# GRAPHENE FOR US

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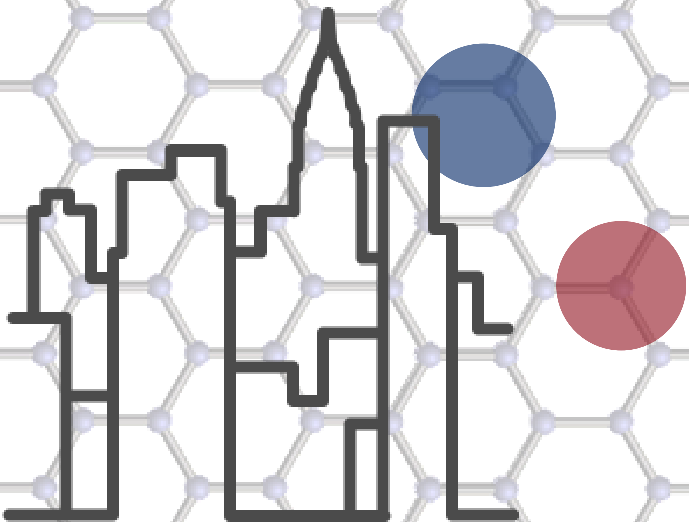

# ABSTRACTS BOOK

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# FOREWORD

On behalf of the Organising Committee we take great pleasure in welcoming you to New York for the second edition of the **GrapheneforUS** 2019 International Conference.

A plenary session and thematic workshops with internationally renowned speakers will feature current and future "Graphene and 2D Materials" developments.

**GrapheneforUS** 2019 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 and 2DM commercialization.

We truly hope that **GrapheneforUS** 2019 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), Elsevier (FlatChem), Millipore (Sigma-Aldrich), The National Electrical Manufacturers Association (NEMA), Columbia University, The Graduate Center and The Advanced Science Research Center (ASRC) of City University of New York.

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 2020.

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**Eva Y. Andrei**
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# Poke, twist, buckle: strategies for band structure engineering in 2D materials

Historically materials discovery has been the result of serendipity or painstaking exploration of a large phase space of chemically synthesized compounds. A new era of materials started with the breakthrough isolation of the first free standing 2D material, graphene, followed by dozens of new 2D materials since. The distinctive characteristic of these layers is that, with all the atoms residing at the surface, it is possible to access and manipulate their properties with non-chemical "knobs" such as strain, twist, electric and magnetic fields. I will discuss experiments that utilize such knobs to transform the electronic structure of graphene: inducing magnetism and Kondo screening by removing single Carbon atoms; generating flat bands and pseudo-magnetic fields by twist and strain.

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# MXene, Graphene or Their Hybrid? A Guide to Finding the Best Material for the Job

Two-dimensional (2D) materials with a thickness of a few nanometers or less can be used as single sheets, or as building blocks, due to their unique properties and ability to assemble into a variety of structures. Graphene is the best-known example, but several other elemental 2D materials (silicene, borophene, etc.) have been discovered. Numerous compounds, ranging from clays to boron nitride (BN) and transition metal dichalcogenides, have been produced as 2D sheets. By combining various 2D materials, unique combinations of properties can be achieved which are not available in any bulk material. The family of 2D transition metal carbides and nitrides (MXenes) has been expanding rapidly since the discovery of $Ti_3C_2$ in 2011 [1,2]. Approximately 30 different MXenes have been synthesized, and the structure and properties of numerous other MXenes have been predicted using density functional theory (DFT) calculations [3]. Moreover, the availability of solid solutions on M and X sites, control of surface terminations, and the discovery of ordered Double-M MXenes (e.g., $Mo_2TiC_2$) offer the potential for synthesis of dozens of new distinct structures. The versatile chemistry of the MXene family renders their properties tunable for a large variety of applications. Oxygen- or hydroxyl-terminated MXenes, such as $Ti_3C_2O_2$, have been shown to have redox capable transition metals layers on the surface and offer a combination of high electronic conductivity with hydrophilicity, as well as fast ionic transport. This, among many other advantageous properties, makes the material family promising candidates for energy storage and related electrochemical applications, but applications in optoelectronics, plasmonics, electromagnetic interference shielding, electrocatalysis, medicine, sensors, water purification/ desalination and other fields are equally exciting [4,5]. There are many applications in which MXenes outperform graphene (pseudocapacitors, EMI shielding, antennas, etc.), in some other areas graphene may still doing a better job, or offer a less expensive solution (rGO). There are also situations when a MXene-rGO hybrid can perform better than those materials alone [6]. This presentation will provide a comparison of properties and potential applications of MXenes and their hybrids [7] in comparison to graphene based materials.

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# Atomic reconstruction at van der Waals interface in twisted 2D Materials

Control of the interlayer twist of van der Waals (vdW) interfaces has been widely used to engineer an artificial 2-dimensional (2D) electronic systems by the formation of a moiré superlattice. Many exotic physical phenomena occur associated with the incommensurability of the moiré superstructures where the wealth of the nontrivial topology of electronic band structures plays a key role to create exotic physical phenomena. In this presentation, we will discuss the engineered atomic scale reconstruction at twisted vdW interfaces using electron microscopy, optical spectroscopy, and electrical transport. We then will discuss emerging electronic and optoelectronic physics in the vdW interface between homojunctions.

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# Manipulating light flow with 2D materials plasmons

Recent years have observed a plethora of strong dipole type polaritonic excitations in 2D materials owing to the reduced screening. These polaritons can be sustained as electromagnetic modes at the interface between a positive and negative permittivity material. In the case of the plasmon-polaritons (e.g. in semi-metallic graphene), the negative permittivity is provided by the coherent oscillations of the free carriers. For exciton-polaritons (e.g. in semiconducting transition metal dichalcogenides, TMD) and phonon-polaritons (e.g. in diatomic hexagonal boron nitride, hBN), it is associated with their resonant optical absorption, resulting from a highly dispersive permittivity. These optical resonances can also result in a negative permittivity, albeit over a narrow spectral window.

In this talk, I will discuss our recent efforts in understanding plasmons behavior in 2D materials and using them to control the flow of light both in the far- and near-field. The general constitutive materials response of 2D materials, in conjunction with metasurface approaches, can potentially enable arbitrary control of phase, amplitude, polarization of light. The flow of light within the 2D materials can also exhibit rich transport behavior, such as hyperbolic rays, non-reciprocal chiral propagation, time reversal of waves and coupling of light spin to induce one-way propagation.

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# Graphene-based biosensors for diagnostics

Graphene oxide (GO) and graphene quantum dots (GQDs) display advantageous characteristics with interest for building innovative biosensing platforms and even smart devices such as nano/micromotors for a myriad of uses including sensing. Quenching of the fluorescence induced by GO or photoluminescence of GQDs can easily operate in synergy with various other nanomaterials and platforms opening the way to several unprecedented biosensing strategies and unique nanomotor technologies. Taking advantage of GO, GQDs we are developing simple, sensitive, selective and rapid biosensing platforms that include: a) GO – based microarray & laterals flow technologies taking advantages of high quenching efficiency of GO. A “turn ON by a pathogen” device will be shown as a highly sensitive detection system using plastics or paper/nanopaper substrates; b) GQDs–based sensors for contaminants detection based on the use of multifunctional composite materials that enable rapid, simple and sensitive platforms in connection to smartphone; c) A water activated GO transfer technology using wax printed membranes for fast patterning of a touch sensitive device with interest for electronic devices including sensing as well as for a cost-efficient nanomotor building technology for several applications. This work is supported by EU (Graphene Flagship), CERCA Programme / Generalitat de Catalunya.

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# The Graphene Revolution: *From Transistors to Synthetic Cells*

Two-dimensional materials enjoy a vast array of unique properties, from extreme thinness and mechanical flexibility to amazing quantum physics. These properties will have a tremendous impact in future electronics by enabling large area, high speed, ubiquitous sensing and processing. This talk will review some of the recent progress on the use of graphene and other two-dimensional materials in these applications. In particular, it will discuss state-of-the-art $MoS_2$ and $WSe_2$ transistors for ultra-low power CMOS circuits [1-2], graphene-based chemical [3] and infrared sensors [4], large area devices for energy harvesting [5], and a new generation of micro-systems that probe the limits of electronics.

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# Wafer-Scale Synthesis of Single Crystal TMD Monolayers

Monolayer transition metal dichalcogenides (TMDs, $MoS_2$, $WSe_2$, etc.) possess a range of intriguing optical and electronic properties including direct bandgap, large exciton binding energies, valley polarization, etc. Current research is typically carried out using flakes exfoliated from bulk crystals or grown by powder vapor transport which are challenging to scale to large areas. Our research is aimed at the development of an epitaxial growth technology for layered dichalcogenides, similar to that which exists for III-Vs and other compound semiconductors, based on gas source chemical vapor deposition (CVD). This approach provides excellent control of the precursor partial pressures to achieve monolayer growth over large area wafers. Our studies have focused on the epitaxial growth of binary TMD monolayers including $MoS_2$, $WS_2$, $WSe_2$ and $MoSe_2$ using metal hexacarbonyl and hydride chalcogen precursors to deposit on 2" sapphire substrates. A multi-step precursor modulation growth method was developed to control nucleation density and the lateral growth rate of monolayer domains on the substrate [1]. Using this approach, uniform, coalesced monolayer and few-layer TMD films were obtained on 2" sapphire substrates at growth rates on the order of ~1 monolayer/hour (Fig. 1). In-plane X-ray diffraction demonstrates that the films are epitaxially oriented with respect to the sapphire with minimal rotational misorientation of domains within the basal plane [2]. Post-growth dark-field transmission electron microscopy carried out on monolayers removed from the sapphire by a wet transfer method reveals that the monolayer films are largely single crystal (65-95% coverage) but contain inversion domains that result from coalescence of $0^o$ and $180^o$ misoriented islands. This research is part of the 2D Crystal Consortium (2DCC) – an NSF-supported Materials Innovation Platform national user facility focused on advancing the synthesis and applications of 2D layered chalcogenide films and crystals. Further details on the 2DCC facilities, in-house research activities and user program will also be provided.

The authors acknowledge financial support of the U.S. National Science Foundation through the Penn State 2DCC under NSF cooperative agreement DMR-1539916 and EFRI 2-DARE Grant EFRI-1433378.

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## Figures

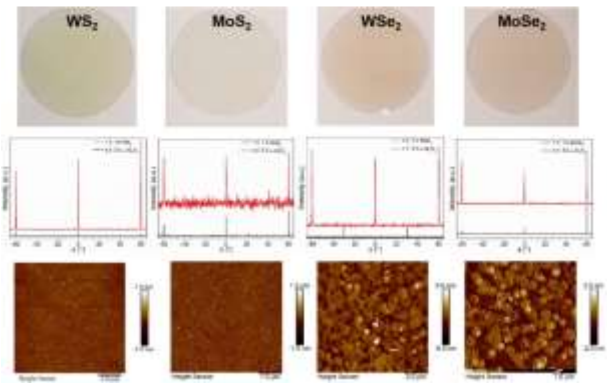


**Figure 1:** Epitaxial TMD films grown on 2" sapphire by gas source CVD

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# The Next Challenge for Graphene

Carbon is a very versatile atom which participates in the structure of different types of organic molecules, carbon nanotubes, single walled and multi-walled, Fullerenes, graphene, graphite, diamond and multiple inorganic compounds. If we restrict our carbon atoms to forming crystals with sp2-like bonding, such as graphene What is next? mathematics provides the answer if we consider that graphene is made of a flat surface embedded in a 3-D space. This surface can be bent to form Fullerenes, closed graphenic molecules which arrange themselves to form crystals, but also the surface can be bent to generate periodic systems named Schwarzites. Schwarzites, are the hyperbolic cousins of graphene and so far have remained elusive despite efforts to synthesize them. In this talk the experimental attempts to synthesize Schwarzites will be reviewed as well as the theoretical results obtained from different structures will be provided. Schwarzites are formed by sp2 carbon atoms in which rings with more than six carbon atoms are introduced, thus introducing the negative Gaussian curvature required for periodicity (See figure 1). Energy minimizations and phonon calculations show that these hypothetical structures are stable. The challenges to generate the first Schwarzites will be discussed.

## Figures

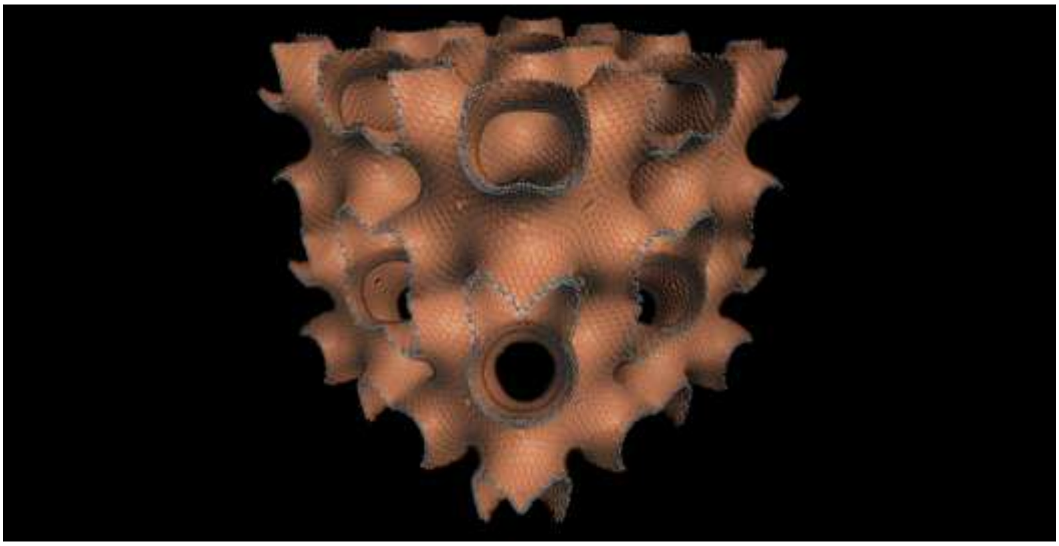

**Figure 1: Several cells of the IWP Schwarzite**

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# 2D Materials for Nanoelectronics: Prospects and Materials Integration Challenges

The size reduction and economics of integrated circuits captured since the 1960's in the form of Moore's Law is under serious challenge. Current industry roadmaps reveal that physical limitations include reaching aspects associated with truly atomic dimensions, and the cost of manufacturing is increasing such that only 2 or 3 companies can afford leading edge capabilities. To address some of the "conventions;" material's physical limitations, "2D materials" such as graphene, phosphorene, h-BN, and transition metal dichalcogenides have captured the imagination of the research community for advanced applications in nanoelectronics, optoelectronics, and other applications. [1] Among 2D materials "beyond graphene," some exhibit semiconducting behavior, such as transition-metal dichalcogenides (TMDs), and present useful bandgap properties for applications even at the single atomic layer level. Examples include "$MX_2$", where M = Mo, W, Sn, Hf, Zr and X = S, Se and Te.

In addition to the potentially useful bandgaps at the monolayer thickness scale, the atomically thin layers should enable thorough electric field penetration through the channel, thus enabling superior electrostatic control. Further, with such thin layers, the integration with suitable gate dielectrics can result in a mobility enhancement. Applications "beyond CMOS" are also under exploration. From an interface perspective, the ideal TMD material may ne expected to have a dearth of dangling bonds on the surface/interface, resulting in low interface state densities which are essential for efficient carrier transport. The ideal TMD materials have much appeal, but the reality of significant densities of defects and impurities will surely compromise the intrinsic performance of such device technologies. This presentation will examine the state-of-the-art of these materials in view of our research on semiconductor device applications, and the challenges and opportunities they present for electronic and optoelectronic applications. [2-4]

This research was supported in part by the Semiconductor Research Corporation (SRC) NEWLIMITS Center and NIST through award number 70NANB17H041 and the Erik Jonsson Distinguished Chair at the University of Texas at Dallas.

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# Moiré-excitons in $MoSe_2/WSe_2$ heterobilayers

The creation of moiré patterns in crystalline solids is a powerful approach to manipulate their electronic properties, which are fundamentally influenced by periodic potential landscapes. In two-dimensional (2D) materials, a moiré pattern with a superlattice potential can form by vertically stacking two layered materials with a twist and/or finite lattice constant difference. This unique approach has led to emergent electronic phenomena, including the fractal quantum Hall effect [1–3], tunable Mott insulators [4, 5], and unconventional superconductivity [6, 7]. Furthermore, theory predicts intriguing effects on optical excitations by a moiré potential in 2D valley semiconductors [8–10], but these signatures have yet to be experimentally detected. In this talk, I will report our experimental evidence of interlayer valley excitons trapped in a moiré potential in $MoSe_2/WSe_2$ heterobilayers. We observe quantum-dot-like photoluminescence of interlayer excitons with the inheritance of unique valley-contrasting properties from the heterobilayer bulk. Twist angle dependent studies further support our observation of moiré excitons. Our results open opportunities for 2D moiré optics with twist angle as a unique control knob.

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# INVITED SPEAKERS

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# National Graphene Action Plan: Progress and commercialization opportunities.

The National Graphene Action Plan 2020 is a five year plan led by NanoMalaysia in enhancing downstream application of graphene within five key focus sectors namely lithium ion battery/ultracapacitor, plastic, rubber, conductive ink and nanofluids which are well aligned in supporting the growth of Malaysia's economy. It is a triple helix program which involves NanoMalaysia, industry and researcher/academia in innovating with graphene. More than 40 projects has been executed since its launch in July 2014 with 14 patents filed. The program has successfully developed 10 graphene-based products and technology which are readily available for commercialization and licensing. Success stories includes graphene-based back up storage for solar and uninterrupted power supply (UPS) application, conductive inks for RFID application, concrete, rubber master batch and emulsion solution. In 2019, an addition of twelve projects were activated with extended sectors supporting the Internet-of-Things & 4th industrial revolution.

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# Synthesis and Characterization of Transition Metal Dichalcogenides

Atomically thin semiconducting transition metal dichalcogenides (TMDs) have promise for a wide range of applications in electronics [1] and optoelectronics [2], and host many novel physical phenomena [3]. However, crystalline disorder obscures intrinsic behavior and limits achievable functionality [4], so that continued progress requires characterization and minimization of crystalline disorder, and correlation of this disorder to macroscopic properties. We characterized intrinsic point defects found in single-crystal TMDs using scanning tunneling microscopy (STM) and scanning transmission electron microscopy (STEM). Crystals grown by chemical vapor transport (CVT), the most commonly utilized approach, show high defect density. We have employed an alternative technique, growing crystals of $MoSe_2$ and $WSe_2$ by a self-flux method in which crystals are grown directly from the molten phase. Under optimized synthetic conditions, the flux-grown crystals show reduced defect concentration by 2-3 orders of magnitude. Monolayers extracted from these high-quality crystals show enhanced electronic mobility, enabling detailed mapping of the Landau level spectrum in applied magnetic fields. Low-temperature photoluminescence spectra of these monolayers show greatly enhanced quantum yield and appearance of a large family of multi-exciton states.

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## Figures

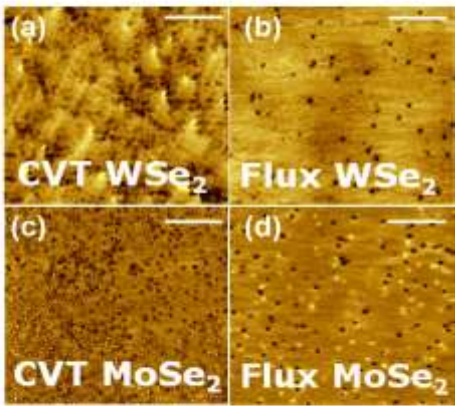


**Figure 1:** STM topographic images of (a) CVT $WSe_2$ (b) flux-grown $WSe_2$ (c) CVT $WSe_2$ (d) flux-grown $MoSe_2$

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# Graphene Flagship: Standardization and Validation

The Graphene Flagship is a research project founded by the EU commission targeting to bring graphene related technologies from research to industry. It coordinates over 150 academic and industrial research groups and more than 60 associated members in 23 countries. From the beginning the Graphene Flagship was active in standardization by establishing a liaison of the Graphene Flagship Standardization Committee (GFSC) with the IEC technical committee 113 (IEC/TC 113) “Nanotechnology for electrotechnical products and systems”. Embedded in the international standardization community scientists of the Graphene Flagship are now leading a number of standardization projects within IEC/TC 113 ensuring that the activities of the GFSC are always according to the IEC strategy.

This talk will provide an overview on the IEC graphene standardization landscape and the contribution of the GFSC to the overall concept. Especially it will be pointed out how standardization supports validation and certification as a pre-condition for the commercial success of the graphene industry.

### Figures

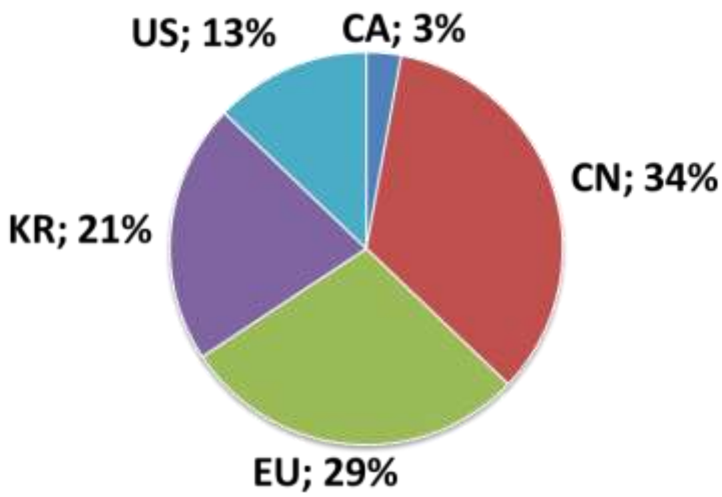


**Figure 1:** Leadership of standardization projects (worldwide)

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# Graphene: Growth Peculiarities on Liquid Substrate and Some Unique Applications

Growth of high qulity and large area graphene or control of its surface topography still remain challanging. The origin of surface ripples of graphene could be associated with the problem of thermodynamic stability of two dimensional membranes, presence of grain boundaries on the substrate, and the difference between the thermal expansion coefficients of graphene and a substrate. Recently the exploitation of graphene growth on liqufied substrate became one of the promising trends to address this challenge. However, we have observed peculiar topographic patterns on graphene surface. In-situ SEM studies on liquified Cu substrate suggest that these patterns originate from the dynamic instabilities caused by solutocapillary forces followed by non equilibrium solidification. These non-equilibrium processes can be well understood based on Mullins-Sekerka and Benard-Marangoni instabilities in diluted binary alloys. The model offers the control parameters over the grown graphene quality. Some unique applications of graphene will be presented too.

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# Graphene Standards – Building a Bigger Business

Electrotechnical products, from the standpoint of their individual components, function as a system. For instance, today's smart phones offer unprecedented functionality in our everyday lives, but this is made possible only by the integrating of different technologies in a system, like the software, the luminescent materials, the touch screen and the audio capabilities. The only way this happens on a mass production scale is through standardization. Standards are at the core of not only every end use product, but to each of the components of that product because these components must perform adequately to work together.

This presentation will explain in general the importance of standards for business and will serve as the introduction to a series of talks that will be a part of the NEMA-sponsored graphene standardization workshop set up for this year's GrapheneForUs Expo.

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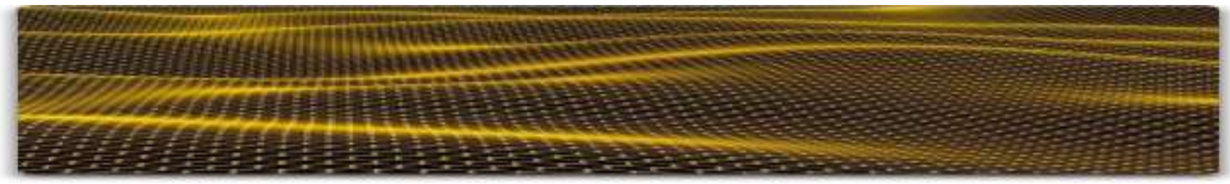

**Figure 1:** Carbon sheet one atom thick

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# Enabling Cutting-Edge Research through Innovative Materials

At MilliporeSigma, we strive to be the trustworthy partner and one-stop source for your research and development. Through academic collaborations and internal development, we are launching innovative materials to accelerate the pace of energy and electronics research. As an example, we partnered with Northwestern University to introduce ready-to-use 2D material inks to the broader academic community. These inks contain well-characterized 2D nanomaterials, including few-layered graphene, boron nitride and transition metal dichalcogenide, which could accelerate device fabrication process through scalable additive manufacturing methods like aerosol, inkjet, gravure, screen printing and 3D printing [1-4]. A variety of applications have since been demonstrated with these materials including printed electronics [5, 6], printed micro-supercapacitors [7], lithium-ion batterie electrodes [8], and photodetectors [9].

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## Figures

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# $PdSe_2$: a Pentagonal Layered Material Bridging the Gap Between 2D and 3D Materials

$PdSe_2$ is a new layered material with an in-plane pentagonal network and stronger-than-vdW interlayer coupling. It offers great trade-off between carrier mobility, band gap, and air stability for nanoelectronics [1]. Because of its unique atomic structure and strong interlayer coupling, it behaves like 2.5D material and many of its properties are different from those of commonly known 2D materials, such as graphene and $MoS_2$. Here I will highlight how first-principles modeling/simulation guided experiments to explore its structural, electronic, and vibrational properties. Because of strong interlayer coupling, its electronic band gap varies significantly from 1.3 eV (monolayer) to 0.06 eV (bulk), based on calculations and measurements [1]. For 2D graphene and $MoS_2$ that have weak interlayer interactions, the layers are quasi-rigid in low-frequency interlayer vibrations, which can be described by a linear chain model (LCM); however, in $PdSe_2$ the layers are no longer quasi-rigid, according to our Raman scattering calculations and measurements. Therefore, the thickness dependence of the interlayer Raman modes' frequencies in $PdSe_2$ deviates significantly from the LCM. A revised LCM was developed to account for the layer non-rigidity [2]. Finally, according to our nudged elastic band calculations, the pentagonal structure and strong interlayer coupling lead to low diffusion barriers for defects, and hence both intralayer and interlayer hopping of defects can occur relatively easily in $PdSe_2$ compared to $MoS_2$, as observed by scanning tunneling microscope [3]. Our works on $PdSe_2$ pave the road for the understanding of 2D materials featuring strong and beyond-vdW interlayer interactions.

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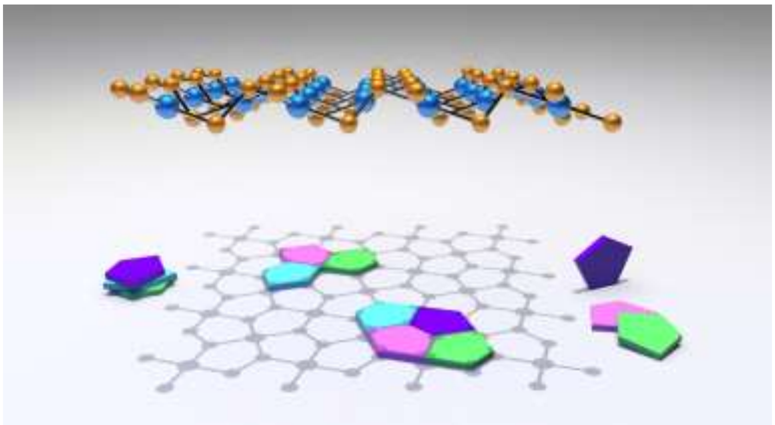

**Figure 1:** $PdSe_2$, a novel layered material with atoms that tile in the famous Cairo pentagonal pattern. It behaves like a 2.5D material due to the unique atomic structure and stronger-than-vdW interlayer coupling.

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# 2D Metallic MXenes: Chemical Vapor Deposition and Structural Characterization

MXenes, a group of emerging two-dimensional (2D) transition metal carbides (TMCs) and nitrides (TMNs), are receiving growing interest given their excellent stability and intriguing properties, notably high conductivity.[1,2] Progress has been made in the synthesis of MXenes via selective etching of the "A" layer from their bulk MAX phases, yet the 2D sheets produced in this manner suffer from small lateral size domains below 10 $\mu$m.[3] This type of MXenes shows great potential in energy storage and electrochemical catalysis,[4,5] but has limited applications in the field of electronic and optoelectronic devices. Developing method for large-area, continuous and crystalline MXenes, like what has been achieved on chemical vapor deposition (CVD) grown graphene and several 2D transition metal dichalcogenides (TMDs), is crucial to extend their applications, and enhance the functionality of the 2D materials family. In this work, I will present our recent work on CVD of ultrathin molybdenum carbide ($Mo_2C$), one of the widely studied MXenes. High-quality $\alpha$-$Mo_2C$ sheets with nanometer thickness are obtained.[6] Moreover, through a systematic Raman spectroscopy study on the synthesized $\alpha$-$Mo_2C$ sheets with diverse shapes including hexagonal, triangular, pentagonal and truncated trapzoid morphologies, We realized that most of the $\alpha$-$Mo_2C$ sheets contain multiple domains and the c-axes of neighboring domains tend to form a 60° or 120° angle (Figure 1), due to the weak Mo-C bonds in this interstitial carbide and the low formation energy of the carbon chains along three equivalent directions. In addition, to overcome the challenges of conventional CVD method in obtaining diverse MXenes and their heterostructures with other 2D materials, we propose a chemical conversion strategy. A variety of MXenes are obtained successfully using this novel strategy (unpublished).

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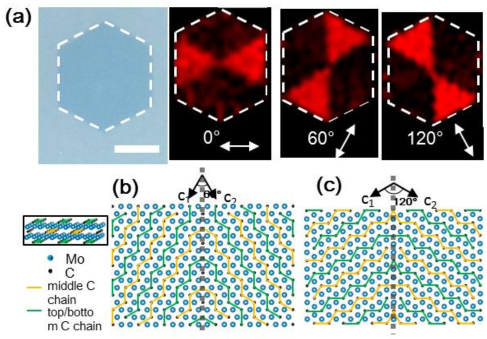


**Figure 1.** (a) Optical images and corresponding Raman maps of the intensity for a hexagonal $\alpha$-$Mo_2C$ flake under incident laser polarization at 0°, 60° and 120°. (b-c) Schematics of the atomic structure at the interface between two adjacent domains with a 60°-boundary (a) and 120° boundary (b) in one layer of $\alpha$-$Mo_2C$.

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# Uniform doping of graphene close to the Dirac point by polymer-assisted assembly of molecular dopants

Tuning the charge carrier density of two-dimensional (2D) materials by incorporating dopnats into the crystal lattice is a challenging task. An attractive alternative is the surface transfer doping by adsorption of molecules on 2D crystals, which can lead to ordered molecular arrays. However, such systems, demonstrated in ultra-high vacuum conditions (UHV), are often unstable in ambient conditions. Here we show that air- stable doping of epitaxial graphene on SiC-achieved by spin-coating deposition of 2,3,5,6-tetrafluoro-tetracyano-quino-dimethane (F4TCNQ) incorporated in poly(methyl-methacrylate)-proceeds via the spontaneous accumulation of dopants at the graphene-polymer interface and by the formation of a charge-transfer complex that yields low-disorder, charge- neutral, large-area graphene with carrier mobilities ~70,000cm2V-1s-1 at cryogenic temperatures. The assembly of dopnats on 2D materials assisted by a polymer matrix, demonstrated by spin-coating wafer-scale substrates in ambient conditions, opens up a scalable technological route toward expanding the functionality of 2D materials.
This work was published in Nature Communication 9, 3956 (2018) by Hans He, et. al., as a result of an international cooperation between the Chalmers University of Technology, Sweden and the Seoul National University, Korea

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# Spectroscopy of Twisted Bilayer Graphene

The electronic properties of heterostructures of atomically-thin van der Waals (vdW) crystals can be modified substantially by Moiré superlattice potentials arising from an interlayer twist between crystals. Moiré-tuning of the band structure has led to the recent discovery of superconductivity and correlated insulating5 phases in twisted bilayer graphene (TBLG) near the so-called "magic angle" of ~1.1°, with a phase diagram reminiscent of high Tc superconductors. However, lack of detailed understanding of the electronic spectrum and the atomic-scale influence of the Moiré pattern has so far precluded a coherent theoretical understanding of the correlated states. I will describe the atomic-scale structural and electronic properties of TBLG near the magic angle using scanning tunneling microscopy and spectroscopy (STM/STS). We observe two distinct van Hove singularities (vHs) in the LDOS which decrease in separation monotonically through 1.1° with the bandwidth (t) of each vHs minimized near the magic angle. When doped near half Moiré band filling, the conduction vHs shifts to the fermi level and an additional correlation-induced gap splits the vHs with a maximum size of 7.5 meV. We also find that three-fold (C3) rotational symmetry of the LDOS is broken in doped TBLG with a maximum symmetry breaking observed for states near the Fermi level, suggestive of nematic electronic interactions. The main features of our doping and angle dependent spectroscopy are captured by a tight-binding model with on-site (U) and nearest neighbor Coulomb interactions. We find that the ratio U/t is of order unity, indicating that electron correlations are significant in magic angle TBLG. Superconductivity arises in TBLG at angles where the ratio U/t, rather than the density of states, is largest, suggesting a pairing mechanism based on electron-electron interactions.

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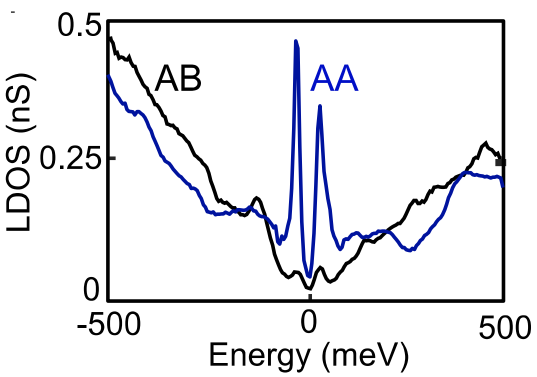


**Figure 1:** STM spectrum of magic-angle graphene.

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# Graphene composites for energy storage and sensors

Graphene has been widely used in many fields due to its superior electrical conductivity, excellent mechanical flexibility, and high thermal and chemical stability, [1]. The extraordinary properties of graphene including high (ballistic) charge mobility and the potential for n- or p-doping can provide high conductivity materials depending on their structural quality. Multiple applications including as materials for gas and energy storage could be within reach if irreversible aggregation, or re-stacking, of graphene nanosheets could be inhibited. Furthermore, its chemical inertness makes it difficult to attach gas molecules on the surface of graphene directly and interfacing the graphene surface with other nanoparticles is a possible solution [2,3]. In our recent work, graphene oxide was enlisted as a substrate to induce nanosized MOFs. By growth nanosized Cu-BTC on the surface of graphene, the GO/Cu-BTC composite shows improved hydrogen storage and $CO_2$ capture performance.The composite material exhibited about a 30% increase in $CO_2$ and $H_2$ storage capacity (from 6.39 mmolg$^{-1}$ of Cu-BTC to 8.26 mmol g$^{-1}$ of CG-9 at 273 K and 1 atm for CO2; from 2.81 wt% of Cu-BTC to 3.58 wt% of CG-9 at 77 K and 42 atm for $H_2$) [4]. By doping graphene with polyaniline and Pd nanoparticles, The resulting Pd–PANI–rGO nanocomposite was highly sensitive and selective to hydrogen gas, with fast response time in air at room temperature. The significantly enhanced sensitivity resulted from the faster spill-over effect, dissociation of hydrogen molecules on Pd, and the high surface area of the PANI–GO composite [5]. By doping graphene oxide with flower-like cobalt–nickel–tungsten–boron oxides, The Co–Ni–W–B–O/rGO composites resembled three-dimensional flowers with high surface area; they also exhibited superior electrochemical performance when compared to most previously reported electrodes based on nickel–cobalt oxides. Furthermore, the Co–Ni–W–B–O/rGO composite prepared in an ethanol solution showed much higher electrochemical performance than that the composite prepared in water. The Co–Ni–W–B–O/rGO electrode showed an ultrahigh specific capacitance of 1189.1 F g$^{-1}$ at 1 A g$^{-1}$ and exhibited an high energy density of 49.9 Wh kg $^{-1}$ along with remarkable cycle stability, which is promising for application in energy storage devices [6]. By spontaneous polymerization of pyrrole and formation of PB nanocubes on GO, The resultant supercapacitor based on PPy–PB–GO exhibits both double-layer and pseudocapacitance. The hybrid electrode showed a maximum specific capacitance of 525.4 F g$^{-1}$ at a current density of 5 A g$^{-1}$. It also exhibited excellent cyclic stability of 96% retention for up to 2000 cycles [7]. Furthermore, we found that three-dimensional graphene aerogel encapsulated n-octadecane can enhance phasechange behavior and thermal conductivity [8].

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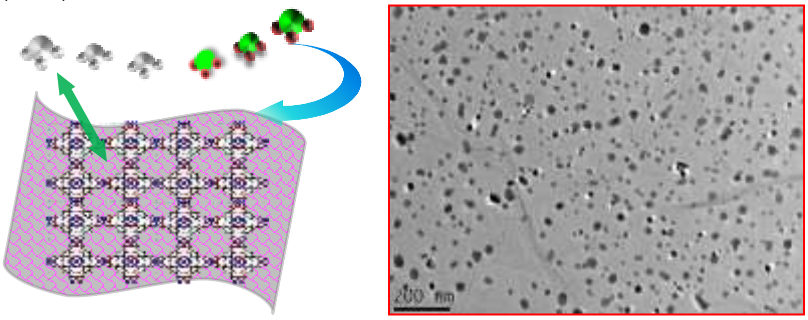


**Figure 1:** Graphene oxide induced nanosized Cu-BTC for gas adsorption.

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# Recent Advances in 2D Materials and Devices Processing

Some of the two dimensional (2D) materials hold great promises to be used for future nano-electronics, beyond current semiconductor technology which faces serious limitation in performance enhancement due to short channel effect and excessive power generation, while the 2D materials present ultra-thin body realizing short channel effect-free state and their heterostructures can be designed to form facile heat dissipation path. These advantages render 2D materials to be promising candidates towards high performance electronic and photonic devices that can be operated under the future mobile and internet of things (IoT) environment. However, research towards the realization of the 2D materials based future electronic and photonic devices faces serious challenges, particulartly in materials and devices processing. In this talk, I would like to address challenges and advances in 2D materials and devices processing, mainly on doping of charge carriers into 2D active layers, Fermi level pinning arising from interface states present at van der Waals surface, uncontrollable contact resistance induced at the interfaces with metal electrodes, impact ionization occurring in small bandgap 2D materials, and power dissipation occurring in 2D hetero-structures.

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# Topological Kink States and Valleytronics in Bilayer Graphene

The advent of two-dimensional materials with hexagonal crystal symmetry offers a new electronic degree of freedom called valley, the manipulation and detection of which could potentially be exploited to form new many-body ground states as well as new paradigms of electronic applications. In this talk, I will describe our effort in creating and understanding valley-momentum locked quantum wires in Bernal stacked bilayer graphene. These quantum wires arise in a topological band structure of bilayer graphene created by state-of-the-art nanolithography and can carry current ballistically with a mean free path of several um's. They are signatures of the quantum valley Hall effect. I will also demonstrate the operations of a topological valley valve and a tunable electron beam splitter, which exploit unique characteristics of the valley Hall kink states. Remarkably the operation of the valley valve does not require valley-polarized current. The high quality and versatile controls of the system open the door to many exciting possibilities in valleytronics and in pursuing fundamental physics of helical 1D systems.

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# Photodetectors based on CVD-grown 2D materials in a van der Waals heterostructure

2D van der Waals heterostructures have great potential for optoelectronic applications [1,2]. High-quality, atomically thin layers are essential for high performance optoelectronics because of their very high responsivity under illumination, due to high excitonic binding energy and Van Hove singularities in the density of states that increase absorption, and photogating effects from careers trapped in localized states that increase carrier concentration by local gating [2]. In this context, $ReSe_2$ is a promising transition-metal dichalcogenide (TMDC), which has a weakly layer-dependent bandgap (it increases from 1.29 eV to 1.31 eV when passing from bulk to atomically thick layers) but a high photo-responsivity when in few-layer form [3]. Here, we report on the fabrication of a $ReSe_2$-based photodetector with high photosensitivity (~$10^6$ photo-to-dark conductivity ratio, see Fig.1d) and fast switching time. The device has a planar architecture (Fig.1b) based on high-quality CVD-grown 2D materials that are van der Waals stacked. The contacts to the absorbing layer are millimeter-sized graphene single crystals (Fig.1a). The crystals are obtained by controlling the nucleation density (<600 nuclei/cm$^2$) on $FeCl_3$/HCl pretreated and ultrasonically cleaned Cu foils inserted in a confined graphite reaction box with narrow slits that effectively suppress Cu sublimation during growth, for reduced substrate roughness and diffusion-limited growth kinetics. The surface oxygen in the partially oxidized substrates not only passivates the Cu active sites to diminish the graphene nucleation density, but also lowers the surface reaction barrier to accelerate its growth rate.
Hexagonal boron nitride serves as an insulating substrate for the device, which is built using a deterministic transfer set up to place the TMDC flake centered on the gap defined by two graphene single crystals that were previously transferred onto a glass cover slip covered with hBN, as shown in Fig. 1c. Metal (AlSiCu) contacts were pre-patterned to the graphene crystals by use of a hard mask, before $ReSe_2$ transfer. This configuration is ideally advantageous to couple the photodetector with light-emitting molecules (fluorophores) or to integrate it with microfluidic devices, in view of biosensing applications.
We also report a direct van der Waals growth of large-scale Graphene/hBN vertical bilayer. CVD grown $MoSe_2$ is then stacked using the same all dry visco elastic stamping setup on to the graphene/hBN vertical bilayer. The direct growth of high-quality van der Waals junctions is an important step toward high-performance integrated optoelectronic devices and systems.

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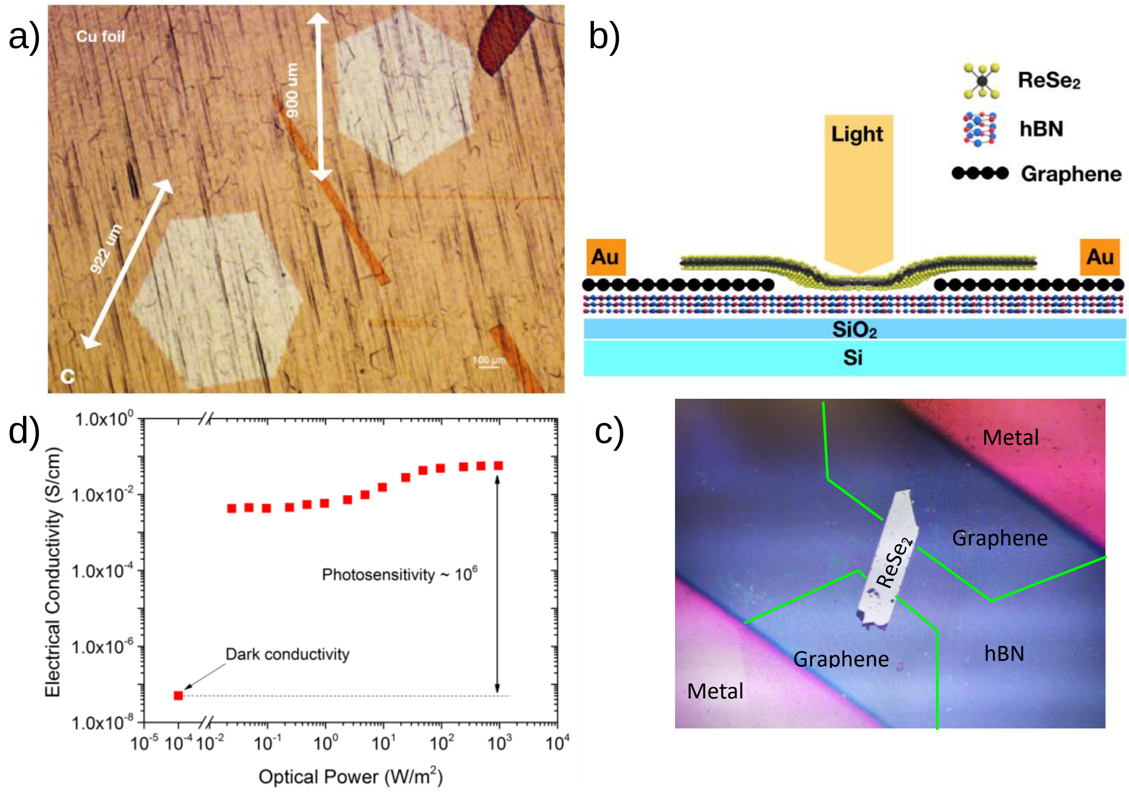


**Figure 1:** a) Micrograph of millimeter-sized single-crystal graphene on Cu used as electrodes for the device; b) Schematic of the photodetector device;.c) Top view of van der Waal stack device; d) Electrical conductivity as a function of irradiance under white light illumination.

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# Transferred via contacts for high quality 2D and hetero-structured devices

The semiconducting transition metal dichalcogenides (TMDCs) have been considered as a promising candidate for Si-based electronics. However, it is notorious particularly for a contact of semiconducting TMDCs especially when their thickness scales down to extreme thinness since fabrication processes such as polymer-based lithography and electron beam evaporation can contaminate and damage the semiconducting layers significantly. [1],[2] The technique of transferred contacts have been recently reported to minimize the damage and contact resistance.[1],[3] The availability of the technique to the various semiconducting TMDCs and its van der Waals (vdW) heterostructures have not been studied. In this study, we demonstrated the high-quality devices for various semiconducting TMDCs ($MoS_2$, $MoTe_2$, $WSe_2$) contacting with transferred via contacts (TVCs). The fabricated devices showed highly performed and reliable field effect transistor (FET) characteristics with comparatively low contact resistance. Moreover, the TVCs composed of different metals allow us to fabricate vdW hetero-structured devices such as $MoS_2$-$WSe_2$, as a high-quality p-n junction device revealing gate-tunable rectifying behavior. This study provides a promising way to discover an intrinsic property of 2D electronics and photonics.

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# Differential ion adsorption in graphene electrodes quantified by *in situ* Raman spectroscopy

Understanding the ion adsorption phenomena is crucial when working with graphene electrodes, extensively used nowadays for biosensing or energy storage, among others. In this work, we assess the change in the Fermi level of graphene via capacitance measurements and correlate it with *in situ* Raman spectroscopy [1,2]. From this study, an intriguing behavior has been observed. Differently supported graphene was immersed in ionic solutions and the Fermi level was assessed using the energy of the G Raman band [3]. The data show that meanwhile the Fermi level is shifted when graphene is supported on an insulating substrate, due to ion adsorption, the same does not occur for conductive substrates, neither for CVD grown multilayer graphene.
By combining Raman and capacitance measurements (in the dominating quantum capacitance regime) on graphene electrodes we will shed some light into the ion absorption and charge transfer mechanisms involved. For this purpose, two types of electrodes (>1 mm diameter), graphene/$SiO_2$ and graphene/ITO, are fabricated and immersed in KCl and NaCl solutions of increasing concentration. We hypothesize that charge delocalization may happen in graphene supported on metallic substrates, making the Fermi level remain unaltered.

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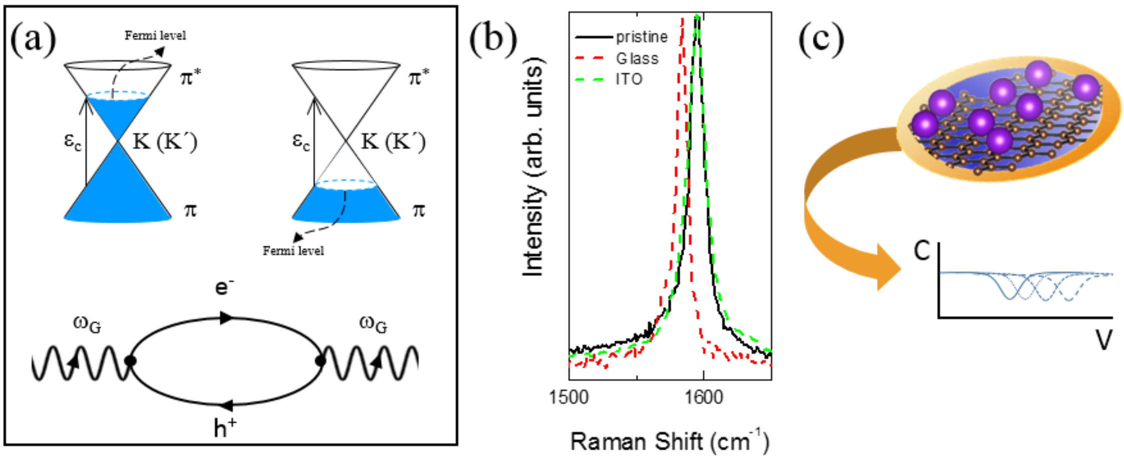


**Figure 1:** (a) Schematic view of graphene´s Fermi level with doping and the renormalization of the G phonon. (b) Raman shift of the G band of graphene on different substrates in presence on 4 mM KCl solution. (c) Schematic representation of a graphene electrode for capacitance measurements with increasing KCl concentration.

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# Wet jet mil exfoliation: High-quality 2D crystals at the fingertips for industrial applications.

The production of two-dimensional (2D) crystals is facing serious issue linked with the exploitation of such materials at the industrial level[1]. However, the practical realization of any commercial application requires efficient synthesis methods[2]. Although many production techniques have been developed,[2] the most promising approach for large-scale production of 2D crystals is the liquid-phase exfoliation (LPE) of their bulk counterparts[3]. However, the main limitations of LPE are the low production rate (g/h) of 2D crystals, and no control in the flakes sizes during the exfoliation processing. In fact, by exploiting ultrasonication[3], it is possible to get an average production rate of 1 g/h, with sizes ranging from tens of nm to few microns[3,4].
To tackle the aforementioned limitations, here we present the latest results on the LPE of bulk-layered crystals. The process is founded on high-shear wet jet milling (WJM, Fig. 1). This technique allows us to have a production rate of ~24 g/h. The developed WJM process has been applied to a large variety of layered crystals ranging from graphite to hexagonal boron nitride, transition metal dichalcogenides, and black phosphorus. The obtained 2D crystals have been employed for several applications, ranging from energy devices (storage and generation) to polymer composites.

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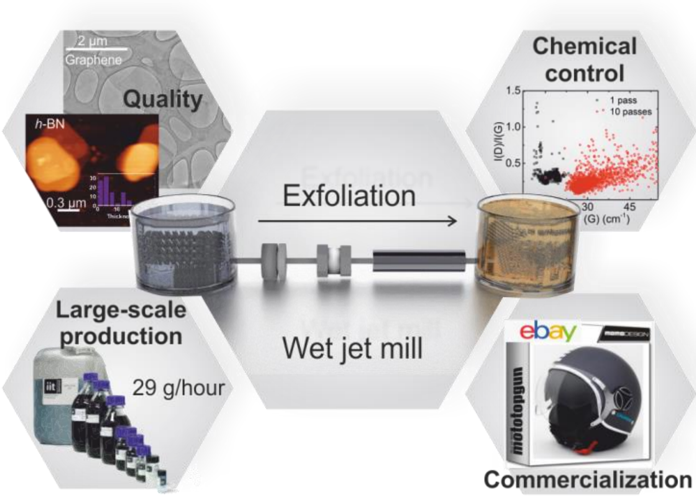


**Figure 1:** Central hexagon, schematic of the wet-jet mill. Top-left, AFM of BN flakes and TEM of graphene. Top-right: Analysis Raman on the defect type. Bottom-left, 20L of graphene dispersion synthesized in 8.5 hours. Bottom-right, a commercially available application of the crystals exfoliated using the WJM.

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# Graphene-enabled, directed nanomaterial placement from solution for large-scale device integration

Placing of nanomaterials at predefined locations with nanoscale precision is still one of the unsolved problems that inhibit their large-scale integration in the domain of semiconductor industry. Various methods that rely on surface functionalization[1] have a drawback where undesired chemical modifications can occur that are detrimental to deposited material's performance. The application of electric-field assisted placement techniques[2] eliminates the need for chemical treatment; however, it requires the use of conductive placement electrodes that limit the performance, scaling, and integration density of electronic devices[3]. Here, we report a method for directed, electric-field assisted placement of solution-based nanomaterials by using large-scale graphene layers featuring patterned nanoscale deposition sites. The structured graphene layers are fabricated by transfer or synthesis on standard substrates, then are removed without residue once nanomaterial deposition is completed by a plasma-based process, yielding material assemblies with nanoscale resolution that cover surface areas larger than $1 mm^2$. We demonstrate the broad applicability by assembling representative zero-, one-, and two-dimensional semiconductors at predefined substrate locations and integrate them into nanoelectronic devices. This graphene-based placement technique affords nanoscale resolution at wafer scale and could enable mass manufacturing of nanoelectronics and optoelectronics involving a wide range of nanomaterials prepared via solution-based approaches.[4]

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# The Computational 2D Materials Database: High-throughput modeling and discovery of atomically thin crystals

Here we present the Computational 2D Materials Database[1] (C2DB), a comprehensive open-access database of around 2000 two-dimensional materials which organizes a large variety of structural, thermodynamic, elastic, electronic, magnetic, and optical properties. The material properties have been systematically calculated by state-of-the-art density functional theory and many-body perturbation theory ($G_0W_0$ and the Bethe–Salpeter equation for ~250 materials) following a semi-automated workflow for maximal consistency and transparency. The C2DB is fully open and can be browsed online (http://c2db.fysik.dtu.dk) or downloaded in its entirety and is constantly expanding by including new crystal prototypes following our lattice decoration approach (Fig. 1). Applications of the database will be presented, identifying a large number of new potentially synthesizable 2D materials for applications within plasmonics, spintronics and (opto-)electronics. The C2DB offers a comprehensive and easily accessible overview of the rapidly expanding family of 2D materials and forms an ideal platform for computational modeling and design of new 2D materials and van der Waals heterostructures.

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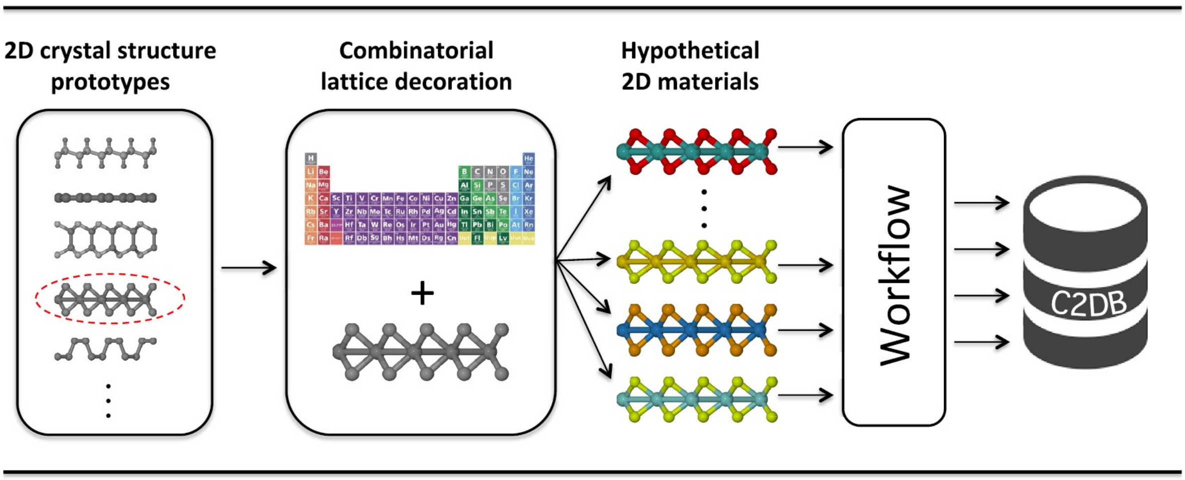


Figure 1: The materials in the C2DB are initially generated by decorating an experimentally known crystal structure prototype with atoms chosen from a (chemically reasonable) subset of the periodic table.

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# Process Safety and Scale-up of Graphene Oxide Synthesis and Storage

Graphene oxide (GO) has been demonstrated as an effective additive for energy storage and composite applications, and large-scale production of GO is of increasing commercial interest. However, a number of process safety issues need to be addressed in this scaleup process. In this work, the safety issues with GO production are addressed in two studies. The first study addresses the exothermicity of the oxidation reaction during modified Hummer's Method. The oxidation reaction is studied in a Reaction Calorimeter, and the data show that the heat of reaction of the system is capable of reaching the decomposition temperature of manganese heptoxide. The second study focuses on the thermal stability of as-produced GO. The explosive decomposition of GO is studied in an Advanced Reactive System Screening Tool (ARSST). The data indicate that the explosive decomposition temperature of GO strongly depends on sample size, and pressure generation can reach 1000s of psi per minute for less than a gram of material. These results are beneficial in evaluating safer operating conditions for synthesis, post-processing, and storage of GO, particularly in large batches.

## Figures

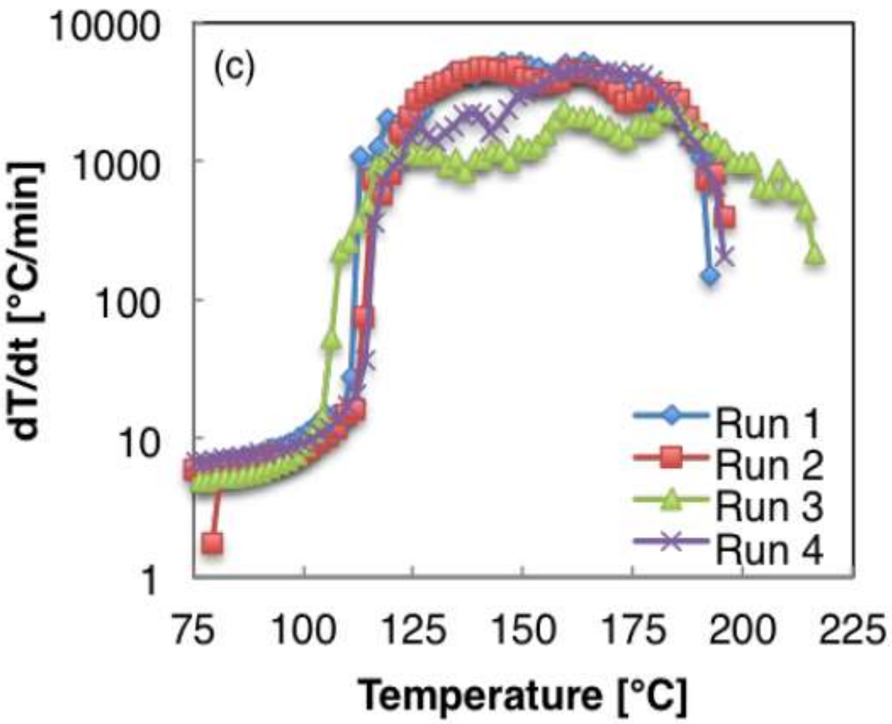


**Figure 1:** Heating rates for graphene oxide in the Advanced Reactive System Screening Tool.

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# Selectivity and functionality on graphene

Graphene is well known as archetype of the 2-D materials, widely recognized for a broad range of applications, including (opto)-electronics due to its outstanding ambipolar charge carrier mobilities and high transparency. These factors together with the highly ordered 2-D structure, makes graphene an ideal substrate for the growth of layered structures, enabling the assembly of heterostructures with graphene as the key step for the realization of complex hybrid device architectures. Although this potential is well known, very often some of these properties need to be tuned. Functionalization of graphene can help in both tuning its properties and providing extra tools making it even more versatile. The functionalization has to overcome three challenges: Reaction, Characterization, Use. While the reactivity of graphene is nowadays quite understood, the characterization is complicated by the intrinsic monolayer character of the material. The most important aspect is the extended functionality of the material that can be made of a certain functionalization. In our research we were investigating the formation of graphene heterostructures in a selective fashion and we wanted to explore their potential for (opto)-electronic applications. In this topic, we achieved highly selective growth of PEDOT on patterned graphene, providing unique hole-conducting/electron-blocking heterostructures. Following this trend, we developed a highly efficient process of selective and oriented growth of various 2-D crystalline materials (optically active) on monolayer graphene. By varying the organic precursors for the active material which is composed of alternated organic and inorganic layers, different interactions leading to selective perovskite self-assembly on graphene were achieved. Varying the length of the aliphatic chain or size of the aromatic moiety (present in the organic part) affects the selectivity of film formation on graphene due to the hydrophobic interactions and/or π–π stacking, respectively. Using the self-assembly principle, high spatial resolution and uniform coverage was achieved in the range from 5 μm up to centimeter scale.

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# Chemical Vapor Synthesis of Ultra Flat Crack-Free Highly-Crystalline Single-Layer Graphene on Cu substrates

Due to its extraordinary physical properties, graphene is regarded as an ideal material to improve the performances of a wide range of technological applications. As the production of pristine graphene constitutes the core foundation for future fundamental discoveries or the realization of next-generation devices, scalable and cost-efficient manufacturing methods have been the subject of intense research worldwide.

Chemical vapor deposition of graphene (CVD) on copper catalysts is presently the most industrially-viable approach to produce graphene. However, the maturity level is not sufficient yet to concomitantly and precisely control (i) the deposition uniformity over large areas, (ii) the number of layers, (iii) the structural quality, (iv) the physical integrity, and (v) the surface planarity, which are key requirements to fully exploit graphene's potential. This talk presents the recent progresses that have been made in this regard.

First, we show how to produce highly crystalline graphene resulting from the coalescence of millimeter-size single-crystalline domains. Such result has been achieved thanks to the customization of the CVD setup and the use of optimal CVD conditions for both the Cu annealing and graphene growth steps [1]. Our findings point out that injecting minute amount of oxygen in the CVD furnace prior to the graphene growth step is a facile and efficient way to reduce the carbon content of the substrate, and hence drastically decrease the graphene seeding density [2]. Secondly, this presentation shows that various physical phenomena can be responsible for the formation of additional graphene layers. Single layer graphene can be achieved by controlling the chemical vapor reaction of methane on the Cu foil topside and by completely suppressing it on the Cu foil backside [2]. We also compare the most widely used Cu catalysts (foils, polycrystalline films and epitaxial films) in order to benchmark the roughness of the Cu surface which serves as a template for graphene growth. It is found that epitaxial Cu(111) films pre-deposited on C-plane sapphire wafers represent the most promising Cu-based catalyst for the synthesis of graphene with superior planarity and physical integrity [3]. Finally, we demonstrate that graphene can be produced on a batch of closely-packed vertically-standing Cu films pre-deposited on rigid 3-inch wafers [4]. Such configuration provides a new route to increase the yield of production of graphene while strictly controlling its thickness, crystallinity, integrity and planarity.

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# Plasmon-pole approximation for many-body effects in graphene

We present the plasmon pole approximation (PPA) theory for calculating the electron-electron interaction-induced many-body effects in the spectral function of graphene as a function of doping density within the GW random phase approximation (GW-RPA). Since the single-band effective chiral linear dispersion model for graphene does not obey the simple f-sum rule by virtue of the infinite filled Fermi sea in the valence band, the PPA is not unique as it is in 3D or 2D metals. We introduced three distinct approximations for obtaining the effective plasmon pole frequency using static RPA, the Thomas-Fermi approximation, and the hydrodynamic dielectric function, respectively. We find that all three PPA schemes, as we show through explicit calculations, give many-body renormalization, specifically the interacting spectral function, very similar to that obtained with the full GW-RPA theory, thus validating all three approximation schemes more or less equivalently and establishing the general validity of the plasmon pole approximation scheme. We also provide a comparison between the PPA and the hydrodynamic approximation in graphene, and comment on the experimental implications of our findings.

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# Lithographic band structure engineering of graphene

By miniaturisation and careful shaping, any material can be pushed into a (quantum) regime, where the dimensions and shape become essential for the overall behaviour, and the electronic band structure is significantly altered. Materials with a low intrinsic dimensionality, such as the two-dimensional material graphene, allow direct access to the entirety of atoms constituting the crystal, making engineering of the band structure particularly attractive. While high-density nanostructuring has been predicted to provide customisation of the properties of graphene, there has been limited progress in realising this in practice; even high-end top-down fabrication procedures introduce enough edge-disorder and contamination to obscure the predicted behaviours. Here we demonstrate band structure engineering by direct, ultra-dense lithographic patterning of graphene. We fabricate a 35 nm-period superlattice of etched holes separated by as little as 12-15 nm in a graphene sheet encapsulated in hexagonal boron nitride. We observe a distinct magnetotransport regime, with nonlinear Landau levels, and a band gap of 156 meV, which can be tuned with an external magnetic field. The transport measurements are in excellent agreement with both tight-binding simulations and an analytical model. A moiré superlattice from the underlying substrate is observed both before and after nanostructuring, and we see transport features unique to our engineered band structure both at the main and moiré charge neutrality points, indicating that the engineered band structure is cloned by the moiré superlattice. Band structure design in two-dimensional materials by top-down patterning enables the realisation of a number of exciting predictions and opportunities such as spin qubits [1], valleytronics [2] and waveguides [3].

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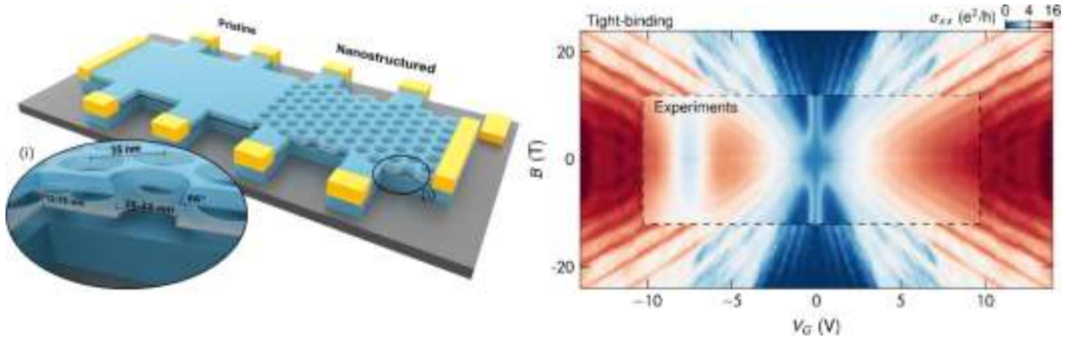


**Figure 1:** (left) Schematic of a measured device with high-quality nanostructured graphene, leading to an engineered bandstructure. (right) Magnetotransport measurements, directly overlaid on tight-binding simulations of the system.

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# Unprecedented transport properties of monolayer TMD devices: Experiment and theory

Experimental low-temperature transport in monolayer transition metal dichalcogenides (TMDs; $MX_2$) is – like in conventional semiconductor heterostructure based 2DEGs – typically found to be limited by Coulomb scattering due to, e.g., charged substrate impurities with mobilities not exceeding μ~5000 $cm^2/(V.s)$ [1]. Here we demonstrate unprecedented transport properties in TMD devices based on *p*-type monolayer $WSe_2$ showing record-high low-temperature mobilities as high as μ~25.000 $cm^2/(V.s)$ [2]. The mobility surprisingly *decreases* with the carrier density *n*, which is *not* in accordance with charged impurity scattering for which a $\mu \sim n^\alpha$ scaling (with α>0) is anticipated [3].

Using a microscopic, density-functional based method for modeling scattering by realistic atomic-scale defects with the *T*-matrix formalism [4], we investigate the effect of point defects on (i) quasiparticle scattering, (ii) spectral properties, (iii) midgap states, and (iv) transport in 2D TMDs. We demonstrate that the observed density dependence of the mobility is consistent with short-range disorder scattering off atomic point defects, such as, e.g., vacancies, thus pointing to a concomitant breakdown of the widely used Born approximation [4]. At the same time we note that defects in 2D TMDs may act as combined Coulomb and short-range scatterers due to filling of their associated midgap states upon doping [3]. To exclude the existence of the former in our devices, we show that common defects in $WSe_2$ – in contrast to many other TMDs – do not have filled midgap states above the valence-band edge, and do therefore *not* give rise to Coulomb disorder scattering for *p*-type doping. This points to strongly material, defect and doping (*p* vs *n*) dependent transport properties in monolayer TMD devices.

In conclusion, our combined experimental and theoretical study has shown unprecedented transport properties in monolayer TMD devices with record-high mobilities limited by short-range disorder scattering. This points to extremely clean TMD monolayers with defect densities as low as $10^{11}$ $cm^{-2}$ as well as high-quality vdW heterostructure devices free of residual charged impurity scatterers.

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# Covalent functionalization of graphene for chromatographic separation of chiral pharmaceuticals

Graphene continues to be in the focus of scientific and practical interest thanks to its unique properties and promising potential applications. In recent years, chemical modifications of this material have further broadened its appeal and possibilities. Covalent modifications of graphene are particularly interesting in light of the expected high chemical and mechanical stability of the functionalized material. Our research, initially driven by a purely academic interest in the covalent attachment of functional groups to graphene, has recently progressed toward a brand new and exciting avenue of graphene biochemical and pharmaceutical applications. We began with the reaction of benzyne cycloaddition, one of many variants of graphene functionalization, developing a method of benzyne [2+2] or [2+4] cycloaddition modification of epitaxial graphene and bulk graphite [1]. Next, we explored another promising reaction – the modification of graphene with tetracyanoethylene oxide (TCNEO). Recently, Cao and Houk reported on the computational prediction of the pristine attachment of carbonyl ylide to graphene [2]. In our work, among other results, we provided experimental verification of this prediction [3]. TCNEO attachment to graphene introduces reactive cyano groups to the material, opening a wide spectrum of possible secondary modifications and uses. For instance, we have found that mesoporous three-dimensional graphene nanosheets (3D GNS) functionalized with TCNEO and (S)-(+)-2-pyrrolidinemethanol can work as chiral stationary phases (CSPs) for chromatographic separation of chiral pharmaceuticals [4]. Graphene-based CSPs are chemically stable at the pH values ranging from below 1 to 10, and up to an order of magnitude less expensive than standard silica-based analogues.

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# Physicochemical Characterisation of Reduced Graphene Oxide for Conductive Thin Films

Graphene is a desirable material for next generation technology. However, producing high yields of single-layer flakes with industrially applicable methods is currently limited. We introduce a combined process for the reduction of graphene oxide (GO) via vitamin C (ascorbic acid) and thermal annealing at temperatures of <150 °C for times of <10 minutes, resulting in electrically conducting thin films with sheet resistances reducing by 8 orders of magnitude to as low as ~1.3 kΩ $\square^{-1}$, suitable for microelectronics, display technology and optoelectronic applications. The in-depth physicochemical characterisation of the products at different stages of GO preparation and reduction allows for further understanding of the process and demonstrates the suitability for industrial production methodologies due to an environmentally-friendly reducing agent, solution processability and no requirement for high temperatures. The presence of the vitamin C lowers the temperature required to thermally reduce the GO into an electrically conducting thin film, making the technique suitable for thermally sensitive substrates, such as low melting point polymers. Simultaneous spray coating and reduction of GO allows for large area deposition of conductive coatings without sacrificing solution processability, often lost through particle agglomeration, making it compatible with industrial processes, and applicable to, for example, the production of sensors, energy devices and flexible conductive electrodes for touchscreens.

## Figures

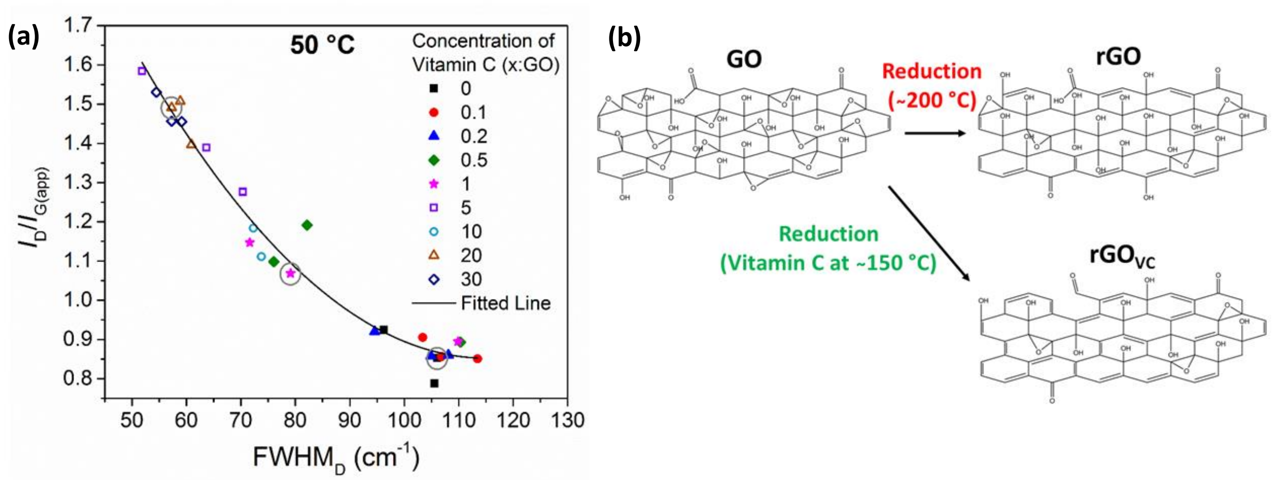


**Figure 1:** (a) $I_D/I_{G(app)}$ versus FWHM$_D$ for Raman spectra from 3 areas on each GO film with different concentrations of vitamin C present, heated at 50 °C for 10 minutes to remove any remaining solvent. (b) Chemical structure of GO before and after reduction at 200 °C and with Vitamin C at 150 °C.

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# Characterization of Solution Processable Graphene for Electronic Applications

Many of the envisaged applications of graphene (i.e. printed electronics, batteries, composite materials) require few layer graphene flakes or graphene nanoplates that can be dispersed in solution. A variety of powders and dispersions purporting to contain graphene are now commercially available, However, the variable quality of these materials and lack of standardized protocols for their assessment is hampering the development of applications. Here we will describe ongoing work at the NRC aimed at developing characterization methods and standard protocols to characterize graphene powders and dispersions. We employ a variety of experimental techniques including scanned probe microscopies (AFM and STM), Raman spectroscopy, X-ray diffraction, X-ray photoelectron spectroscopy and dynamic light scattering in order to characterize the structure and chemical composition of these materials. These methods allow us to measure key parameters to assess the quality of these materials such as flake thickness and lateral size, carbon to oxygen ratio and impurity content.

Solution processable routes to graphene can be grouped into three approaches- a) bottom-up growth of flakes in the gas phase, b) exfoliation of graphite without oxidation and c) exfoliation via oxidation to graphene oxide (GO) followed by reduction. While the fabrication of GO produces a large fraction of large single layer flakes that are readily dispersed in water, reduction is usually incomplete and results in defective graphene which will reduce electrical conductivity. On the other hand, methods to produce graphene without oxidation typically result in few layer graphene nanoplatelets that are rather difficult to disperse, Properties of films made from these dispersions are dependent on both the quality of the individual flakes and details of how the flakes assemble into films. The preferred route for obtaining a graphene film will depend on the required properties and process constraints for a given application. Transparent conductive films have been fabricated from different in-house and commercially available GO and graphene containing dispersions and processed by various routes. The performance of these films can be characterized by a figure of merit based on the optical transmission and conductivity of the film. Performance of films made via reduction of GO will be compared with those based on directly exfoliated graphene.

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# Quantum-electrodynamical approach to the exciton spectrum in Transition-Metal Dichalcogenides

**Manipulation of intrinsic electron degrees of freedom, such as charge and spin, gives rise to electronics and spintronics, respectively. Electrons in monolayer materials with a honeycomb lattice structure, such as the Transition-Metal Dichalcogenides (TMD's), can be classified according to the region (valley) of the Brillouin zone to which they belong. Valleytronics, the manipulation of this electron's property, is expected to set up a new era in the realm of electronic devices. In this work, we accurately determine the energy spectrum and lifetimes of exciton (electron-hole) bound-states for different TMD materials, namely WSe2, WS2 and MoS2. For all of them, we obtain a splitting of the order of 170 meV between the exciton energies from different valleys, corresponding to an effective Zeeman magnetic field of 1400 T. Our approach, which employs quantum-field theory (QFT) techniques based on the Bethe-Salpeter equation and the Schwinger-Dyson formalism, takes into account the full electromagnetic interaction among the electrons. The valley selection mechanism operates through the dynamical breakdown of the time-reversal (TR) symmetry, which originally interconnects the two valleys. This symmetry is spontaneously broken whenever the full electromagnetic interaction vertex is used to probe the response of the system to an external field.[1]**

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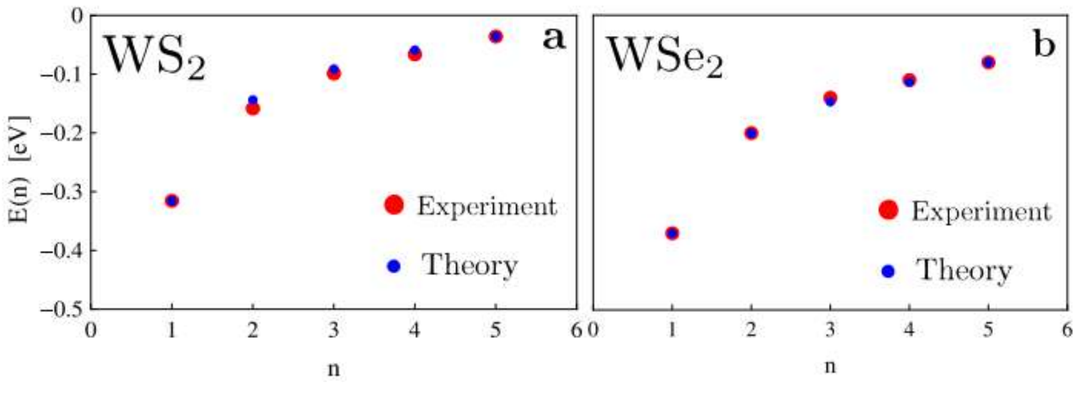


**Figure 1: a)** Comparison between the experimental data of the exciton energy measured in Ref. [2] for monolayer WS2 and our theoretical exciton energy; **b)** Comparison for monolayer WSe2 [3]..

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# Going beyond copper

It's insulating nature as well as its optical transparency make sapphire an appealing substrate for graphene for a vast number of optoelectronic applications. However, direct growth of graphene on sapphire has proved to be challenging, usually requiring metal-catalysts or yielding defective graphene. Here, we report that high-quality monolayer graphene obtained via chemical vapour deposition (CVD) on the c-plane of $Al_2O_3$ (0001) substrates with a catalyst-free approach. The structural and chemical properties of the synthesized graphene are investigated by Raman spectroscopy, atomic force microscopy (AFM), low-energy electron diffraction (LEED) scanning-tunneling microscopy (STM) and low energy electron microscopy (LEEM). We are successfully able to scale up the process from batch to wafer scale (up to 4-inch wafer) keeping comparable quality and uniformity. The carrier mobility measured at room temperature is above 2200 $cm^2/Vs$. Besides, we can transfer full wafer graphene from sapphire to any other desired substrate by polymer-assisted technique. The presented metal-free CVD approach is of sure appeal in virtue of its implementation in a commercial system and it might be an ideal graphene production approach for front-end-of-line (FEOL) integration. Furthermore, by scalably yielding high-quality monolayer graphene, it might have a positive impact on many optoelectronic applications. Finally, industrially impacting in-line coating of graphene will be discussed.

## Figures

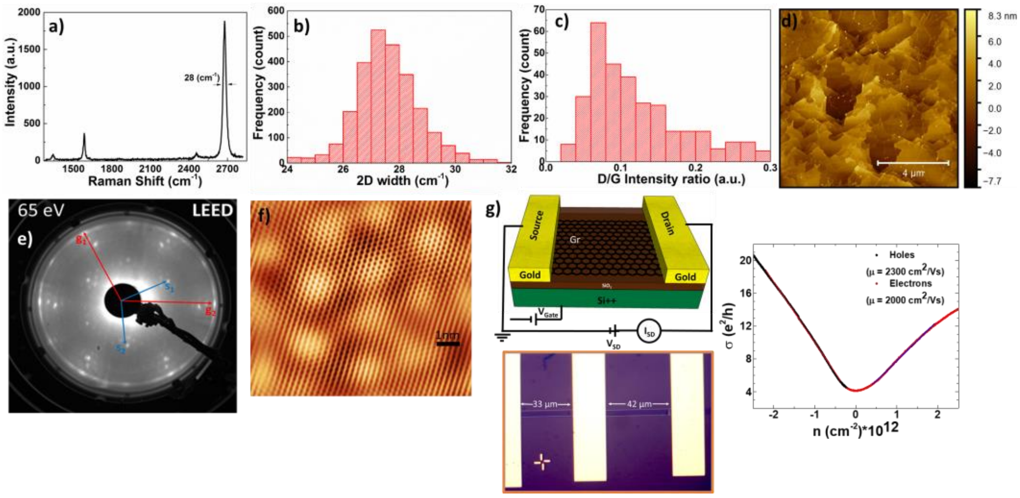

**Figure 1: Graphene on sapphire characterization via** (a) Typical Raman spectra of graphene (b) Peak width of 2D (c) D/G intensity ratio, (d) AFM (e) LEED at 65 eV; (f) 2D-FFT filtered STM topography image (g) Transport measurements.

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# Graphene Environmental Health and Safety Considerations

Scientists and professionals involved in the research, development, and commercialization of graphene should be aware of how past nanoscale materials have been treated, and in some cases targeted, for environmental, health, and safety (EHS) purposes over the past decade. In some cases, adverse EHS studies materially affected commercialization efforts for other nanoscale materials. By understanding what has come before, the industry can take substantive steps to ensure graphene's continued positive reputation. This presentation will provide an overview of EHS, regulatory, and potential liability issues from an attorney's perspective and draw comparisons and distinctions between how other nanoscale materials have been treated and how these lessons can be applied to graphene.

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# $CO_2$ chemical trapping on two-dimensional MXenes

Carbon dioxide ($CO_2$) concentration in the Earth atmosphere is a critical issue since it is behind the greenhouse effect, global warming, and oceans acidification. The need to reduce the $CO_2$ amount in the atmosphere has triggered diverse research into $CO_2$ sequestration, also oriented towards its ulterior utilization as a chemical feedstock in the chemical industry. Therefore, $CO_2$ chemical trapping on active solid-substrates emerges as one of the most feasible routes for this purpose. The so-called carbon capture and storage (CCS) strategy requires specific solid substrates that are able to absorb $CO_2$ in a sufficiently strong way. However, $CO_2$ adsorption on most solid surfaces is very weak, which constitutes CCS a real challenge. Inspired by recent work on the $CO_2$ adsorption on transition metal carbides [1] and by the discovery of an entirely new family of two-dimensional (2D) transition metal carbides and nitrides, termed MXenes [2], with general $M_{n+1}X_n$ chemical formula (M stands for an early transition metal, and X for C or N), we launched a systematic study to inspect whether these new 2D materials provide promising candidates for efficient $CO_2$ abatement.

Hereby, we will present results for adsorption/desorption rates derived from state-of-the-art density functional theory (DFT) based calculations including dispersion, coupled to transition state theory (TST). The present results strongly suggest that these 2D $M_2C$ and $M_2N$ materials (M=Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, and W) have a great potential for $CO_2$ storage and activation. This claim is supported by calculated high adsorption energies, ranging from -1.03 to -3.69 eV, and a significant MXene→$CO_2$ charge transfer. Adsorption and desorption rates derived from TST predict that these materials can adsorb $CO_2$ up to elevated temperatures and low partial pressures, with $CO_2$ uptakes ranging from 2.32 to 8.25 mol $CO_2$ kg$^{-1}$ of substrate, quite competitive to other nowadays-existent material solutions [3,4]. Our predictions have been confirmed experimentally showing single sheets of $Ti_3C_2$ MXene as a potential solid adsorbent for carbon capture applications [5].

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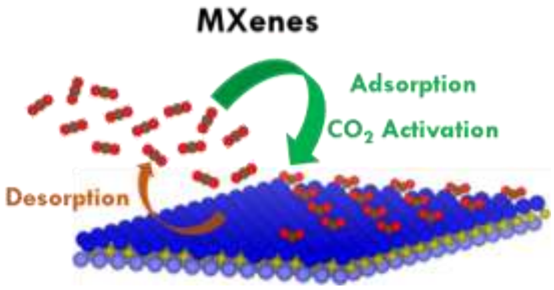


**Figure 1:** Scheme of the $CO_2$ chemical trapping on $M_2X$ (X=C, N) MXenes.

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# Non-contact measurement of graphene conductivity using a microwave cavity; IEC standard 62607-6-4 and its benefit to the graphene industry

Abstract

Recent years have witnessed many breakthroughs in research as well as a significant investment to advance the mass production of graphene materials. Currently, there are several methods being used and developed to prepare graphene-like materials of various dimensions, shapes and number of layers. The most commonly reported quality parameter of graphene materials is the conductivity. In this context, the availability of a standard conductivity measurement technique and graphene reference material for which the 2D surface conductivity can be related to number of layers, mobility and fundamental physical constants, can be a breakthrough that may change the face of the industry. Here we describe a non-contact measurement technique to reliably determine surface conductivity of single-layer or multi-layer atomically thin nano-carbon graphene structures [1]. The measurements are made in an air filled standard R100 rectangular waveguide configuration at one of the resonant frequency modes, typically at $TE_{103}$ mode in the range of 7.435 GHz. Surface conductivity measurement involves monitoring a change in the quality factor of the cavity as the specimen is progressively inserted into the cavity in quantitative correlation with the specimen surface area. The specimen consists of a nano-carbon-layer supported on a low loss dielectric substrate. The thickness of the conducting nano-carbon layer does not need to be explicitly known, but it is assumed that the lateral dimension is uniform over the specimen area. The non-contact surface conductivity measurements are illustrated for a typical graphene grown by chemical vapor deposition process (CVD), and for a high quality monolayer epitaxial graphene grown on silicon carbide wafers for which we performed non-gated quantum Hall resistance measurements [1, 2]. The non-contact cavity method for nano-carbon graphene layers has been standardized [3], and like other non-contact methods (i.e., ellipsometry and optical density) it allows characterization with high speed and efficiency, compared to transport measurements where sample contacts must be defined and applied in multiple processing steps. We believe that the described non-contact microwave cavity test method standard [3] can enable the industry to assess the quality and the corresponding electronic properties of their product, without ambiguity. The effort can also aid manufacturing of many other 2D crystals, which are structurally related to graphene.

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# Generalized Voigt broadening in graphene-based electromechanical nanosensors

New nanosensors and protocols for molecular detection in aqueous environments at room temperature are highly desirable for their potential application in DNA sequencing and in vivo cell studies. Due to their electromechanical properties, graphene provides a platform for electromechanical sensing under these conditions. We have investigated this idea by analyzing representative models. In particular, we have derived analytic expressions for the current, the electromechanical susceptibility, and signal-to-noise ratio. These expressions reveal the relative importance of thermal fluctuations, strain and geometric properties in the signal and electromechanical response. We find that as a result of the environmental fluctuations, electromechanical structures have an electron transmission function that follows a generalized Voigt profile, in close analogy to the inhomogeneous lineshapes found in spectroscopic and diffraction studies. These results allow us to formulate optimal sensing protocols in terms of detector parameters, and give the underlying mechanics and fundamental operational principles for graphene deectometry.

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# Terahertz time-domain spectroscopy as novel metrology tool for liquid-phase exfoliated few-layer graphene

Few-layer graphene flakes produced by liquid-phase exfoliation have become one of the most widely used forms of graphene and related materials. The ability to obtain large masses of graphene at low cost, in a form that can be easily processed, has opened a commercially viable route to a wide range of applications[1]. These include reinforced polymer composites[2] and printed electronics such as batteries and supercapacitors, as well as sensors[3]. Although liquid-phase exfoliation is commonly used to produce defect-free and non-functionalised material, for many applications performance is improved by a chemical modification. A wide range of characterisation techniques have been developed for these few-layer graphene flakes, including rapid, high through-put techniques[4]. However, there is still a need for a simple approach to characterise the electronic properties of these materials, especially in situations where chemical modification has been carried out on the flakes.
In this paper I will present measurements of free-carrier concentration and mobility in few-layer graphene flakes using THz time-domain spectroscopy [6]. By incorporating the flakes into a non-absorbing matrix (PTFE) the absorption of the flakes have been measured, and related to the electrical conductivity (figure 1). By fitting the conductivity to a Drude-Smith model, the free carrier concentration can be extracted. I show how this technique can be used to discriminate between graphene materials with varying degrees of chemical modification, highlighting the possibility to use THz spectroscopy as a quality control technique. This offers a rapid tool to characterise the electronic properties of graphene and related 2D materials, both before and after processing steps to give final products.

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# Characterization of chitosan-graphene oxide membrane and its application in ethanol fuel cells

Graphene oxide (GO) nanoparticles were blended with environmentally-friendly polysaccharide (Chitosan) yielding the membrane for alkaline direct ethanol fuel cells (DAEFC). This type of fuel cells show high potential for applications due to their low environmental impact and high power efficiency [1]. Recently, addition of graphene impressively boosted the performance of polymer-based DAEFC [2]. Herein we present the results of structural, chemical and transport characterization of novel polysaccharide membranes, which were prepared from dispersion chitosan, and functionalized GO. Nitrogen-doped GO was investigated using XRD, XPS, FTIR, and Raman spectroscopy. We characterized membranes morphology using SEM and AFM microscopy. Ionic and electronic charge transport were studied in the direction perpendicular to the plane of the membrane, which is relevant for the DAEFC operation. Alternating current impedance spectroscopy reveals existence of two separate conductivity channels, assigned to ions and electrons. Ionic conductivity as high as 74 (± 10) mS/cm was obtained. Membranes embedded in DAEFC exhibited peak power density of 70 mW/cm$^2$ and an open-circuit voltage of 0.8 V. These results of ionic and electronic charge transport in GO composites will contribute to the improvement of chitosan-based DAEFCs as well as other GO-based composites.

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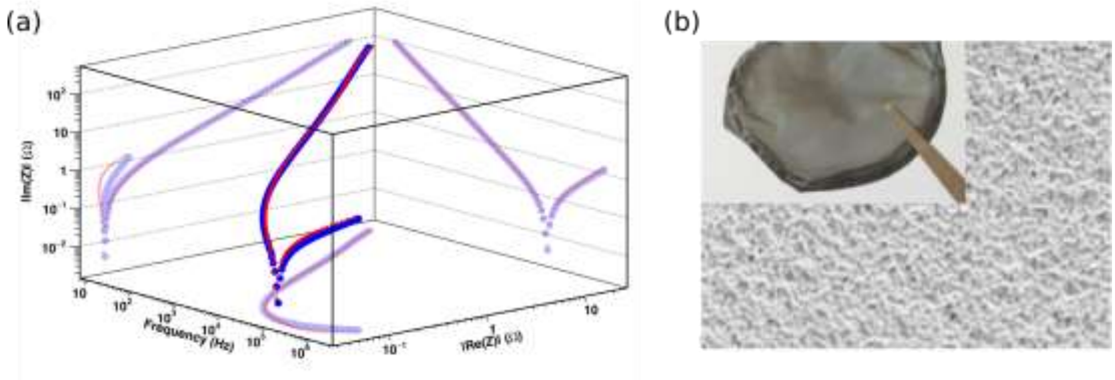


**Figure 1:** (a) Alternating current impedance spectroscopy of graphene oxide (GO) blended with chitosan in 6mol/L potassium hydroxide (measurement - blue, model - red). (b) SEM image of chitosan and 0.01% wt. GO membrane.

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# Plasmon−Plasmon Interactions and Radiative Damping of Plasmons in Nanostructured Graphene

While graphene absorbs only 2.3% in the mid infra red (IR) spectral region, graphene plasmons have much stronger absorption in the far IR. Plasmons tunability by the external electric fields and by the spatial confinement offer a promising platform for opto-electronic and sensor applications. In this work [1], we demonstrate both theoretically and experimentally that the plasmon−plasmon and plasmon−radiation interactions modify strongly the plasmon resonance energy, radiative damping, and oscillator strength in graphene nanoribbon arrays, as shown in Fig. 1. Even for the moderate filling factors of about 50%, plasmon radiative lifetime reduces to a ps time scale from a conventional ns time scale in the isolated graphene nanoribbon. We find scaling of plasmons with respect to the graphene doping level and filling factor, which both modify the strength of the long-range Coulomb and plasmon-radiative interactions. The surprisingly large plasmon energy shift and radiative damping significantly affect the graphene-based plasmonic device performance.

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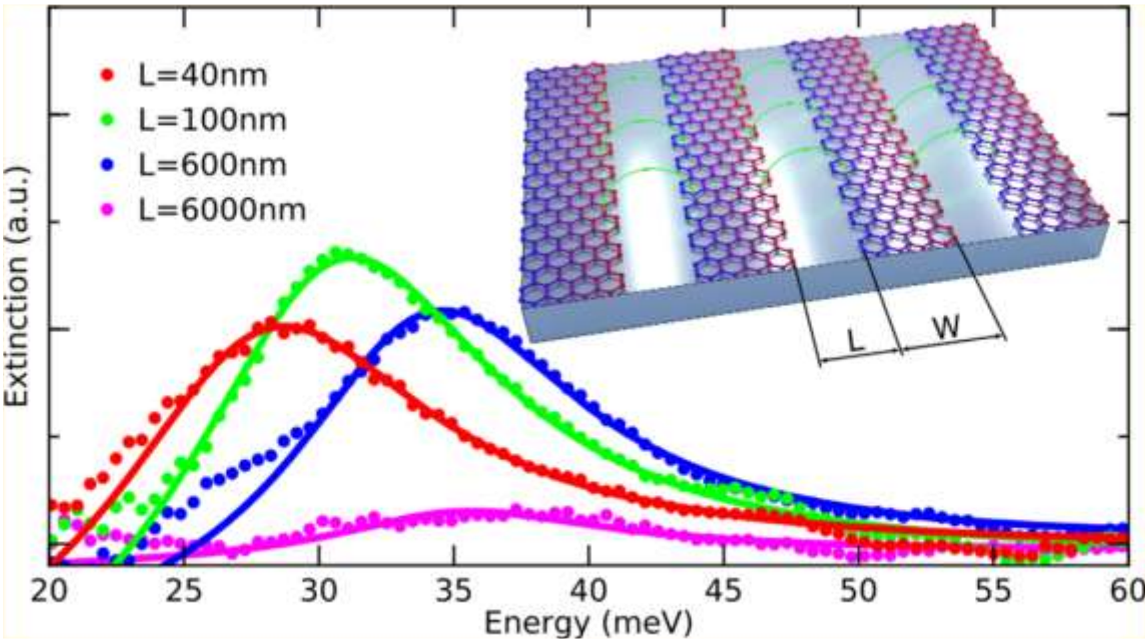


**Figure 1:** Extinction coefficient of graphene nanoribbon arrays as a function of spacing between the nanoribbons at a fixed width of 600 nm.

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# Rapid characterisation of the lateral size of commercially-produced graphene and graphene oxide flakes

Commercial powders and liquid dispersions containing graphene and graphene oxide flakes are difficult to characterise, due to the nanoscale dimensions of the material, as well as the shape and range of sizes of the flakes typically present. Although standardised measurement protocols are being developed within international standardisation committees such as ISO and IEC[1], these characterisation routes are typically time consuming and costly, albeit accurate and precise. Thus, there is an industry requirement for rapid, inexpensive techniques, which need to be small, easy-to-use and produce results in minutes rather than days.

In this work, dynamic light scattering (DLS) and differential centrifugal sedimentation (DCS), which are designed to determine the range of spherical nanoparticle size present in a liquid dispersion, have been compared to determine the lateral size of graphene and graphene oxide flakes. These flakes were already characterised using techniques with more well understood uncertainties, such as scanning electron microscopy (SEM) and atomic force microscopy (AFM)[2]. The parameters required for simple data interpretation that provides quantified ranges of flake size were determined, which allows the material characterisation to be performed on the order of minutes, allowing batch-to-batch quality control and monitoring for large-scale graphene producers worldwide.

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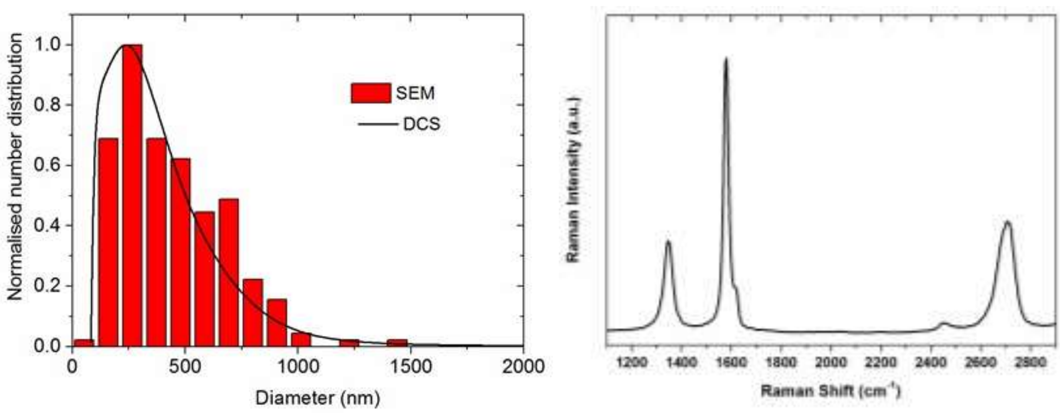


**Figure 1:** (Left) Histogram of the number distribution of lateral flake size as found using SEM and the corresponding distribution calculated using DCS. (Right) Corresponding Raman spectra for the same flakes in powder form.

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# Non-contact and non-destructive characterization of mobility, carrier density, and conductivity of graphene

Onyx is a turnkey, non-contact and non-destructive device for the inspection of several properties of graphene and other 2D materials. Onyx generates full-area maps of mobility, carrier density, conductance, resistance, thickness and other parameters from materials such as graphene, TiN, GaN, PEDOT, ITO, NbC, ALD, spin coated photo-resins. The maps provide information about the homogeneity and quality of the deposition process. Similar characterization is currently realized by nano-scale methods, such as confocal Raman spectroscopy, Atomic Force Microscopy, or Transmission Electron Microscopy, and/or macro-scale methods [1], such as van der Pauw or optical microscopy. However, nano-scale methods are slow and cannot characterize large surfaces. Macro-scale methods generate characterization that average the magnitudes and, thus, cannot provide localized information. Onyx provides meso-scale characterization and covers the gap between nano-scale and macro-scale methods. Onyx is a terahertz-based system [2] that works in reflection geometry as opposed to state-of-the-art methods [1-3] and provides mobility, carrier density, and conductance maps in the terahertz range[4]. Figure 1 shows the conductance maps of a sample of CVD monolayer graphene over quartz substrate. Image (a) shows the conductance measured in reflection configuration while image (b) presents the conductance in transmission configuration. As it is shown in (c), the correlation between the two measurements is strong (98%). The results are in excellent correlation with van-der Pauw method. Images (d) and (e) show the mobility and carrier density of another CVD graphene sample. The mobility and carrier density is extracted without any bias according to model described in [5]. Onyx can be integrated with reactors and enable monitoring production in real-time. Therefore, Onyx could support the production of graphene at industrial scale. Onyx can implement characterization standardized protocols for accurate and repeatable measurements.

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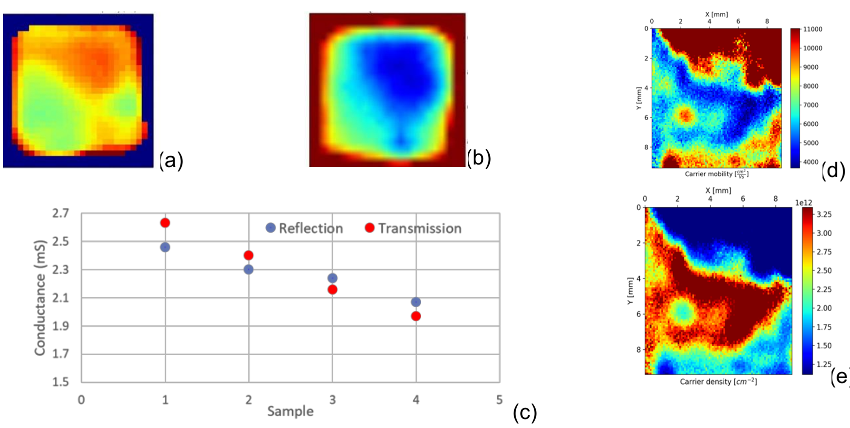


**Figure 1:** Conductance maps of CVD monolayer graphene over quartz substrate sample: (a) reflection configuration, (b) transmission configuration, (c) correlation graph, (d) mobility, (e) carrier density.

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# Gateless carrier density tunability in epitaxial graphene devices functionalized with chromium tricarbonyl

Monolayer epitaxial graphene (EG) has been shown to have clearly superior properties for the development of quantized Hall resistance (QHR) standards. One major difficulty with QHR devices based on EG is that their electrical properties drift slowly over time if the device is stored in air due to adsorption of atmospheric molecular dopants. The crucial parameter for device stability is the charge carrier density, which determines the energy spacing of the Landau levels and thus the magnetic flux density required for precise QHR measurements. This work presents one solution to this problem of instability in air by functionalizing the surface of EG devices with chromium tricarbonyl - $Cr(CO)_3$ [1]. Observations of carrier density stability in air over the course of one year are reported, as well as the ability to tune the carrier density by annealing the devices. For low temperature annealing (< 360 K), the presence of $Cr(CO)_3$ stabilizes the electrical properties and allows for the reversible tuning of the carrier density in millimeter-scale graphene devices close to the Dirac point. Precision measurements in the quantum Hall regime show no detrimental effect on the carrier mobility.

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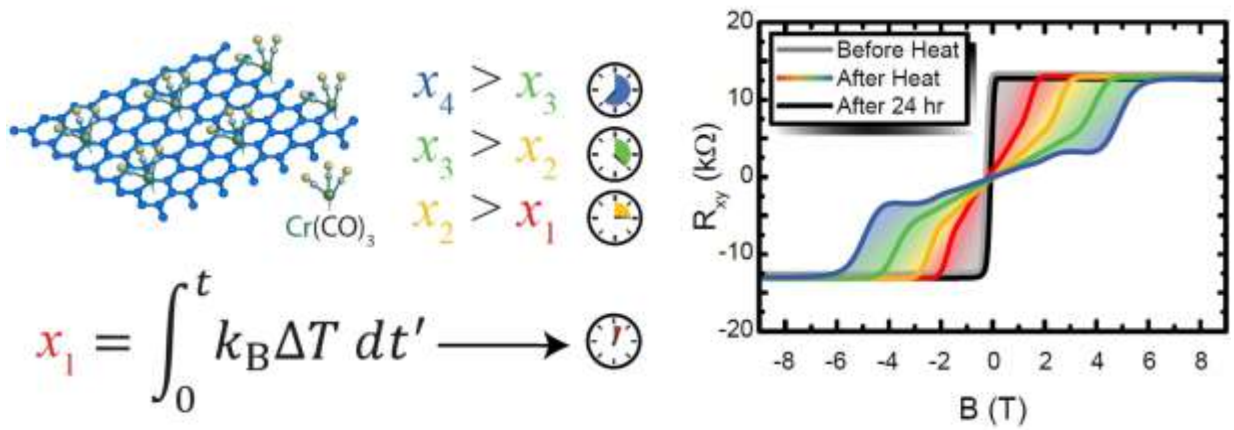


**Figure 1:** Rendering of the graphene crystal structure is shown functionalized with $Cr(CO)_3$. The Hall resistance indicates the increase of the electron density based on the amount of integrated heat exposure. In all cases following application of heat, the device is left in air for a period of at least one day, the device's carrier density returns to a value on the order of $10^{10}$ cm$^{-2}$.

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# Anisotropic Oxidation and Unexpected Stability in Suspended Graphene

We study the oxidation of clean suspended mono- and few-layer graphene in real-time by in situ environmental transmission electron microscopy. At pressures below 0.1 mbar we observe anisotropic oxidation and the formation of hexagonal holes with armchair-oriented edges and edge roughness below 1 nm. At higher pressures we observe increasingly isotropic oxidation, and eventually irregular holes at a pressure of 6 mbar. In addition, we find that few-layer flakes are stable against oxidation at temperatures up to at least 1000 °C in the absence of impurities and electron beam-induced defects. These findings show first that the oxidation behavior of mono- and few-layer graphene depends critically on the roughness, cleanliness and supporting substrate. Second, the activation energy for oxidation of pristine suspended few-layer graphene is up to 43 % higher than previously reported for graphite. In order to study the oxidative etching of suspended graphene, we have developed a cleaning scheme that results in the near complete removal of hydrocarbon residues over the entire visible sample area (~50 μm$^2$) [1, 2]. These results have implications for applications of graphene where edge roughness can critically affect the performance of devices, and more generally highlights the surprising (meta)stability of the basal plane of suspended bilayer and thicker graphene towards oxidative environments at high temperature.

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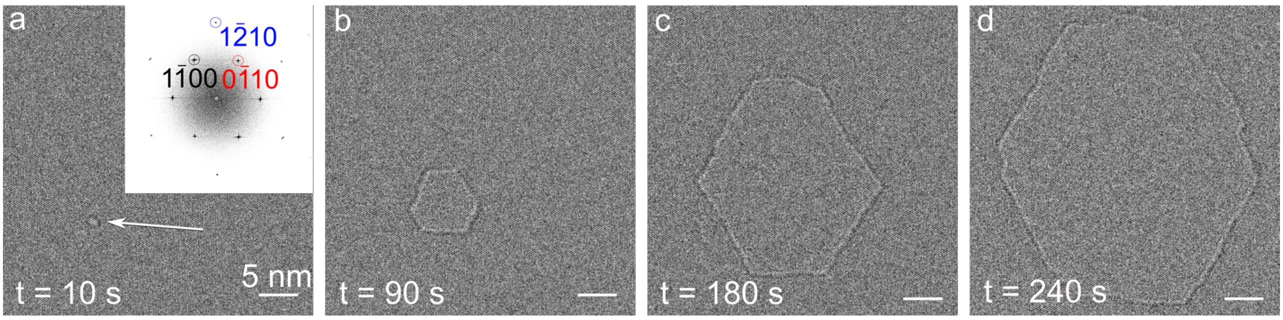


**Figure 1:** TEM images of suspended graphene etched in 0.1 mbar oxygen at a temperature of 800 °C

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# Vibrational Analysis Beyond the Harmonic Regime in Few-Layer Black Phosphorus

In non-metallic materials the heat transfer is dominated by phonons, the quanta of vibrational modes. At 0 K, the vibrational properties of nanostructures can be studied based on the harmonic model. However, harmonic phonons are non-interacting, have an infinite lifetime and the corresponding thermal conductivity is infinite. Therefore, a more realistic approach needs to include the phonon anharmonicity, which results in phonon-phonon scattering. Black phosphorus (BP) features a tunable band gap and its high electrical conductivity and low thermal conductivity along the armchair direction make it a promising material for thermoelectric devices. In this work, we report a Raman spectroscopy study of few-layer BP with varied incident polarization. The active modes $A_g^1$, $B_{2g}$ and $A_g^2$ exhibit a frequency downshift, while the linewidth tends to increase with increasing temperature. To understand the details of these phenomena, we perform first-principles density functional theory calculations on freestanding single-layer BP. The effect of thermal expansion is included by imposing the temperature dependent lattice constant. The temperature induced shift of the phonon frequencies is carried out using ab initio molecular dynamics simulations. The normal mode frequencies are calculated by identifying peak positions from the magnitude of the Fourier transform of the total velocity autocorrelation. Anharmonicity induces a frequency shift for each individual mode and the three- and four-phonon process coefficients are extracted. These results are also obtained from many-body perturbation theory, giving access to phonon lifetimes and lattice thermal conductivity. In general, these theoretical results are in good agreement with experiment.

## Figure

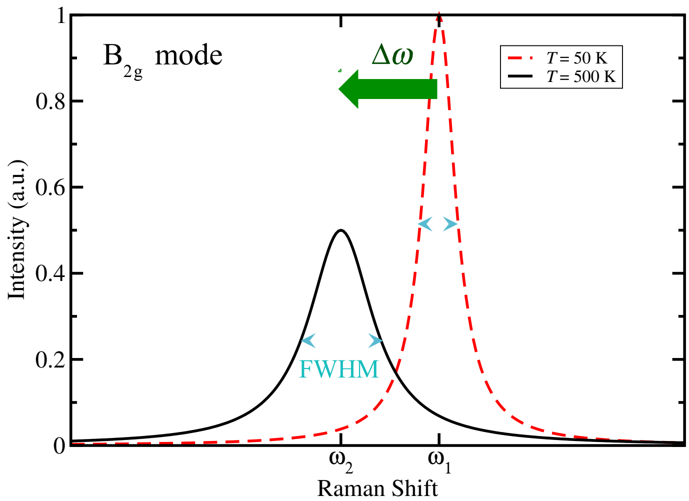


**Figure 1:** Temperature dependent Raman response in few-layer black phosphorus

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# Enhanced performance of a Graphene/n-GaAs Schottky Barrier Solar Cell by means of an AlGaAs/GaAs thin multi-quantum well layer

Insertion of a multi-quantum well (MQW) AlGaAs/GaAs layer thin film between the graphene layer and the bulk n-GaAs layer is expected to improve cell performance in the following way: solar photons generate photo-excited carriers in all three regions of the cell (a) electrons thermionically escaping from the graphene side to the mqw and bulk side (b) electron-hole pairs photogenerated in individual quantum wells and (c) holes generated in the bulk n-GaAs (1.42eV) and diffusing to the junction. We propose a unified model for total current and open-circuit voltage, for all three transport processes in such a cell. The device is a Schottky Barrier cell with a thin region between graphene and n-semiconductor regions, which provides a wider solar photon window (1.80eV, with 30% Al content). On the other hand, mqw's (lattice-matched AlGaAs and GaAs layers) offer an optical gap of 1.59eV, for further photon absorption with 25Angstrom well-widths. Photogeneration in quantum wells splits electron/holes pairs (EHP) in opposite directions. Under the influence of the local junction electric field, electrons join the majority carriers in the n-GaAs and holes diffuse to the Graphene/AlGaAs junction. GaAs quantum well geometry (well width) is pre-selected to confine only one eigen-energy (the ground state) while the second one is coinciding with the edge of the wide band gap conduction band. This ensures increase of thermionic escape of electrons to the conduction band continuum, before recombination. The existence of quantum wells also ensures separation of electron-hole pairs (reducing recombination). We calculate such thermionic currents from MQW's from first principles. We also calculate thermionic currents from the graphene layer over the Schottky Barrier (G/AlGaAs). In both cases, thermionic currents (TE) are found to vary with T^3/2 due to 2D-dimensionality of the quantum well density of states and of the unique properties of the graphene density of states respectively. Simultaneously, photo-generated holes from the bulk and the mqw region diffuse fast to the junction. Such an existence of an MQW layer in the depletion region of the G/AlGaAs junction offers (a) wider band gap for absorption (b) wider optical gap for further absorption due to MQW's (c) higher device current due to two thermionic emission currents (TE) form the graphene and the quantum wells along with reduce recombination. Insertion of AlGaAs layer at the junction increases the Schottky barrier by 0.247eV, thus increasing open-circuit voltage. Under AM1.5 conditions, we predict 1.113V as open-circuit voltage, short circuit current 18.4mA/cm^2, and fill factor 75% leading to a clear improvement of a 15.35% collection efficiency.

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# Physisorption-Mediated Exfoliation of Centimeter-Sized Monolayer $MoS_2$ on Gold

The conflict between the material quality and production scalability is one of the major challenges for future applications of two-dimensional materials. The typical lateral size of monolayer transition metal dichalcogenides (TMDCs), such as $MoS_2$, achieved by mechanical exfoliation is currently limited to ca. 100 µm on insulating substrates [1]. Recently, direct exfoliation of TMDCs on metallic substrates of larger dimensions has been reported, with the focus on potential applications in optoelectronics and catalysis [2].

Herein, we report mechanical exfoliation of centimeter-sized monolayer $MoS_2$ on gold substrates (Figure 1), which is facilitated by strong physisorption between the two materials and also extends to other TMDCs [3]. The surface contamination and roughness of the Au substrates are found to be the key parameters for successful high-yield exfoliation. Microscopic and spectroscopic characterization, and first-principles density functional theory calculations of the $MoS_2$/Au heterostructures confirm the existence of a strong van der Waals interaction (physisorption) between $MoS_2$ and Au, resulting in a significant charge transfer between the two materials without compromising the structural integrity of the monolayer $MoS_2$. Furthermore, electrochemical characterization reveals that the monolayer $MoS_2$ passivates the chemical properties of the underlying Au, and that the Au significantly modulates the electronic band structure of the $MoS_2$.

This simple and reproducible exfoliation technique facilitates the production of large-area TMDCs, enabling studies previously limited by their small lateral size. It is likely that these findings will be applied in research areas such as electrode modification, photovoltaics, and photocatalysis.

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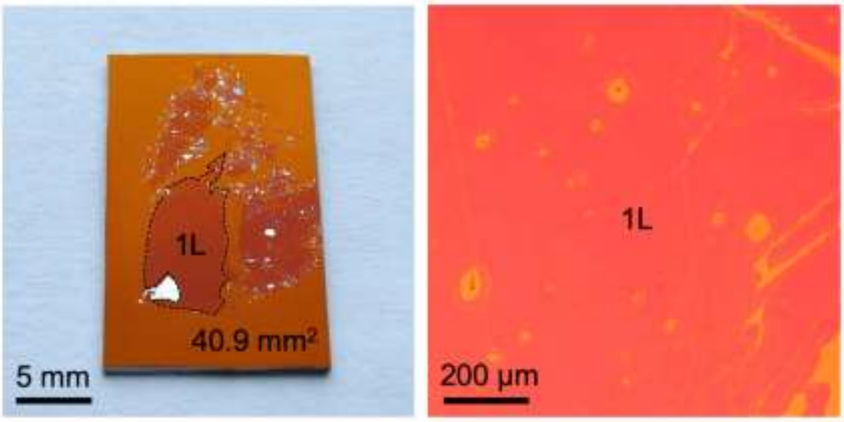


**Figure 1:** Macroscopic (a) and microscopic (b) optical images of monolayer $MoS_2$ on an Au substrate

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# The role of dark excitons in biexciton states of 1L-$WSe_2$

Abstract:
Monolayer tungsten diselenide (1L-$Wse_2$) is an interesting material hosting versatile manybody states. In this talk, I will discuss our recent study of its nonlinear luminescence emission features due to four-particle biexciton and five-particle exciton-trion (aka charged biexciton) states [1]. Through thermal activation measurements, the binding energy of the two species are found to be about 20 and 15 meV respectively, in good agreement with theoretical calculations. Interestingly, both complexes are composed of a spin-one dark exciton bound to a bright exciton or a bright trion located in the opposite valley. This intervalley, bright-dark configuration gives rise to large, negative valley polarization of the biexciton and the exciton-trion emission. This counter-intuitive observation originates from the spin of the dark exciton which makes its Zeeman splitting almost twice that of the bright exciton.

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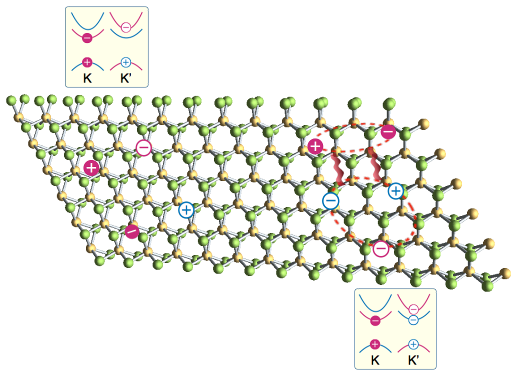


**Figure 1:** Schematic illustration of the four-particle biexciton and the five-particle exciton-trion in a $WSe_2$ monolayer. The biexciton in the figure is due to a ‘dark’ exciton in valley K bound to a ‘bright’ exciton in valley K’; similarly, the exciton-trion is composed of a K-valley ‘dark’ exciton and a K’-valley ‘bright’ trion.

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# Light-Emitting Transition Metal Dichalcogenide Monolayers under Cellular Digestion

Two-dimensional (2D) materials cover a wide spectrum of electronic properties. Their applications have been extended from electronic, optical, and chemical to biological. Regarding biomedical uses of 2D materials, the interactions between cells and 2D materials are of paramount significance. However, bio-interfacial studies are still in their initial stages. This work studies how living organisms interact with transition metal dichalcogenide monolayers. For the first time, we observe cells digest tungsten disulfide (WS2) monolayer. After digestion, cells intake WS22 and become light-emitting. Also, these light-emitting cells are not only viable but are also able to pass fluorescent signals to their progeny cells during cell-division. By combining synthesis of 2D materials and a cell culturing technique, we develop a procedure to real-time monitor the interactions between WS2 monolayers and cells. This observation, with its procedures, opens the door to develop novel cellular labeling and imaging approaches and will trigger further studies on bio-interface between 2D materials and living organisms.

We report that LMH cells can digest fluorescent WS2 monolayers. After digestion, photoluminescence of the original WS2 monolayers is quenched, and LMH cells become light emitting. More importantly, light-emitting (fluorescent) cells are not only viable but also able to pass fluorescent signals to their progeny cells during cell division. This work sheds light on interfacing 2D materials with live organism, and in particular on utilizing the optical properties of semiconducting TMDs for developing next generation of cellular labeling and imaging. From a materials science perspective, this report also introduces an unprecedented approach to engineer structural defects of TMDs using cell digestion. These defective TMDs containing nanopores and vacancies may open up new possibilities of magnetism, basal plane functionalization, and enhanced catalytic performance in hydrogen evolution reactions, and DNA translocation through nanopores.

# POSTERS

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# Heat spreading in 2D material black phosphorus (BP) *via* van-der Waals heterostructure

Two-dimensional (2D) layered materials have sparked significant interest due to their versatile properties. One of the biggest challenges in all the operational electronic devices is the generation of excessive heat. This problem is very severe in nano-devices due to the reduction of their physical dimension that may cause catastrophic failure. [1] The devices based on 2D material BP exhibit promising electronics, photonics, thermal and mechanical properties. [2] However, BP exhibit low thermal conductivity ($\kappa \approx$ is merely 28.8 W/m·K) and large power density due to their miniaturized physical structure that causes early Joule breakdown and thermal spreading problems.[3] Therefore, we study the heat spreading issue in 2D material BP devices to understand the self-heat spreading mechanism.

Here, we report that the back-gate BP device suffers Joule breakdown merely under few $MVm^{-1}$ electric field value with the centrally localized fracture due to non-uniform temperature distribution in BP channel and the hot-spot is located at the center of the cannel. Further we confirmed this by getting the position dependent Raman peaks from spatial micro-Raman spectroscopy as shown in Fig.1a. Furthermore, to mitigate the early breakdown and uneven spreading, we assemble vertical van-der Waals structure. We observed that the vertical devices are more thermally stable and showed more than 5 times higher electrical power than the lateral devices as shown in Fig.1b, due to favorable device geometry for self-heat removal.

This work was supported by the Global Research Laboratory (GRL) program (2016K1A1A2912707) funded by the Ministry of Science, ICT & Future Planning via National Research Foundation of Korea (NRF).

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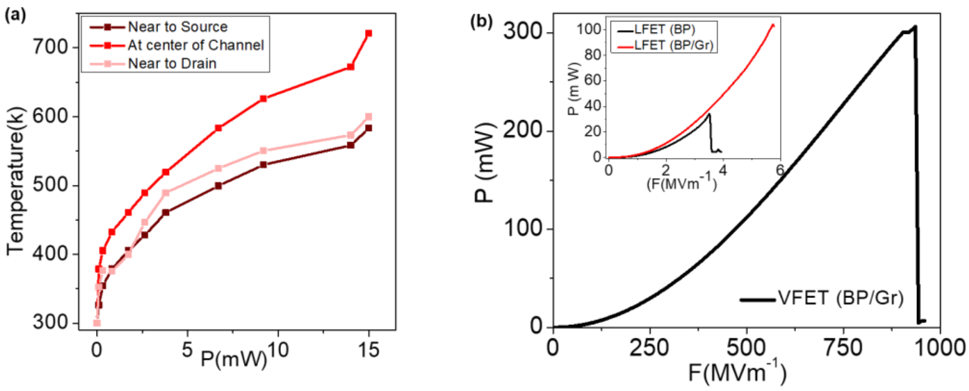


**Figure 1**: (a) Comparison of obtained temperature values by analyzing $A^2_g$ Raman mode of BP at different position as a function of applied electrical power.(b) Comparison of breakdown phenomena of verical device and Insets shows the results from lateral device.

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# Controlled Layer-by-Layer Thinning of $WSe_2$ by Self-limiting Oxidation

Thickness-dependent properties of transition metal dichalcogenides (TMDs) are of immense interest in exploring low-dimensional physics for potential application in electronics and optoelectronics. These studies call for a method to achieve the desired thickness at monolayer precision, without damaging the pristine material properties. We investigate such a method for layer-by-layer thinning of $WSe_2$ using self-limited oxidation with ozone in the presence of UV light. We show that the intrinsic properties of the material remain unaltered in the process by preforming electrical and optical measurements on devices fabricated from etched layers and comparing the results with devices fabricated from pristine exfoliated layers. Our method provides an efficient way to fabricate structures to study layer-dependent properties (e.g. contact resistance, transport and optical properties) and multilayer-monolayer homojunctions of TMDs.

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# Ultra-low Loss Electro-refractive Modulation of Monolayer $WS_2$ Embedded in Photonic Structures

Integrated Electro-Optic Phase modulators play a vital role in the field of dynamic switching, network reconfiguration, phased arrays and optical communication. The need of the hour is to demonstrate efficient low power, high-speed integrated phase shifters, where the index modulation is significant, but with minimal absorption. In traditional accumulation and depletion based silicon modulators, the measured $V_\pi L$ is in the range 1.2 - 3.5 V cm with the doping absorption loss of about 5 - 10 dB/cm. The recently demonstrated graphene on silicon capacitive modulators have a very low $V_\pi L$ of 0.28 V · cm, but come at the expense of a very high absorption loss of 236 dB/cm. The metal-oxide-semiconductor based capacitive devices on silicon on insulator platform similarly have low $V_\pi L$, but have a very high modulation loss of 50 - 60 dB/cm.

2D materials such as monolayer transition-metal dichalcogenides (TMD) have been predicted to experience massive changes in optical response with carrier densities [1]. This can overcome the limitation of today's integrated photonics by providing electro-optic properties to traditionally passive optical materials. Recently discovered TMDs are atomically thin semiconductors with unique electrical and optical properties [2]. These materials enable strong light–matter coupling, with optical absorption around 10–20% in layers as thin as 0.6 nm [3] at visible wavelengths and extremely efficient Coulomb interactions, as manifested in the exciton binding energies on the order of 0.5 eV [ 1] [4].

Here, we show a platform independent, integrable phase modulator designed to endow electro-optic properties to optically passive materials. We demonstrate the electrostatic doping of monolayer $WS_2$ integrated on a $Si_3N_4$ photonic structure by embedding a $WS_2$–$HfO_2$–ITO capacitor on nitride waveguide. We measure a $V_\pi L$ of 1.33 V · cm with an absorption modulation of 0.004 dB/cm for a mode overlap of 0.2 % between the waveguide and monolayer $WS_2$. The extracted change in the optical sheet conductivity of the monolayer $WS_2$ is about (63 ± 4) % with an electrostatic doping of $2.8 \pm 0.2 \times 10^{13}$ / $cm^2$. By designing photonic structures, where the monolayer $WS_2$ overlaps more with the optical mode, the TMD/photonic structure can open up avenues to explore low power efficient phase modulators, with minimal absorption.

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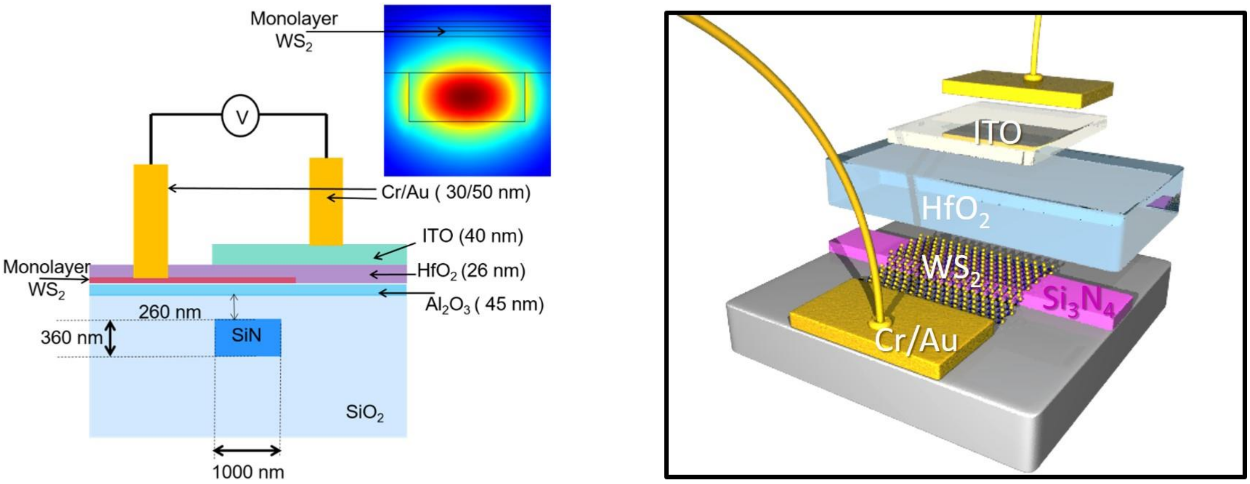


**Figure 1:** Schematic of monolayer WS2 phase modulator

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# Understanding and improving the properties of polycrystalline graphene: Synthesis and Simulations

Graphene's mechanical properties are superior due to its low dimensionality and defect density. The immense strength of graphene was first measured through the nanoindentation of suspended circular membranes; proving graphene to be the strongest material ever characterized [1]. In an effort toward scalable and reliable production, chemical vapor deposition (CVD) methods on copper substrates have proven to be a fruitful method to synthesize large-area monolayer polycrystalline sheets of graphene. While grain boundaries are consequently introduced during synthesis, subsequent nanoindentation methods have shown the strength is still significant. Herein we present methods to significantly improve the quality of CVD-grown graphene. First, we employ rotating-disk electropolishing of copper substrates to obtain nanometer-scale surface roughness over large areas. This allows for control over nucleation density and leads to improved transfer methodologies. Second, the construction of an ultra-high-purity, custom-designed CVD furnace utilizes high-quality purifiers to reduce the oxygen contamination to one part per-billion. This significant reduction in oxidizing species significantly improves growth rate and domain size [3]. Lastly, we further optimized existing electrochemical delamination techniques of graphene from the ultra-flat copper substrates. The combination of these factors is expected to lead to improved and more consistent material properties of CVD-grown graphene; in particular, better-stitched grain boundaries. In parallel, we have formulated a semi-analytical probability density function (PDF) of the critical failure load for polycrystalline two-dimensional materials that we seek to validate against future nanoindentation experiments in order to more accurately understand the mechanical properties of grain boundaries in graphene.

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# Symmetry Engineering and Competing Moiré Potentials in Doubly Aligned Graphene-Boron Nitride Systems

A long-wavelength superlattice moiré potential emerges in heterostructures of graphene and boron nitride (BN) with small interlayer twist. The bandstructure of graphene is substantially modified by this moiré potential, with secondary Dirac cones emerging at finite energy and band gaps opening at both the original and secondary Dirac points [1-4]. We investigate the behavior of BN-encapsulated monolayer graphene in which the bottom BN is perfectly aligned to the graphene via optical alignment of crystal edges [2-4], while the top BN can be rotated freely [5]. Whereas rotations of 60° are equivalent in typical graphene on BN heterostructures [1-5], we observe symmetry under 120° rotations of the top BN in our devices owing to the inequivalence of the boron and nitrogen atoms in the BN unit cell. We observe a significant enhancement of the graphene band gaps when the top and bottom BN are at 0˚ alignment owing to a doubling of the moiré potential. In contrast, rotation of the top BN by 60˚ restores inversion symmetry in the graphene and results in a strong suppression of the gaps. For small twist angles of the top BN (<1˚), we observe two distinct secondary Dirac point features at high carrier density corresponding to the presence of the moiré potentials from the top and bottom BN in superposition. This multi-moiré tunability provides a powerful method by which band structure can be significantly modified in layered two-dimensional systems.

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# Investigating the Integrity of Graphene towards the Electrochemical Hydrogen Evolution Reaction (HER)

Mono-, few-, and multilayer graphene is explored towards the electrochemical Hydrogen Evolution Reaction (HER). Careful physicochemical characterisation is undertaken during electrochemical implementation revealing that the integrity of graphene is structurally compromised. Electrochemical perturbation, in the form of electrochemical potential scanning, as induced when exploring the HER using monolayer graphene, creates defects upon the basal plane surface that increases the coverage of edge plane sites/defects resulting in an increase in the electrochemical reversibility of the HER process. This process of improved HER performance occurs up to a threshold, where substantial break-up of the basal sheet occurs, after which the electrochemical response decreases; this is due to the destruction of the sheet integrity and lack of electrical wiring/conductive pathways. Importantly, the severity of these changes is structurally dependent on the graphene variant utilised. This work indicates that multilayer graphene has more potential as basis of an electrochemical platform for the HER, rather than that of mono- and few-layer graphene. There is huge potential for this knowledge to be usefully exploited within the energy sector and beyond.

## Figures

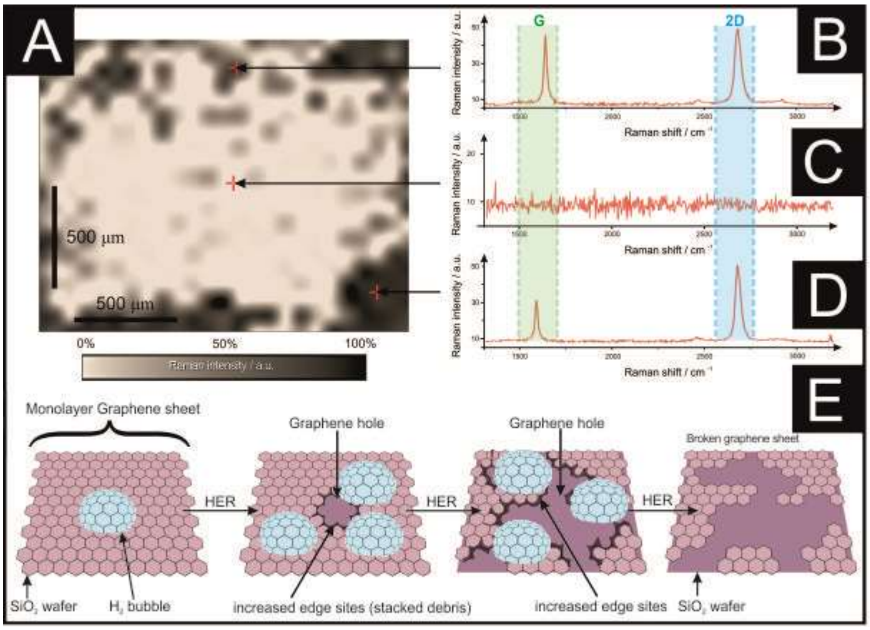


**Figure 1:** (A) Monolayer graphene following 20 LSV scans. Part (B) depicts the Raman profile near a hole, showing that it is few-layer graphene, with the characteristic ratio of the G/2D peaks near to 1:1. (C) Depicts the Raman profile of a broken area where there is no characteristic graphene peak (or signal) present. (D) Shows the Raman profile of an intact area where there is monolayer graphene including its typical G (1590 cm$^{-1}$) and 2D (2690 cm$^{-1}$) peaks. (E) Is a schematic representation of the behaviour identified within this figure (A–D), where the emergence of a bubble on the graphene surface (due to the HER) leads to the creation of some rips when the bubbles explode/move. The debris created due to the graphene breakdown is stacked in areas near to the holes/rip. When many bubbles explode, there is an incremental rise of the edge sites caused by the broken graphene pieces, which eventually lead to the complete destruction of the graphene sheet.

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# Correlated insulator behavior in twisted WSe2 bilayer

Two-dimensional van der Waals materials have become an exciting field. One of the reasons is that this system can be tuned in multiple ways, including stacking order, interlayer spacing and interlayer twist angle, to engineer the material band structure. Manipulating these degrees of freedom has led to observation of several emergent phenomena, including the fractal quantum Hall effect, tunable Mott insulators, and unconventional superconductivity. In particular, interlayer interaction in van der Waals heterostructures at different twist angle could induce many exotic phenomena. How the interlayer interaction affects the electronic structure of a material is a fundamental question. In this study, we report magnetotransport of twisted bilayer WSe2 and show the onset of a correlated insulating behavior at half filling of the moiré unit cell. These results expand magnetotransport results of many body physics beyond graphene.

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# Boron and Nitrogen co-doping of Graphene by CVD

Substitutional doping of graphene offers a chance to modify its properties for various applications. Here using low pressure chemical vapor deposition we grow graphene doped simultaneously by both boron and nitrogen. Theoritcal calculations have shown that in such systems boron and nitrogen dopants tend to segregate and form hexagonal boron-nitride like islands within the graphene sheet.[1,2] Using STM we are able to observe these dopant structures with atomic resolution and show the results here.

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# Towards Intrinsic Optical Properties of Transition Metal Dichalcogenides

Transition metal dichalcogenides (TMDs) have drawn attention due to their potential applications for electronics, optoelectronics, and spintronics. Moreover, TMDs show many novel physical phenomena such as high order excitonic species. In order to explore such intrinsic properties of TMDs, reducing point defect is needed because of their high density of point defect. It has been known that defect density of TMDs is reported as $10^{12}$-$10^{13}$ $cm^{-2}$ with Chemical Vapor Deposition (CVD) [1] and $10^{12}$ $cm^{-2}$ with Molecular Beam Epitaxy (MBE) [2] or Chemical Vapor Transport (CVT) [3] technique. In this study, we have reduced point defect density of $MoSe_2$ and $WSe_2$ to mid$10^{10}$ - low$10^{11}$ $cm^{-2}$ by using self-flux method for growing TMD crystals. Investigating the cleaner $MoSe_2$ and $WSe_2$ allow us to study their intrinsic optical properties. With gate dependent photoluminescence (PL), we have shown clean high order excitonic species such as biexciton and negatively charged biexciton with low laser fluence in $WSe_2$. Narrow linewidth and 100 times higher integrated PL in flux $MoSe_2$ compared to those in CVT $MoSe_2$ also show their properties are getting closer to their intrinsic properties.

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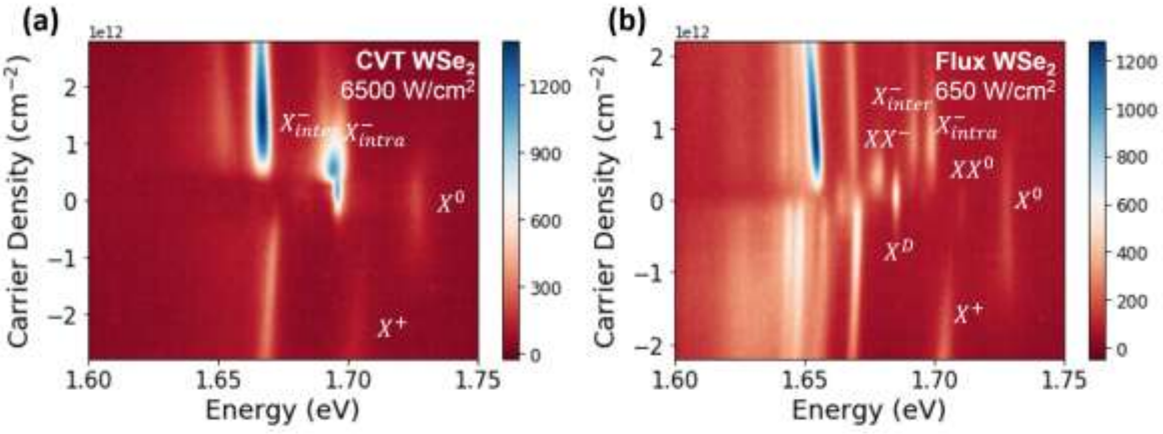


**Figure 1:** Gate dependent PL images of (a) CVT $WSe_2$ taken with a laser fluence of 6500 $W/cm^2$ (b) flux-grown $WSe_2$ taken with a laser fluence of 650 $W/cm^2$

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# Fermi level tuning of $MoS_2$ and $MoTe_2$ via bottom electrical metal contact

Electrical metal contact to two dimensional (2D) materials play important roles in device performance and application. [1] However, atomically thin structure and defects in 2d materials make difficult to investigate the interface between metal and 2d materials. [2] Here, we investigated metal-2d material interaction based on Fermi level change and electrical properties. We transferred MoS2 and MoTe2 on bottom metal electrode with low and high work function metal. Interestingly, MoS2 on Ti and Pd show all n-type performance, but MoTe2 on Ti and Pd show strong n-type ambipolar and strong p-type performance, depending on metal work function. The Fermi level change of 2d material on metal are also confirmed by Kelvin probe force microscopy (KPFM). The Fermi level of MoS2 on Ti and Pd are ~4.42eV. However, the Fermi level of MoTe2 on Ti and Pd are 4.54eV and 4.71eV, respectively. Based on these, we try to understand the carrier transport at the interface between metal and 2d materials.

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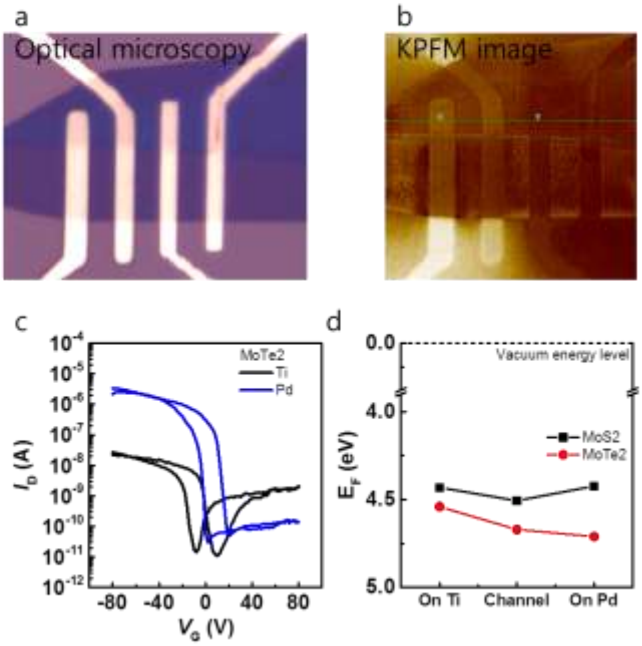


**Figure 1:** a) optical microscopy b) KPFM image of MoTe2 on bottom electrode transistor. c) transfer curves of MoTe2 on Ti and Pd. d) Fermi level change of MoTe2 and MoS2 on different metal.

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# Super-ideal diodes at the Schottky-Mott limit in gated graphene-$WSe_2$ heterojunctions

Metal-semiconductor interfaces, known as Schottky junctions, have long been hindered by defects and impurities. Such imperfections dominate the electrical characteristics of the junction by pinning the metal Fermi energy. We report measurements on a boron nitride encapsulated graphene-tungsten diselenide ($WSe_2$) Schottky junction which exhibits ideal diode characteristics and a complete lack of Fermi-level pinning. The Schottky barrier height of the device is rigidly tuned by electrostatic gating of the $WSe_2$, enabling experimental verification of the Schottky-Mott limit in a single device. Utilizing this exceptional gate control, we realize a "super-ideal" gated-Schottky diode which surpasses the ideal diode limit. Our results provide a pathway for defect-free electrical contact to two-dimensional semiconductors and open up possibilities for circuits with efficient switching characteristics and higher efficiency optoelectronic devices.

## Figures

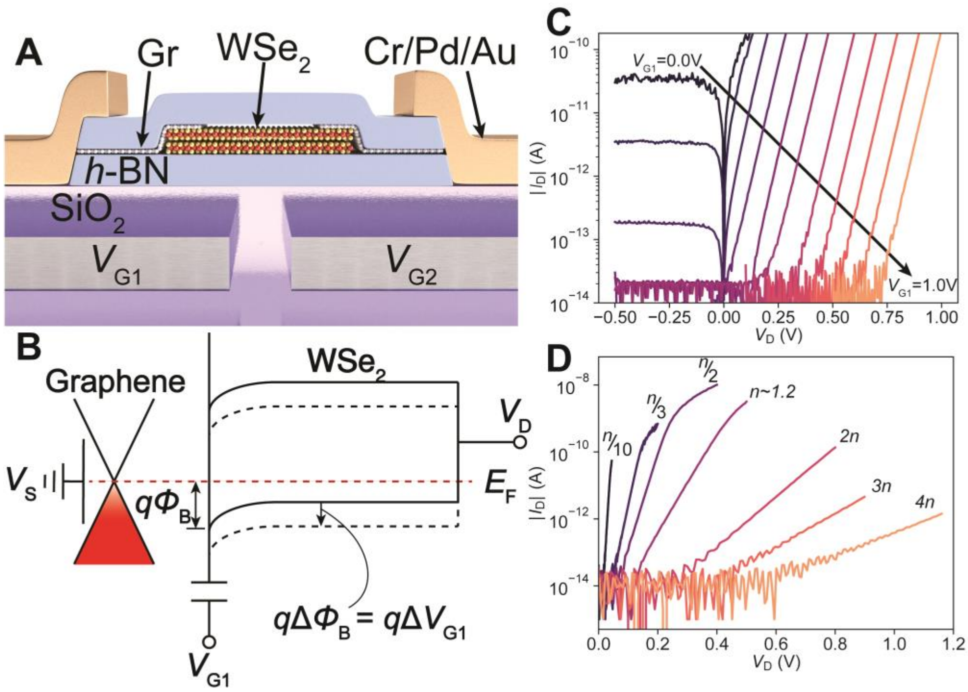


**Figure 1: (A)** Schematic of our device. **(B)** Band diagram of gated Gr-$WSe_2$ junction. **(C)** Gate tunable Schottky diode I-V characteristic for $V_{G2}$=-10V and varying $V_{G1}$. **(D)** Tunable ideality factor beating $n$ = 1 with simultaneous sweeping of $V_{G1}$ and $V_D$.

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# Pressure-induced formation of a new ultra-hard, ultra-thin diamond-like structure: from graphene to *diamene.*

The study of the nanomechanical behavior of atomically thin graphene has led to the discovery of fascinating novel mechanical properties, such as its outstanding in-plane stiffness and out-of-plane flexibility, as well as unique frictional and wear characteristics at the nanoscale. Here we further explore the elastic properties of supported 2D films of graphene by the use of modulated Å-Indentation, a technique capable of achieving sub-Å indentations depths during force-indentation measurements. We experimentally demonstrate that at room temperature and under localized indentation pressure, a single layer of graphene on top of a carbon interface layer (buffer layer), both epitaxially grown on the Si-face of a SiC(0001) substrate, exhibits transverse stiffness superior to that of CVD bulk diamond (Fig.1), is resistant to perforation by a diamond indenter and shows a reversible change in electrical conductivity. Density functional theory (DFT) calculations indicate that the 1-layer graphene film undergoes a pressure-induced reversible phase transformation to a new ultra-stiff, ultra-hard diamond-like structure, named *diamene*, followed by $sp^2$-to-$sp^3$ chemical bond transitions. Furthermore, we find that the formation of ultra-stiff *diamene* is exclusive of 1-layer epitaxial graphene plus buffer layer films grown on SiC(0001), and it is not observed in the buffer layer alone, nor in thicker epitaxial graphene (2-layer or more) nor in exfoliated graphene films of any thickness on $SiO_2$ substrate.

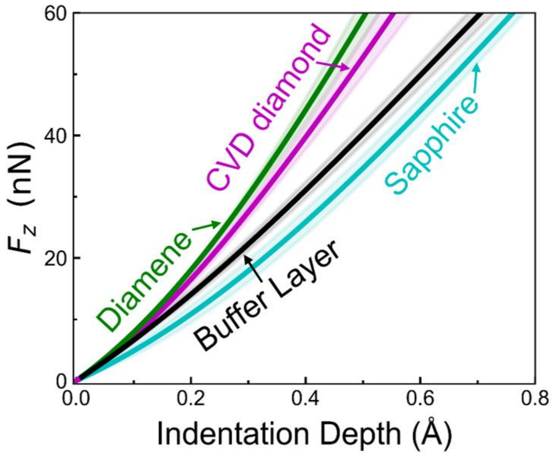


**Figure 1:** Experimental force vs indentation curves showing that *diamene* (1-layer graphene + buffer layer) exhibits stiffness larger than CVD bulk diamond.

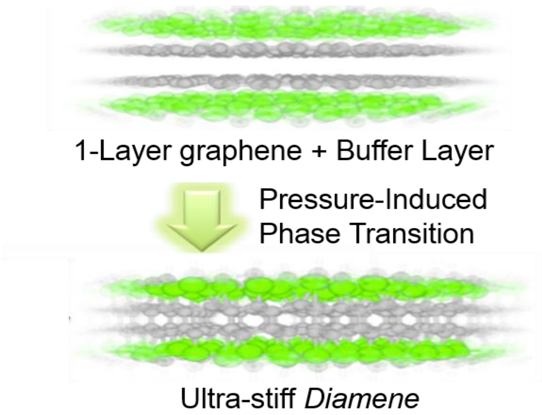


**Figure 2:** Ilustration of the pressure-induced phase transition of the 1-layer graphene + buffer layer film to an ultra-sitff diamond-like structure (*diamene*).

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# Fermi level de-pinning induced by metallic edge-contact to TMDC

Future semiconductor technology can be realized by employing atomically thin two-dimensional (2D) structures, eg. transition metal dichalcogenides (TMDCs). Fermi-level pinning occurs when a metal is in contact with a semiconductor. In most cases, semiconducting characteristics of TMDC are expected to be ambipolar, but that of $MoS_2$ showed strong n-type behavior. To achieve p-type behavior from $MoS_2$ semiconductor devices, de-pinning of the contact metal is required, since pinning is very strong in them. In this work, we demonstrate that, when the high work function of palladium (Pd) is used to form edge contact on multi-layer $MoS_2$, p-type behavior is realized. In contrast, multi-layer $MoS_2$ device fabricated with edge-contact of low work function chromium (Cr) did not show p-type behavior. Furthermore, to understand interfacial properties of another 2D material, we employed the same metals (Cr & Pd) on multi-layer $MoTe_2$ devices. The surface-contact samples of $MoTe_2$ using these metals showed only ambipolar behaviour, and no changes in electrical results were observed despite the use of different work function metals. However, when edge-contact made with low work function metal Cr showed n-type behavior, while edge-contact with high work function Pd showed p-type due to de-pinning of Fermi level at the $MoTe_2$ and metal interface. This opens up a new area of study to designs polarity control of 2D TMDC materials based electronic devices.

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# Enhancement of carrier transport in black phosphorus through via contacts embedded in h-BN

Black phosphorus (BP), one of the allotropes of phosphorus, is a promising candidate for future nano-electronics and nano-photoelectronics. Unlike conventional two dimensional semiconducting materials which show n-type property and high electron mobility, BP shows p-type property and high hole mobility [1]. However, BP faces limitations in application to future electrical devices since BP is easily degraded in air atmosphere, and therefore attempts are made to prevent BP from being oxidized under air ambient. Here, we employed the via contact method [2] for suppressing degradation of BP. The method is to make direct electrical contact by using metal embedded hexagonal boron nitride (hBN) on BP which was not exposed to air. The fabricated devices showed enhanced carrier transport properties because of the suppressed degradation of BP. The devices also showed low contact resistance since ultraclean interface between metal and BP was formed. Furthermore, by applying forces on the contact interface between metal and BP by atomic force microscopy (AFM) probes, the electrical performance of the devices were enhanced, attributed to the better electrical contact formed between metal and BP.

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## Acknowledgements

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# Correlated insulator behavior in twisted WSe2 bilayer

MoS2 and other two dimensional transition metal dichalcogenides has long been predicted with very high intrinsic activity for hydrogen evolution reaction (HER). However, reports have demonstrated that the activity of these layered materials have been hindered by intrinsic and extrinsic factors, especially the bad contact performance between MoS2 and its current collector. In order to improve the contact quality1, efforts were made by selecting proper contact material (such as Graphene)2, or changing the phase of the MoS2 at the contact area1. Here, we found that inherent top gate field effect of proper device configuration can significantly increase the current through the contact barrier, resulting in ignorable energy cost for electron transfer through the MoS2/substrate interface. Our device platform could also allow us to monitor in situ resistance of MoS2 device during HER scanning. We found that the contact resistance can be reduced by more than 6 orders of magnitude, and the HER overpotential can be reduced by hundreds of millivolt with our device platform.

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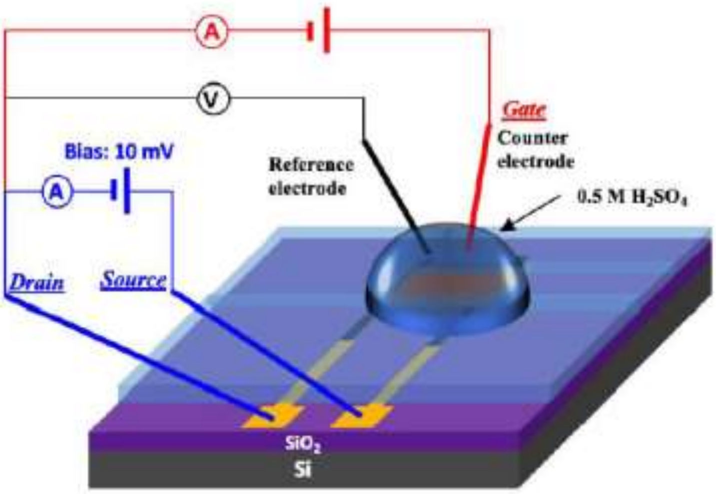


**Figure 1:** Illustration of device platform.

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# Direct Determination of Band Gap Renormalization in Photo-Excited Monolayer $MoS_2$

Abstract
A key feature of monolayer semiconductors, such as transition-metal dichalcogenides, is the poorly screened Coulomb potential, which leads to large exciton binding energies ($E_b$) and strong band renormalization ($DE_g$). The latter has been difficult to determine due to the cancellation between $DE_b$ and $DE_g$ at different carrier densities, resulting in little change in optical transition energy. Here we quantify bandgap renormalization in macroscopic (>3 mm) single crystal $MoS_2$ monolayers on $SiO_2$ using time and angle resolved photoelectron spectroscopy (TR-ARPES). At excitation density above the Mott threshold, $-DE_g$ is found to be as large as 360 meV for the n-doped MoS2 monolayer. We compare the excitation density dependent $DE_g$ with theoretical calculations and show the necessity of knowing the doping/excitation densities in quantifying the bandgap.

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# Nanotopography and Ion Transport in Centimeter-Scale $MoS_2$ Membranes

Nanoporous atomically-thin membranes (NATMs) based on two-dimensional (2D) materials have received attention as catalysts for energy generation and membranes for liquid and gas purification but controlling their porosity and facilitating large-scale production is challenging. In this work, we first show the growth of centimeter-scale molybdenum disulfide ($MoS_2$) films through a simple sulfurization procedure. Aberration-corrected scanning transmission electron microscopy (AC-STEM) of these films reveals a topography consisting of monolayer grains encased in few-layer thick regions. A semiconductor industry etching technique is then utilized to etch away these thin, primarily monolayer areas with tunable porous areas up to ~10% of the membrane and average nanopore diameters as large as ~30 nm. During the etching process, thicker regions essentially remain intact, thus preserving the mechanical robustness of the membrane. Ionic transport measurements through nanoporous membrane devices yield variable ionic conductance values between 0.1 and 16 uS per um$^2$ as a function of etch time while AC-STEM imaging is used to provide insights into the pore formation mechanism at the atomic scale. By employing the often under-utilized form of 2D materials, this work affords a new route for the scalable production of NATMs.

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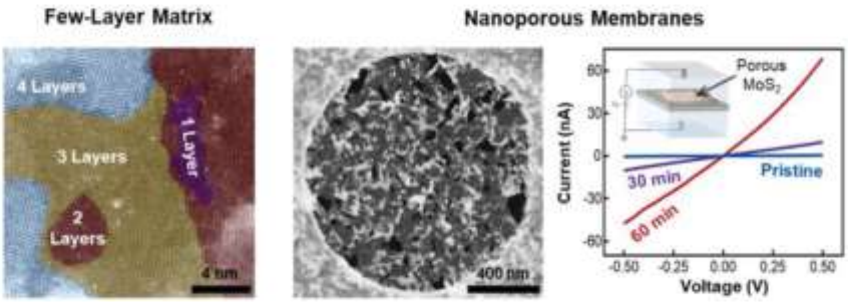


**Figure 1:** (Left) High-angle annular dark field (HAADF) AC-STEM image of few-layer matrix-like structure in $MoS_2$ films grown via Mo foil sulfurization. (Middle) Low-magnification AC-STEM image of nanoporous $MoS_2$ membrane etched for 90 minutes. (Right) Ionic conductance measurements for pristine and variably-etched nanoporous membranes.

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# Measurements of Fermi Level and Doping Concentration of 2D Transition Metal Dichalcogenide Using Kelvin Probe Force Microscopy

Some of atomically thin two-dimensional (2D) materials show good electrical performances. Many of the interesting electrical properties can be realized more diversely by controlling dopant concentration. In this work, we used plasma techniques to control the Fermi level of 2D transition metal dichalcogenide (TMDC), which can be strongly related to dopant concentration (or it can be understood as carrier concentration many cases). As 2D TMDC, we found that semiconducting WSe2 and MoTe2 were effectively doped as p-type, attributed to surface oxidation induced by N2 and O2 plasma. To make the quantitative analysis of the plasma doping effects, the Kelvin probe force microscopy (KPFM) was employed in this work and we confirmed the Fermi level shifts, strongly related to the doping concentrations of 2D TMDC. The validity of the KPFM results were confirmed by measuring electrical characteristics of FET devices fabricated from the 2D TMDC.

ACKNOWLEDGMENTS
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# Rapid characterisation of the lateral size of commercially-produced graphene and graphene oxide flakes

Commercial powders and liquid dispersions containing graphene and graphene oxide flakes are difficult to characterise, due to the nanoscale dimensions of the material, as well as the shape and range of sizes of the flakes typically present. Although standardised measurement protocols are being developed within international standardisation committees such as ISO and IEC[1], these characterisation routes are typically time consuming and costly, albeit accurate and precise. Thus, there is an industry requirement for rapid, inexpensive techniques, which need to be small, easy-to-use and produce results in minutes rather than days.

In this work, dynamic light scattering (DLS) and differential centrifugal sedimentation (DCS), which are designed to determine the range of spherical nanoparticle size present in a liquid dispersion, have been compared to determine the lateral size of graphene and graphene oxide flakes. These flakes were already characterised using techniques with more well understood uncertainties, such as scanning electron microscopy (SEM) and atomic force microscopy (AFM)[2]. The parameters required for simple data interpretation that provides quantified ranges of flake size were determined, which allows the material characterisation to be performed on the order of minutes, allowing batch-to-batch quality control and monitoring for large-scale graphene producers worldwide.

## References

[1] ISO TC229 'Nanotechnologies' and IEC TC113 'Nanotechnology for electrotechnical products and systems' Standardisation Committees
[2] Pollard et al., Characterisation of the Structure of Graphene, NPL Good Practice Guide 145, 2017.

## Figures

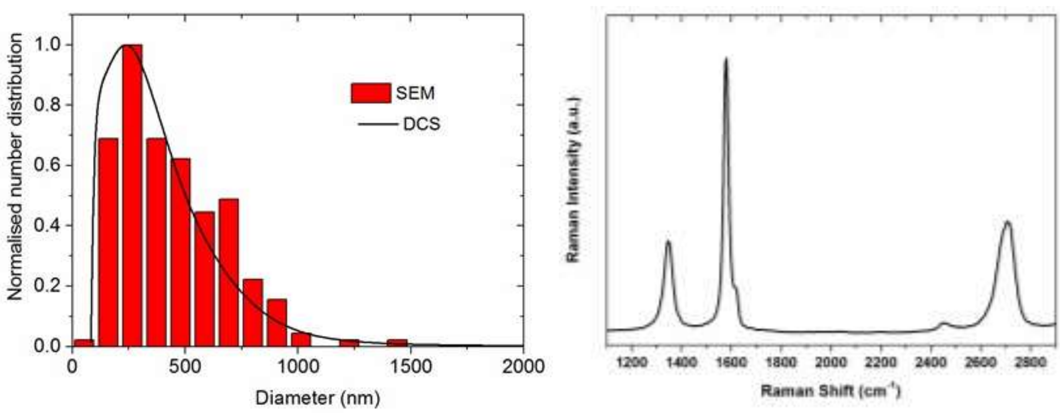


**Figure 1:** (Left) Histogram of the number distribution of lateral flake size as found using SEM and the corresponding distribution calculated using DCS. (Right) Corresponding Raman spectra for the same flakes in powder form.

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# Correlated electron states in monolayer and bilayer $WSe_2$ probed by compressibility and transport measurements

2D transition metal dichalcogenides (TMD) semiconductors have attracted a great deal of attention due to their unique properties including strong spin-orbit coupling, large effective mass and high tunability. Here we report on complementary capacitance and transport measurements on high-quality monolayer and bilayer WSe2 subject to a perpendicular magnetic field. Capacitance measurements probe the bulk electronic compressibility and are sensitive to discontinuities in the chemical potential, resulting from either the single-particle band structure or gaps in correlated electron states. Our compressibility measurements have revealed odd- and even-denominator fractional quantum Hall states, and interlayer exciton condensate. On the other hand, the transport properties turn out to be sensitive to the spin degree freedom at the Fermi level. The spin-selective transport leads to anomalously wide quantum Hall plateau and resistance spikes at the occurrence of quantum Hall ferromagnets. Our results establish 2D TMD as a unique platform for the study of correlated electron states, and pave the way for future exploration in TMD-based systems.

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# Twisted bilayer graphene plasmonic crystal

Twisted bilayer graphene (TBG) consists of two layers of graphene rotated relative to each other. At very small twist angle, the atomic lattices relax and form a periodic array of Bernal-stacked domains separated by solitons. The solitons host topologically protected states and have previously been shown to efficiently scatter propagating surface plasmon polaritons (SPPs) [1]. Therefore, an array of such solitons with a periodicity similar to the wavelength of SPPs should act as a photonic crystal for the SPPs. In this work, we use infrared nano-imaging to verify this proposition and demonstrate the interference of propagating SPPs in TBG. Furthermore, our calculations predict that a full plasmonic band gap is possible in this system.

## References

[1] Jiang et al, Nano Lett, 17:7080 (2017)

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# Finite-size correction scheme for supercell calculations in Dirac-point two-dimensional materials

Modern electronic structure calculations are predominantly implemented within the super cell representation in which unit cells are periodically arranged in space. Even in the case of non-crystalline materials, defect-embedded unit cells are commonly used to describe doped structures. However, this type of computation becomes prohibitively demanding when convergence rates are sufciently slow and may require calculations with very large unit cells. We have shown [1] that a hitherto unexplored feature displayed by several 2D materials may be used to achieve convergence in formation- and adsorption-energy calculations with relatively small unit-cell sizes. The generality of our method is illustrated with Density Functional Theory calculations for diferent 2D hosts doped with diferent impurities, all of which providing accuracy levels that would otherwise require enormously large unit cells. This approach provides an efcient route to calculating the physical properties of 2D systems in general but is particularly suitable for Dirac-point materials doped with impurities that break their sublattice symmetry.

## References

[1] C.G. Rocha, A. R. Rocha, J. H. Garcia, P. Venezuela and M. S. Ferreira, Scientifica Reports, 8 (2018) 9348.

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# Probing graphene- superconductor interface in quantum Hall regime

At metal-superconductor interfaces, Andreev processes occur where an electron tunneling into the superconductor carries with it a second electron, effectively reflecting a hole with opposite momentum back into the metal. This is due to the superconducting gap, which, at low energies, only allows the formation of cooper pairs inside the superconductor, representing an accessible way to measure Cooper-pair tunneling phenomena. An important requirement for strong Andreev processes is a clean interface with a high transmission probability. Graphene is a promising candidate for achieving an extremely clean interface to superconductors[1], however recent results show achieving a transparent interface is non-trivial[2]. In this work, we use controlled assembly in inert atmosphere to create high-quality interfaces between graphene and superconductors. With dual graphite gated graphene, low disorder broadening around charge neutrality point (CNP) could be achieved, which gives opportunities to understand Andreev processes which happen near CNP. In addition, large upper critical fields of 2D superconductors allow us to reach different quantum hall states in graphene while preserving superconductivity. In this work, we report high field measurements of graphene/NbN junctions, in which NbN make edge contact to graphene. Transport measurements at zero field demonstrate clear features associated with both retro and specular Andreev reflection. Zeeman splitting is induced in graphene by applying in plane magnetic field. We observe changes in the Andreev spectrum that are consisting with spin splitting of the graphene band structure. This edge contact technique provides the opportunity to create hybrid SC/graphene or SC/QH system to illustrate new physics such as non-Abelian zero modes of Majorana physics.

## References

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[2] D. K. Efetov; L. Wang; C. Handschin; K. B. Efetov; J. Shuang; R. Cava; T. Taniguchi; K. Watanabe; J. Hone; C. R. Dean; P. Kim. Specular interband Andreev reflections at van der Waals interfaces between graphene and NbSe2. Nature Physics 2016, 12, 328–332.

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# Optical Generation of High Carrier Densities in 2D Semiconductor Hetero-Bilayers

Abstract:
Controlling charge density in two dimensional (2D) materials is a powerful approach for engineering new electronic phases and properties. Such control is traditionally realized by electrostatic gating. Here, we report an optical approach for generation of high carrier densities utilizing transition metal dichalcogenide hetero-bilayers, $WSe_2/MoSe_2$, with type II band alignment. By tuning the optical excitation density above the Mott threshold, we realize the phase transition from interlayer excitons to charge-separated electron/hole plasmas, where photoexcited electrons and holes are localized to individual layers. Remarkably, high carrier densities up to $4\times10^{14}$ $cm^{-2}$ can be sustained under both pulsed and continuous wave excitation conditions. These findings open the door to optical control of electronic phases in 2D hetero-bilayers.

## Figures

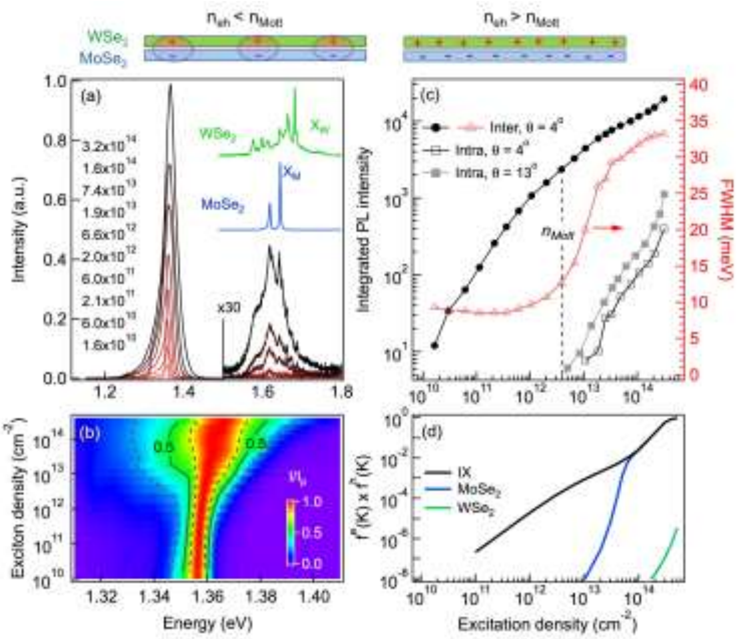


**Figure 1:** Excitation density dependent photoluminescence (PL) and Mott transition in the $WSe_2/MoSe_2$ hetero-bilayer.

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# Fermi Level Pinning-Free 1D Electrical Contact at a Metal-2D $MoS_2$ Junction

Currently 2D crystals are being studied intensively for use in future nano-electronics, as conventional semiconductor devices face challenges in high power consumption and short channel effects when scaled to the quantum limit. Toward this end, achieving barrier-free contact to 2D semiconductors has emerged as a major roadblock. In conventional contacts to bulk metals, the 2D semiconductor Fermi levels becomes pinned inside the bandgap, deviating from the ideal Schottky-Mott rule and resulting in significant suppression of carrier transport in the device. Here we achieve near-ideal alignment of the Fermi level with a pinning factor of 0.98, by employing a 1D edge contact scheme. Use of high work function palladium (Pd, 5.6 eV) achieved ambipolar contact to $MoS_2$, which typically shows unipolar n-type characteristics. Field-effect transistors (FET) with Pd edge contacts show high performance with hole mobility reaching 330 $cm^2V^{-1}s^{-1}$ at 300 K with on/off ratios of $10^8$. The ideal Fermi level alignment allows creation of p- and n-type FETs on the same $MoS_2$ flake using Pd and molybdenum (Mo, work function 4.5 eV) contacts, respectively. This device acts as an efficient inverter – a basic building block for future 2D semiconductor integrated circuits -- with gain reaching 15 at $V_D$=5 V.

## Figures

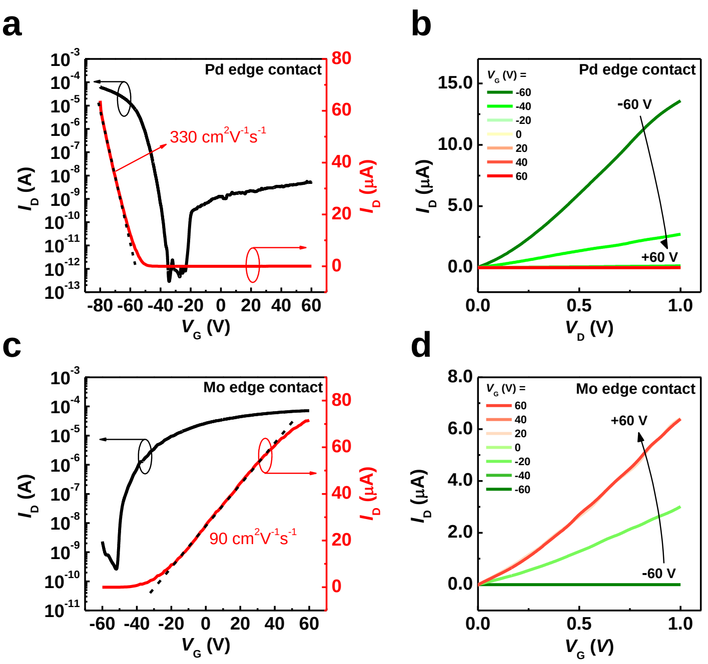


**Figure 1: Electrical performance of Mo/ $MoS_2$ and Pd/ $MoS_2$ edge contact FETs.** Transfer curves on the log (black) and linear (red) scales, for Pd (**a**) and Mo (**c**) at $V_D$ = 1 V (Pd) and 2 V (Mo). Output curves with different gate voltages of Mo (**b**) and Pd (**d**). Mo edge contact FET (L= 6 μm, W=2 μm). Pd edge contact FET (L= 10 μm, W=16 μm).

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# Twistable Electronics and Plasmonics with Dynamically Rotatable Heterostructures

We have reported our innovative technique of using AFM in contact mode to dynamically tune angular alignment of adjacent layers in 2D heterostructures with better than 0.2 degrees of precision [1]. We have been studying electronic transport, optical and mechanical properties of graphene/BN Moiré superlattices in our research through the on-demand control of crystallographic alignment in graphene/BN heterostructures. Our low temperature transport measurements revealed new observations of graphene band structures in graphene/BN moiré superlattice as a pioneering example. Graphene Raman spectra as a function of moiré wavelength were measured in one device eliminating sample variances comparing to more than 30 samples used in previous studies. We also reported rotational friction measurement of graphene and BN in the same device. This new technique will enable a vast amount of research of 2D heterostructures with active and dynamical control of angular alignment. In our recent studies, we extended our capability of rotating 2D materials to extremely thin layers. To reduce the friction between graphene channel surface and extremely thin BN layer in our device, we further invented methods to shape graphene Hall bar with AFM contact mode instead of using traditional e-beam lithography and dry etch. With same methods, we were also able to utilize graphite split gate in our device. All these new techniques enabled near-field plasmonic and photocurrent measurements in dynamically rotatable graphene/BN heterostructures as well.

## References

[1] R. Ribeiro-Palau*, C. Zhang*, K. Watanabe, T. Taniguchi, J. Hone & C. R. Dean, Twistable electronics with dynamically rotatable heterostructures. Science 361, 690 (2018).

## Figures

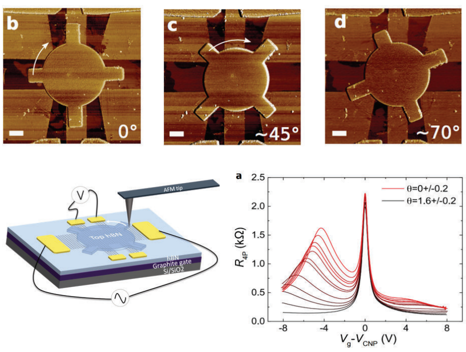


**Figure 1:** Graphene/BN moiré superlattice device with dynamically rotatable BN/HSQ handle [1].

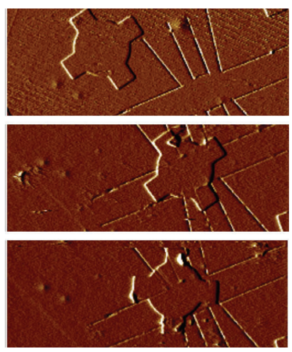

**Figure 2:** 3nm BN handle rotation on graphene Hall bar cut by AFM in contact mode.

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