GRAPHENE FOR US

International Conference

New York ★ Feb. 22-23, 2018

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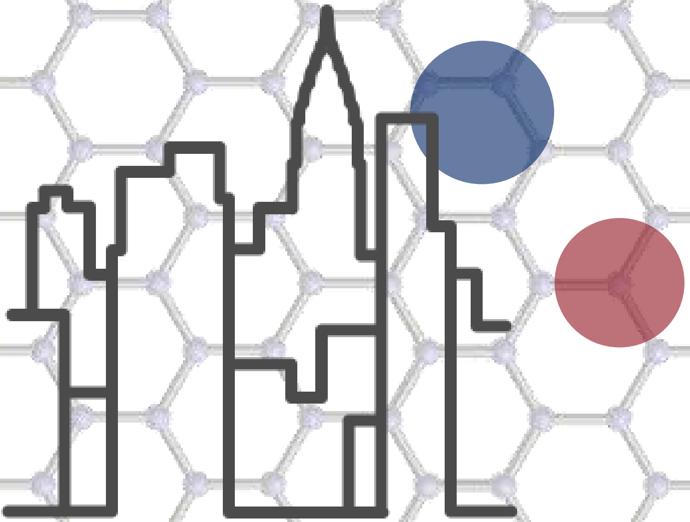

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FOREWORD

On behalf of the Organising Committee we take great pleasure in welcoming you to New York for the first edition of the **GrapheneforUS**2018 International Conference & Exhibition.

A plenary session with internationally renowned speakers, an industrial forum with extensive thematic workshops in parallel and a significant exhibition featuring current and future Graphene developments will be highlighted at the event.

GrapheneforUS2018 will bring together, from a global perspective, scientists, researchers, end-users, industry, policy makers and investors in an environment of cooperation and sharing towards the challenges of Graphene commercialization.

We truly hope that **GrapheneforUS** 2018 serves as an international platform for communication between science and business.

We are also indebted to the following Scientific Institutions and Companies for their help and/or financial support: Grafoid Inc., Texas Instruments, PennState (Materials Research Institute) / 2D Crystal Consortium, Center for 2-Dimensional and Layered Materials (2DLM), Rensselaer, Elsevier (FlatChem) and Columbia University.

We also would like to thank all the exhibitors, speakers and participants that join us this year.

One thing we have for granted: very few industries, one way or another, will escape from the influence of Graphene and 2D Materials and the impact on businesses is here to stay.

Hope to see you again in the next edition of **GrapheneforUS** to be held in 2019.

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SwissLitho is a young high-tech company with the vision to change the way nanostructures are commonly made. Their unique nanolithography tools, called NanoFrazor, trace their origins to the Millipede project from IBM Research Zurich. The multiple-patented technology uses heatable silicon tips for patterning and simultaneous imaging of arbitrary high-resolution nanostructures. The NanoFrazor opens up new and unprecedented possibilities for nanofabrication in order to accelerate scientific and technological progress in all fields of nanotechnology. Since its foundation in 2012, SwissLitho has received many of the most prestigious national and international start-up and technology awards. They are a multi-national and interdisciplinary team of engineers and scientists from more than 10 countries and with customers from all over the world.

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BeDimensional is an innovative start up born in 2016 from the Technology Transfer program of the Istituto Italiano di Tecnologia (IIT), being inspired by the initiative of researchers from the Graphene Labs. BeDimensional aims to develop new materials for the industry through the introduction of two-dimensional crystals. BeDimensional provides new recipes to the market in order to add or enhance the performances of the existing materials through the introduction of graphene and other two-dimensional crystals, improving the characteristics and functionalities of existing products/devices.

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A $MoTe_2$ LED and photodetector for silicon photonics

One of the current challenges in photonics is developing high-speed, power-efficient, chip-integrated optical communications devices to address the interconnects bottleneck in high-speed computing systems. Silicon photonics has emerged as a leading architecture, in part because of the promise that many components, such as waveguides, couplers, interferometers and modulators, could be directly integrated on silicon-based processors. However, light sources and photodetectors present ongoing challenges. Common approaches for light sources include one or few off-chip or wafer-bonded lasers based on III–V materials, but recent system architecture studies show advantages for the use of many directly modulated light sources positioned at the transmitter location. The most advanced photodetectors in the silicon photonic process are based on germanium, but this requires additional germanium growth, which increases the system cost. The emerging two dimensional transition-metal dichalcogenides (TMDs) offer a path for optical interconnect components that can be integrated with silicon photonics and complementary metal-oxidesemiconductors(CMOS) processing by back-end-of-the-line. In this talk, I will show that one type of 2D layered material, molybdenum ditelluride ($MoTe_2$) could bring us one-step closer to chip-integrated devices based on silicon photonics architectures by acting as an active light source or bias-free high speed photodetectors[1].

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Figures

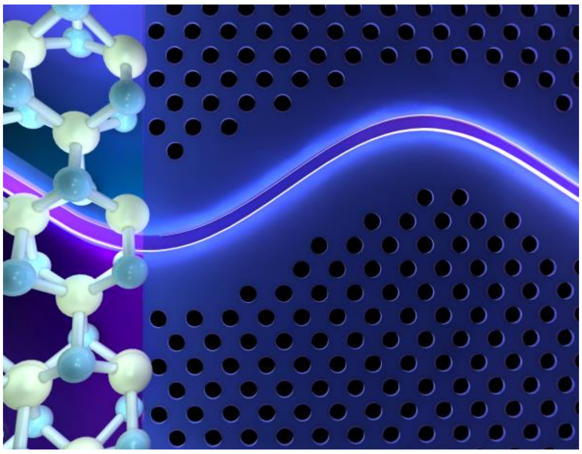

Figure 1: A molybdenum ditelluride light source for silicon photonics

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2D-crystals-based composites for energy applications

Graphene and other 2D crystals are emerging as promising materials[1-5] to improve the performance of existing devices or enable new ones.[1-5] A key requirement for flexible electronics or energy applications is the development of industrial-scale, reliable, inexpensive production processes,[2] while providing a balance between ease of fabrication and final material quality.

Solution-processing[2,6] is a simple and cost-effective pathway to fabricate various 2D crystal-based (opto)electronic and energy devices, presenting huge integration flexibility compared to conventional methods. Here, I will present an overview of graphene and other 2D crystals for flexible and printed (opto)electronic and energy applications, starting from solution processing of the raw bulk materials,[2] the fabrication of large area electrodes[3] and their integration in the final devices.[7,8,9,10,11,12]

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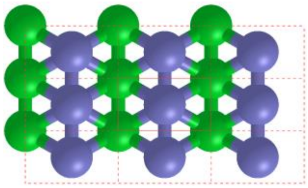
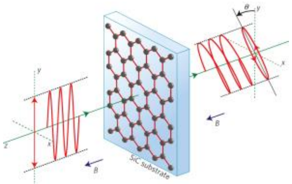
Electronic and optical properties of strained graphene and borophene





When passing an optical medium in the presence of a magnetic field, the polarization of light can be rotated either when reflected at the surface (Kerr effect) or when transmitted through the material (Faraday rotation). This phenomenon is known as a direct consequence of the optical Hall effect arising from the light-charge carrier interaction in solid state systems subjected to an external magnetic field, in analogy with the conventional Hall effect. The optical Hall effect has been explored in many thin films and also more recently in 2D materials. Here, an alternative approach based on strain engineering is proposed to achieve an optical Hall conductivity in graphene without magnetic field [1]. Indeed, strain induces lattice symmetry breaking and hence can result in a finite optical Hall conductivity. First-principles calculations also predict this strain-induced optical Hall effect in other 2D materials. Combining with the possibility of tuning the light energy and polarization, the strain amplitude and direction, and the nature of the optical medium, large ranges of positive and negative optical Hall conductivities are predicted, thus opening the way to use these atomistic thin materials in novel specific opto-electro-mechanical devices.

Borophene, a recently synthesized two-dimensional monolayer of boron atoms, is expected to exhibit anisotropic metallic character with relatively high electronic velocities [2]. At the same time, very low optical conductivities in the infrared-visible light region have been reported. Based on its promising electronic transport properties and *a priori* high transparency, borophene could become a genuine LEGO piece in the 2D materials assembling game. Such early suggested properties demand for an in depth investigation of borophene electronic structure. Moreover, borophene is naturally degraded in ambient conditions and it is therefore important to assess the mechanisms and the effects of oxidation on borophene layers. Optical and electronic properties of pristine and oxidized borophene have been investigated using first-principles techniques [3]. Optical response of the oxidized layer is found to be strongly modified suggesting that optical measurements can serve as an efficient probe for borophene surface contamination.

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“Graphene and 2D Materials” EUREKA Cluster: Fostering European Competitiveness

The “Graphene & 2D Materials” EUREKA cluster is defined as a complementary enabling and accelerator instrument in the European scene, fully piloted by industries to further take graphene from the mature research developed at academic laboratories into the European society in the space of 5 years, boosting economic growth, jobs creation and international leadership and investment attractiveness. This cluster will help Europe having a more dominant position in graphene patenting, will deploy the proper winning industrial strategies to gain worldwide competitiveness, and will ensure that for all promising industrial sectors of technology innovation, a fully integrated EU-value chain is established, integrating into consortia the relevant actors from low to high Technology Readiness Levels (TRL).

The cluster will clarify the differentiating potential in all sectors where EU-industries is strong and could further gain in competitiveness and will develop proper incentives towards the achievement of EU-leadership in the fields of graphene commercialization and graphene-driven technology improvement. The cluster will elaborate and foster industrially-driven innovation strategies, that will take advantage of the existing excellent science and transnational platforms in Europe (national networks, Graphene-Flagship, etc.), and will focus on solving current challenges which are limiting the time to market and business growth of graphene-related EU companies.

Graphene has a huge potential to impact established industrial sectors, building new emerging industries and niche segments and creating economic value. The “Graphene and 2D Materials” Strategic Research Agenda currently targets 7 interlinked priority R&D areas for Europe. These areas are (1) Standardization, (2) Production and Scalability, (3) Composites, (4) Energy, (5) Biosensors and Health, (6) Optoelectronics and Electronic Devices; (7) Functional coatings. Currently, 243 Institutions from 27 countries (among them 154 companies) expressed interest in joining the Cluster...

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Spin transport in graphene interfaced with strong spin-orbit materials

Owing to its small spin-orbit coupling (SOC), graphene has proven to be an efficient carrier of spin [1], making it promising for spintronics applications. However, a small SOC prevents the active manipulation or generation of spin currents. Recent work has thus focused on interfacing graphene with high-SOC materials such as transition metal dichalcogenides (TMDCs) or topological insulators (TIs), in the hope of inducing strong SOC in graphene while maintaining its superior charge transport properties [2-5].

In this talk, I will present our group's recent efforts to describe the nature of SOC and spin transport induced in graphene by proximity to TMDCs and TIs. We find that spin transport in these systems is distinguished by a giant spin lifetime anisotropy, with spins oriented in the graphene plane relaxing much faster than spins pointing out of the plane [6,7]. This anisotropy arises from the specific nature of the SOC induced in the graphene layer, which depends on the symmetry of the graphene/TMDC or TI interface. In addition to serving as a probe of SOC induced in graphene, giant spin lifetime anisotropy may also prove useful for spintronics, for example serving as an orientation-dependent spin filter.

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Figures

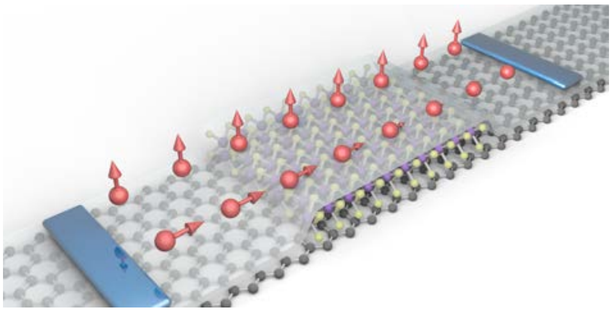

Figure 1: Schematic of anisotropic spin relaxation in a graphene/TMDC heterostructure.

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Tunable degrees of Freedom in van der Waals heterostructures

Graphene, a single layer of carbon atoms arranged in a hexagonal lattice, is probably the best known, and most extensively characterized two-dimensional material. However, this represents just one of a larger class of van der Waals materials, in which atomic monolayers can be mechanically isolated from the bulk. By integrating these materials with one another, an exciting new opportunity has emerged in which layered heterostuctures can be fabricated with properties beyond those of the constituent materials. In this talk I will present some of our recent efforts where we explore new degrees of freedom available in these strucutures that allow us to realize yet a new level of control over their electronic properties.

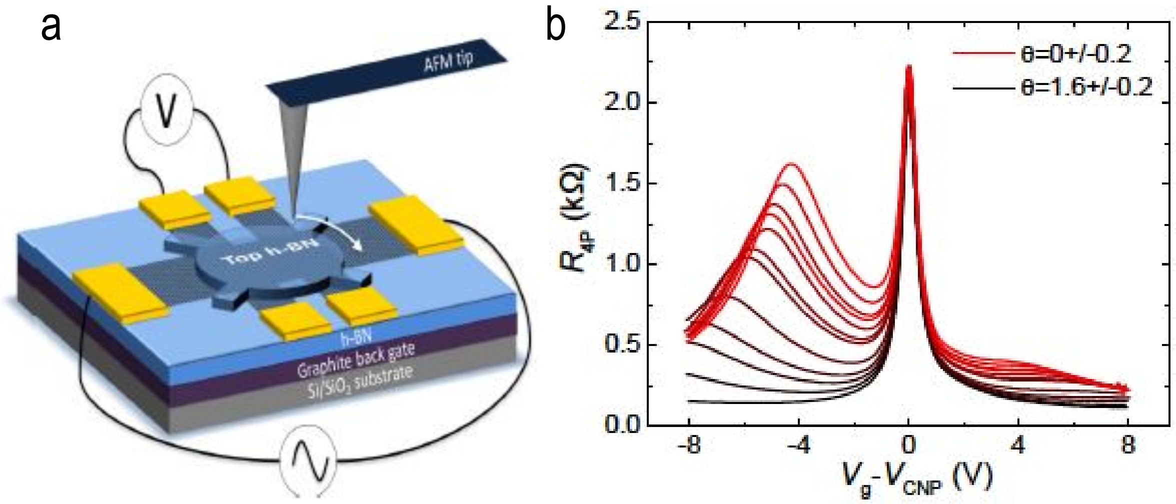

Figure 1: (a) Cartoon schematic of an example device where the crystallographic orientation between a graphene Hall bar and encapsulating BN layer can be varied resulting in a dynamically tunable moire-pattern. (b) Transport measurement acquired from a device similar to that illustrated in (a). Rotating the BN layer allows in-situ modification of the density at which the moire pattern- induced satellite Dirac point appears. Control of the angular orientation to better than 0.2 degree precision is demonstrated.

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The Scaling of Reproducible Graphene for Industry Use

Over the last few years, Graphenea has invested in expanding its team, facility and production capacity of both the Graphene Oxide and CVD Graphene Films to supply the needs of the growing graphene market. By making these strategic investments and developing a clear roadmap for both GO and CVD graphene, Graphenea has been able to keep pace with the demand of the graphene market. Ultimately, the key to success will come from working hand in hand with our industry partners to achieve their research milestones.

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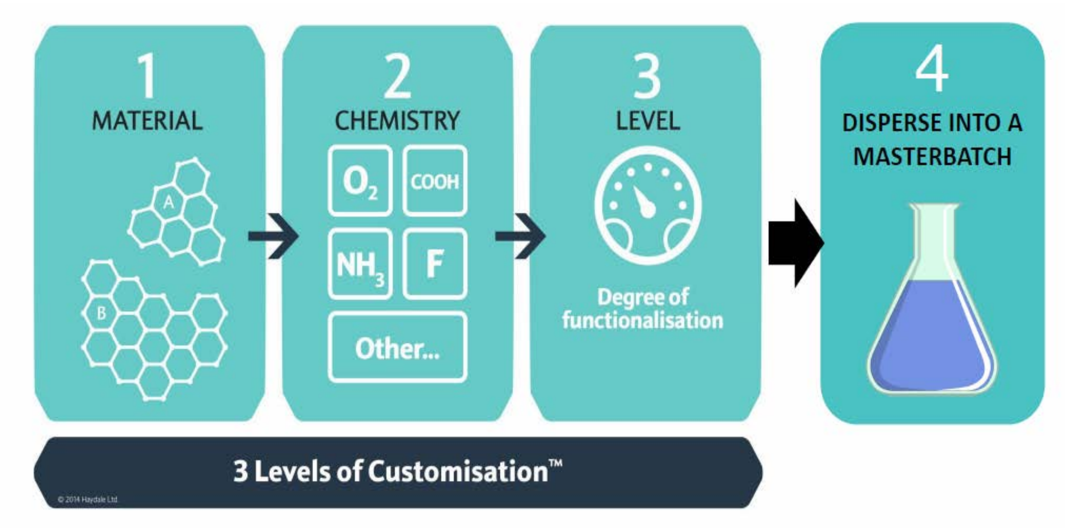
Near term commercial applications for Graphene, Composites and Conductive Pastes

Abstract

The potential for graphene and other nano particles to significantly enhance material properties has been well documented. However, as carbon is inert and does not mix well with other materials it needs to be homogeneously dispersed and bonded into the host material in order to realise its potential. There are hundreds of “graphene’s” in the market today and all display different characteristics, from flake size, to thickness and chemical groups on the surface and ends to the supply chain issue in delivery of volume at a commercial cost. Some supply may well require scale up and the likelihood is that the volume output will be different from the pilot plant. Knowing which one material works best and applying a sympathetic surface treatment for a specific application is the Haydale expertise. This functionalisation treatment plus the years of processing know how sets Haydale apart in the ability to commercialise nano materials.



For industry to adopt these new materials we need to demonstrate a repeatable and cost effective supply chain that delivers a “masterbatch” to the customer. One of the challenges industry faces is that there is currently no standard definition of graphene which means that R&D and general procurement departments may not know exactly what it is they are buying nor be able to replicate test results with a subsequent batch of material. Industry requires a standardisation of materials to remove this uncertainty. The recent ISO paper has helped but there is a way to go.

Recent work at Haydale has now confirmed significant improvements in electrical, thermal and mechanical performance of Carbon Fibre pre preg, opening up many applications NOW. Haydale has significant expertise in GRP and Thermoplastic pipes for water, sewerage, and the Oil & Gas industry. With latter suffering for significant repair issues, leak detection and a desire to replace pipes with “non-metallics”, the Haydale team has unique solutions for these needs. These breakthroughs plus new pastes for bio medical sensors offers real short term commercial opportunities for Graphene, and nano particles. The industrial and financial world has been waiting for these commercial applications to bear fruit.

Further, in order to persuade industry to adopt the new materials we need to be able to incorporate the functionalised materials into existing production facilities thus avoiding the need for replacement of existing capital equipment. Ray Gibbs will examine these challenges and explain how Haydale has established a consistent supply chain of the nanomaterials and are addressing the commercial adoption challenges through the establishment of Centres of Excellence in strategic locations across the globe in the three dominant continents of The Far East, USA and Europe.

Biography
Ray is a Chartered Accountant, and former Deloitte audit and corporate finance partner for 9 years. He has over 20 years' experience in high technology and fast moving consumer goods businesses and is a former CFO of Chemring Group Plc. Ray was part of Haydale Graphene Industries' management team that acquired Haydale Limited in 2010, became CEO in 2013 and successfully took the business through to IPO in April 2014, defined the strategy and driven for globalization and now sales. Since IPO the company has doubled its market value, currently at over £35m and grown from 6 to over 65 staff. He has been immersed into the graphene and nano world for 7 years. An accomplished international speaker now seen at many Graphene conferences and seen as a leader in the industry, Ray offers a rare insight into industry and the ability to make the bridge with the academic world.

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Printable Two-Dimensional Nanomaterial Inks for Electronic and Energy Applications

Layered two-dimensional nanomaterials interact primarily via van der Waals bonding, which has created new opportunities for heterostructures that are not constrained by epitaxial growth [1]. In order to efficiently explore the vast phase space for van der Waals heterostructures, our laboratory employs solution-based additive assembly [2]. In particular, constituent two-dimensional nanomaterials (e.g., graphene, boron nitride, transition metal dichalcogenides, and black phosphorus) are isolated in solution, and then deposited into thin films with scalable additive manufacturing methods (e.g., aerosol, inkjet, gravure, and screen printing) [3]. By achieving high levels of nanomaterial monodispersity and printing fidelity, a variety of electronic, electrochemical, and photonic applications can be enhanced including digital logic circuits [4], lithium-ion batteries [5], and photodetectors [6]. Furthermore, by integrating multiple nanomaterial inks into heterostructures, unprecedented device function is realized including anti-ambipolar transistors [7], gate-tunable photovoltaics [8], and neuromorphic memristors [9]. In addition to technological implications for electronic and photonic technologies, this talk will explore several fundamental issues including band alignment, doping, trap states, and charge/energy transfer across two-dimensional van der Waals heterointerfaces [10].

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Graphene Flagship: bridging the gap from research to commercialization

With a budget of €1 billion, the Graphene Flagship represents a new form of joint, coordinated research on an unprecedented scale, forming Europe's biggest ever research initiative. The Graphene Flagship's principal mission is to take technologies based on graphene and related materials from the laboratory to commercial applications. As such, innovation is a key focus of the Flagship.

Bringing together research community and companies adding industry viewpoints to discussions has a great boosting effect on the innovation activities, which leads to new initiatives and paves the way for commercialization efforts. The innovation process in general together with the innovation approach applied in graphene flagship will be discussed.

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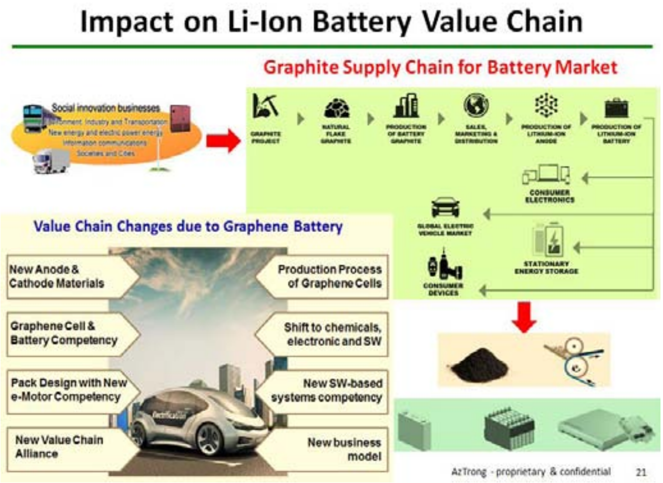
Challenges of Graphene Battery Commercialization

Abstract

Graphene is considered the most revolutionary, world-changing material since plastic. With the emergence of smart mobile devices (MD), electric vehicles (EV), grid and distributed energy (G&DE), sensors and Internet of Everything (IOE) the world is moving rapidly toward a more connected and more sustainable place. Graphene will play a key role to help transform many industries. We believe the success to of its commercialization for applications will depend largely on the availability of quality mass production and functionalization equipment.

All these advances hinge upon the development of next generation of energy storage technologies that can deliver high energy and power densities at a low cost (i.e. > $350/kWh) and high safety. This talk will discuss the technical parameters and performance factors underlying the use of graphene-based technologies – which we feel presents a compelling performance upgrade for the replacement of conventional Li-ion batteries in use today for mission-critical, extreme-duty applications of battery systems. Graphene has emerged as important candidates for electrode materials in lithium-ion batteries (LIBs) due to their unique physical properties. A comparison on the current state-of-the-art and most recent advances in graphene-containing nanocomposite electrodes and their derivatives will be provided along with the synthetic routes of their electrochemical performance in LIBs will be discussed. More importantly, the issues of graphene relate to materials, electrode coating, safety for energy storage applications will be highlighted, with an emphasis on anode and cathode materials. Several directions for near future R&D will be discussed. AzTrong is a leading production equipment supplier of high quality functional GO/rGO (ink, powder, slurry, film) for various applications & solutions. We will share his experiences in graphene battery, graphene mass production as well as commercialization for energy storage and other applications.

Figures


Impact on Li-Ion Battery Value Chain

Graphite Supply Chain for Battery Market

Value Chain Changes due to Graphene Battery

New Anode & Cathode Materials
Graphene Cell & Battery Competency
Pack Design with New e-Motor Competency
New Value Chain Alliance
Production Process of Graphene Cells
Shift to chemicals, electronic and SW
New SW-based systems competency
New business model

AzTrong - proprietary & confidential 21

Figure 1: Transform the Li-Ion battery supply chain

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Atomic reconstruction at van der Waals interface between two-dimensional materials

Crystal interfaces at the boundary between two materials have been essential in engineering material properties in modern materials physics. The interface in two-dimensional (2-D) van der Waals (vdW) heterostructures differs from classical heterogeneous interfaces since it can create high-quality interface structure without any limitation on lattice commensurability between the two layers. Indeed, adjusting stacking angle or lattice mismatch between the layers has proved a fruitful way to tune the electronic properties by producing additional quasiperiodic structure described by a Moiré pattern. However, the interplay between vdW interaction energy and elastic energy at the interface can cause atomic reconstruction, leading into intriguing structures which have not yet been clearly understood. In order to understand the atomic reconstruction mechanism and details of the resulting structures, we choose the simplest form of vdW interface: two layers of graphene with controlled twist angle. Here we show that the atomic-scale reconstruction at the vdW interface can be manipulated to form arrays of commensurate domain structures. A combination of transmission electron microscopy (TEM) with finite element method (FEM) simulation reveals the reconstruction mechanism: periodic rotational modulation of the lattice following the Moiré periodicity forms the local commensurate configurations. More interestingly, a systematic study on a series of different twist angles shows how the commensurability of those domains is modified by tuning the twist angle, revealing a gradual transition from commensurate to incommensurate configuration. We note that the commensurate domain structures in bilayer graphene are topologically nontrivial, providing a network of one-dimensional (1-D) topological channels along their boundaries. The signature of transport behavior through the network of 1-D channels can also be observed in the presence of transverse electric field. Reconstructed vdW interface structures and their correlation with transport properties indicates the importance of understanding the intriguing behavior of atomic reconstruction at the vdW interface for engineering 2-D heterostructures in various applications.

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The Transformation of Graphene and 2D Materials into Biomaterials

The use of nanomaterials in medicine is growing at an unprecedented rate for a variety of therapeutic, diagnostic or combinatory applications. Graphene and other 2D materials possess properties that make them attractive materials for biomedical applications, however, their impact on the physiology of live organisms is still unexplored. What is needed today is the determination of the specific characteristics graphene and 2D materials should possess in order to determine the toxicological and adverse reaction risks following administration or implantation. This talk will illustrate how biological-grade graphene oxide (GO) sheets exhibit very interesting behaviour on interaction with tissues of living animals (*in vivo*). The pharmacokinetic and toxicokinetic profile of the GO sheets in correlation with their physicochemical characteristics (thickness, lateral dimensions) can allow the determination of the critical parameters that can allows their further development towards the clinic. Development of GO for therapeutic or diagnostic applications requires determination of the fundamental *in vivo* pharmacological parameters such as blood circulation half-life, tissue biodistribution, excretion rates, and kinetics of material biodegradation which will constitute the emerging research area of graphene pharmacology.

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Graphene composites: from lab to market

In this talk I shall present our recent progresses on the large-scale production of graphene, two-dimensional crystals and related composites for industrial applications [1,2,3]. I will first discuss several two-dimensional crystal-based compounds and show the impact of the flake morphology and the compounding process on the thermal/electrical/mechanical properties of the final compound. I will then present a few examples of graphene products and discuss a strategy to fill the gap between research in the lab and final product in the market.

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Figures

Figure 1: MOMO DESIGN motorcycle helmet with graphene shelter technology developed by IIT Graphene Labs.

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Recent Progress in Commercialization of Graphene-based Thermoplastic and Thermoset Composites.

Graphene materials completely dispersed in various polymer matrices represent the first commercially feasible use of graphene. In this talk, we focus on our current developments in high performance graphene composites based on both thermoplastic and thermoset resins. One of our first graphene products is PLA-based conductive filament with volume resistivity as low as 0.6 Ω·cm. This material is compatible with most of the commercial FDM printers, and suitable for creating conductive traces and sensors. In addition, we have created a line of graphene composites and master batches that can then be diluted for further processing into parts by extrusion or injection molding.

Another area of significant progress in functional graphene materials is the launch of several graphene-enhanced conductive adhesives distributed under trademark G6-EPOXY TM (visit www.g6-epoxy.com for full list of specifications). We have developed metal-free carbon-based epoxy with volume resistivity below 5 Ω·cm, making it one of the best metal-free conductive adhesives currently available in the market. We have also developed hybrid epoxies (highly electrically conductive adhesives) with a proprietary formulated blend of graphene, silver fillers and other additives. With the development of this proprietary formulation, we have not only guaranteed the electrical conductivity of these epoxies to be at par with the existing commercial products but have also successfully managed to substantially reduce the percentage of silver content in the epoxies.

The critical belief behind reducing silver content had 2 major points: improving the mechanical properties and ease of processing and keeping the cost price of the product low thereby making it more commercially viable and attractive for variety of applications.

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Diamene: Ultrahard Single Layer Diamond formed from two-layer Epitaxial Graphene upon Impact

Atomically thin graphene exhibits fascinating mechanical properties, although its hardness and transverse stiffness are inferior to those of diamond. So far, there has been no practical demonstration of the transformation of multilayer graphene into diamond-like ultrahard structures. Here we show that at room temperature and after nano-indentation, two-layer graphene on SiC(0001) exhibits a transverse stiffness and hardness comparable to diamond (Fig. 1), is resistant to perforation with a diamond indenter and shows a reversible drop in electrical conductivity upon indentation. Density functional theory calculations (Fig. 2) suggest that, upon compression, the two-layer graphene film transforms into a diamond-like film, producing both elastic deformations and sp2 to sp3 chemical changes. Experiments and calculations show that this reversible phase change is not observed for a single buffer layer on SiC or graphene films thicker than three to five layers. Indeed, calculations show that whereas in two- layer graphene layer-stacking configuration controls the conformation of the diamond-like film, in a multilayer film it hinders the phase transformation.

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Figures

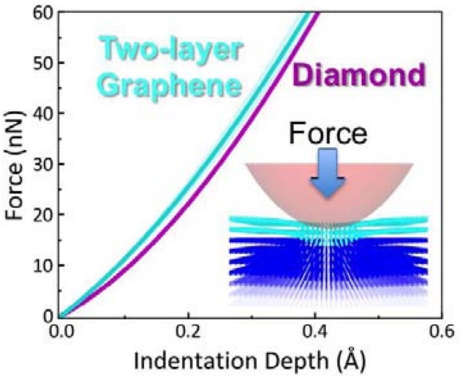

Figure 1: Experimental load vs. indentation curves showing that two-layer epitaxial graphene is stiffer than diamond.

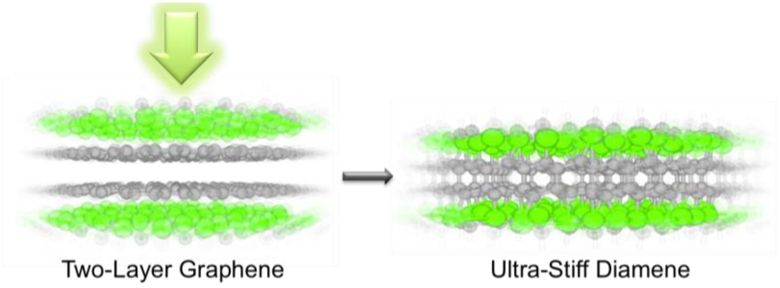

Figure 2: DFT simulations of the transformation of two-layer graphene into diamene under pressure.

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Atomically-Thin Materials and Heterostructures

The last decade has seen an exponential growth in the science and technology of two-dimensional materials. Beyond graphene, there is a huge variety of layered materials that range in properties from insulating to superconducting. Furthermore, heterogeneous stacking of 2D materials also allows for additional "dimensionality" for band structure engineering. In this talk, I will discuss recent breakthroughs in two-dimensional atomic layer synthesis and properties, including novel 2D heterostructures and realization of unique 2D allotropes of 3D materials (e.g. 2D-GaN and Ga_2O_3). Our recent works demonstrate that the properties and doping of 2D materials, especially synthetic 2D materials, are extremely sensitive to the substrate choice. I will discuss substrate impact on 2D layer growth and properties, doping of 2D materials, selective area synthesis of 2D materials, and 2D nitrides beyond hBN. Our work and the work of our collaborators has lead to a better understanding of how substrate not only impacts 2D crystal quality, but also doping efficiency in 2D materials, and stabalization of nitrides at their quantum limit.

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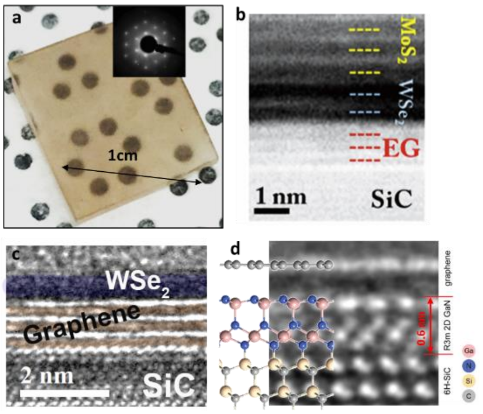

Fig.1: Examples of (a) wafer-scale WSe2, (b,c) 2D heterostructures, and (d) 2D-Gallium Nitride.

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When molecular science meets 2-D materials: combining multiple functions

The combination of the molecular science with 2-dimensional materials, by mastering the supramolecular approach, allows the tuning of the dynamic physical and chemical properties of 2D materials, making it possible to generate multifunctional hybrid systems for applications in (opto)electronics and energy.[1] Towards this end, both covalent and non-covalent strategies can be exploited. My lecture will review our recent findings on:

(i) The harnessing of the yield of exfoliation of graphene in liquid media by mastering the supramolecular approach via the combination with suitably designed functional molecules possessing high affinity for the graphene surface, leading ultimately to the bottom-up formation of optically responsive graphene based nanocomposites for electronics. [2]

(ii) The combination of bottom-up grown copper nanowires with graphene oxide sandwiched in a layer-by-layer fashion, followed by a mild reduction in water, yielded flexible hybrid electrodes with transparencies and conductivities matching those of indium-tin oxide. As a proof-of-concept, such hybrid structures have been used as electrodes in electrochromic devices.[3]

(iii) The development of artificial heterostructure devices with a variety of different electronic and optical properties by self-assembly of atomically precise supramolecular lattices on CVD graphene. This approach made it possible to generate controllable 1D periodic potentials in the resulting organic–inorganic hybrid heterostructures.[4]

(iv) The exploitation of thiol-chemistry to covalently graft functional molecules to the basal plane of MoS2.[5]

Our approaches provide a glimpse on the chemist's toolbox to generate multifunctional 2D materials based nanocomposites with ad-hoc properties to address societal needs in electronics and energy applications.

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Spectroscopy of 2D Materials with Low Energy Electron and Photo Electron Emission Microscopy

It is well known that Low Energy Electron Microscopy (LEEM) and Photo Electron Emission Microscopy (PEEM) are powerful methods for high-resolution imaging of surfaces and interfaces, both in static and in dynamic situations. Time resolution in pump-probe type experiments can be on the order of picoseconds, spatial resolution below 2 nm has been demonstrated in aberration-corrected instruments, and spin-resolved instruments are capable of imaging magnetic domain structures. In recent years, these instruments have also seen rapid development of a range of spectroscopic capabilities that greatly expand and enhance their utility and application range. Many of these novel capabilities have been developed in the context of 2D materials science and exploration. Examples include structure analysis and correlated workfunction measurements of inhomogeneous 2D systems, surface potentiometry in simple 2D device structures, quantitative determination of 2D strain fields in epitaxial 2D materials, Electron Energy Loss Spectroscopy (EELS), area-selected Angle-Resolved Photo-Electron Spectroscopy (ARPES) as well as state-selected imaging of electron states below the Fermi level, and Angle-Resolved Reflection Electron Spectroscopy (ARRES) of electron states above the vacuum level. For example, figure 1 shows ARPES and ARRES spectra obtained in the same instrument on graphite and hexagonal boronnitride (hBN), compared with band structure calculations [1]. In this talk I will give an overview of recent developments and results.

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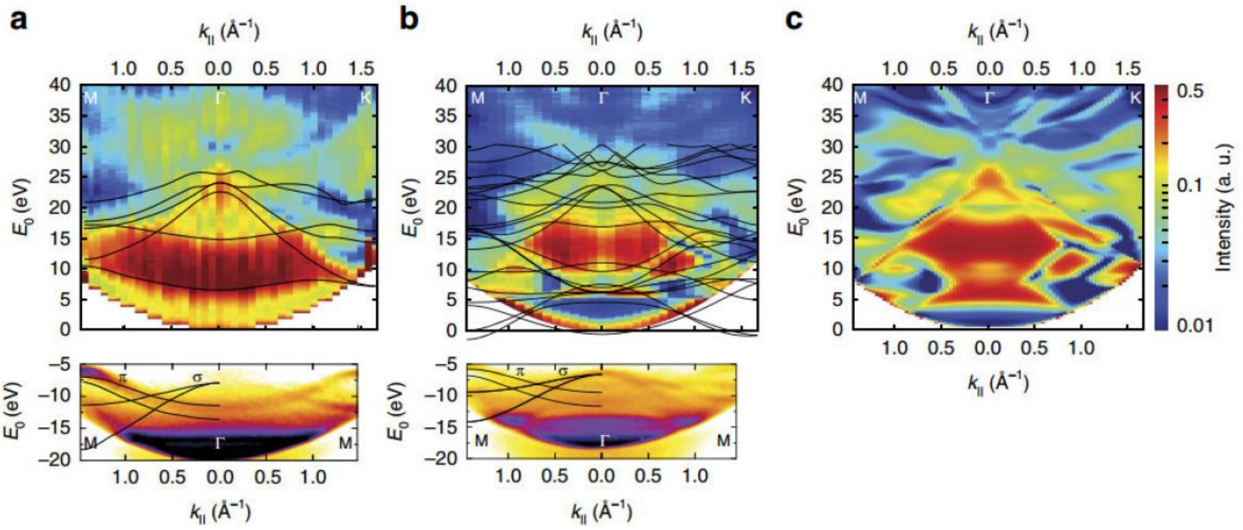

Figure 1: ARPES (lower panels) and ARRES (upper panels) spectra on graphite (a) and hBN (b). Solid lines show theoretical bandstructures. (c): Theoretical ARRES spectrum for bulk hBN. Red regions (high reflectivity) correspond with bandgaps in the unoccupied valence band. A close correspondence with seen with the experiment result in (b).

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Graphene-based Interlayer Tunneling Field-Effect Transistors: Device Physics and Applications

Graphene has attracted significant research interest in the past decade, and spearheaded a larger effort on other two-dimensional (2D) materials and their van der Waals heterostructures. Motivating in part this effort is the interest in emerging devices, which may augment functionalities of existing technologies. We discuss here the realization and device physics of graphene- and transition metal dichalcogenide-based interlayer tunneling field-effect transistors, a new class of devices that operate via energy and momentum conserving (resonant) tunneling between two 2D layers (Figure 1). We examine the case of double bilayer graphene heterostructures [1] separated by hexagonal boron-nitride [2,3] or WSe_2 [4], which show gate-tunable resonant tunneling when the two layers are rotationally aligned. In devices where the two graphene bilayers are separated by WSe_2, the interlayer current voltage characteristics show room temperature negative differential resistance with large peak-to-valley ratios, and high current densities. We discuss intrinsic benchmarks and potential applications.

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Figures

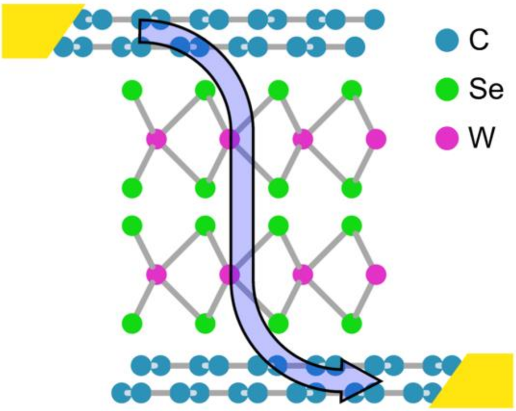

Figure 1: Schematic representation of an interlayer tunneling field-effect transistor consisting of two bilayer graphene separated by WSe_2.

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Grafoid: Collaboration Is the Key to Graphene's Commercialization

Bilateral co-operation in the low carbon economy offers opportunities for graphene producers. In the coming years, strong bilateral relationships for the commercialization of graphene will flourish. These relationships will bring together mine-to-market industry players to propel application development to meet market demand.

The natural flake graphite market has changed dramatically in the last five years from a dig-and-sell commodity business to a value-added product business and, driven by national and international factors, the industry is being shaped by two colliding forces: climate change and the graphene revolution.

Globally, national governments are committing to stringent emission targets and implementing policies to foster and propel new material advancements. Traditional mining industries, weakened by the global commodity downturn, are searching for ways to revive their businesses, while new material enterprises, such as value-added graphite and graphene start-ups, are looking to leverage these game-changing opportunities.

The impact has been significant and long-term implications will dramatically change the critical material sectors. As more and more countries ratify the Paris Accord and mandate domestic policy, the faster industry will adopt change.

Grafoid is poised to take advantage of the change. As a graphene research, development and investment company, it has positioned itself for collaborative commercial alliances in graphene application development. Based on an investment in a patented one-step process to produce an affordable suite of graphene products, the company develops applications with joint venture partners at Grafoid's Global Technology Centre (GGTC), in Kingston, Canada. Further, it has partnered with the Canadian Government to build the world's first automated mass production graphene line and is positioned as a founding member of the 2GL Platform (www.2GLPlatform.com) of critical material companies and the GO Foundation.

No one company can do it alone. Commercialization of graphene will only successfully happen when we work together in collaboration, fitting all the necessary pieces together – the science, material and innovation – and matching it with financial resources and industry's products and ideas. This requires cooperation, education and outreach on our part.

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How Clean is My Graphene?: Understanding the Impact of Contamination Using ToF-SIMS Characterization

Due to the extensive research carried out on graphene and related 2D materials over recent years, the fundamental physical and electrical properties are generally well understood, however uptake by industry is still at a relatively low level. One of the major barriers to this has been a lack of consistency in the properties of commercial scale materials, whether that is in exfoliated graphene powders or chemical vapour deposition (CVD) grown 2D layers on metal catalysts. One major reason for this is likely to be the significant variations in chemistry and contamination which can be observed for these materials[1]. Sample handling, processing, and even inherent variations in source materials can lead to measureable differences between samples. In this study, we use Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS), a highly surface sensitive measurement technique, to explore in detail the variation in contamination species present with different graphene material systems, and show how this can impact on graphene composite material properties [2], and CVD growth mechanisms [3], where contamination can be directly linked to changes in nucleation densities.

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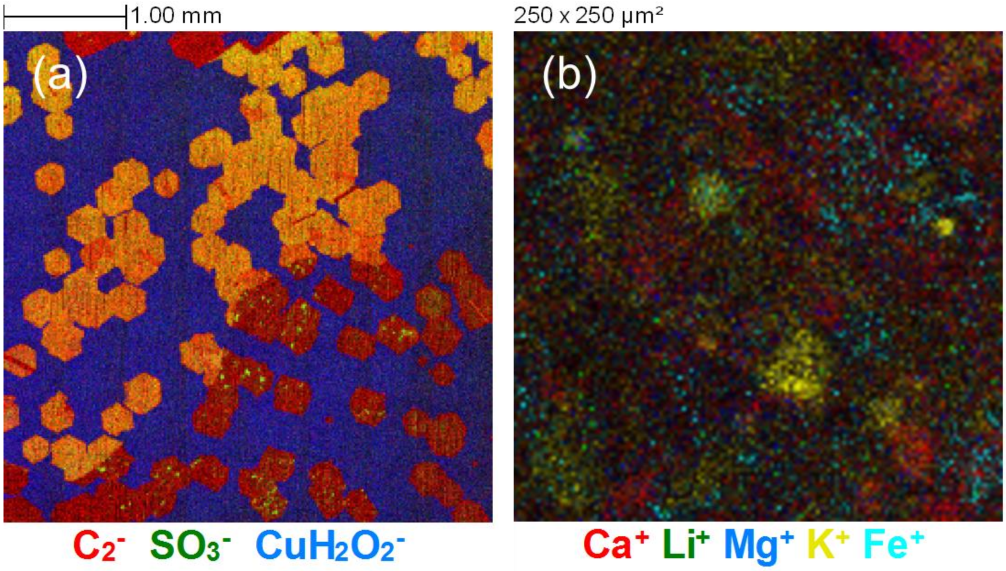

Figure 1: ToF-SIMS images of (a) CVD single crystal graphene grown on copper foil, and (b) pressed exfoliated graphene powder, showing the presence of various contaminant species associated with each sample.

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Multi-Purpose Functionalization of Boron-Doped Graphene: insights from in silico experiments

We use DFT calculations to explore different kinds of functionalization of boron doped graphene and their possible applications describing their structures at atomistic level as well as providing information about their electronic properties. Exploiting our understanding of the “socket-plug” mechanism [1], we show that thanks to the doping with boron atoms it is possible to create dative bonds between the graphene surface and molecules with a lone-pair or metal surfaces. In particular, we envisage a possible use of graphene as a platform for custom-made receptors to create selective bio-sensors, for example for glucose in blood [2], as well as we describe its behavior as catalyst in NOx reduction [3]. Moreover, we show that the boron atoms can act as anchoring sites for a more efficient coating of metal surfaces enhancing the binding between the two materials and the resistance of the metal to corrosion, as it has been detailed for a copper surface [4-5]. Finally, we demonstrate how boron doped graphene can be used together with another 2D material, such as iron selenide, to create a novel heterostructure with enhanced superconductivity properties [6].

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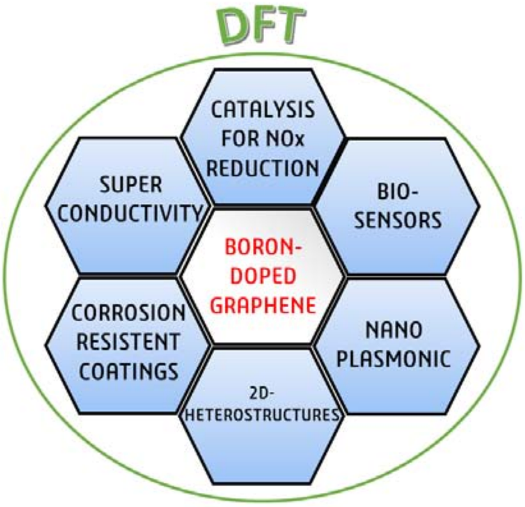

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Pressure-induced phase transition of bilayer epitaxial graphene: Computations meet the experiment

Graphene exhibits unique electronic and mechanical properties. Recent AFM-based nano-indentation measurements show that two-layer graphene (2G) on SiC(0001) exhibits a transverse stiffness and hardness comparable to those of diamond [1]. Our density functional theory (DFT) calculations indicate that these mechanical properties originate from a phase transition from a graphitic to a diamond-like structure of 2G. Upon compression, a 2G film can transform into a diamond-like film in contact with SiC(0001) (Fig. 1(a)). The sp^2-to-sp^3 structural and chemical changes occur regardless of the stacking configuration (contrary to the case of a 3-layer and 4-layer graphene film) of the two graphene layers. The DFT calculations also show that a diamond-like film forms a hard contact with the SiC(0001) substrate, exhibiting an interfacial layer of bonds with a transverse elasticity as stiff as that of the substrate material. Moreover, regardless of the stacking configuration, two graphene layers buckles to form a diamond-like film, exhibiting a transverse elastic modulus ranging between 0.30 and 1.01 TPa close to that of bulk diamond. At last, I will also report classical indentation simulations, showing that a SiC(0001) substrate coated by a stiff diamond-like film yields a force vs. indentation depth curve steeper than that of the bare SiC substrate, whereas a 5-L or 2-L graphene film on SiC lead to a significant softening of the transverse mechanical response. These results are in agreement with the experimental indentation curves.

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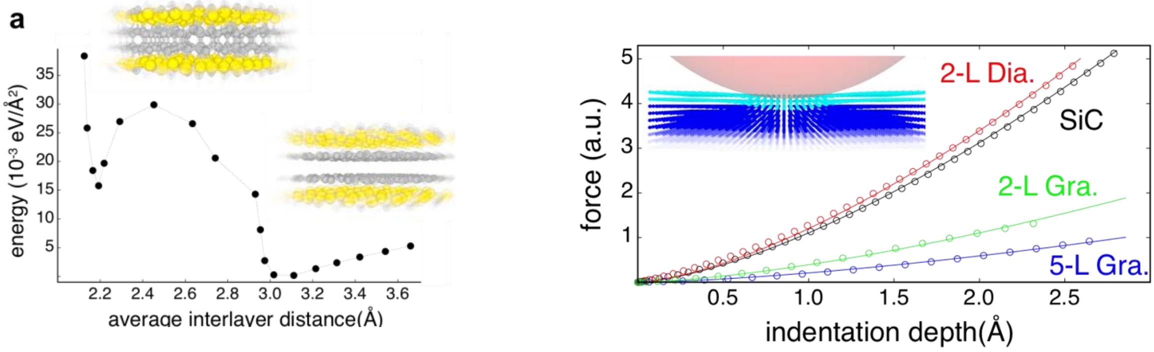

Figure 1: a) Energy per unit area obtained by DFT calculations for a two-layer graphene film sandwiched between mirroring H-SiC layers; Force vs. indentation curves obtained by using a classical scheme based on atomistic model structures and Hookean force fields.

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A Graphene Oxide 2D Platform for Intracellular siRNA Delivery

Development of efficient and safe nucleic acid delivery vectors remains an unmet need holding back clinical translation of such gene therapeutics. Graphene oxide (GO), among other two-dimensional (2D) nanomaterials, could help resolve this bottleneck thanks to its large surface area, versatile chemistry and biocompatibility, which could boost transfection efficiency while providing a less controversial safety profile than that of viral vectors [1]. However, complexation of double-stranded nucleic acids onto the GO surface is thought to be compromised by electrostatic repulsion and by steric hindrance of hydrophobic and π-π interactions from the nucleobases. To deliver double-stranded oligonucleotides, GO is decorated with positively-charged materials that generally induce cytotoxicity [2]. Here, we demonstrate for the first time the capacity of bare GO, without cationic functionalization, to complex a short, double-stranded nucleic acid of biological relevance (siRNA) and mediate its intracellular delivery. Atomistic molecular dynamics simulations, in combination with a variety of experimental techniques, demonstrated the binding between GO and siRNA. Confocal microscopy and stem-loop RT-qPCR allowed monitoring the efficient uptake of GO:siRNA complexes in a primary mouse cell culture **(Figure 1)**. 4 h after transfection, GO:siRNA complexes delivered sufficient oligonucleotide levels to induce significant gene silencing. However, time-lapse tracking of internalized GO and siRNA evidenced a sharp decrease of intracellular siRNA from 4 to 12 h and the entrapment of GO in large intracellular vesicles. Such intracellular behavior may explain the deficient biological performance of GO:siRNA complexes compared to a lipid-based benchmark transfection reagent. Overall, these results underline the potential of bare GO flakes to act as 2D siRNA delivery platforms, avoiding cationic functionalization, but warrant further vector optimization to achieve efficient gene silencing.

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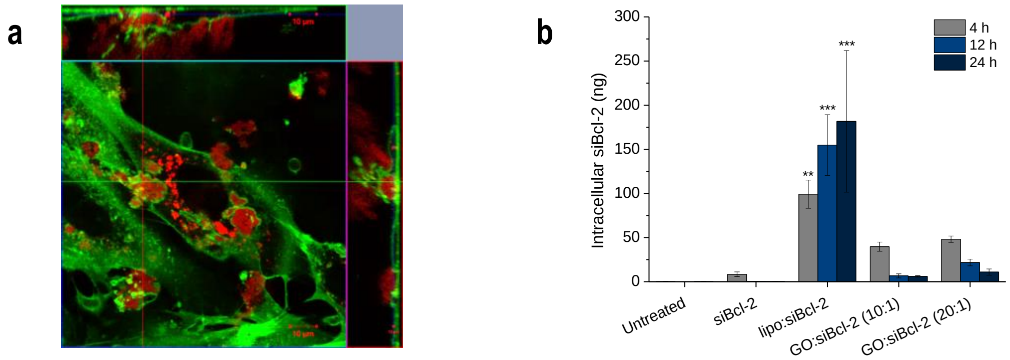

Figure 1: GO as 2D platform for intracellular siRNA delivery. (a) GO internalization in mouse primary fibroblasts was monitored by confocal microscopy (in green, cell membrane; in red, GO intrinsic fluorescence). **(b)** Stem-loop RT-qPCR evidences a rapid decrease in intracellular siRNA levels upon GO-mediated delivery. **p<0.01 and ***p<0.001, one-way ANOVA and Tukey's post-hoc test, n=3.

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2D TMDC Materials Foundry and Wafer-Scale Synthesis

2DLayer is the world leader in commercially-available 2D TMDC materials and is bringing the world ever-closer to wafer-scale TMDCs. Our vision is in to see fully-functional devices composed solely of 2D materials, as well as the potential to integrate into existing CMOS technology. We realize the necessity for collaboration among the academic field, and offer customized TMDC solutions in order to further extend the capability and quality of research around the world. As a pillar for the field, we hold ourselves to the highest standard for material quality and customer service, completely guaranteeing our product.

In this talk we discuss the progress and challenges in wafer-scale synthesis of high-quality TMDs, and the next steps to bring this new technology closer to commercial realization.

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Light polarization and carrier density dependence of photocurrent in few layer graphene and monolayer MoS_2

Helicity dependent photocurrent (PC) in single layer graphene (SLG) has been the subject of intense debate, and was recently ascribed to the photon drag (PDE) and the circular photogalvanic effects (CPGE) [1]. Here we report the experimental determination of the PC response of few layers graphene and 2D semiconductors as a function of light intensity and state of polarization, as well as carrier density and polarity. The bilayer graphene (BLG) data show qualitative features in common with the photocurrent that is expected to arise from the PDE and the CPGE, as seen in SLG except an anomaly which seems to have an origin similar to the CPGE [2]. Also, we present helicity dependent PC data of trilayer graphene (TLG) ABA-stacked (which consists of SLG-like and BLG-like subbands) and ABC-stacked (approximately cubic band dispersion and band gap opening by gating). While the PC due to LPDE of TLG samples are similar to SLG and BLG; we noticed a large enhancement in the PC due to the CPGE of ABC-stacked TLG (~15 pA), while the PC due to CPGE in ABA-stacked TLG is similar to SLG. In addition, we investigated the excitonic physics of monolayer MoS_2 with high valley polarization, by light polarization dependent PC. We demonstrate that large PC dichroism can be achieved, due to the CPGE upon resonant excitations [3]. Also we observed anomalous linear photogalvanic effect in a monolayer MoS_2 sample which could be attributed to spin polarization at the edges. These results highlight the richness of photoresponse in graphene and 2D semiconductors, providing an opportunity to establish light helicity as a means to manipulate the photoconductive behaviour of future 2D optoelectronic devices.

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Scalable production of pristine graphene using electrochemical exfoliation

In the electrochemical exfoliation method, an applied voltage drives ionic species to intercalate into graphite where they may form gaseous species that expand and exfoliate individual graphene sheets. However, a number of scientific obstacles have prevented this method from becoming a feasible manufacturing approach; the disintegration of the graphite electrode as the method progresses is the chief difficulty. Our data show that if graphite powders is contained and compressed within a permeable, expandable containment system, then these graphite powders can be continuously intercalated, expanded, and exfoliated to produce graphene at high yields. Our data indicate both high yield and extraordinarily large lateral size in the as-produced graphene, as shown by AFM, SEM, and optical microscopy. This process is scalable with no diminished efficiency in large sizes and parallel electrodes.

Figures

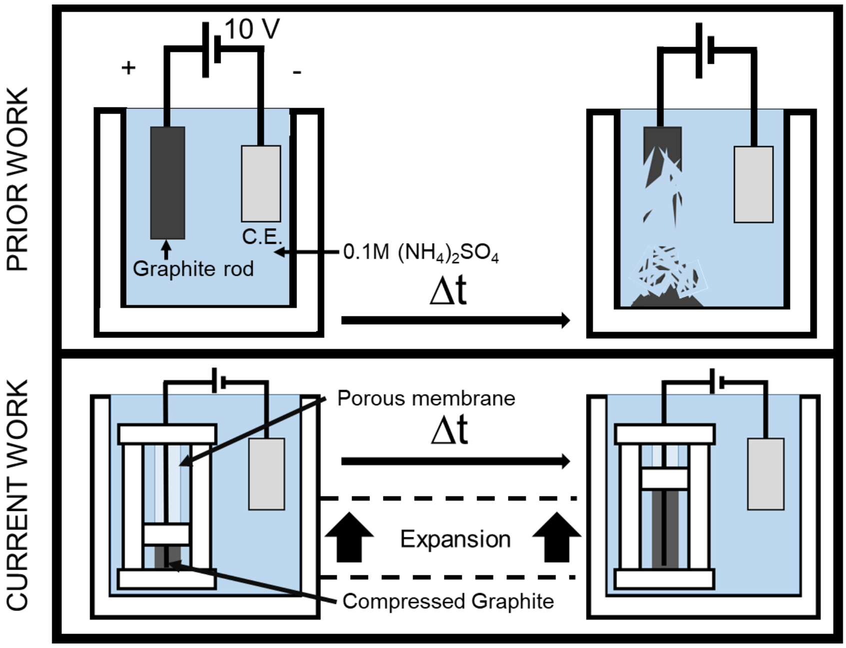

Figure 1: (top) Prior efforts to use electrochemical exfoliation have resulted in the graphite working electrode disintegrating during intercalation (C.E. denotes the counter electrode). (bottom) Schematic illustration of our process for electrochemical exfoliation of graphite flakes in a permeable expandable container.

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Full Title - Highly Conductive Free-Standing Reduced Graphene Oxide Thin Films for Fast Photoelectric Devices

Compared to mechanically exfoliated and chemical vapor deposited graphene, reduced graphene oxide (RGO) has unique advantages such as wet process, high yield and capability of assembling large-area thin films on varied substrates. However, RGO is normally not recommendable for advanced devices due to its poor electrical conductivity. Here we report a new method to prepare highly conductive free-standing RGO thin film. The as-prepared RGO thin film possesses the highest conductivity of 87100 S m^{-1}, the second-lowest sheet resistance of 21.2 Ω sq^{-1} and the medium level mobility of 16.7 $cm^2 \cdot V^{-1} \cdot s^{-1}$ among all the RGO films reported so far. To demonstrate the application potential of the free-standing RGO thin films in photoelectric devices, a fully suspended RGO photodetector is constructed using the free-standing RGO thin film, which exhibits the fastest (*ca.*100 ms) and broadest (from ultraviolet 375 nm to terahertz 118.8 μm spectral range) photoresponse among all RGO film photodetectors to date. The response speed is even comparable to those of CVD grown-graphene photodetectors and mechanically exfoliated graphene photodetectors. This work would pave the way to high-conductivity RGO thin films by wet process assembly, thus facilitating applications of RGO in advanced electronic, optoelectronic and sensing devices.

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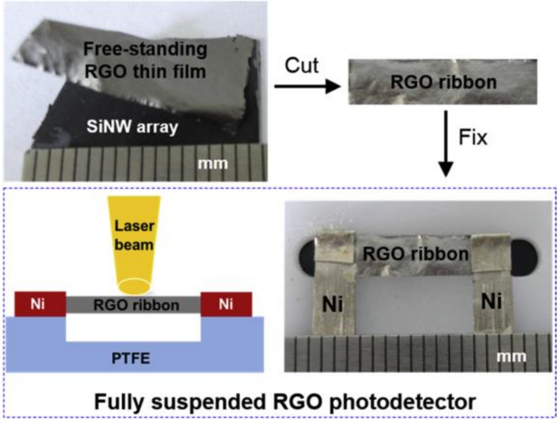

Figure 1: Digital photograph and schematic diagram of the fully suspended RGO thin film photodetector for photoresponse measurement. The incident laser spot was positioned in the middle of the free-standing RGO thin film.

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Large thermoelectric figure of merit in graphene layered devices at low temperature

Nanostructured materials have emerged as an alternative to enhance the figure of merit (*ZT*) of thermoelectric (TE) devices. Graphene exhibits a high electrical conductivity (in-plane) that is necessary for a high *ZT*; however, this effect is countered by its impressive thermal conductivity. In this work TE layered devices composed of electrochemically exfoliated graphene (EEG) and a phonon blocking material such as poly (3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS), polyaniline (PANI) and gold nanoparticles (AuNPs) at the interface were prepared. The figure of merit, *ZT*, of each device was measured in the cross-plane direction using the Transient Harman Method (THM) and complemented with AFM-based measurements. The results show remarkable high *ZT* values (0.81 < *ZT* < 2.45) that are directly related with the topography, surface potential, capacitance gradient and resistance of the devices at the nanoscale.

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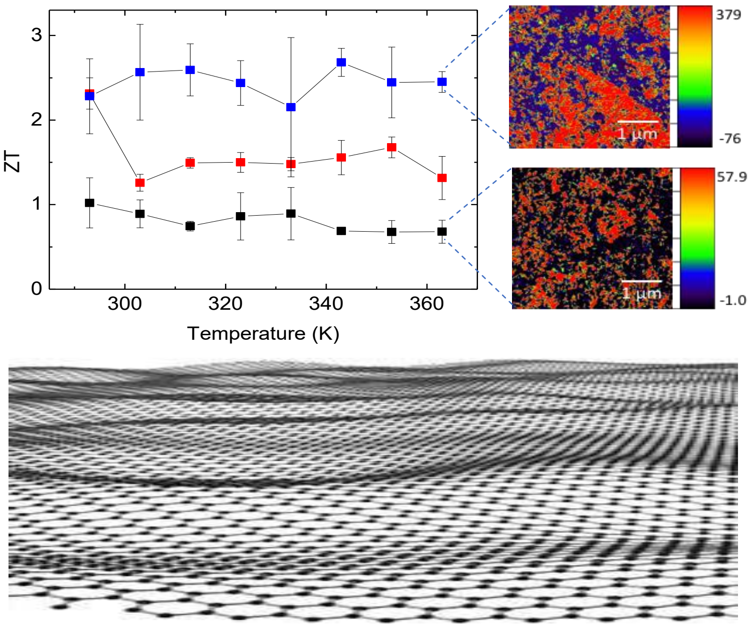

Figure 1: Thermoelectric figure of Merit of Graphene-based heterostructures.

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Probing the Charge Density Wave State in Bulk to Monolayer 2H-TaSe$_2$ by Raman Spectroscopy

Tantalum diselenide (TaSe$_2$) is a metallic, layered transition metal dichalcogenide that can be cleaved into 2D layers. Bulk 2H-TaSe$_2$ undergoes a structural phase transition to an incommensurate charge density wave state (CDW) at 122 K and a commensurate CDW state at 90 K [1]. The CDW amplitude modes are Raman-active and well understood [2-4]. Additionally, there are previously unanalyzed Raman peaks associated with the CDW that can be observed. We report the temperature and polarization dependence of all CDW modes and the undistorted-state Raman modes of TaSe$_2$ for 633 nm, 515 nm, and 476 nm excitation. The intensity, frequency, and width of these peaks are monitored for samples from bulk down to monolayer thickness. We also track the transition temperature of the incommensurate and commensurate CDW states as a function of thickness. Finally, our DFT calculations provide insight into the nature and behavior of the CDW Raman modes.

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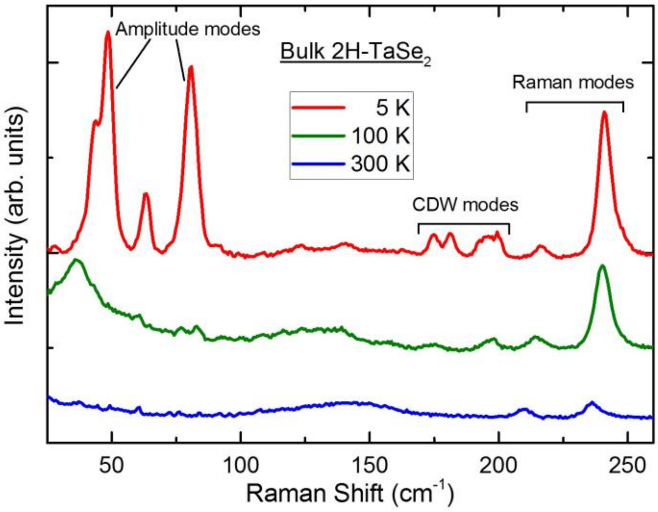

Figure 1: Raman spectra of bulk 2H-TaSe$_2$ taken in the undistorted state (300 K), the incommensurate CDW state (100 K), and the commensurate CDW state (5 K) using 514 nm excitation. The normal Raman modes, the CDW amplitude modes, and other CDW modes are indicated.

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THz Near-field Nanoscopy at 25 Nanometer Spatial Resolution

Terahertz (THz) imaging and spectroscopy has emerged as a powerful tool for analysis of biological specimens or for studying and controlling low-energy excitations in solid-state systems [1]. One major limitation of THz spectroscopy is, however, the spatial resolution that is limited by diffraction to about 100-1000µm, making it impossible to extract intrinsic, local material characteristics of nanoscale Graphene or other 2D-material structures or devices.

Scattering-type scanning near-field optical microscopy (s-SNOM) bypasses the diffraction limit, enabling optical measurements with extreme subwavelength spatial resolution of below 20nm [2]. THz time-domain s-SNOM spectroscopy of a semiconductor SRAM sample enables quantitative analysis of free carrier concentration and scattering rates of nanoscale device structures at unprecedented surface sensitivity (Fig. below). Similarly, THz s-SNOM measurements at single frequencies enabled highlighting highly conductive nanostructures in transistor devices [3]. Using a similar experimental concept to generate a local photo-current by THz radiation allows for studying nanoscale conductivity in a biased Graphene device [4] or to characterize carrier scattering in a graphene sheet that has been encapsulated in h-BN and placed on a split metallic film [5].

Extending the already established concepts of mid-IR s-SNOM imaging and spectroscopy of 2D materials [6] to the THz frequency range a plethora of fundamental and applied new insights into Graphene and other 2D device structures can be expected from THz near-field nanoscopy measurements.

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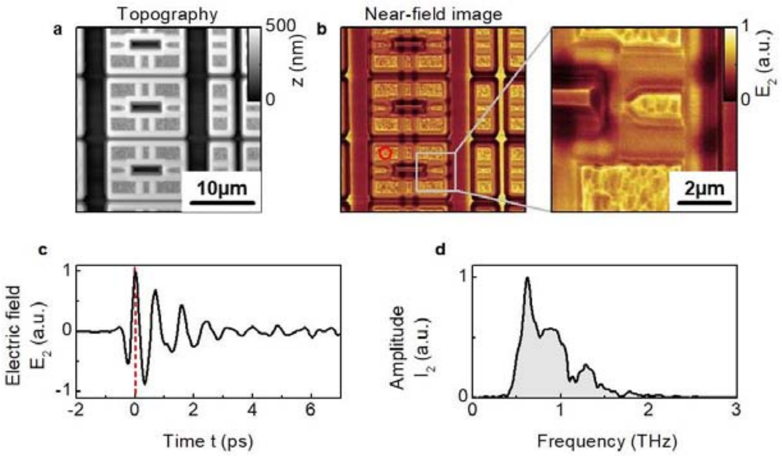

Figure 1: a Topography image of the SRAM. **b** Spectrally integrated near-field image measured at THz-TDS delay-time t=0ps (see red-dashed line in c) featuring a spatial resolution <20nm. Variations in the scattered electric field intensity indicate changes in the local carrier density of the different doping regions. **c** THz-TDS waveform measured on the n+ -doped region (see red cross in b) with <20nm spatial resolution. **d** Near-field spectrum of the waveform shown in c.

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Correlative in-situ AFM & SEM mechanical analysis of suspended 2D materials

Understanding of mechanical properties of Graphene and other two dimensional (2D) materials is crucial for almost all current and future applications regarding those materials. Although the mechanical properties of Graphene have been investigated intensively by atomic force microscopy (AFM) and other techniques, experiments on freestanding 2D membranes still remain challenging and interpretation of the results are controversial. Hence, to obtain a thorough understanding of mechanical AFM experiments on freestanding membranes, complementary measurements (e.g. Raman Spectroscopy [1], Scanning Tunneling Microscopy (STM) [2]) are necessary. Here, we will show recent results of our in-situ corrleative AFM & SEM (scanning electron microscopy) study on suspended graphene. By using our novel AFSEM™ technology [3], we are able to investigate the effect of a scanning probe on freestanding few-layered graphene with full force control of the AFM and directly visualize the deformation of the membrane with the SEM. Since we are capable of performing several other AFM modes (conductive, magnetic force, thermal, KPFM) AFSEM™ allows for a range of characterization techniques and direct correlation with scanning electron images.

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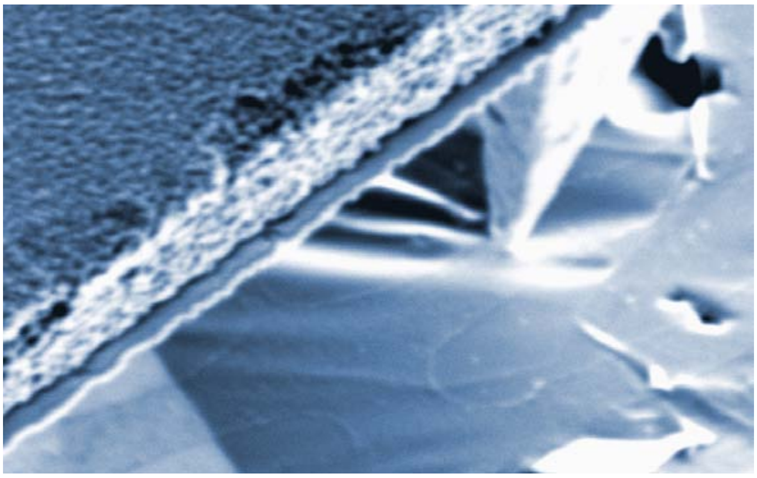

Figure 1: In-Situ SEM image of a scanning AFM tip on suspended, few-layered graphene

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Graphene and water-based elastomers thin-film composites

Elastomers are viscoelastic polymers with weak inter-molecular forces that exist in an amorphous state above their glass transition temperature. Elastomers can be classified as thermosets or thermoplastics. The most common thermoset elastomer is vulcanized natural rubber latex (NRL), which is most commonly processed in the form of a latex, a stable dispersion (emulsion) of polymer microparticles in an aqueous medium. Also common are thermoplastic polyurethanes (PU), in this case an anionic aliphatic polyester polyurethane dispersion in water.

We demonstrate composites with both graphene oxide and reduced graphene oxide, the reduction being undertaken in-situ or ex-situ using a biocompatible reducing agent in ascorbic acid. The graphene/wPU composite incorporates graphene flakes in between polymer chains, whereas the graphene/NRL composite incorporates the graphene in between polymer microparticles. The ultrathin films were cast by dip molding. The transparency of the elastomer films allows us to use optical microscopy image and confirm the uniform distribution as well as the conformation of the graphene flakes within the composite.

We show that graphene can be used to reinforce 20 micron thin elastomer films, resulting in over 50% increase in elastic modulus at a very low loading of 0.2 wt%, while also increasing the elongation to failure. This loading is below the percolation threshold for electrical conductivity.

Thin-film elastomers (elastic polymers) have a number of technologically significant applications ranging from sportswear to medical devices.

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Figures

Figure 1: Optical images of water-borne polyurethane thin-films reinforced with 0%, 0.05%, 0.1% and 0.2% by weight of reduced graphene oxide.

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A study on the growth of WS$_2$ homobilayers with controlled 0 and 60 degree stacking using two-step van der Waals epitaxy

The crystallographic alignment (0 or 60 degree stacking) of homobilayer shows strong interlayer coupling and leads to magnetoelectric effects for quantum manipulations [1-3]. However, 0 or 60 degree stacked homobilayers are typically fabricated by manually stacking the TMD layers through transfer, which is a low yield process with a high possibility of contaminant trapping between the layers.

In this report, we introduce two-step epitaxial growth technique to synthesize WS$_2$ homobilayer with a controlled 0 or 60 degree stacking. Since edges of the first monolayer have dangling bonds which work as nucleation sites for second growth, the second WS$_2$ monolayer grows from the edges and subsequently covers the first WS$_2$ monolayer. This growth process allows the two- step WS$_2$ homobilayer growth always gives perfectly aligned 0 or 60 degree stacking, attributed to the edge structures of first grown WS$_2$ monolayer. In order to elucidate the growth mechanism, we model the growth by *ab initio* first-principles scheme based on density functional theory (DFT), which identifies the most stable inter-layer stacking interactions (0 or 60 degree stacking) as a function of their binding energy. Furthermore, presence of dangling atoms/bonds in between the layers is corroborated from the formation energy calculations.

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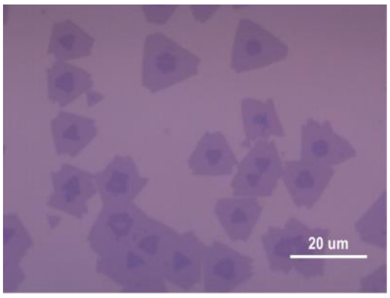
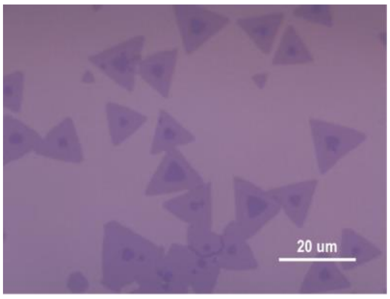


60° of WS2 homobilayer



0° of WS2 homobilayer

Figure 1: Insert caption to place caption below figure (Arial Narrow 11)

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Nanoscale Heterogeneities in Monolayer $MoSe_2$ and WSe_2 Revealed by Correlated SPM and TERS

Two-dimensional semiconductors, specifically the broad class of transition metal dichalcogenides (TMDs) attract significant attention of research community in recent years due to the wealth of interesting and potentially applicable phenomena observed in these materials. In order to control the performance of devices based on TMDs, they must be characterized at the scale relevant to the corresponding application, which in most cases today corresponds to a few tens of nanometers [1].

Here we report on the direct application of scanning probe microscopy (SPM) cross-correlated with tip enhanced Raman scattering (TERS) imaging for characterization of rather unexpected locations of grain boundaries in single layer CVD grown $MoSe_2$, as well as the evolution of these grain boundaries in the course of sample aging and their transfer from the original substrate via wet etching transfer procedures. Detailed analysis of the TERS maps of $MoSe_2$ on Au revealed that there exist two types of nanoscale (few to several tens of nm across) domains, one featuring a resonant response (as should be expected for 638 nm laser), and the other featuring mostly a single peak near 240 cm^{-1} (typical for non-resonant conditions).

Additionally, TERS maps on WSe_2 revealed the presence of small, 100 - 300 nm triangular areas with zero Raman response. Cross-correlation of the TERS data with the topography, surface potential and friction images revealed that large flakes had a significant number of perfectly triangular holes. Such perforations in TMD flakes can be extremely beneficial for hydrogen evolution reactions, as it has been demonstrated that the most efficient way of improving the performance of TMDs in fuel cells is to increase the ratio of edge length to surface area [2]. This ratio in the samples examined here was up to 3 - 4 times higher compared to homogenous continuous flakes. These perforated flakes can be transferred to any surface, including corrugated ones, which should inevitably cause some strain also beneficial for hydrogen catalytic activity.

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Low Damage NanoFabrication for 2D Material Devices and Beyond

NanoFrazor lithography – or thermal scanning probe lithography (t-SPL) - has recently entered the lithography market as first true alternative to electron beam lithography (EBL) [1]. Core of the technology - which has its origins at IBM Research and their Millipede project - is a heatable, ultrasharp probe tip which is used both for patterning and simultaneous inspection of complex nanostructures. The heated tip creates very high-resolution (down to <10 nm half-pitch) nanostructures by locally evaporating resist materials at a patterning speed comparable to high-resolution Gaussian shaped EBL [2]. The written nanostructures are inspected by the cold tip in parallel with the patterning process, enabling very accurate markerless overlay with sub-5 nm accuracy having been demonstrated [3,4]. Pattern transfer by reactive ion etching [5], lift-off [5], directed self-assembly [6] and more have been demonstrated. Here, we show how devices based on low-dimensional materials such as MoS_2 (Figure 1) or graphene flakes, carbon nanotubes and nanowires can be fabricated by NanoFrazor. The topography of the atomically thin 2D materials can be imaged through the resist enabling easy and accurate overlay. Furthermore, the patterning process involves no injection of charged particles into the sensitive materials which enables measurements and applications at as near as their pristine state as possible.

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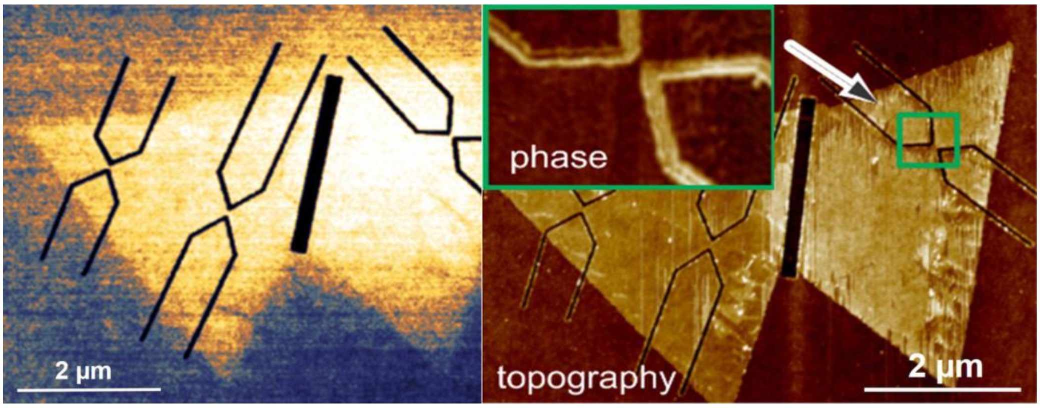

Figure 1: Left: NanoFrazor image of CVD grown single-layer MoS_2 flakes (courtesy of EPFL) after NanoFrazor patterning. The atomically thin material is clearly visible under the resist layer enabling very accurate overlay of the patterns. Right: AFM images of the same flake after the patterns have been etched into the material.

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Predictive models for low-frequency Raman scattering in 2D materials

Two-dimensional (2D) layered materials have been extensively studied owing to their fascinating and technologically relevant properties. Their functionalities can be often tailored by the thickness and stacking. A quick, non-destructive and inexpensive tool is highly desirable for thickness and stacking characterization of 2D materials. Recently, low-frequency (LF) Raman spectroscopy quickly rises up as such tool, since LF interlayer modes, including the shear and breathing modes, are much more sensitive to the interlayer coupling compared to the typically studied high-frequency (HF) intralayer Raman modes [1,2,3]. The frequencies of LF modes are sensitive to the number of layers, which is explained by a linear chain model [1,2]. Meanwhile, the intensities of LF modes are sensitive to the stacking pattern [4,5]. We proposed a simple and generalized interlayer bond polarizability model [2] to explain and predict how the LF Raman intensities depend on complex stacking sequences for any thickness in a broad array of 2D materials, including graphene, MoS_2, $MoSe_2$, WSe_2, $NbSe_2$, $PdSe_2$, Bi_2Se_3, GaSe, h-BN, etc. Additionally, a general strategy is proposed to unify the stacking nomenclature for these 2D materials. Our model reveals the fundamental mechanism of LF Raman response to the thickness and stacking, and provides general rules for thickness and stacking identification of 2D materials.

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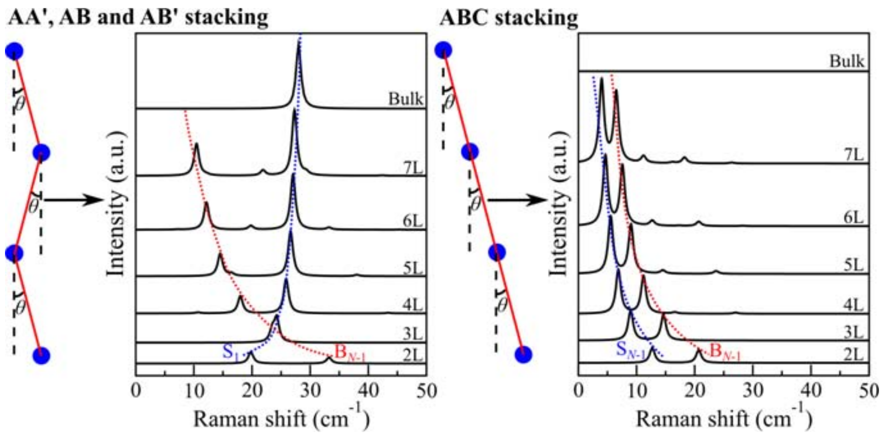

Figure 1: Calculated low-frequency Raman scattering of 2D materials for different stacking configurations at different number of layers, based on the interlayer bond polarizability model [2].

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Scalable metal-free CVD growth of graphene on sapphire

Here, we report that high-quality monolayer graphene can be obtained via chemical vapor deposition (CVD) on the c-plane of $Al_2O_3(0001)$ substrates with a catalyst-free and single-step approach in a commercially available CVD reactor (HT-BM, Aixtron). The growth temperature in the presented CVD approach, i.e. 1200 °C, is lower than what typically reported in literature [1-2]. The structural and chemical properties of the synthesized graphene are investigated by Raman spectroscopy, atomic force microscopy (AFM), low-energy electron diffraction (LEED), Scanning tunnelling microscopy(STM) and X-ray photoelectron spectroscopy (XPS). Raman analysis reveals high-quality monolayer graphene over the entire sample through a high (I_{2D}/I_G) intensity ratio, which is more than 4.2, and a small D peak (I_D/I_G averages at 0.55). The full width at half maximum (FWHM) of the 2D peak ranges from 29 to 35 cm^{-1}. AFM investigations show atomically flat sapphire surfaces and confirm the presence of graphene by imaging wrinkles, typical of CVD graphene upon thermal stress release. The wrinkles are several micrometers long and cross over the substrate terrace structure. C 1s binding energy is measured by XPS as 284.4 eV, confirming the sp2 nature of the grown carbon layer. No evidence of covalent interaction with the substrate is observed, indicating truly suspended graphene. In the acquired LEED micrographs, the diffraction spots of graphene and sapphire are clearly visible. Graphene preferential orientation is 30° rotated with respect to the sapphire substrate. The carrier mobility is above 2000 cm^2 /V.s. at room temperature. The presented metal-free CVD approach is of sure appeal in virtue of its implementation in a commercial system and by scalable yielding high-quality monolayer graphene it might have a positive impact on a number of optoelectronic applications.

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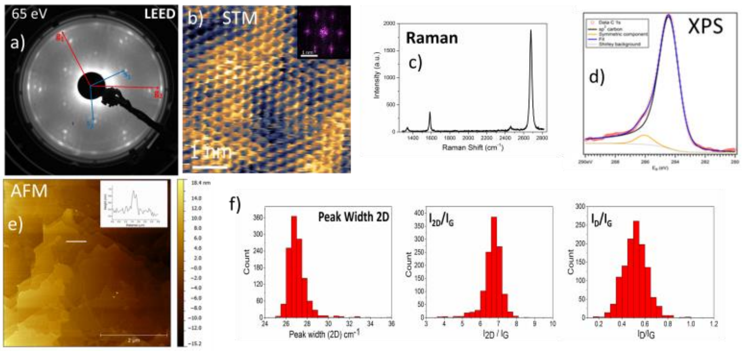

Figure 1: Graphene on sapphire characterization via (a) LEED at 65 eV; (b) STM; (c) Raman; (d) XPS - C1s spectrum; (e) AFM. (f) Histograms of 2D FHWM intensity ratio of 2D and G peaks and of D and G peaks.

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Analytic approach to magneto-strain tuning of electronic transport through a graphenenanobubble: perspectives for a strain sensor

Abstract
We consider the scattering of Dirac particles in graphene due to the superposition of an external magnetic field and mechanical strain [1,2]. As a model for a graphene nanobubble, we find exact analytical solutions for single-particle states inside and outside a circular región submitted to the fields[1]. Finally, we obtain analytical expressions for the scattering crosssection, as well as for the Landauer current through the circular region. Our results provide a fully-analytical treatment for electronic transport through a graphene nanobubble, showing that a combination of a physical magnetic field and strain leads to valley polarization and filtering of the electronic current[1]. Moreover, our analytical model provides an explicit metrology principle to measure strain by performing conductance experiments under a controlled magnetic field imposed over the simple[1].

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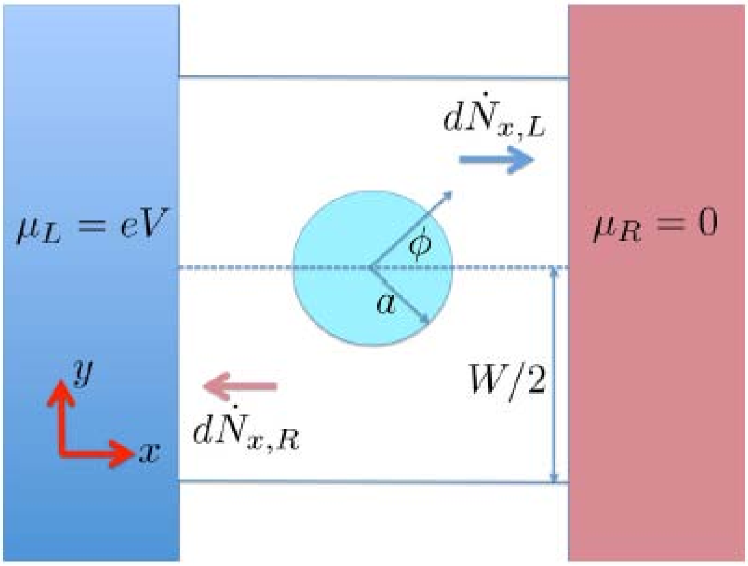

Figure 1: Transport through a graphene nanobubble of radius a, between two semi-infinite contacts

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Graphene biosensors for label-free detection of DNA and protein disease biomarkers

Graphene is an excellent candidate for high sensitivity biosensors for detection of disease biomarkers for clinical diagnostic applications. In this talk, I will review our work on two novel biosensors developed for detection of protein and DNA biomarkers: an ultrasensitive label-free graphene immunoFET for detection of Human Chorionic Gonadotrophin (hCG) and an rGO-graphene double layer structure for detection of human immunodeficiency virus 1 (HIV1) gene. For immunoFET, an argon etching technique and deep UV treatment was developed for patterning clean graphene channels. The rGO-graphene structure was achieved by immobilization of GO on graphene followed by electrochemical reduction by cyclic voltammetry. The immunoFET showed a unique resistance change pattern with high reproducibility and an ultralow label-free detection limit of 1pg mL^{-1} and high sensitivity of 0.30 Ω/ng/mL. The hCG concentration gradient demonstrated a broad analytical range of 0.01~15 ng mL^{-1} exhibiting a sensor potency of approximately 4.95 ng mL^{-1} which is significantly lower than the clinical limit for hCG. In case of rGO-graphene structure, 42% higher redox current was observed in compared to graphene electrode. The hybridized dsDNA demonstrated a linear range from 10^{-7} M to 10^{-12} M with a detection limit of 1.58 x 10^{-13} M.

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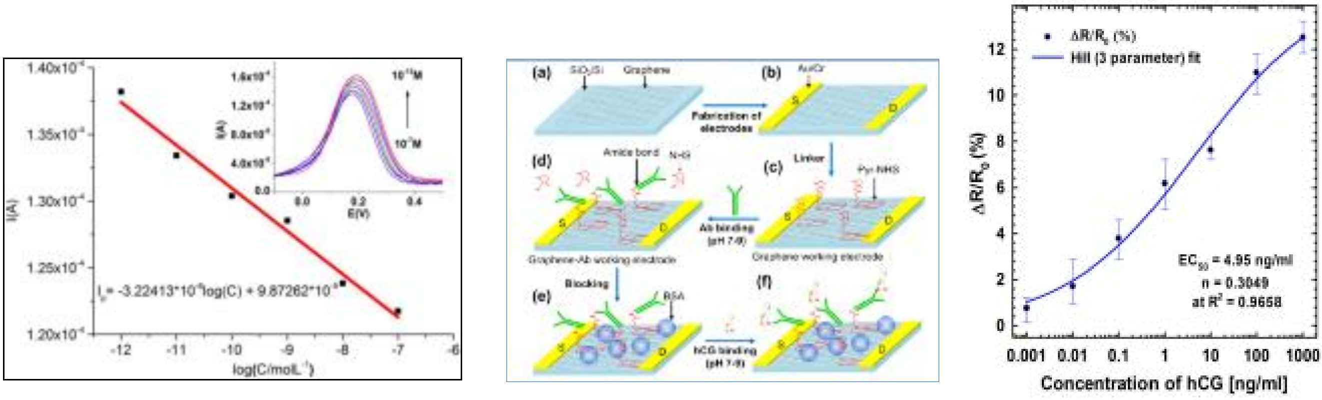

(A) (B) (C)

Figure 1: (A) Dependence of peak currents of DPV spectra of the rGO DNA sensor on the concentration of target cDNA; (B) Surface modification of back-gated immuno graphene field effect transistor (immunoFET); (C) Dependence of relative resistance changes of the immunoFET sensor on hCG concentration.

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Standardisation of terminology and measurement for graphene and related 2D materials

Potential innovators of real-world graphene products 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. This may be because the material has been characterised in a way that leads to large uncertainties, or because a lack of batch-to-batch reproducibility means the original characterisation is only accurate for the initial batch of material. Thus companies developing commercial products do not truly understand the effects the different properties of the material have on the final desired properties of their application.

There is an obvious need for reliable, accurate and precise measurements for off-line material testing that are standardised across the industry and therefore allow end-users to be able to compare materials commercially available around the world. At the same time, these accurate and precise measurement techniques and protocols are required before any reliable quality control (QC) methods can be developed for either the production of material or intermediates in the production chain. Crucially, international standardisation of the terminology and measurement methods is required so that graphene can be a truly global industry, allowing materials to be traded between producers and end-users in the many different countries currently pursuing graphene applications.

The current state of international standardization in this area will be detailed. Importantly, the recent publication of the first ISO (International Organization for Standardization) standard, 'ISO/TS 80004-13:2017: Nanotechnologies -- Vocabulary -- Part 13: Graphene and related two-dimensional (2D) materials'[1,2] will be described, including several of the key terms and definitions.

Furthermore, the new NPL Good Practice Guide entitled 'Characterisation of the structural properties of graphene', developed in collaboration with the University of Manchester, UK, will also be explored, as will how this guide will be the basis of new ISO measurement standards being developed to ensure the reliable, reproducible and comparable characterisation of graphene, worldwide.

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Probing the dielectric response of the interfacial buffer layer in epitaxial graphene via optical spectroscopy

Monolayer epitaxial graphene (EG) is a suitable candidate for a variety of electronic applications. One advantage of EG growth on the Si face of SiC is that it develops as a single crystal, as does the layer below, referred to as the interfacial buffer layer (IBL), whose properties include an electronic band gap. Though various electrical and non-optical probing experiments have been conducted on this buffer layer, most recently reported in Nano Letters by *Nair, et al. (2017)* [1], studies pertaining to its optical properties have not yet been rigorously explored. In this work, we combine measurements from Mueller matrix ellipsometry, differential reflectance contrast, atomic force microscopy, and Raman spectroscopy, as well as calculations from Kramers-Kronig analyses and density functional theory (DFT), to determine the dielectric function of the IBL within the energy range of 1 eV to 8.5 eV.

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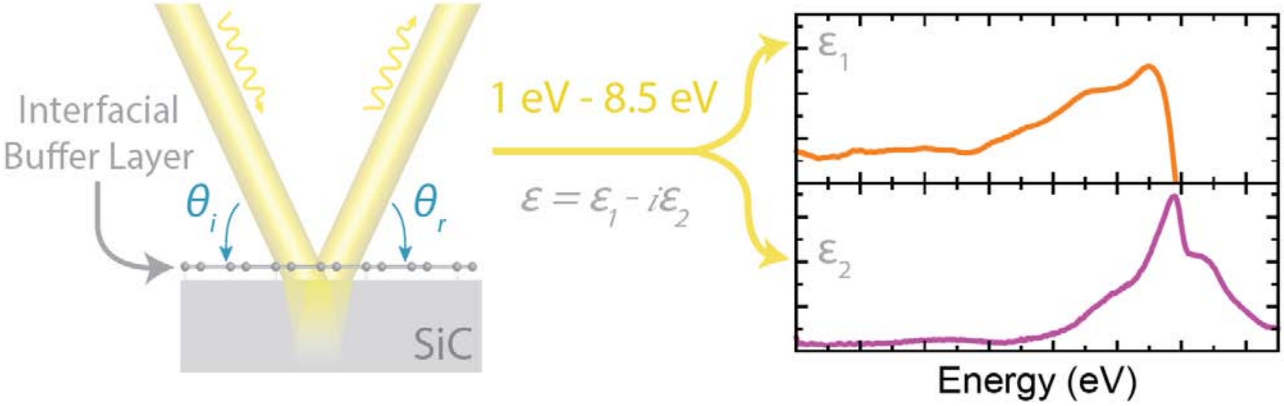

Figure 1: A schematic of the Mueller matrix ellipsometer measurement is shown. Broadband light is directed to the IBL at variable incident angles, and the tool evaluates the change in polarization and intensity as a function of the incident angle. Both the real and imaginary portions of the dielectric function for the IBL are extracted using this technique and are subsequently compared to differential reflectance contrast measurements and density functional theory calculations.

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Monitoring the translocation of single polypeptides through MoS$_2$ nanopores from ionic current fluctuations, lessons from all-atom molecular dynamics simulations

Solid-state nanopores (SSN) have emerged as versatile devices for single-molecule biomolecule detection and sequencing [1]. SSNs offer promises as high-rate and low cost sequencing devices of DNA and proteins with potential applications for early diagnosis of diseases. The idea behind nanopores sequencing is based on experimental ultrafast monitoring of the ionic current through nanometer-sized channels [2]. Because the channel conductance of the ionic flow through nanopores scales inversely with the membrane thickness, few-atoms thick materials are ideal candidates with an expected high signal-to-noise ratio [3]. Beyond graphene, transition metal dichalcogenides such as molybdenum disulfide (MoS$_2$) are potentially advantageous due to their rich optoelectronic and mechanical properties. This study reports the results of all-atom molecular dynamics simulations that investigate the feasibility of using MoS$_2$ nanopores for protein sequencing. First, we investigate the dynamics of KCl ions through MoS$_2$ nanopores using non-equilibrium molecular dynamics (NEMD) simulations. MoS$_2$ nanopores with different diameters, from 1.0 to 3.0 nm and nanoporous membranes with different thicknesses, from single-layer to trilayers MoS$_2$ are studied. We provide open pore benchmark signals and new models for ionic conductance of such devices for further translocation simulations/experiments [4]. Second, we investigate uding NEMD simulations the translocation of model peptides in the presence of an electric field. The aim is to estimate the performances of MoS$_2$ nanopores for protein sequencing applications.

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Optical and electrical properties of CVD grown monolayer graphene samples subjected to ion irradiation

Optical and electrical properties in series of CVD grown monolayer graphene samples subjected to ion irradiation by different ions and doses were studied. Ion irradiation results in a redistribution of the intensity of main Raman scattering lines and to a significant increase of resistivity (about four orders of magnitude), accompanied by the change in the mechanisn of conductuvuty. Stability of a disorder introduced by ion irradiation was studied during the long-term ageing as well as reversibility of the destroyed graphene structure after annealing of radiation damage.

Asymmetry of electron and hole mobility was observed in pristine samples with metallic conductivity. It was shown that in irradiated samples with hopping conductivity, magnetoresistance is negative in perpendicular magnetic fields and positive in parallel fields. Explanatory models for the observed effects are discussed

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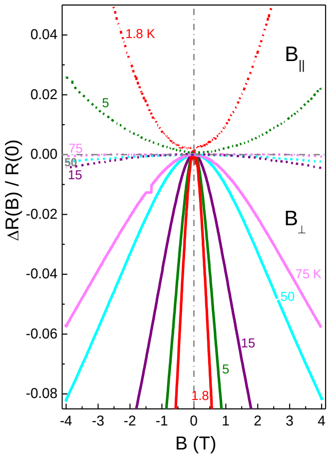
Figure 1: ΔR/R as a function of B for irradiated sample with hopping mechanism of conductivity in parallel and perpendicular magnetic fields at different temperatures shown near each curve



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Dynamical Stability of Supported Black and Blue Phosphorus

Bulk black phosphorus (BP) is an attractive material for applications in nanoelectronic and photonic devices due to its high carrier mobility and anisotropic in-plane properties. Similar to graphite, BP is made of layers which are held together by weak interlayer van der Waals (vdW) forces. Recently, single-layer BP has been obtained by mechanical exfoliation and single-layer blue phosphorus (bP) has been synthesized on a Au(111) substrate by molecular beam epitaxy [1,2]. Theoretical works have predicted a phase transition between single-layer BP and bP [3], but it has not yet been observed experimentally. In addition, to study the stability of two interacting continuous materials, such as BP or bP adsorbed onto an Au(111) substrate, vibrational modes must be taken into account. Based on density functional theory (DFT) calculations, we demonstrate the importance of including the vdW interaction to accurately describe the properties of BP and bP allotropes. The temperature dependent Helmholtz free energy, lattice constants and linear thermal expansion coefficients of BP and bP have been studied using the quasiharmonic approximation. We find that a phase transition between these materials appears around 168 K using a semi-local exchange-correlation (xc) functional. However, single-layer BP is found to remain the most energetically stable phase regardless of temperature when a non-local vdW xc functional is used. To gain insight into how one phase transforms into another, we used the climbing image nudged elastic band (cNEB) method to show that BP must overcome an energy barrier of 0.48 eV/atom to transform into bP. This value is ~10% higher than that obtained without including any vdW interactions. Finally, we extend this study of energetics by adsorbing single-layer BP and bP onto an Au(111) substrate. We propose an improvement of the frozen phonon method to include the vibrational modes located at the interface between these materials. Breathing and shearing modes emerge which contribute to the stability of a surface adsorbed on a substrate.

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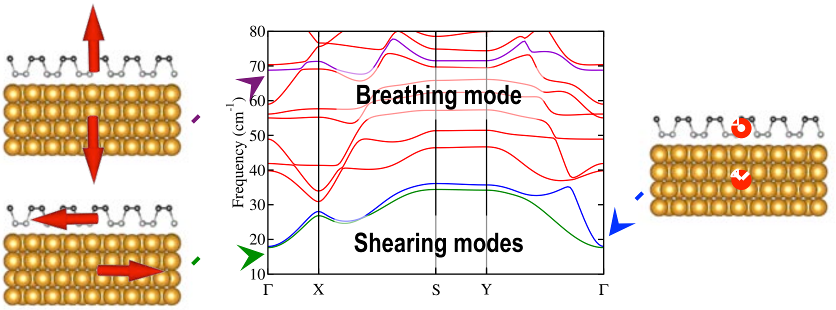

Figure 1: Phonon dispersion of black phosphorus on an Au(111) substrate.

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New modeling for thermionic-photo-current and open-circuit voltage in (GIS) Schottky Solar Cells

Abstract

Grown oxide layers (insulators) bridging a graphene layer to n-silicon in G/I/S solar cells have been shown to reduce recombination at the cell junction. Under illumination, the built-in field at the Graphene-Silicon junction, forces minority photo-generated holes to the interface and ultimately to the G-side, while photoelectrons thermionically escape from the G-side to the semiconductor. Electrons from the graphene side may obtain sufficient energy to overcome the junction barrier by simultaneous thermionic emission (TE) and tunneling through the oxide layer to the semiconductor side. Graphene-based Schottky solar cells illuminated from the G-side respond to solar photons at energies above the semiconductor's band gap, hence minority-hole photo-generation. Minority holes diffuse to the junction and aided by the built-in field tunnel through the junction to the graphene side. The interface is essentially a double barrier as a combination of junction Schottky barrier ($q\Phi_B$) and the ox-layer. In this communication, we model the following currents crossing the GIS junction (a) thermionic current from the Graphene side to the semiconductor J_{TE} and (b) hole-current J_P from the n-Si side to the G-side. We derive J_{TE} as a thermionic current that depends on a number of parameters, such as temperature T, Schottky barrier height q□$_B$, and voltage V across the device, specifically, we find that TE current is a strong function of $T^{3/2}$ as $J_{TE} \sim T^{3/2} \exp(-q\Phi_B/kT) \exp(-\chi^{1/2}\delta) [\exp(qV/kT)-1)]$. Once these electrons migrate to the n-region, they join the majority electron flow to the load under illumination. The electron tunneling probability $\exp(-\chi^{1/2}\delta)$ guarantees electron flow to the semiconductor (δ = the oxide thickness). On the other hand, photo-generated hole-current is derived from standard techniques leading to $J_p = (qD_p p_n^*/L_p) \exp(qV/kT)-1)-(\alpha L_p qF_\lambda (e^{-\alpha w}/(1+\alpha L_p))$, where F_λ is the solar photon flux, with flat quasi-Fermi level through the depletion region ($p_n^* = p_{no}(e^{qV/kT})$, p_{no} = background hole in the n-region, w is the depletion width at the junction, a is the absorption coefficient, and L_p is hole diffusion current). These holes eventually will tunnel through the oxide to the graphene side. By neglecting recombination at the depletion region, we calculate the total current $J = L_{ight} - J_{dark,}$ and the deduce open-circuit voltage. Based on the two current expressions above, we deduce increased open circuit voltage as follows:

$$V_{oc} = \frac{kT}{q}\left[\ln\left(\frac{\alpha L_p q F_\lambda e^{-\alpha w}}{J_{oo}(1+\alpha L_p)}\right) + \frac{q\Phi_B}{kT} + \chi_n^{1/2}\delta\right];$$

$J_{oo} = A^* T^{3/2}$ is a new current pre-factor, with A* an appropriate (and explicitly derived) Richardson's constant.

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Capacitive pressure and touch sensors with suspended graphene-polymer heterostructure membranes

Single layer chemical vapor deposited (CVD) graphene has shown great promise in enabling Micro and Nano-electromechanical Systems (MEMS/NEMS) that can outperform current state of the art. However, existing methods in forming single layer graphene electromechanical devices result in low yields during the graphene device fabrication process. In addition, the suspended membranes that survive often suffer from a distorted topography due to transfer polymer residue, limiting the in-plane span, and poor device reproducibility.

We present the fabrication and characterization of a suspended graphene/polymer heterostructure membrane that aims to tackle the prevailing challenge of constructing high yield, environmentally robust suspended graphene devices whilst preserving the mechanical and electronics properties. [1] The fabrication method enables the construction of suspended membrane structures that can be multiplexed over entire wafers with 100% yield.

Further, we describe the fabrication and characterization of a capacitive pressure sensor formed by a graphene-polymer heterostructure membrane spanning a large array of micro-cavities each up to 30 µm in diameter with 100% yield. Sensors covering an area of just 1 mm^2 show reproducible pressure transduction under static and dynamic loading up to pressures of 250 kPa. The measured capacitance change in response to pressure is in good agreement with calculations. Next, we demonstrate a novel strained membrane transfer and optimizing the sensor architecture. This method enables suspended structures with less than 50 nm of air dielectric gap, giving a pressure sensitivity of 123 aF/Pa per mm^2 over a pressure range of 0 to 100 kPa. [2]

Lastly, we demonstrate a touch-mode capacitive pressure sensor (TMCPS) incorporating a SU-8 spacer grid structure. [3] This results in a partially suspended membrane configuration, which produces reproducible deflection, even after exposing the membrane to pressures over 10 times the operating range. The device shows a pressure sensitivity of 27.1 ± 0.5 fF/Pa over a pressure range of 0.5 kPa to 8.5 kPa.

We demonstrate the operation of the above devices as air pressure, water pressure and force touch sensors.

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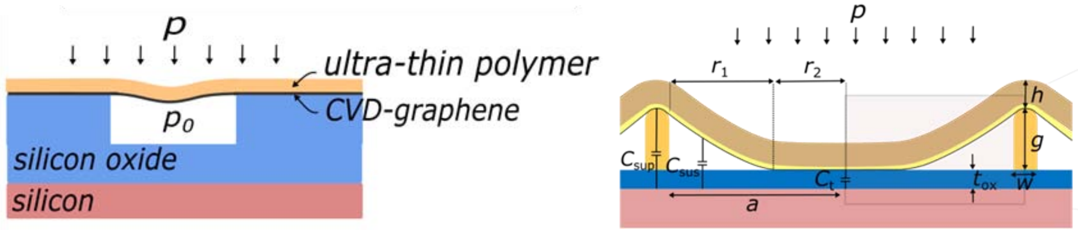

Figure 1: Schematic of a graphene-polymer heterostructure membrane based pressure sensor operating in (a) fully suspended more and (b) touch mode.

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Luminescent emission from 1s, 2s, 3s and 4s excitons of monolayer WSe_2 in high magnetic fields

The strong Coulomb interaction in 2D-TMDCs provides an outstanding platform for investigating exciton physics. We found that in ultrahigh quality BN/1L-WSe_2/BN heterostructures, we can observe 2s luminescence up to 150K. Remarkably, the 2s emission exhibits much better valley polarization and coherence than 1s. In a strong magnetic field, we further observed excitonic luminescence up to the 4s excited state (see Fig.1 below). By analyzing the diamagnetic shift of the ground and excited exciton emission, we determine the size ratio of the different exciton species. Moreover, the Zeeman splitting measurement shows monotonic increase of *g* factor from 1s to 3s, indicating the existence of nontrivial differences of magnetic moment and effective mass between different Rydberg states. Complementary to PLE and absorption measurements in literature, our results provide an alternative approach to optically investigate tightly-bound electron-hole pairs and their valleytronics in 2D atomic layers.

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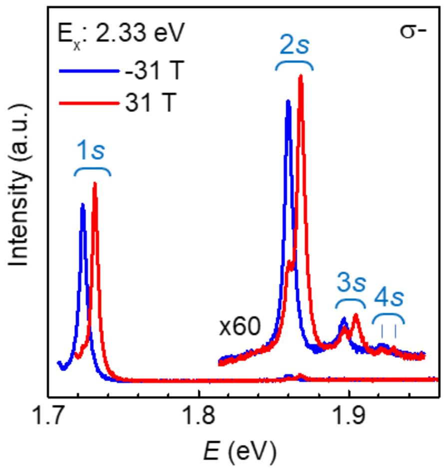

Figure 1: Luminescence emission of 1L-WSe_2 in magnetic fields of ±31 Tesla. Zeeman-split 1s, 2s, 3s and 4s emissions are visible.

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Scalable production of defect-free graphene sheets using rotor–stator mixer in supercritical CO_2 and their applications

Abstract

A green and scalable approach was presented for the production of defect-free graphene sheets by the exfoliation of graphite using a rota-stator mixer in supercritical CO2. The synergistic effects of the fluid dynamic force coupled with the supercritical CO2 were investigated by the combination of experiments and CFD simulation. The characterization results by transmission electron microscopy, Raman spectroscopy and atomic force microscopy confirmed that the total exfoliation yield reached more than 70%. Up to 80% of the produced graphene was less than five layers. The CFD simulation showed that the geometry of the mixer and the velocity gradient influenced greatly the exfoliation efficiency. The graphene-based flexible films with high electrical conductivity were fabricated by inkjet printing the ink which was formulated using the as-prepared graphene, ethyl cellulose and cyclohexanone. Also, the polyaniline/graphene/MnO2 composite paper electrode with the area capacitance of 3.5 F/cm2 and excellent stability was constructed. Accordingly, the all-solid-state supercapacitors were assembled and could lighten a green LED light.

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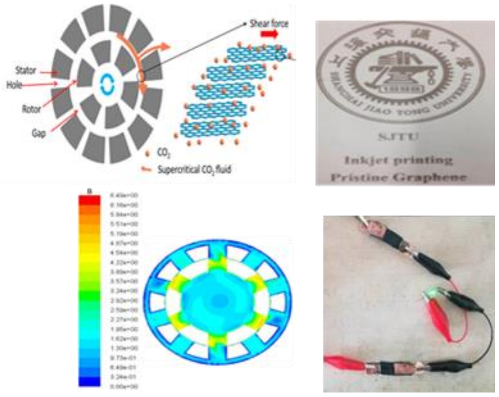

Figure 1: Rotor and stator mixer, fluid flow pattern, printing conductive pattern and supercapacitor

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Characterization of solution processable graphene related materials

As graphene based materials move from the laboratory to production, there is increasing interest in a wide range of applications such as membrane filtration, batteries, printable electronics, and graphene-polymer composites, which require graphene related materials in solution. In this case the graphene is in the form of flakes dispersed in organic or aqueous solvents. Solution processable routes to graphene generally fall into two categories direct exfoliation of graphite or oxidation to graphene oxide (GO) followed by reduction to graphene. Properties of films made from these dispersions are dependent on both the quality of the individual flakes and how they are assembled into films. Here we will present results on evaluating the structure, morphology optical and electrical properties of GO and reduced GO samples derived from various protocols using starting materials from a variety of commercial sources. Different sizes of individual GO flakes were prepared by controlling the sonication energies in aqueous dispersion and implemented new approaches to characterize various GO properties as a function of the average flake size. New protocols were developed to determine and compare the flake size of GO dispersions by using dynamic light scattering and atomic force microscopy (AFM). AFM height measurements were also used to determine flake thickness and monitor the thermal reduction of GO. The atomic scale structure of the flakes was observed using scanning tunneling microscopy. Photoluminescence of GO was characterized as a function of sonication energy, excitation wavelength, and pH of dispersion. Strong dependence of photoluminescence intensity on pH control and variation of photoluminescence intensity with different flake sizes was observed. GO concentration dependent cytotoxicity was studied with various flake sizes for multiple cell lines.

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Graphene deflectometry for sensing molecular and ionic processes at the nanoscale

Single-molecule sensing is at the core of modern biophysics and nanoscale science, from revolutionizing healthcare through rapid, low-cost sequencing to understanding physical processes such as ionic hydration at their most basic level. However, rapid and/or weak interactions at the molecular scale are often too fast for the detection bandwidth or otherwise outside the detection sensitivity. Of critical importance, most of the envisioned biophysical applications are at room temperature, which further limits detection due to significant thermal noise. Here, we theoretically demonstrate reliable transduction of forces into electronic currents via locally suspended graphene nanoribbons, which allows for the detection of ultra-weak -- tens of picoNewtons -- and fast -- gigahertz -- processes, at room temperature. The sensitivity of electronic couplings to distance magnifies the effect of the deflection, giving rise to measurable electronic current changes even in aqueous solution. Due to thermal fluctuations, the characteristic charge carrier transmission peak follows the Voigt profile. Room temperature graphene deflectometry presents new opportunities in the sensing and detection of molecular-scale processes, from ion dynamics and DNA sequencing to protein folding, in their native environment.

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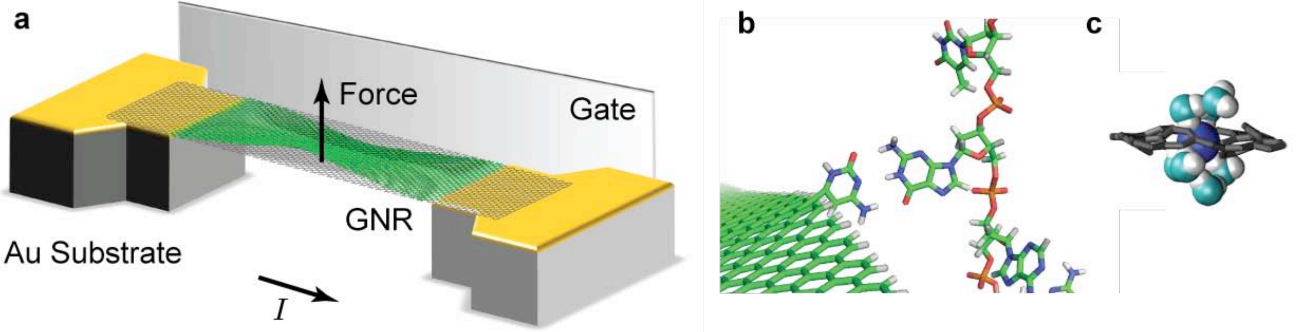

Figure 1: Graphene nanoribbon deflectometer. **a**. Schematic of a graphene ribbon suspended between two gold contacts in aqueous solution (omitted for clarity). Hydrated ions and molecules can deflect the graphene, e.g., **b**., by binding to a functional group at the ribbon edge or, **c**., by passing through a pore. The deformed ribbon is in green with an exaggerated upward deflection for visual clarity.

POSTERS

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High-performance flexible solid-state supercapacitors built from nitrogen-doped hybrid-dimensional nanocarbon materials

Abstract
The rapid development of portable electronics has increasingly demanded advanced power supply devices with enhanced energy/power efficiency as well as improved portability and durability. Flexible solid-state supercapacitors (FSSSCs) show great potential to fulfill this demand owing to their multiple structural and functional superiorities [1-3]. Herein, we demonstrate a high-performance FSSSC built from nitrogen-doped hybrid-dimensional nanocarbon (N3C) based paper-like electrodes (N3CPs) and a polyvinyl alcohol-potassium hydroxide (PVA-KOH) based gel polymer electrolyte. Three types of representative carbon materials with different dimensions including graphene nanosheets, carbon nanotubes and carbon black nanoparticles are used together as building blocks to construct N3C composites via microwave-assisted solvothermal assembly combined with post-annealing. With melamine serving as both a superior structure-directing agent and a highly effective nitrogen source, an interconnected highly-porous 3D hierarchical structure and a high nitrogen doping level of 10.8 at.% can be achieved. A stepwise negative-pressure filtration process is employed to fabricate the sandwich-structured N3CPs with enhanced flexibility, conductivity and mechanical strength. The as-prepared N3CP possesses a high specific capacitance of 294 $F \cdot g^{-1}$ at 1 $A \cdot g^{-1}$ in a KOH electrolyte, as well as excellent rate capability and cyclic stability, which can be ascribed to its optimized composition and micro-/nanostructure. A further fabricated FSSSC exhibits high areal/volumetric capacitance, remarkable energy/power density and satisfied operational reliability/durability. The results hold promising prospects towards practical applications of N3CP based FSSSCs for powering future portable electronics.

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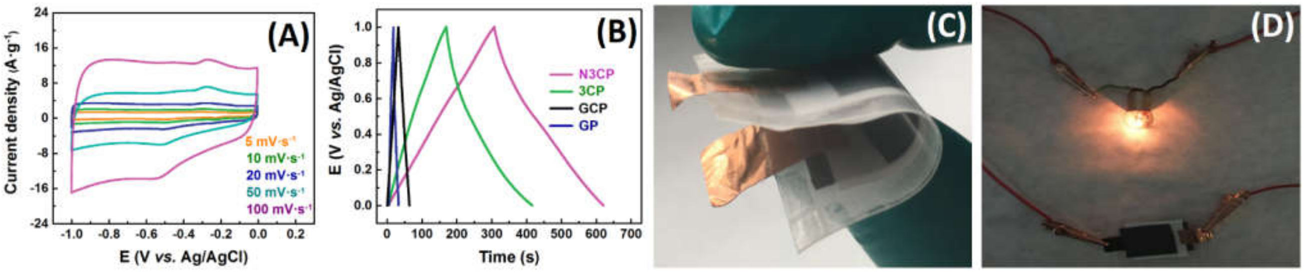

Figure 1: (A) CV curves of the N3CP electrode at different scan rates. (B) Gavalnostatic charge-discharge curves of different paper electrodes at 1 $A \cdot g^{-1}$. (C) A lab-made N3CP based FSSSC. (D) A miniature bulb is lightened up by the FSSSC. Electrolyte: 6 M KOH. Counter electrode: Pt. Reference electrode: Ag/AgCl.

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First-Principles Study of Phonon Anharmonicity in Atomically-Thin Black Phosphorus

Black phosphorus (BP) consists of anisotropic puckered layers held together by long-range van der Waals forces, which allows for the isolation of single-layers [1]. This material is of interest due to its semiconducting band gap which remains direct independent of the number of layers [2], as well as its high carrier mobility [3]. It was shown experimentally that the Raman active modes A_g^1, B_{2g}, and A_g^2 have frequencies which downshift with increasing temperature [4]. In this work we study this phenomenon for the single-layer using first-principles density functional theory (DFT) calculations. To model the temperature-induced shift of the phonon frequencies, we carry out *ab initio* molecular dynamics simulations with varied temperature. The normal mode frequencies are located at the peak positions in the power spectrum, which is calculated as the magnitude of the Fourier transform of the total velocity autocorrelation. We extend this approach to anharmonic systems by approximating the general solution to the classical equations of motion as a superposition of normal modes, with each mode written as a Fourier series. Anharmonicity induces a frequency shift for each mode individually as well as from phonon-phonon coupling, with the latter interpreted classically as an effective damping of a given mode due to its interaction with all other modes. The effect of thermal expansion is also included by imposing the temperature dependent lattice constant in each simulation as calculated within the quasiharmonic approximation. In general we obtain frequency downshifts with increasing temperature in agreement with experiment, with the results visualized in Figure 1.

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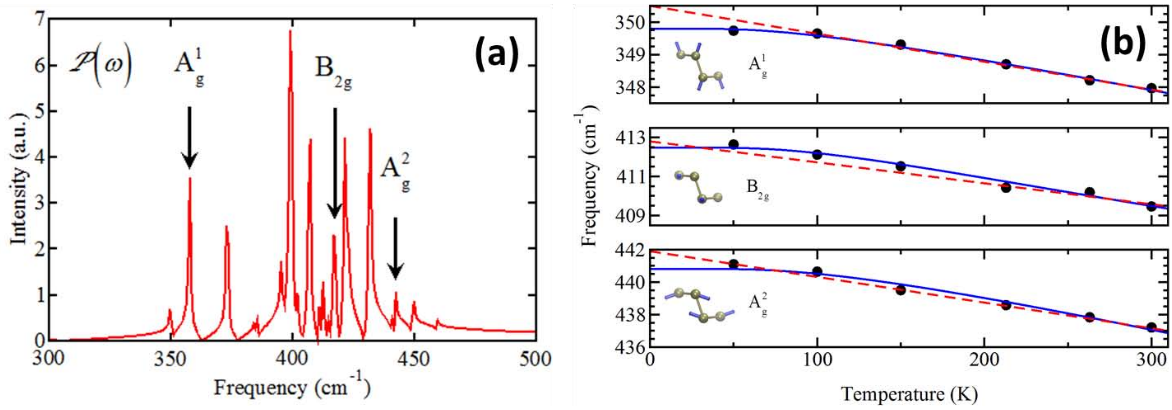

Figure 1: (a) Sample power spectrum with the Raman active mode peaks identified. (b) Predicted frequency shifts with varied temperature.

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Chalcogenide Glass Waveguide-integrated Black Phosphorus Mid-Infrared Photodetectors

Black phosphorus (BP) is a promising 2D material that has unique in-plane anisotropy and a 0.3 eV direct bandgap in the mid-IR [1,2]. However, waveguide integrated black phosphorus photodetectors have been limited to the near-IR on top of Si waveguides that are unable to account for BP's crystalline orientation [3]. In this work, we employ mid-IR transparent chalcogenide glass (ChG) both as a broadband mid-IR transparent waveguiding material to enable waveguide-integration of BP detectors, and as a passivation layer to prevent BP degradation during device processing as well as in ambient atmosphere [4]. Our ChG-on-BP approach not only leads to the first demonstration of mid-IR waveguide-integrated BP detectors, but also allows us to fabricate devices along different crystalline axes of black phosphorus to investigate, for the first time, the impact of in-plane anisotropy on photoresponse of waveguide-integrated devices. The best device exhibits responsivity up to 40 mA/W and noise equivalent power as low as 30 pW/Hz$^{1/2}$ at 2185 nm wavelength. We also found that photodetector responsivities changed by an order of magnitude with different black phosphorus orientations. This work validates black phosphorus as an effective photodetector material in the mid-IR, and demonstrates the power of the glass-on-2D-material platform for prototyping of 2D material photonic devices.

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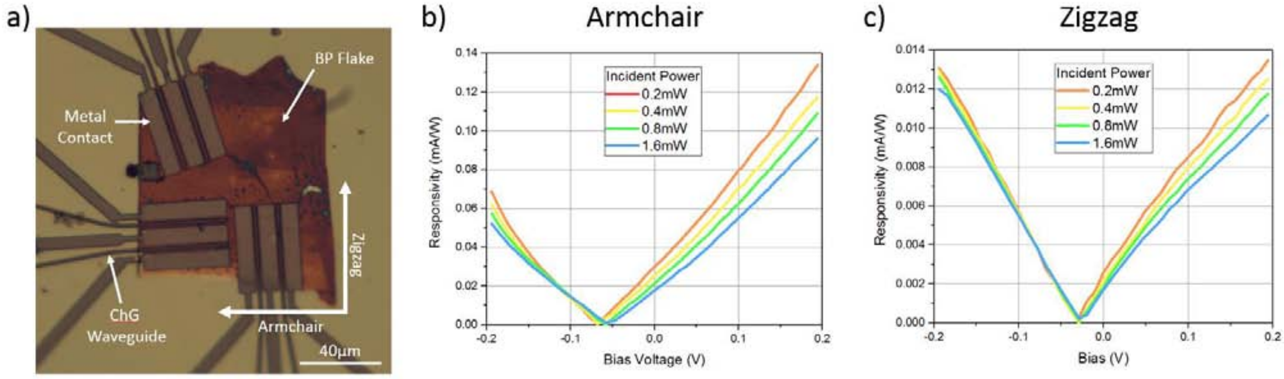

Figure 1: (a) Optical microscope image of six fabricated waveguide-integrated photodetectors on the same BP flake. (b) Responsivity as a function of applied voltage at varying incident 2185nm laser powers for waveguide parallel to armchair directions and (c) zigzag direction.

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The mechanical properties of grain boundaries in chemical vapor deposition grown graphene: Simulations and Experiments

Graphene is the strongest material ever characterized. Its elastic modulus and mechanical strength were first measured through the nanoindentation of free-standing circular membranes [1]. In order to take advantage of graphene's strength in an industrially scalable manner, chemical vapor deposition methods have been developed to synthesize large area continuous monolayer films. Although the subsequent films contain grain boundaries, nanoindentation experiments demonstrate they still achieve a significant portion of their fracture [2]. Herein, we utilize oxygen assisted methods to allow tunability in the nucleation density. We present electropolishing techniques of copper to consistently achieve nanometer scale surface roughness over large areas. This yields an increase in nucleation uniformity, as well as a more mechanically robust film. These methods allow for more meaningful statistics to be built from experiments. In parallel, we present a numerical formulation for a membrane-based cohesive zone model to model the fracture of grain boundaries in graphene through the finite element method within the context of the nanoindentation experiment. Our failure analysis provides a relationship between the critical failure load and the distance of the grain boundary. The results are used to calculate a probability density function of polycrystalline graphene that can be validated against the nanoindentation experiments to understand the mechanics of failure of grain boundaries in graphene.

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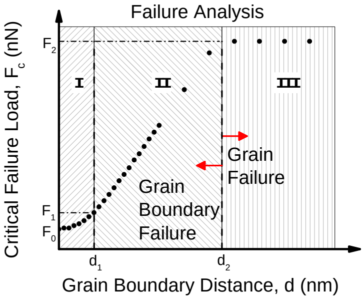

Figure 1: Relationship between the critical failure load and the grain boundary distance in a nanoindentation experiment.

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Cryogenic near-field imaging and spectroscopy at the 10-nanometer-scale

Single-layer materials like graphene, boron-nitride or transition-metal dichalcogenides are of rising interest for novel plasmonic and opto-electronic applications due to their unique characteristics and their broad application range. Being highly sensitive to the local environment, their properties can, however, strongly vary on the nanometer length scale, severely limiting the macroscopic performance of such novel devices. Scattering-type scanning near-field optical microscopy (SNOM) and nanoscale FTIR spectroscopy (nano-FTIR) systems have become the key technology to understand and resolve these limitation by measuring the electronic properties of such nanostructures at the 10-nanometer length scale.
SNOM [1-8] and nano-FTIR [1,2] have already proven themselves vital for modern nanoscopy and have been used in applications such as chemical identification [2], free-carrier profiling [3], or the direct mapping of propagating plasmons [4,5] and polaritons [6]. Hence, key information about the local conductivity, intrinsic electron-doping, absorption or the complex-valued refractive index can routinely be extracted at the nanoscale.
Within this talk we will introduce the newest technological breakthrough in the field of near-field optics - Cryogenic near-field imaging and spectroscopy. Pioneered by the group of Dimitri Basov [7], this novel approach extends ambient near-field measurements to the cryogenic temperature range (<10-300 Kelvin, [1]) and opens a complete new world for nanoscale optical microscopy and spectroscopy. This technology enables for example the direct mapping of phase-transitions in strongly correlated materials [7,8] or the detection of low-energy elementary excitations at the surface of solid-state systems.

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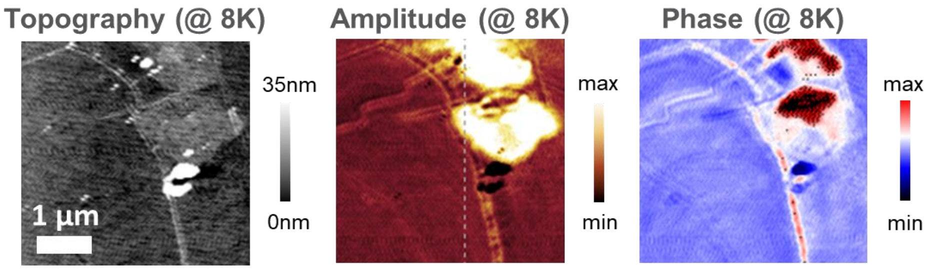

Figure 1: Cryogenic near-field optical microscopy. Topography, near-field amplitude, and near-field phase image of an epitaxial graphene sample measured at an excitation wavelength of 9.7µm. The sample temperature for these measurements is set to 8.0 Kelvin. Clear interference pattern of propagating surface-plasmon polaritons are visible at grain boundaries and defect sites [3,4].

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Engineered Strain of APCVD Synthesized Graphene

The synthesis of graphene on both platinum and copper substrates is well established and is showing great promise towards large-area industrial scale production. However, growth of graphene on platinum substrates shows promise over copper because it can be reused for repeated growth, be grown at atmospheric pressure, be easily transferred to arbitrary substrates, and exhibits higher quality defect-free nanosheets. In addition, the control of strain in nanosheets is of great significance and has shown to open a band-gap in graphene [1], increase sensitivity in resonators [2], and increase photocurrent generation [3]. Despite vast research in the synthesis of 2D materials, there has been little to no discussion on the engineered strain of 2D materials during the thermal growth process. One reason, is due to the extreme temperatures needed for the decomposition of the nucleation gas, which makes incorporating instruments within the thermal chamber at high temperatures prohibitive.

In this work, we demonstrate a tensile test actuator (TTA), fabricated from stainless steel to conduct uniaxial tensile strain of platinum foil within the furnace. The platinum foil is doubly clamped and suspended, then placed within the thermal chamber, where it experiences thermal strain during the synthesis of graphene by atmospheric pressure chemical vapor deposition (APCVD). Growth is conducted within a three zone furnace utilizing mass flow controllers to control the nucleation gas methane (CH_4) and precursor gas hydrogen (H_2). Polycrystalline platinum foil from Sigma Aldrich with 99.9 wt% metal basis at 0.025mm thickness is used as the metal catalyst. The TTA and platinum foil are placed inside the furnace, along with a control sample, to allow for comparison between strained and unstrained conditions.

To investigate growth of graphene on uniaxial tensile strained platinum foils, characterization of the nanosheet structure is conducted utilizing Scanning Electron Microscopy (SEM) and Raman Spectroscopy. SEM of the platinum foil exposed to thermal strain shows evidence of thermal fatigue, consisting of striations along preferential grain directions. Comparison of strain between the control foil and strained foil are conducted by Raman Spectroscopy by observing a downshift in the 2D band, corresponding to increasing strain. Further growth experiments are showing unique morphologies and crystal structure on strained and unstrained substrates.

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Highly Sensitive, Large-Area MoS_2 Photodetectors with Graphene Contacts

Monolayer transition metal dichalcogenides (TMDs) have a direct bandgap and extraordinary light absorption [1-3], making them ideal candidates for atomically-thin optoelectronics. Although there have been previous reports of sensitive photodetectors based on monolayer MoS_2 [2, 4], they were mainly based on material obtained by exfoliation, not suitable for mass production, and using thicker metals such as Au for source and drain electrodes, not ideal for flexible electronics. Here we show that large-area MoS_2 transistors with graphene electrodes, fabricated using CVD-grown material, yield performance that matches or exceeds the performance of photodetectors based on exfoliated materials, with record shot-noise-limited detectivities of 8.7×10^{14} Jones in ambient conditions and even higher when encapsulated. This figure of merit is at least one order of magnitude higher than the values reported for exfoliated devices [4]. The devices with graphene electrodes have a tunable band alignment and are suitable for scalable ultra-thin flexible optoelectronics [5].

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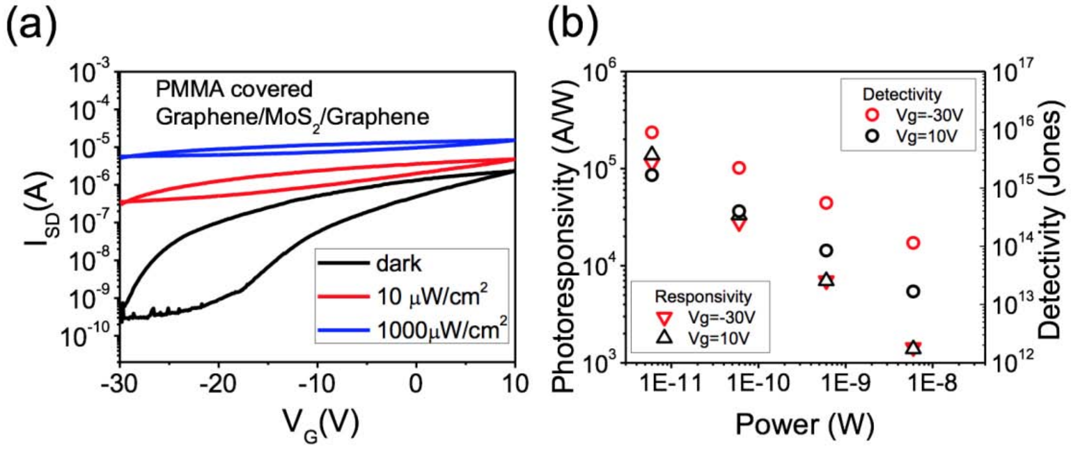

Photoresponse of a PMMA-covered device (a) and power dependence of its photoresponsivity and detectivity (b).

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Synthesis of luminescent graphene by adsorption of an amphiphilic Eu complex

Synthesis of luminescent graphene is an intriguing process that will open new possibilities for making ultrathin and flexible light emitting devices. We attempted a simple approach to synthesizing luminescent graphene, *i.e.* noncovalent physical adsorption of a luminescent Eu complex (EuLC$_{18}$: Fig. 1(a)) on the surface of the graphene sheets grown by chemical vapor deposition (CVD). An amphiphilic complex, EuLC$_{18}$, has bipyridine ligands to wind the Eu ion and two long alkyl chains (C$_{17}$H$_{35}$). The bipyridine ligands, which act as photo-antennae, effectively absorb the photo-excitation energy and transport it for the Eu excitation while sensitizing the sharp ff emissions of Eu ions with high efficiency (photo-antenna effect)[1][2]. In the synthesizing of EuLC$_{18}$-adsorbed graphene sheets, the CVD-grown graphene sheets, which were transferred onto non-luminescent quartz substrates, were simply dipped in a chloroform solvent for five minutes, in which EuLC$_{18}$ was dissolved with a concentration of 1 mM. The EuLC$_{18}$/graphene sheet showed bright red-color luminescence under UV lgith irradiation as shown in Fig.1 (b). The luminescence spectrum of the EuLC$_{18}$/graphene sheet under photo-excitation at a wavelength of 290 nm is shown in Fig.1(c). Several luminescence peaks were clearly observed in a wavelength region from 580 to 694 nm. The luminescence peaks at 591, 616.5, and 694 nm correspond to the ff emissions of the trivalent Eu ion. These peaks can be assigned to the $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, and $^5D_0 \rightarrow {}^7F_4$ transitions, respectively. We confirmed through the measurements of the excitation spectrum that the light emission typical for ff transitions of the Eu ion was obtained via the energy transfer from the ligand to the Eu ions by the photo-antenna effect. We have demonstrated that ultrathin graphene sheets can be made luminescent simply through adsorption of EuLC$_{18}$ on the graphene surface.

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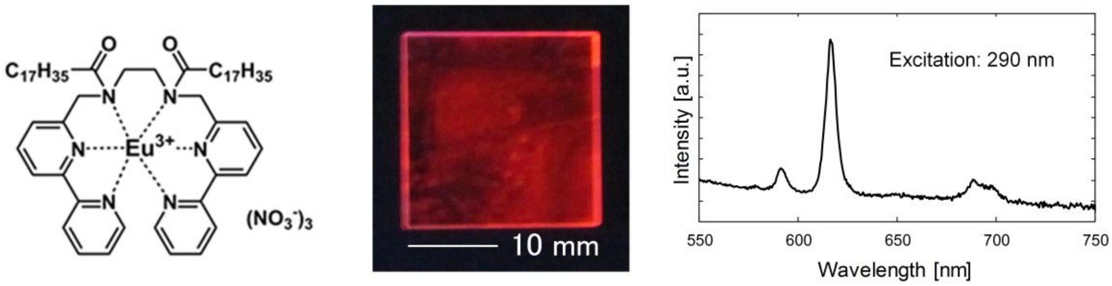

(a) (b) (c)

Figure 1: (a) Structure of EuLC$_{18}$ (b) EuLC$_{18}$/graphene sheet under UV light irradiation and (c) luminescence spectrum

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Oxygen Plasma Functionalized 3D Graphene/Sulfur/ Polypropylene Cathode Composite for Li-S Batteries

In recent times, lithium-sulfur (Li-S) battery has been extensively studied due to its high theoretical energy density (~2500 Wh/kg)[1]. Graphene has been employed as conductive scaffolds to improve the electrical conductivity of sulfur[2–4], and also as a coating layer of separator to restrain the shuttling effect of polysulfide by physical interception[5] or via introducing functional groups[6,7]. However, previous designs of the Li-S battery lack a good interface between the cathode and the separator, thus challenging the battery community to come up with new design of the overall battery in order to achieve optimal performance. In this work, a novel mesoporous, three-dimensional graphene (3DG)-separator structure is reported for multifunctional applications in a Li-S battery. In the proposed and tested design, we achieved seamless integration of the current collector, the cathode material and part of the separator, where the latter behaves as a “Janus structure”. Our studies demonstrated that the mesoporous 3D graphene exhibits a bulk electrical conductivity of ~22 S/cm, with good mechanical integrity[8,9][10], making it a promising candidate for using as a flexible current collector, as well as a scaffold for sulfur particles. The unique surface morphology of 3D graphene contributes to strong van der Waals forces that enable 3D graphene to intimately attach to the polypropylene (PP) separator thus enabling a Janus separator structure. The fabricated devise does not use any binder materials, conductive additives or metal current collector. It is described here as a “3-in-1” structure or Tri-Function Structure (TFS) consisted of oxygen plasma functionalized 3D graphene/sulfur/PP, which showed a capacity of ~1400 mAh/g at 0.1 C with a sulfur loading of ~70 wt%. This design of the novel 3-in-1 structure contributed to a high cyclic performance of the Li-S battery. This improvement was further enhanced by the employed oxygen plasma functionalization, since it creates oxygen-containing functional groups that have a strong binding energy to polysulfide. This fabricated 3D graphene structure along with the proposed novel concept of cell design for Li-S battery provide an improved battery concept that facilitates reduced weight and high performance of the energy storage device.

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Flexible, Fabric-integrated Supercapacitors based on Nanosized MnO_2 and Polypyrrole - Carbon Nanotube/Graphene Composite

A flexible, fabric–integrated supercapasitor has been designed and fabricated using carbon nanostructured materials. Carbon Nanotube (CNT) sheet was surface-modified by laser milling using a solid-state laser to create nano-sized defect sites. The latter have been identified in a previous study predominately as amorphous carbon particles [1]. MnO_2 nanoparticles were selectively precipitated onto the defect carbon particles when the sheet was exposed to $KMnO_4$ and ethanol. Polypyrrole was introduced by exposing the Laser Milled (LM)-CNT sheet to $KMnO_4$ and pyrrole in an acidic pH, where the MnO_2 particles acted as an oxidizing agent. The LM-CNT composite displayed energy densities that were an order higher as compared to the non – LM – CNT composite. It also revealed a higher cyclic stability, retaining 96% capacitance after 5000 cycles at 4A/g current density. The asymmetrical full device utilizing MnO_2 and PPy showed a peak energy density of over 55 - 60 Wh/kg at 1kW/kg power density . The porous nature of the 3D graphene was utilized for fabric integration [2]. A sandwich structure was created with fabric as a base, graphene as a highly conductive paste (150 S/cm), and CNT composite sheet as electrode, to assemble a flexible super capacitor. Details are presented in Fig. 1.This devise is easy to fabricate in a scalable manner, which makes it a promising candidate for wearable electronic applications.

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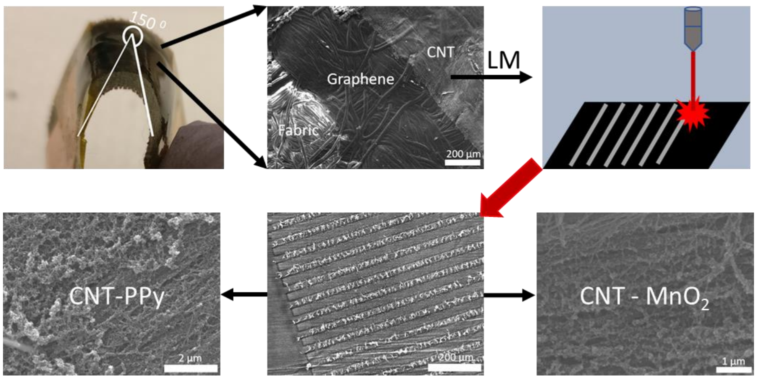

Figure 1: Figures on first row show (left to right) fabric integrated CNT composite supercapacitor, SEM image of fabric/graphene/CNT interface and schematic of the Laser Milling (LM) process. Second row figures display (middle) LM-CNT sheet, (left) CNT – Ppy composite and (right) CNT – MnO_2 composite.

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MoS_2 Quantum Dots Decorated 2-Dimensional Bi_2S_3 for Photocatalytic Hydrogen Production under Broad Solar Spectrum

Hydrogen (H_2) is a promising candidate to replace fossil fuels owing to its high fuel value of ~143 kJ/g. Furthermore, the combustion of H_2 produces only water as by-product, rendering the process environmentally benign [1]. There are a variety of methods to produce H_2, among them photocatalytic splitting of water to generate H_2 has been widely regarded as one of the most sustainable approaches [2, 3]. In view of solar energy utilization, the search for semiconductor photocatalysts that can harvest the wide spectrum of solar light, from ultraviolet (UV) to near-infrared (NIR) wavelength, and simultaneously achieve efficient solar energy conversion remains is one of the most challenging missions. Although noble metals have been studied extensively to achieve high photocatalytic activity for H_2 production, the scarcity of these precious metals and high production costs limit the practicality of using noble metals for photocatalytic H_2 production. Molybdenum disulfide (MoS_2) has emerged as an attractive non-noble metal catalyst with high catalytic efficiency based on theoretical and experimental studies. Among the different shapes and sizes of MoS_2, zero-dimensional (0D) MoS_2 quantum dots (MoS_2QDs) possess unique optical and electronic properties, which are vital in many applications, particularly photocatalysis [1, 4]. The quantum size of MoS_2QDs not only results in an increase in unsaturated bonds, but higher exposed edges per surface area as well. The latter will in turn enable more hydrogen atoms to be bonded to the photocatalyst, thereby increasing the photocatalytic activity for H_2 generation. In this work, MoS_2QDs decorated 2D-bismuth sulfide (Bi_2S_3) photocatalyst was synthesized via a facile solvothermal route. Photoluminescence characterization showed that the synthesized MoS_2QDs possessed up-conversion and down-conversion properties, indicating their capability to harness energy from the light spectrum ranging from ultraviolet (UV) to near-infrared (NIR). The performance of the synthesized MoS_2QD/Bi_2S_3 photocatalysts revealed the highest hydrogen yield of 17.7 mmol/h.g was achieved by $0.14MoS_2QD/Bi_2S_3$, which was almost 3 and 4.5 folds higher than that of control MoS_2 nanosheets-decorated Bi_2S_3 and undoped Bi_2S_3, respectively. Furthermore, examination of the $0.14MoS_2QD/Bi_2S_3$ photocatalysts under NIR irradiation showed a significant photocurrent response and an accumulative H_2 yield of 53.6 μmol/g after 6 h reaction. Besides that, $0.14MoS_2QD/Bi_2S_3$ was able to retain more than 90% of photoactivity after 4 consecutive reaction run, thus indicating its superior photostability. Photoelectrochemical measurements also revealed a significant improvement in the charge transfer rate of MoS_2QD/Bi_2S_3 as compared to the control samples. This work demonstrated the importance of MoS_2QDs and their potential in replacing noble metal co-catalysts for photocatalytic H_2 production under broad solar spectrum.

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Engineering MoS_2 for High-Performance Electrocatalytic Hydrogen Evolution

Developing catalysts better than Pt for the hydrogen evolution reaction (HER) consists of one holy grail in the field of clean energy. We demonstrate that monolayer MoS_2 films may be engineered to show better HER catalysis than Pt. This is realized by optimizing the density of sulfur vacancies in the film and leveraging proper interactions of the film with substrates. Pt substrate is used as an example to provide the proper interaction. The substrate does not participate the catalytic reaction, but may boost the activity of the film by forming a lower interface tunneling barrier and affecting the electronic structure of the film, such as through charge transfer. A minimal amount of Pt like 1 nm thick is enough to enable the superior performance at the film, and the performance of the film is very stable with no degradation for more than two months. This result indicates that MoS_2 may be engineered to be better than Pt in HER catalysis, although more studies would be necessary to find out non-noble materials as the proper substrate.

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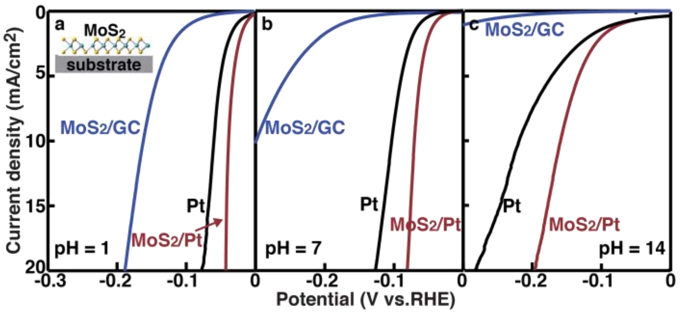

Figure 1. Better-than-Pt HER catalysis of monolayer MoS_2 films over a broad range of pH values. (a) Polarization curves collected from a monolayer MoS_2 film on glassy carbon (GC) substrates (blue curve), a monolayer MoS_2 film on a Pt substrate (red curve), and the bare Pt substrate with no MoS_2 film (black curve) in 0.5 M H_2SO_4. Also given are the polarization curves collected from the monolayer MoS_2 film on Pt substrates (red curve) and the bare Pt substrate (black curve) in (b) neutral media (pH = 7) and (c) alkaline electrolyte (pH = 14). Inset in (a) shows a schematic illustration for the film on substrates.

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Ultra-low energy SEM/STEM of graphene

The development of new types of materials such as 2D crystals (graphene, MoS_2 , WS_2 , h-BN, etc.) requires also the development of new surface sensitive techniques for their characterization. Regarding to “surface” sensitivity, the (ultra) low energy electron microscopy can be a very powerful tool for precise study of these atomic-thick materials and can confirm their predicted physical phenomena occurred on the surfaces. Modern commercial scanning electron microscopes enable imaging and analysis of samples by low energy electrons even at very high magnification. In the case of the SEM, resolution even below 1 nm can be achieved at low landing energy of electrons. [1]

Since specimen contamination increases with increasing electron dose and decreasing landing energy, specimen cleanness is a critical factor in obtaining meaningful data. A range of various specimen cleaning methods can be applied to selected samples. Typical cleaning methods, such as solvent rinsing, heating, bombarding with ions and plasma etching have their limitations. Electron-induced in-situ cleaning procedure can be gentle, experimentally convenient and very effective for wide range of specimens. Even a small amount of hydrocarbon contamination can severely impact the results obtained with low energy electrons. During the scanning of surfaces by electrons, the image usually darkens because a carbonaceous layer gradually deposits on the top from adsorbed hydrocarbon precursors. [2] This effect is called electron stimulated deposition. The surface diffusion of hydrocarbon molecules around the irradiated area serves as a source of additional precursors, responsible for even darker frame of the contaminated field of view. On the other hand, the effect of electron stimulated desorption occurs at the same time, especially at low energies, so fundamental question arises what process, deposition or desorption, will dominate. Examination of the phenomena taking place on surfaces bombarded with very slow electrons may open the door to many surface studies outside an ultrahigh vacuum. [3] [4]

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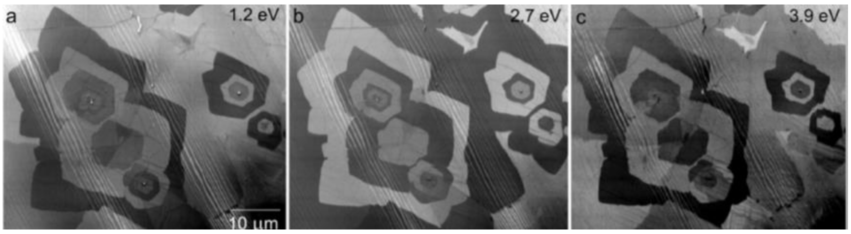

Figure 1: Graphene multilayers observed by ultra-low energy SEM: 1.2 eV (a), 2.7 eV (b), 3.9 eV (c)

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Transient Investigations of Hot-Carrier Transport in BN-Encapsulated Graphene FETs

Graphene is a material with remarkable electrical characteristics, including room-temperature mobility that is unparalleled among semiconductors, electrical conductivity that is better than that of silver, and a current carrying capacity that exceeds 10^8 A/cm^2[1]. Nonetheless, it is also known that the electrical properties of graphene are typically strongly degraded by the interaction of its carriers with substrate. With graphene on SiO_2, common issues are carrier trapping by interface states, and by deep levels within the oxide, and current degradation due to Joule heating of the substrate [2,3]. The latter process typically degrades the maximum saturation velocity to which carriers may be accelerated and, thus, the current-carrying capacity of the device [3,4]. A potential strategy that should allow these issues to be alleviated is that of encapsulating the graphene in high-quality BN. This should allow the graphene to be isolated from the influence of defects in the underlying oxide, and to also minimize transient heating effects. In our presentation, we describe the results of studies that we have performed to investigate transient transport in such encapsulated graphene devices. Utilizing a strategy of nanosecond-duration pulsing, we demonstrate that transport in these devices is essentially free of the influence of defect related carrier trapping. At the same time, we also establish that the influence of Joule heating is significantly suppressed. Our results reveal a transition from current saturation to linear conductance as the charge neutrality point is approached from either the conduction or valence bands.

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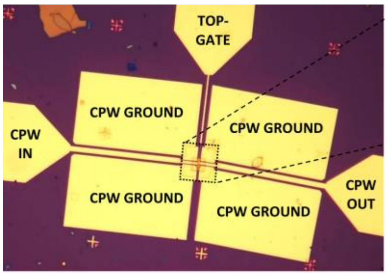

Figure 1: Coplanar waveguides for pulse measurements

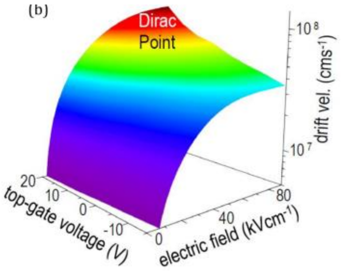

Figure 2: Deviation of drift velocity near Dirac point

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Hierarchical Graphene Foam for Efficient Solar-thermal Conversion

Efficient solar-thermal conversion is essential for the harvest and transformation of the abundant solar energy, leading to the exploration and design of efficient solar-thermal materials. Carbon-based materials especially graphene have the advantages of a broadband absorption, excellent photothermal properties, holding promise in solar-thermal energy conversion [1-4]. Herein, we report the synthesis of hierarchical graphene foam (h-G foam) with continuous porosity via plasma-enhanced chemical vapor deposition (PECVD). This h-G foam consists of vertical graphene nanoplates array on the 3D foam skeleton, which provides much larger heat exchange area. This unique structure dramatically enhance the omnidirectional absorption of sunlight, and thereby could enable a considerable elevation of the temperature. Used as heating material, the external solar-thermal conversion efficiency impressively reaches up to ~93.4% and the solar-vapor conversion efficiency exceeds 90% for seawater desalination with high endurance.

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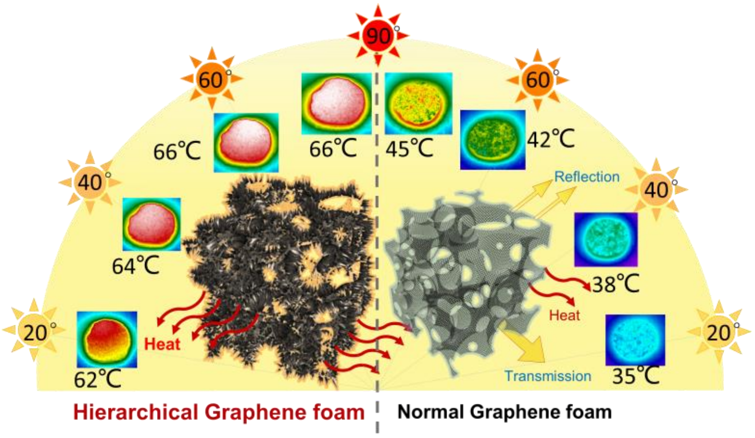

Figure 1: The schematic and IR image of solar-thermal conversion difference between h-G foam and normal G foam under various incident angles.

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First-principles study of Raman active modes in MoS_2 intercalated with Ag

Two-dimensional layered materials have been subject of increased research interest ever since a single layer of graphen has been obtained by mechanical exfoliation in 2004 [1]. In particular, the transition metal dichalcogenides (TMDs) with the general formula MX_2, where M is a transition metal (Mo, W) and X a chalcogen atom (S, Se, Te), have already shown a wide range of technologically relevant properties when scaled down from bulk to few-layer systems. For example, bulk MoS_2 has an indirect band gap of 1.29 eV, which becomes a direct band gap of 1.8 eV when a single layer of MoS_2 is considered [2].

Precise characterization of two-dimensional materials is crucial for exact control of their properties that vary with the number of layers. Raman spectroscopy has become the key experimental technique in this sense, due to its nondestructive nature and the ability to identify even small structural and electronic changes.

Here, we present a combined experimental and theoretical study of the Raman active modes of few-layer MoS2 intercalated with silver. Using Density Functional Theory (DFT) we predict a significant red shift of all Raman active modes of MoS_2 upon Ag intercalation and with increasing Ag concentration in few-layer systems (see figure 1 for results in 2L). However, this effect subsides as the number of MoS_2 layers grows as is supported by the linear chain model for the low-frequency shear and breathing modes for systems with the number of layers corresponding to experimental sample thicknesses. While high-frequency intralayer Raman modes have been extensively studied, we specifically focus on low-frequency interlayer Raman modes that are more susceptible to changes of interlayer couplings [3] and are modified due to presence of silver in the van-der-Waals gap of MoS_2.

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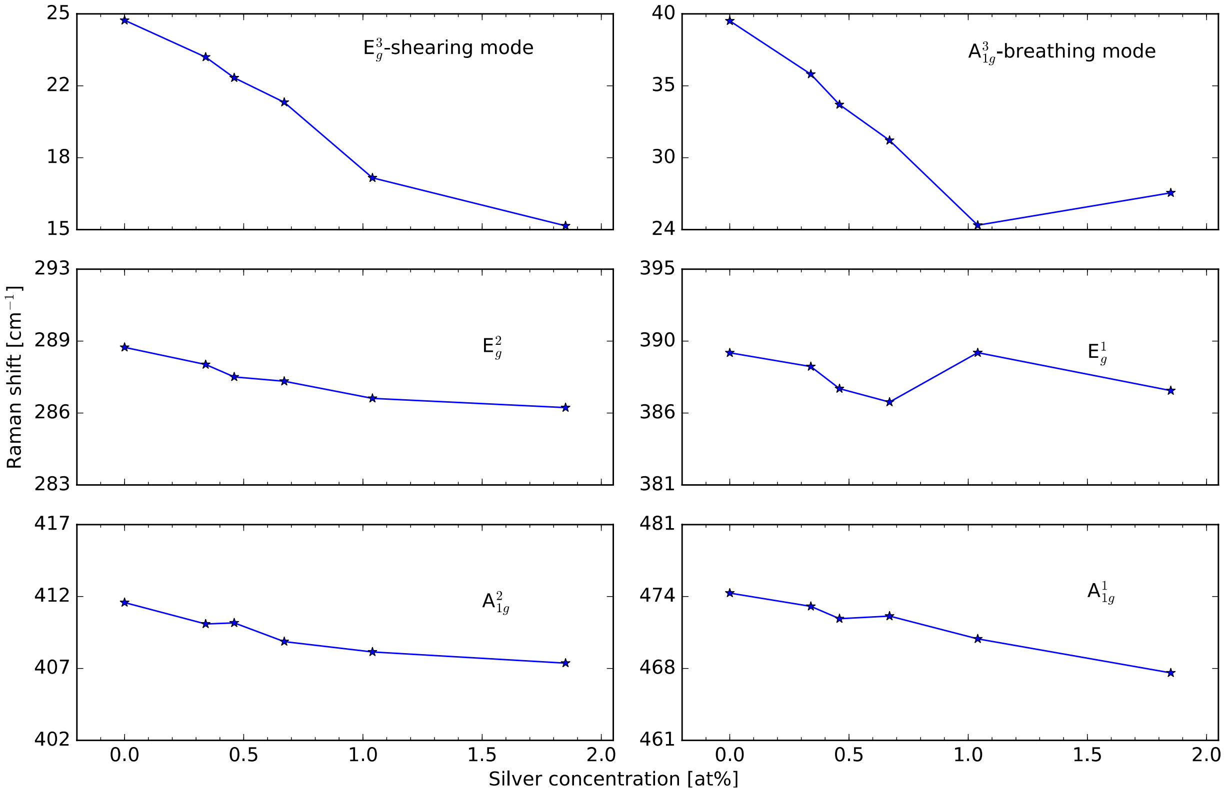

Figure 1: Raman active modes of 2L MoS_2 as a function of silver concentration after intercalation of silver in the van-der-Waals gap of bilayer MoS_2.

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Fluorographene nanosheets used as an interface modification layer of organic phototransistors

Organic field-effect transistors (OFETs) have recently attracted considerable attention due to their potential applications in sensor, memory, smart cards, electronic paper, and display driver circuits. The OFET devices not only exhibit switching functions controlled by electronic fields but also have many other functions, including light emission, light response, signal storage, etc. Organic transistors with light responsive function are called organic phototransistors (OPTs). We fabricated high-performance OPT devices based on bitriisopropylsilylethynyl tetraceno[2,3-b]thiophenes (TIPSEthiotet) or pentacene as a semiconductor layer. Fluorographene (FG) nanosheets were used to modify the interface between an organic semiconductor layer and gate dielectric. The interface modification of FG nanosheets has a large effect on device performance, enhanced photoresponsivity, and increased photocurrent/dark-current ratio. The FG-modified devices based on TIPSEthiotet showed a maximum photoresponsivity of 21.83 A W^{-1} and a photocurrent/dark-current ratio of 1.85×10^6 under white light irradiation. Meanwhile, for the FG-modified OPT device based on pentacene, a high photoresponsivity of 144 A W^{-1} was obtained under white light irradiation with an optical power of as low as 25 μW cm^{-2}.

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Synthesis of Graphene Nanocomposites with Enhanced Thermal Conductivity and Mechanical Strength for Use in Heat Exchanger and Fuel Storage Technology

Stainless steel's high strength and thermal conductivity make it essential in heat exchangers and fuel storage technology. However, steel is corrosive, expensive, and its production is harmful to the environment. Polymer blends with enhanced properties can potentially serve as an alternative to stainless steel, as they have wide applicability due to their flexibility and durability. Graphene is an extremely lightweight, strong, and conductive material. Previous studies that have investigated the use of graphene nanoparticles (GNPs) in plastics to create an alternative to stainless steel in heat exchangers failed to achieve a necessary thermal conductivity coefficient above 2 W/m·K. Polymer blends with GNPs could have the advantage over stainless steel as they would be cheaper, lightweight, recyclable, and non-corrosive. Researchers in this study hypothesized that adding GNPs to immiscible copolymer blends, rather than homopolymer blends, would decrease the percolation threshold of graphene and achieve sufficient thermal conductivity at a lower wt% of GNPs. The GNPs should localize inside one phase while being repelled by the other immiscible polymer. Reducing the amount of graphene used would be optimal for cost-efficiency. Three copolymer compositions of polystyrene/poly(methyl methacrylate) (PS-PMMA), polypropylene/poly(methyl methacrylate) (PP-PMMA), and poly(butylene adipate-co-terephthalate)/poly(lactic acid) (PBAT-PLA) were compared to three homopolymer compositions of PS, PP, and PBAT with increasing concentrations of GNPs. Blends were tested for tensile properties, izod impact strength, and thermal conductivity. The PP-PMMA and PBAT-PLA blends at 25 and 20 wt%, respectively, achieved desirable thermal conductivity coefficients near 2.3 W/m·K while maintaining sufficient strength. The PBAT-PLA blend holds the most potential. Its biodegradability allows for it to be environmentally friendly. It also formed a favorable bicontinuous phase (substantiated by TEM imaging) and proved to have the highest flexibility.

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Monolayer Graphene as Electrode Materials for Electrochemiluminescence Applications

Electrochemiluminescence (ECL) is luminescence phenomenon induced by electrochemical reactions in which species generated at electrodes undergo reactions to light-emitting excited states. The ECL system based on $Ru(bpy)_3^{2+}$ as emitter and tripropylamine (TPrA) as coreactant using platinum electrodes and photomultipliers, has been utilized for commercial applications in clinical analyses. Graphene grown by chemical vapor deposition (CVD) possesses attractive properties such as transparency and chemical stability, as electrode materials for ECL applications. However, there are only a few reports about ECL using CVD graphene.[1, 2] In this work, ECL based on the $Ru(bpy)_3^{2+}$/TPrA system is demonstrated using CVD-grown graphene electrodes with a CMOS image sensor towards realization of portable and high-sensitive ECL bioanalytical devices using graphene. Monolayer graphene films were grown by CVD method on copper foils and transferred onto quartz glass substrates. A gold film was formed on graphene for electrical contact. The ECL measurement cells made of PTFE were constructed as shown in Fig. 1(a). The custom-made CMOS chips (Fig. 1(b)) were placed under the quartz substrate. Visible, orange light was observed at graphene during the ECL measurements (Fig. 1(c)). Figure 2(a) and (b) show faradaic current and ECL emission as a function of time at potentials of 1.5, 2.0 and 2.5 V for 60 sec. The potentials required for ECL emissions were higher against standard redox potentials (E° = 1.20 V for $Ru(bpy)_3^{2+}$ and E° = 0.9 V for TPrA) because of the resistance of the graphene film (R = 0.5~1 kΩ/□) in which applied voltage drops. Consequently, at lower potential, ECL is obtained only by TPrA oxidation, while at higher potential, the ECL process involves two electrochemical reactions (Fig. 2(c)), which result in different time-dependence in the ECL intensity. These results suggest that, with proper cell design, CVD graphene and CMOS image sensor will be excellent combination for portable ECL analytical devices.

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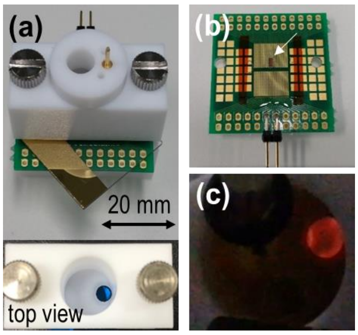

Figure 1: Images of (a) cell for ECL measurement, (b) CMOS chip and (c) ECL at graphene electrode

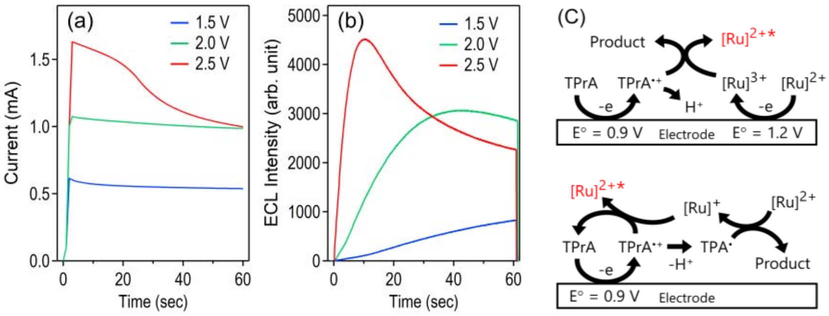

Figure 2: (a) Faradaic Current and (b) ECL emission as a function of time at graphene electrode in a solution of 5 mM $Ru(bpy)_3Cl_2$, 0.5 M TPrA and 0.1 M phosphate buffer (pH 7.0). (c) ECL mechanisms for $Ru(bpy)_3^{2+}$/TPrA.

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Study of correlation between electrochemical properties and density of states of graphene using field effect transistors

Graphene, a carbon material of a single atomic layer, has attracted attention for electrochemical applications such as batteries and sensors due to its high electrical conductivity, chemical and mechanical stability and high specific surface area. The electrochemical properties of graphene are determined by various factors. The density of states (DOS) nearby Fermi energy E_F has major effects on the electron transfer behaver in carbon-related materials that have lower DOS compared with metals.[1] However, general methods to change DOS of carbon materials influence other factors than DOS such as surface structures and impurity concentrations. We fabricated a field effect transistor (FET) with a graphene channel in order to investigate a correlation between electrochemical properties and DOS of graphene. Monolayer graphene films were grown by chemical vapor deposition (CVD) on copper foils and transferred onto SiO_2 (300 nm) /Si substrates. A back gate FET with Au electrodes was fabricated. The electrochemical properties of CVD monolayer-graphene films were evaluated by cyclic voltammetry (CV) measurements in 0.1 M potassium chloride solutions containing 1 mM hexa-ammine-ruthenium(III). The CV measurements were conducted under applying back gate voltages V_{bg} to modulate DOS $\rho\ (E)$ (Figure 1). The reaction rate constants k^0 were estimated as a function of redox peak separations ΔE_p from cyclic voltammograms.[2] As shown in Figure 2, the k^0 values from the CV measurements increased when differences between V_{bg} and the Dirac point became larger. In other words, E_F located at energy levels where $\rho\ (E)$ was higher. Thus, the heterogeneous electron transfer rate (HETR) at graphene surfaces became higher when $\rho\ (E)$ nearby E_F became higher. This work, which combined research fields of electrochemistry and electronics, allowed us to reveal the correlation between HETR and DOS of graphene experimentally without changing parameters other than DOS. These results indicate that electrochemical properties of graphene strongly depend on DOS.

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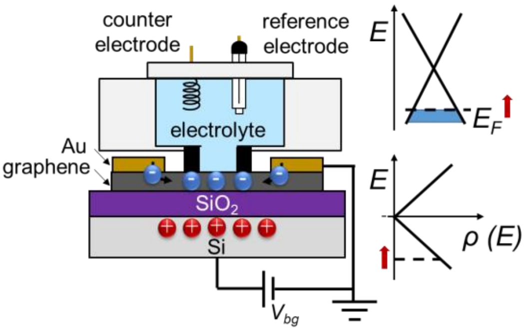

Figure 1: Schematics of cyclic voltammetry measurements under applying a back gate voltage and modulation of DOS.

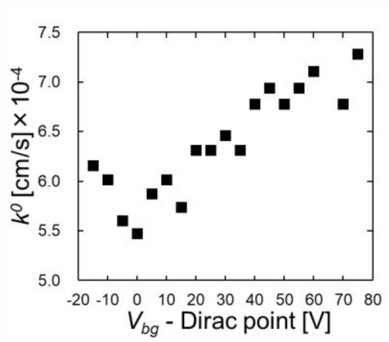

Figure 2: k^0 values as a function of V_{bg} – Dirac point.

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First principles simulation of local response in transition metal dichalcogenides under electron irradiation

Electron beam irradiation by transmission electron microscopy (TEM) is a common and effective method for post-synthesis defect engineering in two-dimensional transition metal dichalcogenides (TMDs)[1]–[3]. Combining density functional theory (DFT) with relativistic scattering theory, we simulate the generation of such defects in monolayer group-VI TMDs, MoS_2, WS_2, $MoSe_2$, and WSe_2, focusing on two fundamental TEM-induced atomic displacement processes: chalcogen sputtering and vacancy migration. Our calculations show that the activation energies of chalcogen sputtering depend primarily on the chalcogen species, and are smaller for TMDs containing Se. Meanwhile, vacancy migration activation energies hinge on the transition metal species, being smaller in TMDs containing Mo. Incorporating these energies into a relativistic, temperature-dependent cross section, we predict that, with appropriate TEM energies and temperatures, one can induce migrations in all four TMDs without simultaneously producing vacancies at a significant rate. This can allow for controlled manipulation of the TMD crystal for targeted functionality, without the risk of substantial collateral damage.

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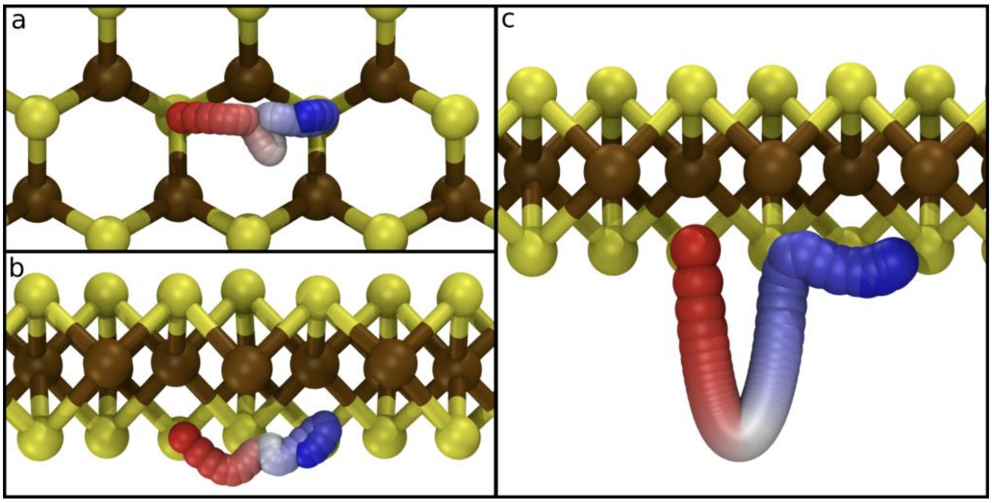

Figure 1: The collision of an incident electron induces the migration of S in MoS_2. (a) and (b) Resulting S trajectory calculated using DFT-based molecular dynamics when 4.10 eV is transferred from the incident electron to the S nucleus

under TEM irradiation of 105 keV. The color gradient from red to blue indicates the time evolution through 300 fs. (c) S trajectory resulting from a more direct collision, with an energy transfer of 7.86 eV. The trajectory runs for 680 fs.

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Controlled CVD growth of graphene and it electronic properties

Graphene is a perfect two-dimensional atomic crystal. It has attracted considerable attention due to its unusual mechanical, optical, and electronic properties. Chemical vapor deposition (CVD) is an effective way to prepare large-area and high-quality graphene becaunse of its ultra-low cost, high controllability, and high scalability. In order to enhance electronic properties of graphene-based devices, we fabricated graphene single crystals with a variety of shapes using CVD method. The twelve-pointed graphene grains were controllably synthesized. Self-aligned single-crystal graphene grains were precisely controllable grown on liquid Cu surface by ambient pressure CVD. Meanwhile, we used an in situ etching method to fabricate large-scale graphene arrays with control over the size, shape, and location. On the other hand, hierarchical graphene architectures with a layer-stacking growth were also fabricated by CVD method. The growth mechanism of graphene and it electrical properties were investigated.

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Ion transport and sensing in porous graphene

Selective ion transport is a hallmark of biological ion channel behavior but is a major challenge to engineer into artificial membranes. We examine ion transport through graphene nanopores and found that, when the size of the pore is comparable to the size of the hydrated ions, the nanopore demonstrates strong nonlinear I-V behavior and has weak selectivity for K^+ over Cl^- ions [1]. Further, bare graphene nanopores yield measurable ion selectivity that varies over two orders of magnitude simply by changing the pore radius and number of graphene layers due to a enhanced water loss in the second hydration layer [2]. Measurement of selectivity and activation barriers from both first and second hydration layer barriers will help elucidate the behavior of biological ion channels. Moreover, for separation of ions from water, one can exchange longer, larger radius pores for shorter, smaller radius pores, giving a practical method for maintaining exclusion efficiency while enhancing other properties (e.g., water throughput) for filtration/desalination applications.

Additionally, we develop the first scaling theory for ion transport that enables all-atom molecular dynamic (MD) simulations to capture the access resistance, i.e., how the bulk electrolyte converges to the pore(s) [3,4]. This resistance is contextual, it depends on the presence of functional groups/charges and fluctuations, as well as the (effective) constriction geometry/dimensions. Addressing the context generically requires all-atom simulations, but this demands enormous resources due to the algebraically decaying nature of convergence with respect to the bulk size. Our finite-size scaling analysis – reminiscent of the treatment of critical phenomena – makes the access resistance accessible in MD. It suggests that there is a “golden aspect ratio" for the simulation that yields the infinite system result with a finite system. We employ this approach to resolve the experimental and theoretical discrepancies in the radius dependence of graphene nanopore resistance.

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Figures

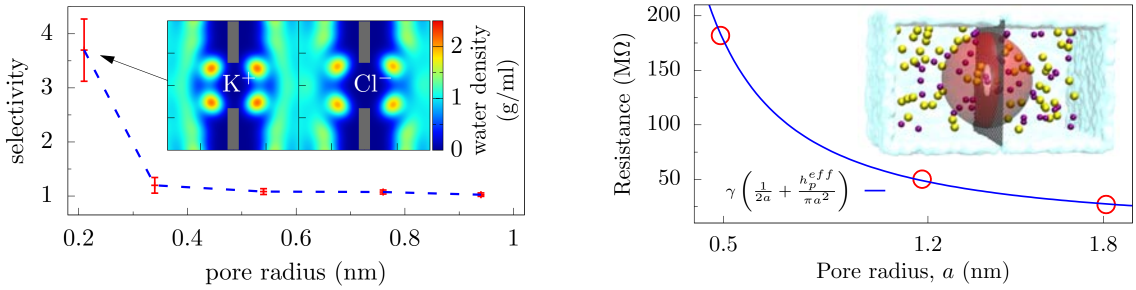

Figure 1: (Left panel) Selectivity (plot) and ion hydration (inset) in sub-nanoscale monolayer graphene pores. When the pore radius reaches the inner hydration layer, selectivity is observed do to partial removal of water molecules. (Right panel) Resistance versus pore radius (plot) and graphene membrane (inset). Using a novel scaling approach, we show that the radius dependence follows the continuum Maxwell-Hall form, which has both pore and access contributions.

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