 μW cm⁻² and applied potential of -0.3 V versus reversible hydrogen electrode (RHE). Meanwhile, GaS flakes can be used to realize innovative PEC-type UV-selective photodetectors. Our results open the way towards the use of 2D metal monochalcogenides in innovative PEC applications, including medical diagnostics, air purification, chemical analysis (ozone sensing) and advanced optical communications.

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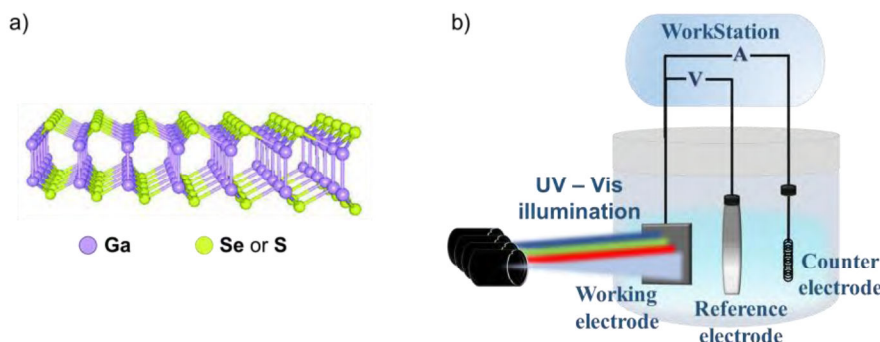


Figure 1: a) Crystal structure of monochalcogenides. b) Sketch of the experimental setup used for characterization of the PEC-type photoelectrodes.

Electronic structure studies of graphene and graphene based functional materials by soft X-ray absorption spectroscopy and spectromicroscopy at Canadian Light Source

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Abstract :

Deeper understanding of the electronic structure of graphene and the interfaces within graphene-based hybrid materials are crucial for a further enhancement of their applications in fuel cell¹ and artificial and batteries^{2,3}. X-ray absorption near-edge structures (XANES) spectroscopy can reveal detailed information on the electronic structure and the local chemistry of the absorbing atom. With soft X-ray, XANES can gain information on the surface with electron yield (probing depth of 5-10 nm) and subsurface with fluorescence yield (probing depth of 100 nm) simultaneously which are perfect to study the surface and interface of materials even under operando. Further, scanning transmission X-ray microscopy (STXM), and Photoemission electron microscopy (PEEM), based on the X-ray absorption process, has a chemical contrast mechanism to allow for imaging at the nano-scale which can nicely correlate performance with structure variation in novel materials^{4,5,6}. In this talk I will introduce how to apply soft X-ray XANES and STXM/PEEM at CLS to gain a deeper understanding of electronic structures in graphene and graphene-based hybrid materials. The emphasizes is XANES at C and O K-edge and transition metal L-edge, which can identify the strong chemical bonding nature in graphene supported novel inorganic hybrid nanostructures, the key in making super active non-precious metal fuel cell catalyst¹ and battery electrode materials with greatly improved performance²⁻⁶.

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ePosters

LEEM imaging of the moiré pattern of twisted bilayer graphene

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The discovery that magic angle twisted bilayer graphene (MABLG) is a superconductor, yields the promise of exciting new solid state physics. In particular, gating enables exploration of the phase diagram not possible in cuprates [1]. However, the influence of inhomogeneity of twist angle, strain and defects on charge transport properties in these exfoliated, torn and stacked flakes remains an important open question.

Here, we demonstrate that Low Energy Electron Microscopy (LEEM) can directly image MABLG on the full device scale, identifying specific areas of the magic twist angle. This has enabled efficient Nano-ARPES measurements confirming the existence of flat conduction bands [2]. Furthermore, we show direct LEEM imaging of the moiré pattern near the magic angle and compare monolayer-on-monolayer to bilayer-on-bilayer graphene. By stitching high magnification images, we map the moiré pattern at 2 nm resolution over large areas of several micrometers. Using this data, local variations in twist angle and strain are extracted from the moiré pattern by geometric phase analysis [3]. The direct observability of these properties establishes the potential of LEEM to this field of physics.

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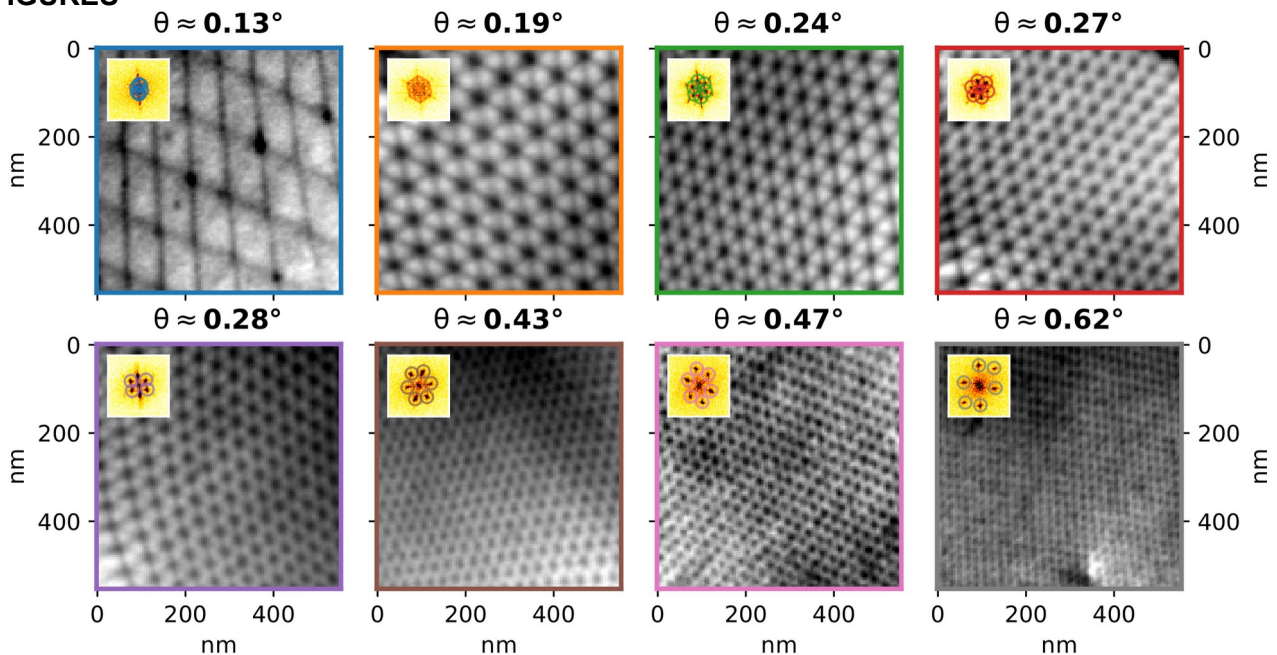


Figure 1: LEEM images of different areas of twisted bilayer graphene, showing moiré patterns of different twist angles, each with clear lattice distortions. Insets show FFTs and extracted reciprocal super lattice vectors indicated by circles.

in-situ Cesium Doping of Monolayer Graphene

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Modifying graphene with surface adsorbates is a widely studied way of modifying graphene's electronic properties. Different graphene/adatom systems have shown that it is possible to open a band gap in graphene¹, engineer topological insulators² and create magnetic moments³. The atomic thickness of graphene maximizes the effect of adsorbates, enabling chemical sensors that achieve single molecule sensitivity⁴. Alkali metal adatoms are a particularly efficient dopant for graphene due to their high electronegativity. Lithium/graphene systems have been studied for in the context of low-dimensional superconductivity⁵ and achieving ultrafast diffusion of lithium⁶ for battery applications.

Doping graphene with alkali metal adatoms bears challenges. Experiments with alkali metals must be conducted in an ultra-high vacuum or inert gas environment due to the high reactivity of the alkali. Alkali metal adsorbed graphene is not air stable, which imposes limits on the available characterization methods. An impurity free graphene surface must be achieved prior to adsorption to achieve efficient adsorption and avoid unwanted parasitic reactions. This problem is particularly acute for graphene samples prepared by the use of polymer handles. Alkali metal atoms can also intercalate under the graphene layer depending on substrate and sample preparation conditions. Moreover, it is possible for adatoms to form clusters on a graphene surface⁷ which negatively impacts both doping uniformity and doping efficiency.

In this work, we report a new method of alkali doping of graphene to reach ultra-high doping ($n \sim 10^{14}$ cm⁻²) for charge transport studies beyond the limit of ionic liquid gating. We work with chemical vapor deposition grown graphene transferred onto quartz substrates. Quartz is the substrate of choice due to its chemical inertness and optical transparency, with the latter enabling non-invasive Raman spectroscopy through the substrate. Micron scale graphene devices were prepared using lithography-based methods and the samples were thermally annealed in a nitrogen glove box environment to desorb water prior to alkali doping. The graphene was subsequently exposed to cesium vapor at different temperatures using a flip-chip method that allows hermetic sealing of the air sensitive samples in an inert gas environment with a liquid cesium source of cesium vapour. We measured the in-situ variation of graphene resistivity as cesium atoms are adsorbed onto the graphene surface, and resistivity is modulated by charge transfer doping. Evidence of high doping is observed via Raman spectroscopy performed through the quartz substrate window, with G-peak Stoke shifts ranging from 1589 cm⁻¹ in low-doped regions up to 1608 cm⁻¹ in heavily doped regions. Approaches to improve homogeneity for charge transport measurements will be discussed.

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Excitons in bulk black phosphorus evidenced by photoluminescence at low temperature

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Atomic layers of Black Phosphorus (BP) present unique opto-electronic properties dominated by a direct tunable bandgap in a wide spectral range from visible to mid-infrared [1]. In this work, we investigate the infrared photoluminescence of BP single crystals at very low temperature [2]. Near-band-edge recombinations are observed at 2 K, including dominant excitonic transitions at 0.276 eV and a weaker one at 0.278 eV (Figure 1). The free-exciton binding energy is calculated with an anisotropic Wannier-Mott model and found equal to 9.1 meV. On the contrary, the PL intensity quenching of the 0.276 eV peak at high temperature is found with a much smaller activation energy, attributed to the localization of free excitons on a shallow impurity. This analysis leads us to attribute respectively the 0.276 eV and 0.278 eV PL lines to bound excitons ($I^{\circ}X$) and free excitons (X) in BP. As a result, the value of bulk BP electronic bandgap is refined to 0.287 eV at 2K, to serve as reference for future work on thin BP layers.

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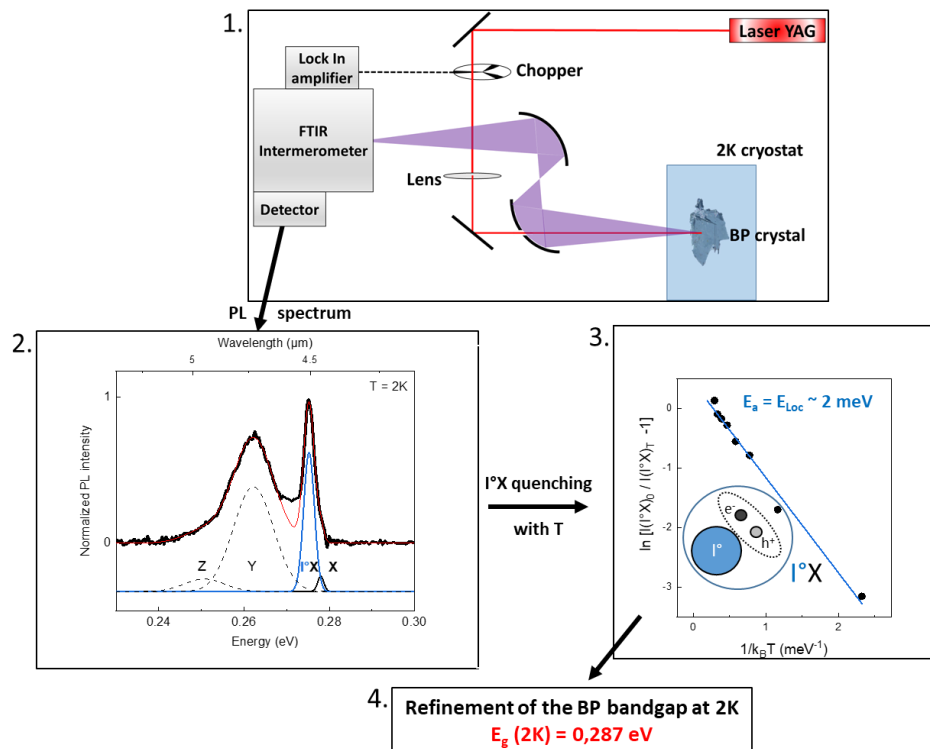


Figure 1: 1. MacroPL setup. 2. PL spectrum of BP crystal at 2 K. 3. Quenching of $I^{\circ}X$ intensity with temperature.

DFT study of curvature effects in graphene flakes

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Curvature effects on mechanical and electronic properties of fixed size graphene hexagonal flakes are studied. Several values of spherical and pseudo-Taub NUT curvatures (figure 1) are applied to a hexagonal-shaped graphene flake generated with a tailor-made numerical software. A hybrid system of molecular mechanics optimizations and Density Functional Theory (DFT) single-point energy calculations is used to get the total energies and the spectra, from which the curvature energy and the gap are extracted. By plotting these results against the curvature parameter k an exponential relationship k^n is expected for both curvature energy and gap. This relationship is confirmed for the pseudo-Taub NUT function flakes, while for the spherical ones a slow change in the exponent n is observed (figure 2). This behaviour is further studied with a nonlinear extrapolation for larger radius, from which an asymptotic exponent of -2, compatible with available continuous models [1], is extracted.

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FIGURES

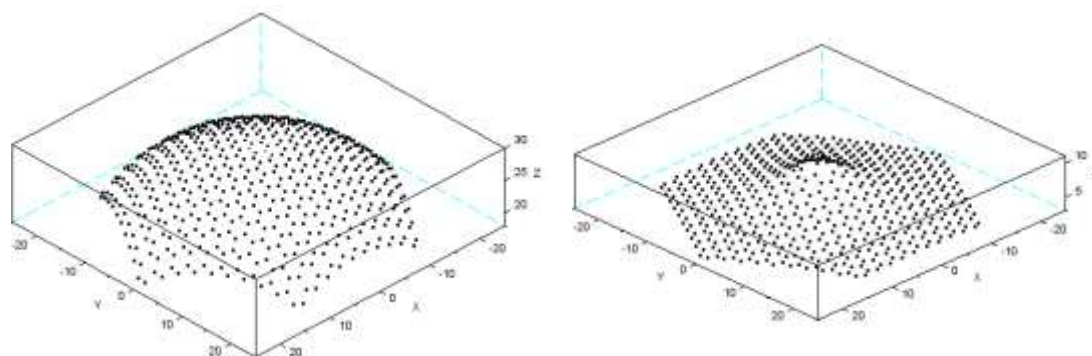


Figure 1: Examples of spherical (left) and pseudo-Taub NUT (right) curvatures in hexagonal graphene flakes.

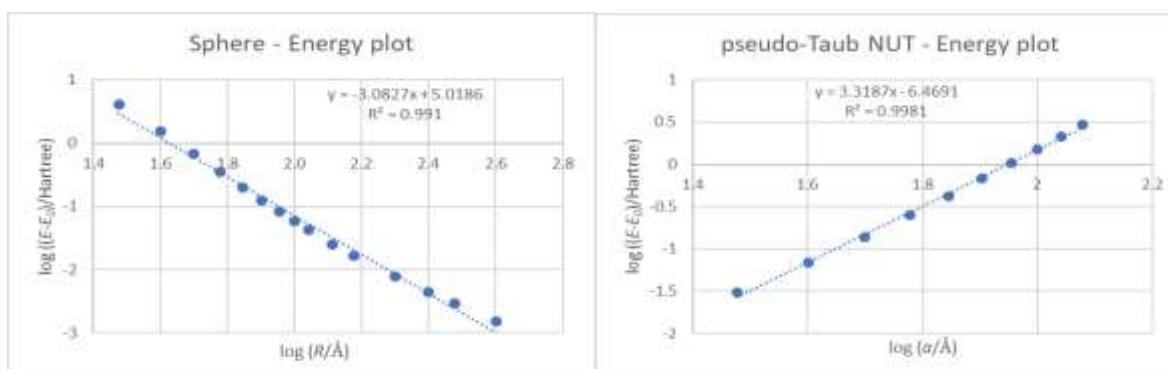


Figure 2: Energy plots for both curvatures studied, with least-squares fittings.

Tip-Enhanced Raman Spectroscopy (TERS) of Transition Metal Dichalcogenides

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Abstract

Two-dimensional (2D) layered materials have been particularly attractive due to their unique structure and excellent optical, thermal, mechanical and electrical properties.¹ In particular, 2D transition metal dichalcogenides (TMDs), such as MoSe₂ and MoS₂, show unique physical and chemical properties when the thickness is limited to a few layers. TMDs have been widely considered for different applications such as in energy storage, electronic devices, optoelectronic and biosensing.²

In this work, MoS₂ flakes are prepared by chemical vapor deposition (CVD) method and the resulting flakes display a variety of shapes and thicknesses. Tip-Enhanced Raman spectroscopy is used to study the lattice vibrations of individual flakes and reveal the presence of defects and the influence of the flake thickness. Specifically, the mapping of the A_{1g} and E_{2g} Raman modes are investigated and the contrast between the far-field and near-field signal was measured. Additionally, the mapping of the surface potential of few layers MoS₂ is collected and correlated with the TERS images

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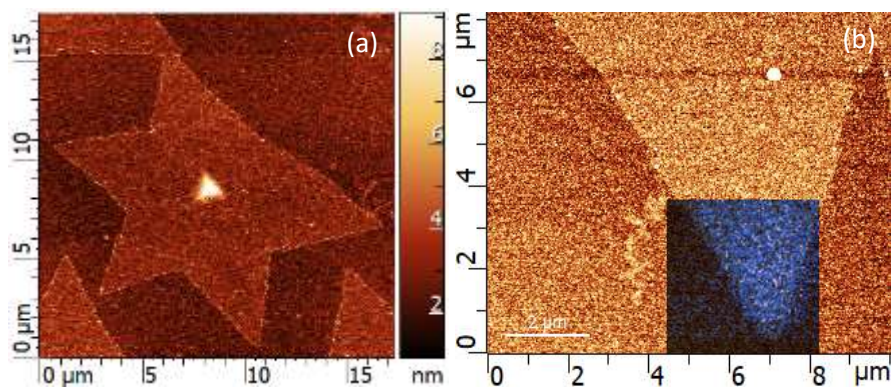


Figure 1: (a) Atomic Force Microscopy (AFM) image of monolayer MoS₂ on SiO₂/Si substrate. (b) AFM image of monolayer MoS₂ on SiO₂/Si substrate and an overlaid TERS map.

MoS₂ Field-Effect Transistors: Transport Properties, Electron Irradiation and Field Emission

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We perform a detailed electrical characterization of CVD-synthesized few-layer MoS₂-based field-effect transistors (FETs), with Ti/Au electrodes, inside a scanning electron microscope (SEM), in order to study the effects of low-energy electron-beam irradiation (up to 10 keV) on the transport properties of the device.

We report an increase of the carrier mobility and a negative shift of the threshold voltage for successive low-energy irradiations that is explained in terms of positive charge trapped in the SiO₂ gate dielectric, during the irradiation [1]. The transistor channel current is increased up to three orders of magnitudes after the exposure to an irradiation dose of 100 e⁻/nm².

Moreover, profiting of the measurement setup with nanomanipulated metallic probe-tips inside the SEM chamber, we also perform a complete characterization of the field emission properties of the MoS₂ nanosheets. Indeed, the sharp edges and high aspect ratio of the nanosheets favour the electron emission, making this material suitable to realize field emission cathodes [1-3].

We report that a field emission current can be extracted from the MoS₂ nanosheets by the application of an electric field as small as 20 V/μm, when the tip anode is placed at 1.5 μm from the emitting surface. In this configuration, we also estimate a field enhancement factor of about 500.

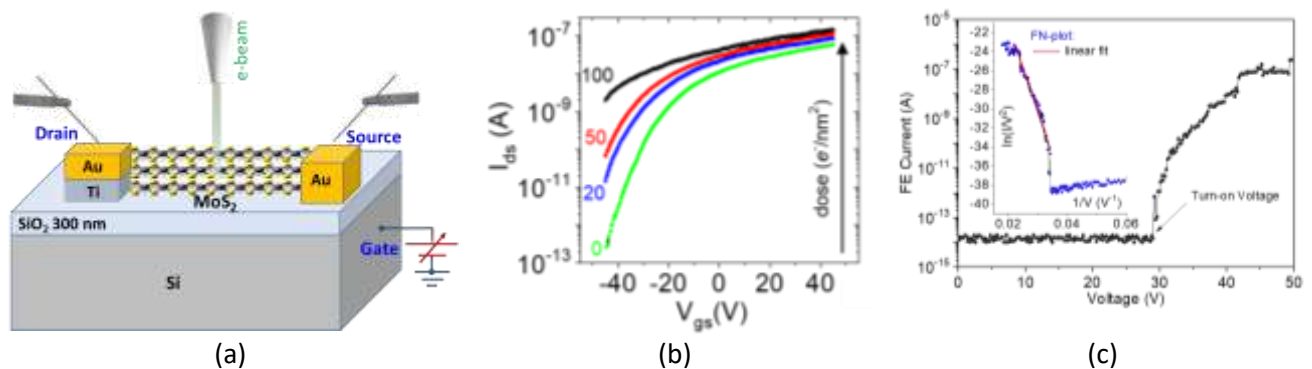


Figure 1: (a) Schematic of the MoS₂ FET under e-beam irradiation. (b) transfer characteristics I_{ds} - V_{gs} measured at $V_{ds} = 1.6$ V for different electron beam irradiation doses. (c) Field emission characterization of MoS₂ flake. I-V curve measured at cathode-anode separation $d = 300$ nm. Left inset: FN-plot of the experimental data. Red line is the linear fit.

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Quantum Transport in Strained Single-Wall Carbon Nanotubes

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Can we control quantum interferences and many-body interactions mechanically, i.e. by pulling on a nano-system? While many idealized theoretical proposals address this question [1], very few have been realized experimentally. To bridge this gap with single-wall carbon nanotubes (SWCNTs), we are developing simultaneously an experimental platform and an applied theoretical model. We nanofabricated high quality strain-tunable suspended SWCNT transistors. For the fabrication, we first located SWCNTs with a diameter smaller than 2 nm using scanning electron microscopy (SEM) and atomic force microscopy (AFM). We then patterned nanometer-scale bowtie-shaped Au break junctions (around 300 nm wide) on top of SWCNTs using electron beam lithography (EBL). Finally, we suspended our devices by removing the supporting SiO₂ beneath them, which after electromigration of the gold junctions [2], it will allow straining of ultra-short SWCNTs with our QTSE platform [3]. To guide the quantum transport measurements in our uniaxially strained SWCNT devices, we developed an applied theory considering dominant uniaxial strain effects and experimental realities. We predict a strong tunability of charge conductance via uniaxial strain in metallic SWCNTs and to a strain-tunable quantum transistor effect. Specifically, for armchair metallic tubes, we observe a valley filter behaviour where electrons are only allowed to flow through certain valleys of the band structure. We also predict the ability of uniaxial strain to modify the electron-hole transport asymmetry in semiconducting SWCNTs, which would permit to engineer two vastly different transport behaviour into a single device [2].

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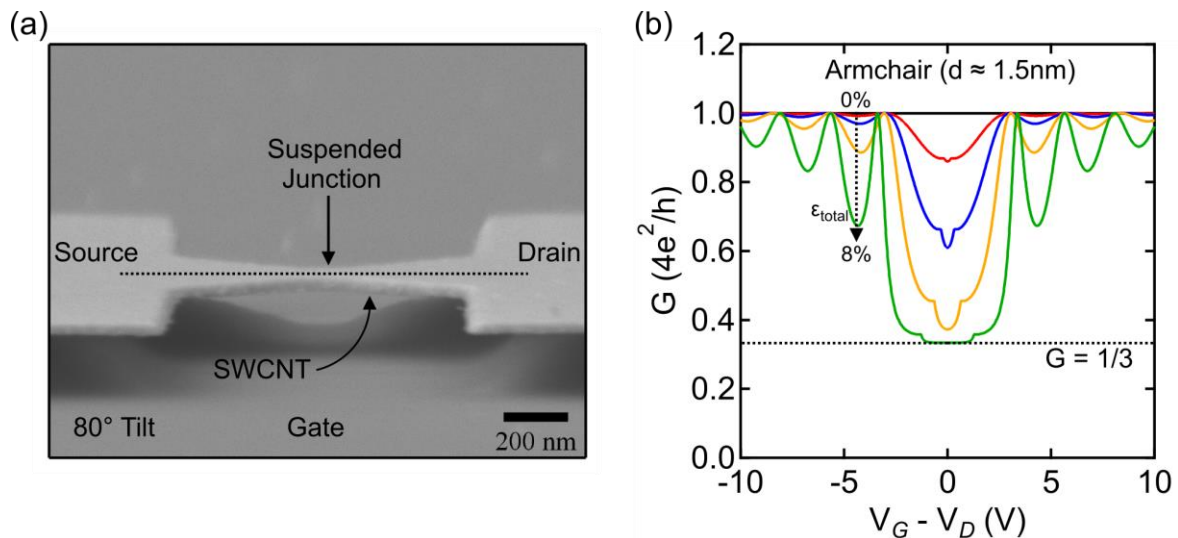


Figure 1: (a) Tilted SEM image of a suspended SWCNT junction. Gold contacts and the SiO₂/Si substrate act as source/drain and gate electrode, respectively, for strain transport measurements. (b) Conductance as a dependant of the gate voltage for uniaxial strain 0 %, 1 %, 2 %, 4 % and 8% (black, red, blue, gold, green) in an armchair SWCNT with the diameter around 1.5 nm. The conductance is suppressed and shows a perfect quantization of 1/3.

On the relationship between microwave plasma flow instability and functional properties of gas phase synthesized graphene nanosheets

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Abstract

Synthesis of graphene with controlled properties such as defect density and chemical doping can be of advantage in wide range of practical applications. In this work we show close relationship between atmospheric pressure microwave plasma instability during graphene nanosheets synthesis by decomposition of ethanol and its functional properties i.e. electrical sheet resistance and high temperature oxidation reactivity. During the synthesis process chemical kinetics and nucleation of graphene depends on the argon gas temperature and optimal formation of growth species in the gas phase [1]. Recently, we have showed [2] that plasma instability caused by high velocity gas flow and plasma discharge movement, caused by combination of central Q_c and secondary Q_s gas flow rate in our dual-channel nozzle configuration, led to increased amount of structural disorder as well as increased amount of carbon-oxygen functional groups and sp^3 phase content in the grown graphene nanosheets (**Figure 1**). These physical and chemical changes were reflected in the change of electrical conductivity and thermal stability of graphene nanosheets layer deposited on the SiO_2 substrate. Further change of ethanol precursor flow rate with increase of microwave power and the substrate temperature led to the transition from horizontal to vertical growth of few-layer graphene layer [3]. Prepared nanomaterial was analyzed by SEM, TEM, Raman and X-ray photoelectron spectroscopy. Information about plasma processes was obtained by optical emission spectroscopy, high speed and ICCD camera imaging.

This work was supported by The Czech Science Foundation under project 18-08520S and in part by project LM2018097 funded by the Ministry of Education, Youth and Sports of the Czech Republic.

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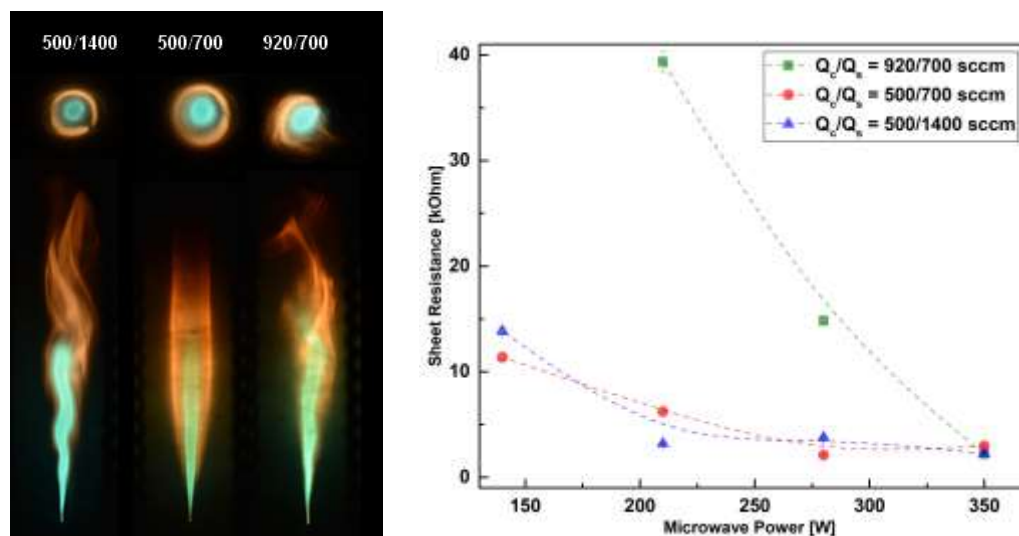


Figure 1: Microwave plasma instability dependence on Q_c/Q_s flow rate on the left and the change of graphene nanosheets layer sheet resistance on the right.

Temperature-induced transition in carbon nanotube on a substrate

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CNTs attract interest of researchers in physics, material science, electronics and biotechnology and nanotechnology due to their unique thermal, mechanical, optical and biological properties. We present the study of single-walled carbon nanotube (CNT) interacting with a plane substrate. We characterize the energy of interaction with the substrate using effective Lennard-Jones-type potential.

Nanotubes have high longitudinal (axial) and relatively weak transverse (radial) stiffness. Because of this, at sufficiently large diameters, nanotubes due to the weak noncovalent interaction of atoms can transform from a hollow cylindrical shape to a collapsed state.

We find energy of the homogeneous open and collapsed states depending on the radius of the carbon nanotube and report on the bi-stability in some range of the CNT diameters. The energy profile of the transition between these two states can be found numerically; for that we solve the problem on the minimum of energy for each fixed value of the distance between the substrate plane and the center of the upper side of the nanotube.

Using the molecular-dynamical simulations we look at the evolution of the CNT with the initial half-opened, half-collapsed state.

With use of the molecular dynamics modelling we demonstrate that the transition area from one state to another is spatially localized and has the features of topological soliton. The transition of a nanotube from one stationary state to another can be described qualitatively as the motion of a kink (topological soliton) in the ϕ -4 model with an asymmetric double-well potential having one, narrow deep hole corresponding to the collapsed state and a second, wide hole higher in energy corresponding to the open state of the nanotube. We show that the value and the direction of the front propagation speed depend significantly on the CNT diameter as well as on the temperature of the system. We discuss the mechanism of the process using a model of effective oscillator in a double-well potential.

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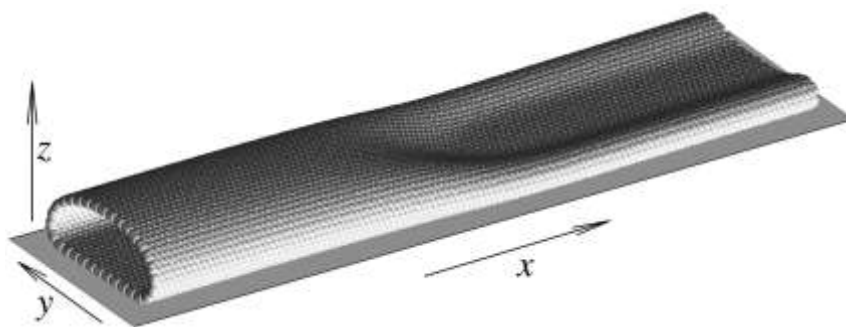


Figure 1: View of a carbon nanotube with a chirality index (31,31) located on a substrate formed by the surface of a silicon carbide crystal 6HSiC (0001). The left end of the nanotube is in an open stationary state (the cross-section of the nanotube has the shape of a convex drop), the right end is in a collapsed stationary state (the cross-section has the shape of an asymmetric dumbbell with a two-layer central part).

In the middle part of the nanotube, a localized region of its smooth transition from one stable stationary state to another is formed.

Layer-controlled single-crystalline graphene film with stacking order via Cu-Si alloy formation

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Multilayer graphene provides both the physically intriguing properties and technologically applications with electronic, optical properties. Several approaches to synthesize the multi layer graphene have been demonstrated but a method of precisely controlling the number of layers with desired stacking sequences is still lacking. Here, we propose an approach for controlling the layer thickness and crystallographic stacking sequence of multilayer graphene films in a wafer-scale via Cu-Si alloy formation using direct chemical vapour deposition (CVD). C atoms are introduced by tuning the ultra-low-limit CH₄ concentration to form a Si-C layer, reaching 1 ~ 4 graphene layers in wafer-scale after Si-sublimation.

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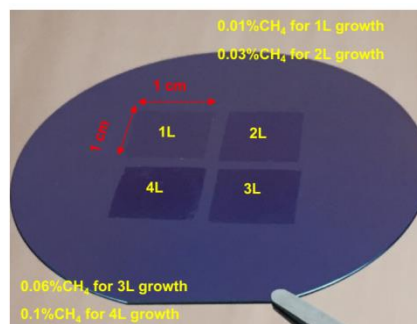


Figure 1: Photograph of centimeter-scale mono-, bi-, tri-, and tetralayer graphene on the SiO₂/Si substrate.

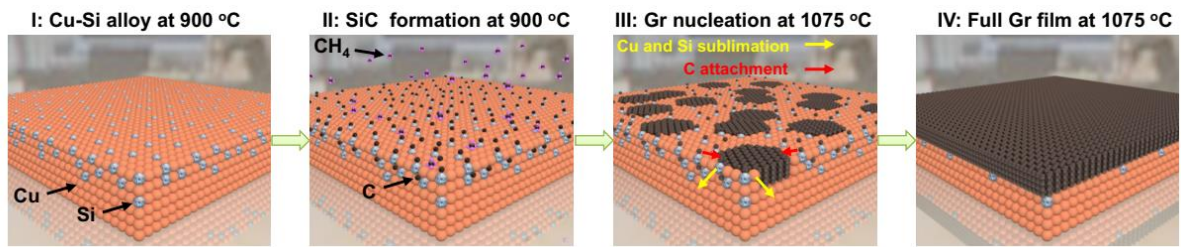


Figure 2: Schematic of growth process. Step I: Si atoms were uniformly distributed in the monocrystalline Cu(111) film; step II: SiC formation at 900 °C in a H₂-rich environment; step III: multilayer graphene islands were grown at 1075 °C; step IV: a full multilayer graphene film was obtained

Transverse Electron Mean Free Path through Few-layer Graphene in eV-Transmission Electron Microscopy

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The transverse electron mean free path (MFP) in graphene has received less attention than its in-plane counterpart, although van der Waals heterostructures often rely on out-of-plane conduction and suspended graphene layers are commonly used as substrates in transmission electron microscopy. In order to probe the transverse MFP in the 0-100 eV range, we added a second electron source to an aberration corrected low energy electron microscopy (AC-LEEM) setup, enabling imaging in both transmission and reflection mode at nanometer (nm) resolution.

We have measured the energy-dependent transmissivity and reflectivity of 2D graphene layers up to 75 eV above the vacuum level and obtained the energy-dependent transverse electron MFP. Below approx. 30 eV we find an increase in MFP. However, the MFP is always much shorter than suggested by the so-called 'universal curve' [1] and exhibits characteristic maxima.

The observed splitting of the elastic MFP maximum around 2.5 eV (see figure) in multi-layer graphene is explained by a model [2] in close analogy to optical multilayer antireflection coatings: The electron wave is partially reflected and partially transmitted at each graphene layer, leading to interference of the multiply reflected waves. By scanning the energy, the electron wavelength is varied and the MFP maxima form whenever transmitted and multiply reflected waves interfere constructively.

Due to their high transmissivity at low energy, graphene membranes are suited as support films in eV-TEM [3]. As the resonant increases in MFP were attributed to interference effects, they can also be expected in other layered materials, providing a new perspective on the 'universal' curve in the low-energy regime.

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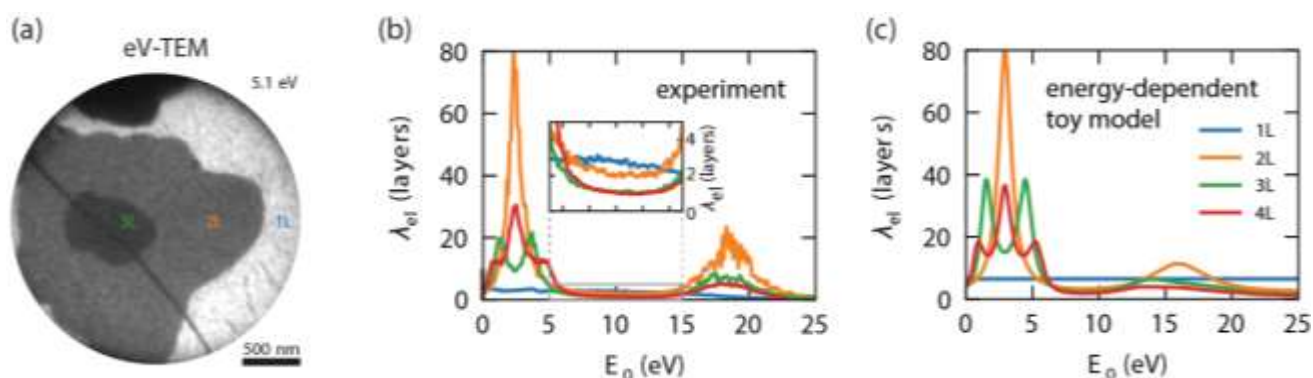


Figure 1: (a) Transmission Electron Micrograph at 5.1 eV electron energy of mono-, bi- and tri-layer graphene areas. (b) Elastic mean free path extracted from transmission and reflection spectra. (c) Elastic mean free path according to a toy model inspired by optical thin-film interference.

Influence of mixing methods on wear rate and frictional properties of graphene nanoplatelet (GNP) reinforced polyethylene

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Although ultra-high molecular weight polyethylene (UHMWPE) has been the warhorse of total knee and hip replacements for several decades, its long-term response is heavily compromised by wear resistance [1]. In order to improve its tribological behaviour, graphene nanoplatelets (GNP) have been added as a reinforcement [2]. In this work, we introduced two different dry-processing methods for UHMWPE/GNPs composites: ball milling and blade mixing. GUR[®] 1050 UHMWPE (Celanese, USA) in powder form was mixed with AvanPLAT-40[®] (Avanzare, Spain) multilayer GNPs in different proportions (up to 3 wt%) by two different mixing methods: ball milling (400rpm, 8 h) and blade mixing. Tribological tests were performed on a ball-on-disk tribometer (CSM Instruments, Switzerland) at 37°C with the sample immersed in deionised water. The 5 N force was applied through a stationary alumina ball (6 mm in diameter, Ra = 0.050 ± 0.002 µm). The coefficient of friction (COF) was registered for 24 h with a total sliding distance of 4320 m. Worn tracks were measured using a confocal microscope SENSOFAR Pµ 2300. The wear response shows a strong dependence in wear factor (k) with processing method, as reflected in Figure 1, where a two times variation in k is shown for a wide range in wt% of GNP reinforcement. Additionally, k seems to be near constant for ball milling composites, opposing to blade mixing composites that where k significantly increases over 1.5 wt%. The presence of GNPs in the ball milled composites has a positive effect on COF, specially over 0.5 wt%. For instance, at 3 wt% of GNPs, a reduction of ~25% is achieved. For blade mixing processed composites, the results shows a similar trend, characterised by a minimum value of COF at 1.4 wt% (a 33% reduction). Accordingly with the results, a reduction in COF has been identified for both processing methods, considering filler percentages over 0.5 wt%.

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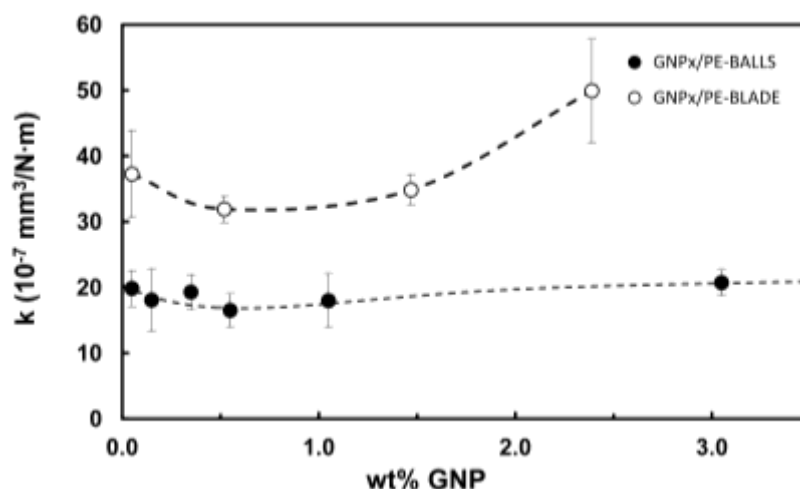


Figure 2: Wear rate vs GNP concentration for Ball Mill and Blade Mixer processed composites.

Solution-processed Layered Double Hydroxides for Energy Applications

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Layered double hydroxides (LDHs) are a class of anionic clays consisting of positive charged brucite-like layers spaced by water molecules and counterbalancing anions[1]. In particular, transition metals LDHs have drawn attention for energy storage and conversion applications[2] because of their electrocatalytic and photocatalytic properties[3][4]. Contrarily to other layered materials[5], LDH layers are held together by electrostatic forces and a dense network of hydrogen bonds[1]. For these reasons, a careful choice of solvent capable to break hydrogen bonds is pivotal for an efficient exfoliation of the LDHs. One of the most effective solvent for LDHs exfoliation is formamide[6]. However, due to formamide toxicity and its high boiling temperature (210°C), other solvents are recommended for the processing of LDHs[7]. In our work, we report that the presence of both acetate and citrate anions during the synthesis of nickel-iron layered double hydroxide (NiFe-LDH) makes possible its exfoliation by simple shaking during the dispersion in ethanol. The formation of single-layer nanosheets is confirmed by X-ray diffraction (XRD) and atomic force microscopy (AFM) data. Lastly, the investigation of NiFe-LDH as electrocatalyst for the OER is showing promising performances for practical applications.

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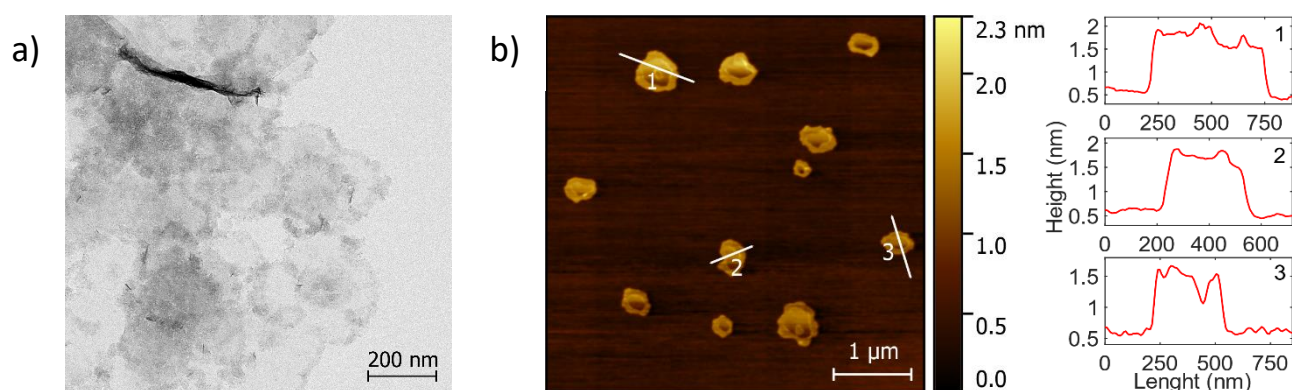


Figure 2: a) Transmission electron microscopy image of citrate containing NiFe-LDH nanosheets. b) Atomic force microscopy image and height profiles of NiFe-LDH nanosheets deposited on mica.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement GrapheneCore3 – 881603

Supressing 1/f Noise in Graphene Field Effect Transistor Sensors

Minh Tran

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Flicker noise or 1/f noise refers to processes in which the power spectral density (PSD) is inversely proportional to frequency and is typically the dominant noise source in transistors at low frequency. We report our work on measurements of unprecedentedly low 1/f noise in graphene field effect transistors, which we attribute to large device area. Large area graphene grown by chemical vapor deposition (CVD) has potential for a variety of applications including biomolecular sensors, bolometric photodetectors and ion sensitive field effect transistors (ISFET) [1]. For all these applications, low-frequency 1/f noise is found to be the dominant factor that determines sensor resolution limits. Hence, the absolute value of 1/f noise PSD serves as a crucial performance metric for graphene sensor applications.

Previous studies of 1/f noise in graphene devices have been performed using both CVD grown graphene and exfoliated graphene. Balandin et al [2] has studied 1/f noise in exfoliated graphene and how it varies with substrate and charge carrier concentration. Karnatak et al [3] has shown that contact resistance can play a dominant role in 1/f noise. To date, there has been no experimental study of 1/f as the graphene channel is scaled up to mm lengths.

We report here our work on 1/f noise measurement of graphene field effect transistors with varying channel geometries[4]. In our experiments, CVD grown graphene on copper was transferred onto fused silica coated with 100 nm of parylene using a wafer scale wet transfer process. Parylene was used as an interface between the graphene and fused silica, which has been shown by Fakih et al [1] to reduce both drift and hysteresis in graphene ISFETs. The transferred graphene was processed with two photolithography steps to fabricate devices with areas ranging from $12 \mu\text{m}^2$ to 36mm^2 . Electrical contact to the graphene was made directly with Au. The 1/f noise was measured by first applying a dc bias using a low noise lithium-ion battery, and the generated voltage fluctuations were then measured using a low noise voltage pre-amplifier and a 24-bit digitizer.

The voltage PSD of 1/f noise in graphene, will typically have the form of $S_V = V_0^2 K/f$. Where V_0 is the dc voltage applied across the device, f is the frequency, and K is the unitless noise constant. K is experimentally approximated to be $(1/N) \sum_{n=1}^N S_{Vn} f_n / V_0^2$, where S_{Vn} is the voltage PSD measured at n different frequencies f_n . The work from Balandin et al [2] demonstrates typical K values of 10^{-8} , and work from Karnatak et al [3] shows K values as low as 10^{-9} . Our devices have unprecedented low measured K values of 10^{-14} , which we attribute to the large device area of 36mm^2 . Our results experimentally demonstrate that the noise parameter K can be decreased by orders of magnitude by working with large area devices. Our work suggests that for graphene based sensor applications, large device area is favourable for improved sensor resolution.

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Enhanced Photoluminescence in Encapsulated TFSI treated MoS₂

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Semiconducting transition metal dichalcogenides (TMDs) such as molybdenum disulfide (MoS₂) are 2D materials which possess a direct band gap at a single-layer thickness [1]. Their electronic bandgap makes them ideal for optical sensing and electronic switching applications. A challenge in using TMDs in optoelectronic devices is their extremely low photoluminescence quantum yield (PLQY) (0.01%-0.6% in MoS₂) [2]. PLQY indicates the percent of photons emitted per photons absorbed above the TMD bandgap. Surprisingly, recent literature has demonstrated methods to drastically increase PLQY using chemical treatments and electrostatic doping [2,3]. Here we demonstrate significantly enhanced photoluminescence (PL) up to an order of magnitude in MoS₂ using trifluoromethanesulfonimide (TFSI) acid treatment (Figure 1). We observe a relative suppression of a charged exciton feature (typically observed at 675nm) suggesting the TFSI treatment may charge-neutralize the TMD monolayer thus reducing non-radiative recombination. Additionally, the PL enhancing effects of TFSI-acid deteriorate after exposure to standard lithography solutions reducing their potential use in device manufacturing. We attempt to remedy this using hexagonal boron nitride (hBN) encapsulation to preserve the TFSI-acid effects (Figure 2). While TFSI-acid treated MoS₂ demonstrates increased PL efficiency, hBN encapsulation is mixed for protecting the enhanced PLQY from standard processing solution.

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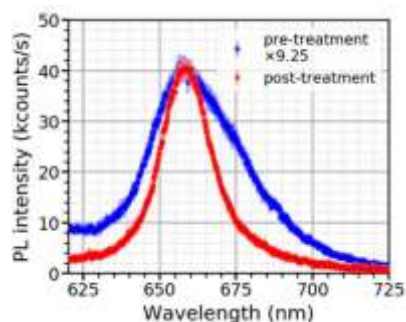


Figure 1: Photoluminescence (PL) spectra of monolayer MoS₂, before and after acid treatment and hBN encapsulation at equivalent power of a 532nm pump.

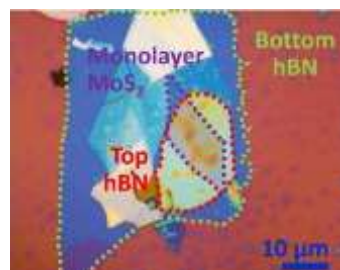


Figure 2: Optical microscope image of TFSI-treated monolayer MoS₂ encapsulated in hBN. Bottom layer hBN (green) and MoS₂ (purple) were TFSI treated followed by placement of the top layer hBN (red).



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