VIRTUAL Graphene 2021

NOVEMBER 02-05, 2021

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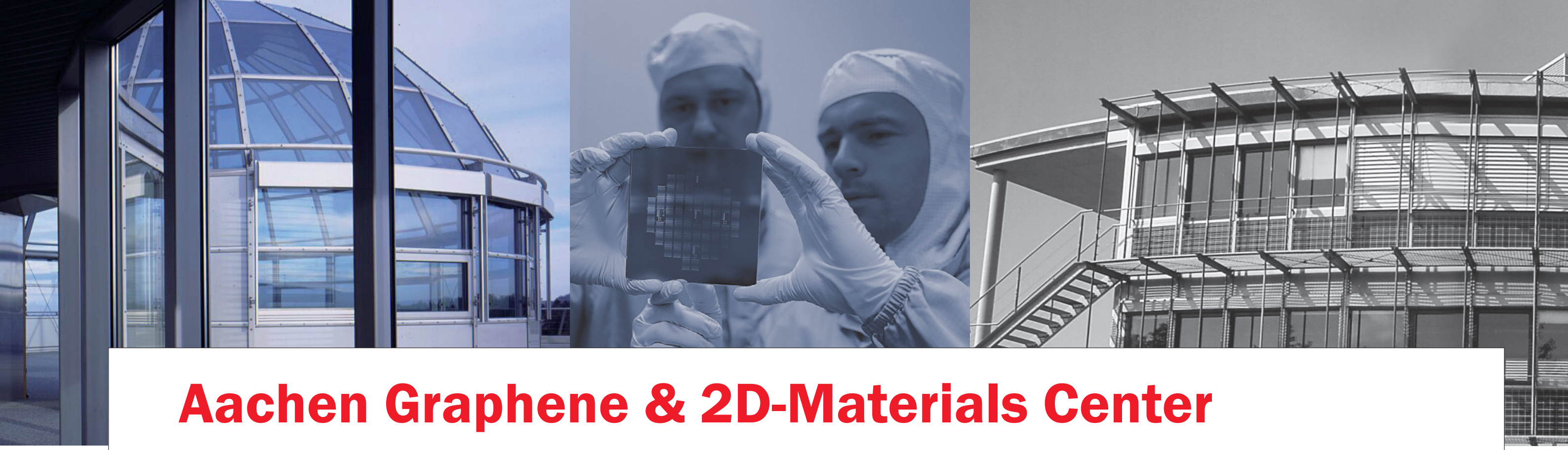
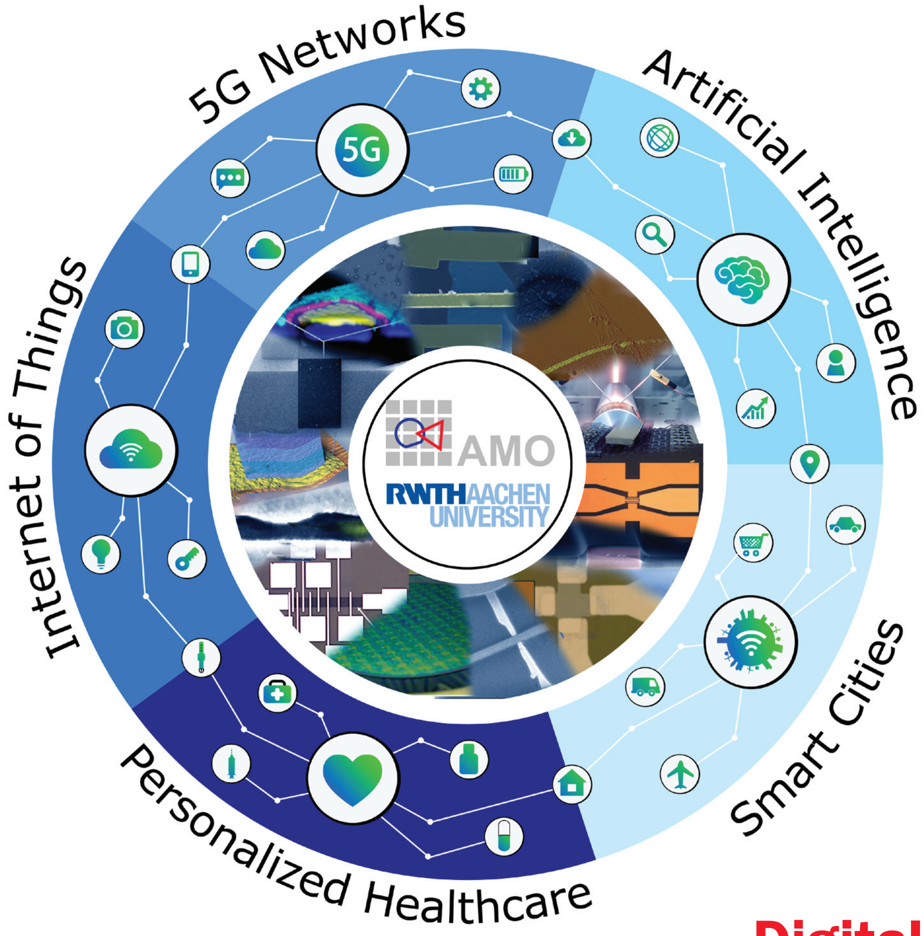


Aachen Graphene & 2D-Materials Center

From basic research to innovation



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FOREWORD

On behalf of the Organising Committee we take great pleasure in welcoming you for the 1st edition of the "Virtual Graphene" 2021 International Conference (November 02-05, 2021) featuring as well 2D-HAPES2021 (2D-Halide Perovskites International Workshop).

2D-HAPES2021
2D Halide Perovskites
from basic science to applications
VIRTUAL
graphene
2021
2D-HAPES2021 International Conference (2D Halide Perovskites)
to be organised within Virtual Graphene as a satellite workshop

Graphene and 2D Materials have a huge potential to impact established industrial sectors, building new emerging industries and niche segments and creating economic value. This four-day online conference will present the whole value chain of "Graphene and 2D Materials innovation" from most recent scientific discoveries to breakthroughs in large scale material production and integration towards the development of innovative and competitive commercial applications.

More than 40 high profile most influential academia worldwide experts in the Graphene and 2DM sector will present speeches in this international event on how advanced materials will change the future of technology and impact positively our daily life.

We are indebted to AMO GmbH (Germany) for their help and financial support. We also would like to thank all the speakers and participants that join us this year and the Institute of Microelectronics and Photonics "Lukasiewicz" for exhibiting at Virtual Graphene2021.

Hope to see you again in-person in the next edition of **Graphene2022 (Aachen, Germany): June 28 – July 01, 2022.**

Virtual Graphene2021 Organising Committee

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AMO GmbH is a German high-tech company that acts as a pathfinder for new technologies and as fabrication-service provider in the field of nanotechnology since more than 20 years.

AMO operates a state-of-the-art clean room with advanced nanostructuring capabilities (UV-Nanoimprint, E-Beam lithography, Interference Lithography), offering research and fabrication services that go from proof-of-concept demonstrators to final technological solutions. Main fields of expertise are nanoelectronics, photonics, sensor technology, as well as graphene and other two-dimensional materials.

https://en.uniroma2.it/

University of Rome Tor Vergata was established in 1982 and is therefore a relatively young University. It was designed on the model of Anglo-Saxon campuses: it stretches on 600 hectares and hosts important research institutions, such as National Research Council – CNR and the Italian Space Agency – ASI.
The mission of the University of Rome Tor Vergata is to contribute to people's education and training, to scientific research and to the technological, organisational and social innovation needed to achieve a truly sustainable development in Italy, Europe and worldwide pursuant to the Sustainable Development Goals approved by the United Nations in September 2015.
As the implementation of the actions needed to accomplish such ambitious purpose requires high skills and management of complex processes, not only is the Tor Vergata University deeply committed to excellent education and scientific research, but it also closely cooperates with the private sector, public institutions and non-profit organisations at national and international level. This aims at favouring the adoption of policies and behaviours focusing on sustainability both in terms of well-being for people and ecosystem conditions.

EXHIBITOR

https://imif.lukasiewicz.gov.pl/en/

Łukasiewicz – Institute of Microelectronics and Photonics (Łukasiewicz-IMiF) is one of 32 research and development institutes in the Łukasiewicz network – Europe's third largest research network, whose mission is to support the development of Polish and international companies.

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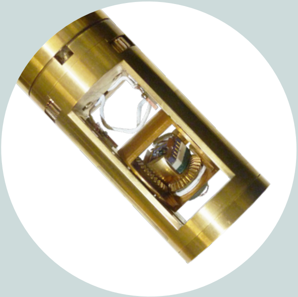
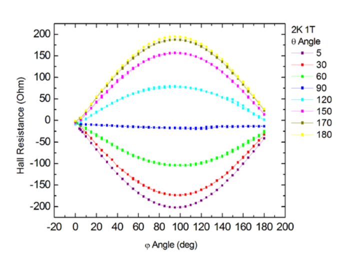
CRYOGEN-FREE MEASUREMENT SYSTEM INSERTS



Two-Axis-Rotator

One-Axis and Two-Axis Rotators

- One-Axis: In-plane or out-of-plane orientation
- Two-Axis: 180 degree in each axis
- Compatiable with resistivity and hall measurement

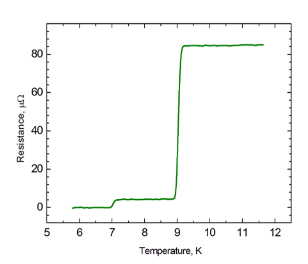


Hall Voltage Measured using a Two Axis Rotator: Theta Sweeps

Fibre Optic Probe with illumination

Resistivity and Hall Effect Measurements

- DC or AC options available
- Temperature range up to 1.6 K up to 700 K
- Compatiable with electro optical measurement

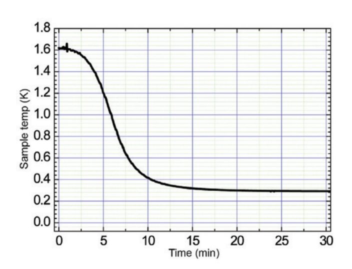


Resistance vs Temperature in zero applied field

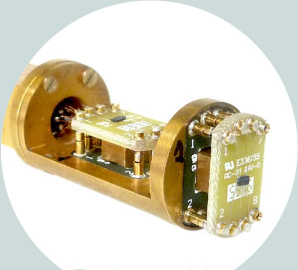
Rotating ^{3}He insert

Ultra Low Temperatures

- 300 mK base temperature with ^{3}He insert
- Rotator available for ^{3}He insert
- <50 mK with DR insert



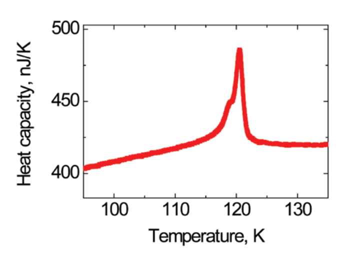
Cooldown of a sample from 1.6 K (IVTI base temperature) to a ^{3}He pot base temperature of less than 300 mK



Probe end for relaxation calorimetry

Thermal Properties

- AC Calorimetry for unparalledled sensitivity
- Relaxation method for high accuracy
- Thermal transport insert for measuring thermal conductivity and Seebeck coefficient



Heat capacity vs Temperature in zero applied field

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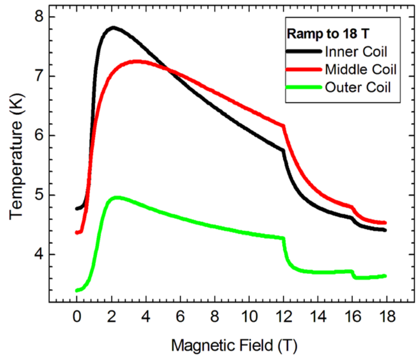
Suitable for physical characterisation of graphene and other two-dimensional structures.

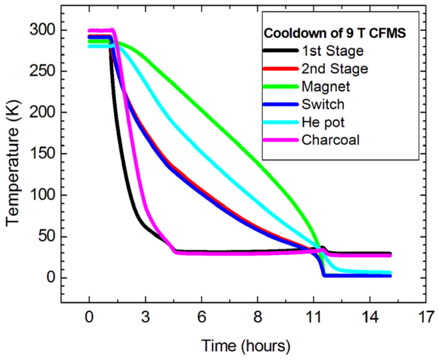
12 T CFM with 50 m iVTi

Two-Axis Rotator Probe

^{3}He Rotator Probe for temperature down to 0.3 K



Ramp of magnetic field to 18 T showing the resistance of a GaAs-AlGaAs hetrostructure at 300 mK, 2 K and 5 K



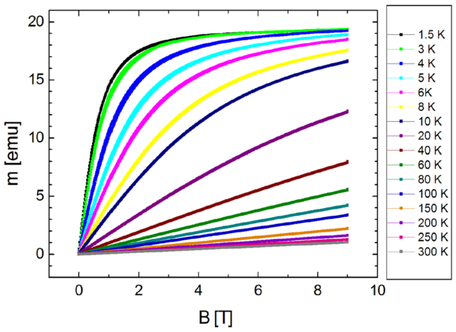
Typical cooldown graph of 9 T cryogen-free system

Key features

- Magnetic fields from 3 T to 18 T
- 1.6 K to 400 K as standard
- mK stability across the temperature range
- 50 mK to 1000 K available with special options
- 20 bit power supply provides precise field control

Magnetic Measurements

- VSM and AC susceptibility options
- Heater options to 700 K or 1000 K
- Ferromagnetic resonance (FMR) insert)



Magnetic moment of the paramagnetic material $Gd_2(SO_4).8H_2O$ as a function of field at different temperatures.

Advances in room temperature 2D ferromagnets

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Sarah Friedensen, Rachael Keneipp, Alice Castan
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Recently-discovered two-dimensional ferromagnetic materials (2DFMs) have rapidly gained much interest in the scientific community. Such materials are potentially transformative in the fields of spintronics and computing, where they may prove powerful tools for miniaturizing devices such as magnetic tunnel junctions and spin-transfer torque memory bits. In addition, heterojunctions and twisted bilayer stacks of such materials may yield interesting and exotic spin textures. However, preparation of such devices is complicated by the air sensitivity of many 2DFMs. Here, we report our progress on the preparation of few-to-monolayer flakes of in-plane ferromagnet vanadium selenide (VSe_2) using electrochemical exfoliation, a detailed study of the change in both surface topology and ferromagnetic properties of VSe_2 in air after different levels of surface passivation, and work towards developing an AFM technique for specifically imaging lateral magnetic fields.

FIGURES

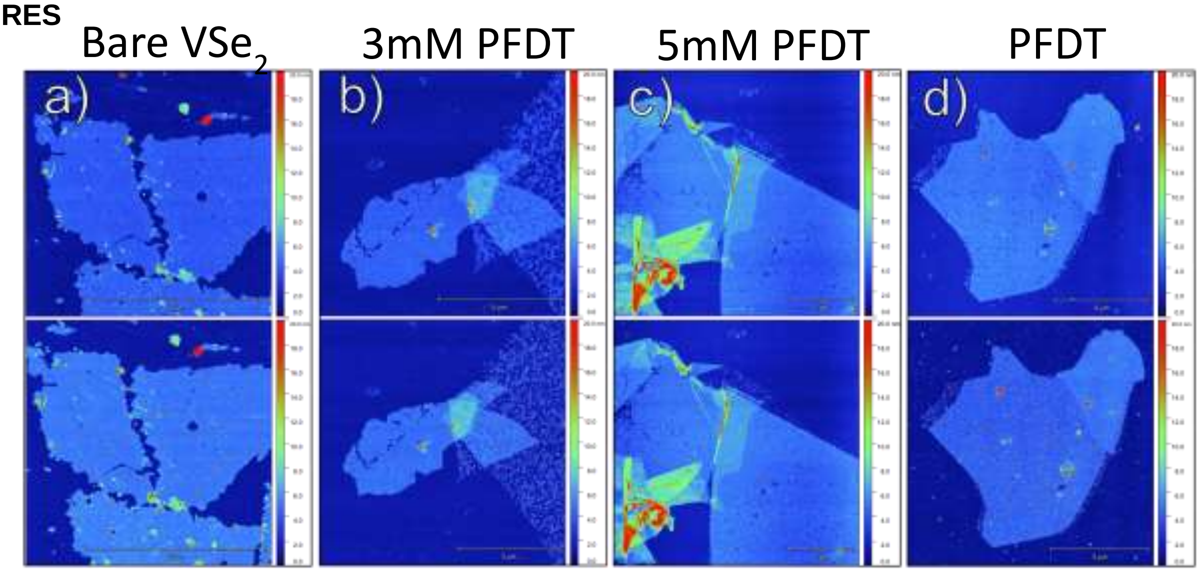

Figure 1: AFM time-series with different concentrations of perfluorodecanethiol (PFDT) surface treatment in ethanol shows that for few-layer VSe_2, concentrations as low as 3mM of PFDT in ethanol prevent oxidation just as well as pure PFDT.

Semiconductor moiré materials

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The discovery of moiré materials has enabled condensed matter experimentation in new regimes. In this talk, I will discuss the general features of moiré materials, with a particular focus on the interplay between strong electronic correlations and non-trivial band topology in semiconductor moiré systems. Specifically, I will discuss how we can explore Hubbard physics and Kane-Mele-Hubbard physics in these materials.

Exciton manipulation and transport in 2D semiconductor heterostructures

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The discovery of graphene marked the start of research in 2D electronic materials which was expanded in new directions with MoS_2 and other layered semiconducting materials. They have a wide range of interesting fundamental properties and potential applications. New opportunities are enabled by the band structure of transition metal dichalcogenides (TMDCs) in which we could harness the valley degree of freedom for valleytronics and next-generation photonics. Long-lived interlayer excitons in van der Waals heterostructures based on TMDCs have recently emerged as a promising platform for this, allowing control over exciton diffusion length, energy and polarization. I will show here how by using MoS_2/WSe_2 van der Waals heterostructures, we can realize excitonic transistors with switching action, confinement and control over diffusion length at room temperature in a reconfigurable potential landscape. On the other hand, the weak interlayer interaction and small lattice mismatch in $MoSe_2/WSe_2$ heterostructures results in brightening of forbidden optical transitions, allowing us to resolve two separate interlayer transitions with opposite helicities and meV-scale linewidths. These have opposite helicities under circularly polarized excitation, either preserving or reversing the polarization of incoming light. By using externally applied electrical fields, we can control their relative intensities and polarization by different regions in the moiré pattern, characterized by different local symmetries and optical selection rules. Our more advanced excitonic devices now also offer the way to manipulate the motion of valley (spin) polarized excitons.

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Electronic, Thermal, and (Some) Unusual Applications of 2D Materials

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This talk will present recent highlights from our research on two-dimensional (2D) materials, including graphene, boron nitride (h-BN), and transition metal dichalcogenides (TMDs). Our results span from material growth and fundamental measurements, to simulations, devices, and system-oriented applications. We have grown monolayer 2D semiconductors over large areas, including MoS_2 [1], WSe_2, and $MoSe_2$ [2]. We also uncovered that $ZrSe_2$ and $HfSe_2$ have native high-κ dielectrics ZrO_2 and HfO_2, which are of key technological relevance [3]. Improved electrical contacts [4] led to the realization of monolayer MoS_2 transistors with high current density [5,6], near ballistic limits [7]. We have also demonstrated new memory devices based on layered Mo-, Sb-, and Ge- tellurides [8,9]. These could all play a role in 3D heterogeneous integration of nanoelectronics, which presents significant advantages for energy-efficient computation [10]. I will also describe a few less conventional applications, where we used 2D materials as highly efficient thermal insulators [11] and as thermal transistors [12]. These could enable control of heat in “thermal circuits” analogous with electrical circuits. Combined, these studies reveal fundamental limits and some unusual applications of 2D materials, which take advantage of their unique properties.

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Production of organic nanomaterials by liquid phase exfoliation

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Liquid phase exfoliation (LPE) has become an important production technique giving access to single and few-layered nanosheets in colloidal dispersion. It has been shown to be applicable to a whole host of inorganic crystals with the nanosheet morphology being defined by the in plane and out of plane binding strength in the parent crystal.[1] In addition to layered inorganic crystals, organic sheet stacks such as 2D polymers or covalent and metal organic frameworks have received increasing attention in recent years. Such organic sheet stacks can be made by a number of techniques, e.g. using reversible solution phase chemistry, polymerisation after assembly on the liquid-air or liquid-liquid interface or polymerisation after precisely aligning monomers in single crystals.

With the single crystal to single crystal transformation, perfectly single crystalline 2D polymer sheet stacks can be synthesised and are an ideal starting point for LPE. We found that crystalline nanosheets are produced after LPE of charge-neutral polymers.[2] By optimising the size selection, mg fractions with up to 29% of monolayers of a model 2D polymer with an average length of ~130 nm were obtained. This is the first time that the amount of monolayers of an exfoliated organic 2D material has been quantified. Overall, LPE of this derivative is equally efficient as graphite exfoliation producing nanosheets with average length/thickness aspect ratios of ~60.[2]

In contrast, LPE of metal organic frameworks (MOFs) yields relatively small and thick sheets. Using a Zr-MOF as model system an average length/thickness aspect ratio of ~6 was determined [3] which is significantly lower than for many layered inorganic materials (e.g. transition metal dichalcogenides). In a comparative study using a range of Ga, Sc and Zr-based MOFs,[4] as well as $Cu(HHTP)_2$ we find that the aspect ratio varies between 4-10 when performing LPE in aqueous surfactant. We attribute this to the typically polycrystalline nature of the starting materials.

Finally, we were intrigued by the question whether materials with only noncovalent bonds could be exfoliated using LPE. With the realisation that the binding strength anisotropy governs the (average) shape of the LPE nanomaterials, it should be possible to obtain nanomaterials with distinct shape from exfoliation of organic molecular crystals. To test this, orthorhombic and triclinic single crystals of the organic semiconductor rubrene with only non-covalent π-π interactions between the molecules were used in LPE.[5] Distinct nanorods and nanobelts of rubrene with only a few molecular layers are formed, stabilized against aggregation in aqueous sodium cholate solution and isolated by liquid cascade centrifugation.

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Metrological framework for quality control of mass-produced graphene

Luiz Gustavo Cançado
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Liquid-phase exfoliation (LEP) is considered, among all forms of producing 2D materials, as the most scalable one [1]. However, production scalability, with quality, can only be reached if critical parameters such as temperature, processing time, and energy are optimized. Postprocessing is also important: the proper choice of electrostatic or steric stabilizers can make the suspensions stable. Mass separation through centrifugation is usually employed to improve homogeneity. All these procedures should be monitored, aiming at the requirements that make the material suitable for the target application. However, because LPE usually generates 2D nanosheets with broad distributions of thickness and lateral size, it is hard to find the right parameters that summarize the yielded material. For this purpose, robust statistical analysis is required. In this talk, I will present statistical methods that summarize and provides deep understanding of morphological attributes of mass-produced nanoflakes from 2D materials. The protocol is based on atomic force microscopy (AFM) [2-4], Raman spectroscopy [5,6], and tip-enhanced Raman spectroscopy (TERS) [7] measurements and automated analysis. The information gathered is rarely accessible even in conventional methods considered as statistical ones, such as thermal or spectroscopic analysis. The key factor is that the statistical essence our protocols is not related to the measurement itself but to the large number of nano-objects individually scrutinized, having their morphological parameters extracted one by one. The amount and type of information that can be extracted from this routine indicate that this is the most adequate way to analyze batch produced nanomaterials, in which the size and shape of each individual nano-object matters to the physicochemical properties of the whole.

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Deep-ultraviolet spectroscopy in hexagonal boron nitride: from bulk to monolayer

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Hexagonal boron nitride (hBN) is an ultrawide bandgap semiconductor with a large range of basic applications relying on its low dielectric constant, high thermal conductivity, and chemical inertness. The growth of high-quality crystals in 2004 has revealed that hBN is also a promising material for light-emitting devices in the deep-ultraviolet domain, as illustrated by the demonstration of lasing at 215 nm by accelerated electron excitation [1], and also the operation of field emitter display-type devices in the deep-ultraviolet [2]. With a honeycomb structure similar to graphene, bulk hBN has gained tremendous attention as an exceptional substrate for graphene with an atomically smooth surface, and more generally, as a fundamental building block of Van der Waals heterostructures [3].

I will discuss here our results on the optoelectronic properties of hBN from bulk to monolayer. I will first focus on bulk hBN, which is an indirect bandgap semiconductor with exceptional properties [4]. I will present our recent measurements revealing the giant light-matter interaction in bulk hBN [5]. I will then address monolayer hBN. In samples epitaxially grown on graphite by high-temperature MBE, the reflectivity minimum is found in resonance with the emission of atomically-thin hBN, thus demonstrating the direct bandgap of monolayer hBN [6]. These results are further confirmed by recent experiments by means of hyperspectral imaging in the deep-ultraviolet in monolayer hBN exfoliated from a bulk crystal [7].

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Sweden aims to be in the top 10 countries at using graphene for industrial needs

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Sweden has a strategic innovation programme – called SIO Grafen – with a focus on graphene and 2D materials. The vision of the programme is that in 2030 Sweden is one of the leading countries at developing and using graphene industrially.

SIO Grafen thus has a national responsibility to:
- Establish graphene as an industrial area of strength
- Develop collaboration
- Stimulate Swedish graphene supply
- Contribute to sustainable solutions

SIO Grafen is now in its seventh year out of a maximum of twelve. SIO Grafen has funded approximately 150 projects where graphene or other 2D materials has been the key factor in solving industrial challenges. About 180 organisations have participated in these projects. Most of these organisations are based in Sweden, but not all. We would now like to encourage even more international collaboration.

This presentation will describe the programme and discuss some examples of the funded projects.

Probing electric polarization on the atomic scale: the case of van der Waals heterostructures and water confined inside

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In this talk, after briefly reviewing scanning dielectric microscopy - a set of scanning probe microscopy methods that probes dielectric properties on the atomic scale [1-3] - I will present our most recent studies applied to van der Waals (vdW) heterostructures [4-6]. First, we succeeded to measure the dielectric constant of few water layers confined into atomically flat nanoslits made of graphite and hexagonal boron nitride (hBN) [4]. Our work revealed the presence of an electrically dead water layer with vanishingly small polarization at the solid/liquid interface, providing much-needed feedback for theories describing interfacial water and water-mediated surface interactions. We then focused on the properties of hBN heterostructures. Our experiments revealed that monolayer hBN is piezoelectric, while we found no piezoelectricity in bilayer and bulk hBN [5]. Our experiments also revealed that marginally twisted hBN heterostructures - two hBN crystals stacked at small twist angle - have ferroelectric-like superlattice domains [6]. These findings open up new possibilities for understanding electric polarization on the atomic scale and designing novel devices with piezoelectric and ferroelectric properties based on van der Waals heterostructures and liquids confined inside.

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Atomic reconstruction in twisted TMD interfaces and their electronic properties.

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Twisted heterostructures of two-dimensional crystals offer a broad scope for the design of novel metamaterials. In this talk I will review our latest work on twisted TMDs bilayers and discuss atomic reconstruction that occurs when the twist angles are small. For small twist near the 2H stacking, stable 2H domains dominate, with nuclei of a second MM metastable phase. This appears as a kagome-like pattern at ~1 degree twist, transitioning below 0.3 degree to a hexagonal array of large 2H domains. The tunnelling measurements show that such reconstruction creates piezoelectric textures, opening a new avenue for engineering of 2D material properties.
For 3R stacking, a pattern of mirror reflected triangular 3R domains merges, featuring layer-polarized conduction band states caused by lack of both inversion and mirror symmetries. Surprisingly, the lack of inversion symmetry in 3R polytype leads to emergence of out-of-plane ferroelectricity due to layer-asymmetric interband hybridisation. The electrically-polarised domains can be switched by external electric field which opens a new pathway towards optoelectronic devices with memory effect..

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FIGURES

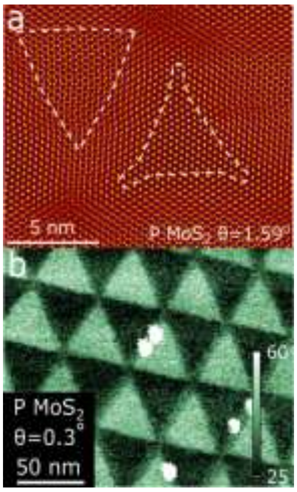

Figure 1: (a) Atomic resolution STEM imaging of the reconstructed lattices in twisted bilayer MoS2 (b)Conductive AMF image of the 3R domain structure indicating layer-polarised electronic wave functions.

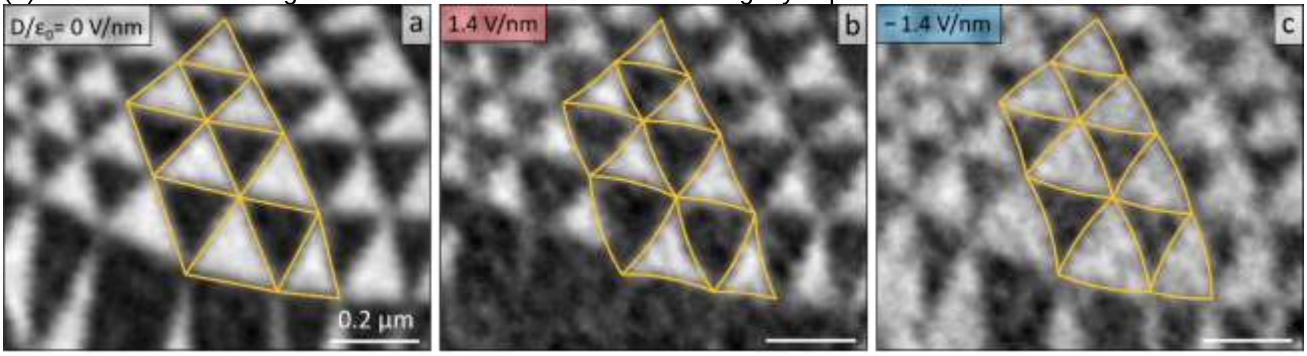

Figure 2: Domain evolution under transverse electric field.

Emergent optical functionalities of van der Waals heterostructures of transition metal dichiacogenides

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Van der Waals (vdW) heterostructures form a rich platform which enables us to fabricate a variety of combination of materials without any constraint of lattice mismatch, sequence, and twisted angles, and consequently to create rich properties and functionalities. Here we introduce our attempts in exploring optoelectronic functions of vdW heterostructures based on the transition metal dichalcogenide (TMD).

One noticeable advantage of vdW heterostructures is that its symmetry can be controlled depending on how and what materials researchers stack. This is in marked contrast with the bulk single crystals, where symmetry is uniquely determined by the space group. When we construct a vdW heterostructure of C3 symmetric WSe2 and C2 symmetric black phosphorous (BP), the combined system becomes C1 symmetric because three-fold and two-fold rotational symmetries can not coexist. Consequently, the heterostructure system becomes in-plane polar despite that both WSe2 and BP are nonpolar materials. This allows the occurrence of bulk photovoltaic effect in WSe2/BP with a relatively large photocurrent density in comparison to the bulk polar crystals [1].

Another example is the exciton/magnon interaction at the vdW interface of MoSe2 and yttrium iron garnet (YIG). YIG films support long-lived magnons that can be coherently driven by microwaves. Magnons play a major role in spintronics circuits as a low-loss information carrier, and in quantum hybrid systems as a macroscopic quantum interface to superconducting quantum bits. Realizing an interfacial coupling between magnons and excitons offers a promising way forward to connect spintronic and quantum technologies to optics. Here we report unambiguous evidence of a dynamical coupling between mangnons in YIG and excitons in TMDs through the interfacial exchange interactions [2].

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Graphene Plasmonic Crystals for Terahertz Radiation Amplification

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More than 40 years ago, a new direction in physics opened up with the arrival of plasma-wave electronics. The possibility that the plasma waves could propagate faster than electrons fascinated all. Therefore, it was initially expected that plasmonic devices, including detectors and generators of electromagnetic radiation, would be able to work effectively in the very high frequencies - terahertz (THz) range, inaccessible to standard electronic devices. However, numerous experimental attempts to realize such amplifiers or emitters failed: the intensity of radiation turned out to be too small, plasma resonances too broad, or devices operated only at cryogenic temperatures. Thus, the creation of compact, tunable, room temperature operating THz amplifiers and sources is still a challenging task.

We study THz radiation absorption by grating graphene nanostructures (see Fig.1) and demonstrate gate voltage tunable resonant plasmon absorption, that with an increase of the current, turns to THz radiation amplification with a gain going up to 9% [1]. The results are interpreted using a dissipative plasmonics crystal model, which captures the main trends and basic physics of the amplification phenomena. Specifically, the model predicts that increasing current drives the system into an amplification regime, wherein the plasma waves may transfer energy to the incoming electromagnetic waves. All results were obtained at room temperature. Therefore, they pave the way towards a future THz plasmonic technology with a new generation of all-electronic, resonant, voltage-controlled THz amplifiers [1].

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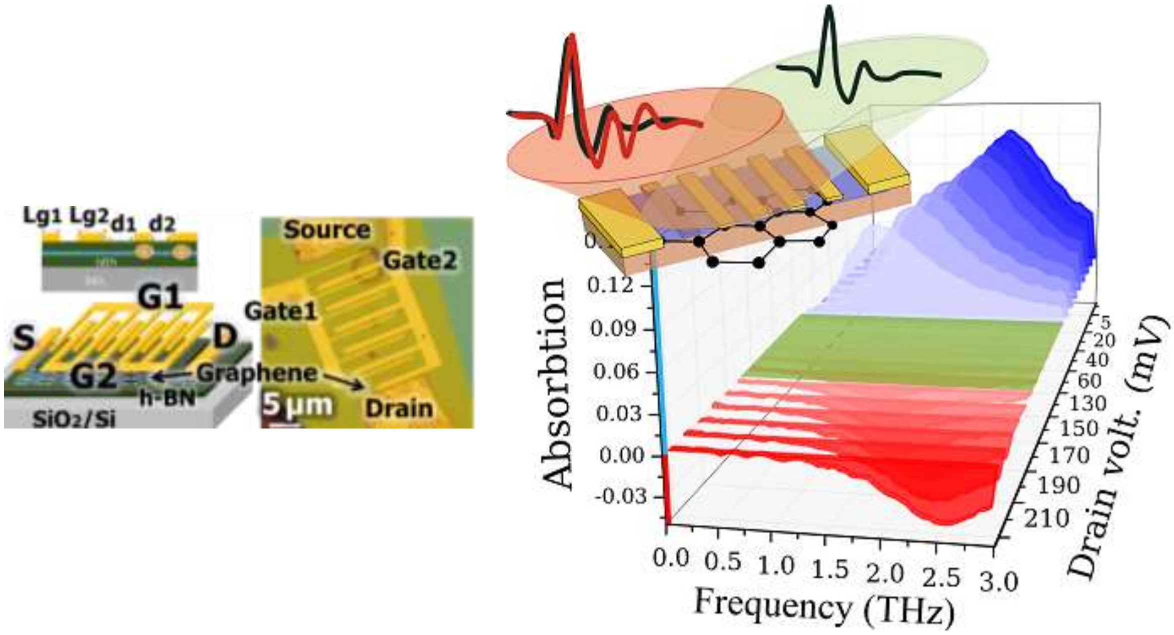

Figure 1: Schematic representing experimental configuration with a grating-gate graphene transistor structure along with incoming and outgoing THz beams. The 3D plot depicts experimentally recorded plasma resonances, highlighting that with increasing drain voltage/current, the resonant absorption (blue) turns to total transparency (green) followed by amplification ("negative absorption" – red)

Graphene based flexible radio-frequency electronics: Current status and major challenges

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Radio frequency integrated circuits (RF ICs) built the core of modern information and communication systems. Graphene based devices like transistors, diodes or varactors have been recognized from the very beginning as promising candidates in future RF ICs, having the potential to significant outperform established devices based on Silicon or III/V semiconductor materials in terms of speed, functionality or mechanical flexibility.

However, so far the potential of graphene in RF electronics has mainly been demonstrated on a single device level because the realization of more complex integrated RF circuits was limited by a non-mature fabrication technology and large variations in the device performances.

In this presentation I will first present the MMIC (monolithic microwave integrated circuit) process for graphene based RF circuits developed at AMO and discuss especially the challenges and possible solutions related to device variability and yield.

Different RF ICs have been realized so far, which are designed for future WiFi communication systems in 5G and for IoT applications.

In the second part of the presentation, I will discuss approaches, challenges and possible solutions for the wafer scale integration of graphene based electronic and sensor devices [1]. The performance will be compared to chip scale production and the current limitations for yield, device to device variation and reproducibility will be discussed.

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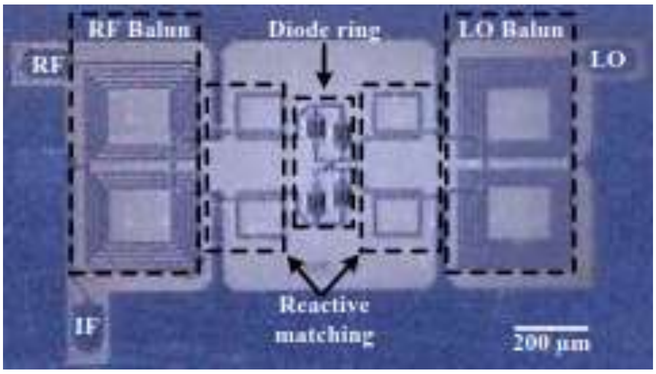

Figure 1: Optical micrograph of an integrated RF circuit (double balanced mixer operating at 6-12 GHz). The different parts of the circuit are indicated.

Atomic defects in 2D materials studied by transmission electron microscopy

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Structural defects are considered as a parameter-tuning knob for tailoring physical properties of 2D materials. The ability to engineer atomic defects at nanometer scale opens up unique opportunities to alter and enhance electrical, optical, mechanical and magnetic properties. Despite the growing interest in 2D materials, growing defect-free 2D materials on desired substrates remains a challenge. Identification and characterization of these inevitable intrinsic growth defects are thus an essential process. Further exploitation of possible defect modification and manipulation might shed light on potential utilization of defect structures in device processing. Aberration Corrected Transmission Electron Microscopy (AC-TEM) is one of the most suitable techniques to study the atomic structure of 2D materials, enabling to visualize atomic defects and simultaneously to form new defects by electron irradiation [1]. In this work, we demonstrate a multi-scale analysis of WSe_2 monolayer grown by molecular beam epitaxy (MBE) in van der Waals regime [2], using a simultaneous real and reciprocal space imaging, so-called 4D-STEM. A possible correlation of atomic defects to large-scale structural analyses obtained by X-ray diffraction will be demonstrated for the purpose to study 2D epitaxial growth. In addition, we study the atomic defects diffusion under thermal electron irradiation inside TEM to explore the possibilities of defect engineering and materials design by combining their intrinsic and extrinsic defects.

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The thermal conductivity of the Dirac fluid at room temperature

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Graphene displays highly exciting fundamental properties, while enabling a range of promising applications, in particular related to the field of optoelectronics, where hot carriers often play a crucial role [1]. Here, we will show recent results [2], where we have studied the flow of electronic heat in graphene, carried by hot carriers, using a novel technique (see Fig. 1). Owing to hydrodynamic behavior – where carrier-carrier interactions are faster than momentum relaxation – we obtain a giant electronic heat diffusivity up to 70,000 cm^2/s. The diffusivity is particularly large upon approaching the Dirac point, where the system enters the quantum-critical Dirac fluid regime. In this regime, theory predicts a diverging thermal conductivity [3], and indeed we find a thermal conductivity up to 40,000 W/m/K. This is an order of magnitude larger than the already extremely high thermal conductivity of the phonon system of graphene [4]. This result is likely relevant for thermal management applications requiring ultrafast heat dissipation from small hot spots.

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FIGURES

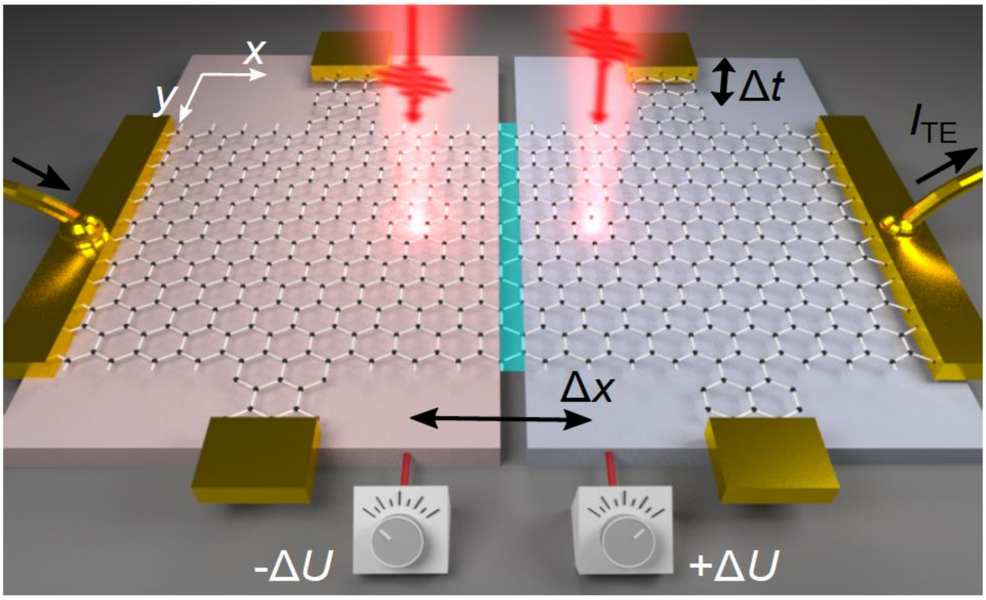

Figure 1: Schematic representation of spatiotemporal thermoelectric microscopy with two spatially (Δx) and temporally (Δt) displaced ultrashort laser pulses that are incident on a graphene device with two backgates at respective gate voltages of $-\Delta U$ and $+\Delta U$. This creates a *pn*-junction (cyan-colored region), where photocurrent is generated. By systematically varying Δx and Δt and measuring the photocurrent generated by interacting heat from the two pules, we obtain the diffusivity of heat carried by the electronic system. This thermal diffusivity becomes extremely high – up to 70,000 cm^2/s – when examined in the hydrodynamic time window, where Δt is smaller than the momentum relaxation time (~350 fs for our device). This is especially the case when ΔU is small, *i.e.* close to the Dirac point, when the system is in the quantum-critical Dirac-fluid regime. See Ref. [2].

Mesoscopic Transport and Twistronics in Gate-defined Van der Waals Nanostructures

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Layers of two-dimensional materials stacked with a small twist-angle give rise to beating periodic patterns on a scale much larger than the original lattice, referred to as a "moire superlattice". As the twist angle approaches ~1.08 degree, isolated flat-bands emerge near zero energy. Correlated superconducting and insulating states were reported near the half-filling of such flat-bands. In this talk, we will discuss a higher-order moiré superlattice of moiré superlattices in a twisted-trilayer graphene architecture [1]. We report transport signatures of superconducting and correlated insulating states near the half filling of the moire of moire superlattice, at an extremely low carrier density on the order of ~1010 cm-2. We also show that the temperature dependence of v=-4 and v=4 states are semi-metallic, distinct from the insulating behavior in twisted bilayer systems, demonstrating that moiré superconductivity may emerge from continuous and non-isolated flat-bands. Towards further understanding and utilizing the rich underlying physics in twisted-trilayer-graphene, we will also talk about our recent effort in building gate-defined nanostructures to locally manipulate charge carriers with electrostatics in graphene [2].

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Advanced 3D printed electrode based on Si and wet-jet milled few layers graphene for Li-ion batteries

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Development of Li-ion batteries with specific geometries and form factors meeting the requirements of the newly emerged technologies is gaining increasing attention [1]. Three-dimensional (3D) printing is an attractive technology for the manufacturing of advanced electrodes for portable electronics and energy storage devices [2]. Herein, we report for the first time,[3] the fabrication of a 3D printed Si-based anode using a simple and cost-effective fused deposition modelling (FDM) for Li-ion batteries. The anode is composed by polylactic acid (PLA) as host polymeric matrix, Si nanoparticles as active material, and wet-jet milled few layers graphene (WJM-FLG)[4] mixed with carbon black doped-polypyrrole (PPy) as conductive additives. This composition has been optimized to produce 3D filament fulfilling the printability and providing a good electrochemical behaviour. The doped-PPy and WJM-FLG nanoflakes uniformly coat the exterior surface of Si nanoparticles, creating a conductive network through the PLA-based filament as well as mitigating the large volume changes during charge-discharge cycling, thus improving the electrochemical performance of the Si-based 3D printed anode [5,6]. The flexible 3D printed anode shows a stable rate capability up to a current density of 50 mA g^{-1}, high coulombic efficiency (97%), a specific capacity of ~ 345 mAh g^{-1} at the current density of 20 mA g^{-1} with the capacity fade rate of only 0.01% after 350 cycles (Figure 1). This work offers a promising strategy for the fabrication of polymeric-based and flexible 3D electrodes with programmable architectures toward next-generation electronic applications.

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Figures

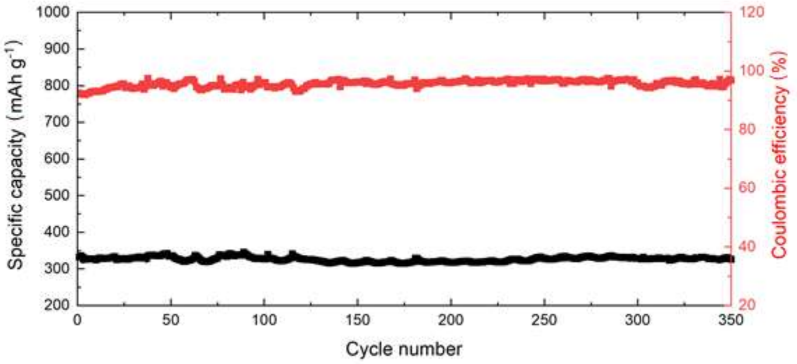

Figure 1: Long-term cyclic performance and coulombic efficiency of the half-cell assembled with the 3D printed optimized electrode at the current rate of 20 mA g^{-1}.

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

In silico polymerization of 2D Polymers at water-surfactant monolayer interfaces

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Two-dimensional Polymers with large crystalline domains and monolayer thickness are challenging to synthesize to this day. A promising approach was introduced by Feng et al. in 2019 [1] where surfactants on a water surface were used to facilitate a 2D templating effect for the polymerization. This happens in three steps: first, spreading of the surfactants on a water surface, second, adding monomer 1 and letting it pre-assemble at the interface, and finally, adding monomer 2 which starts the polymerization. However, the exact mechanisms in each of the steps are poorly understood yet because of the dynamical behavior of the system which is difficult to characterize in experiment. Here, we use Molecular Dynamics (MD) Simulations to account for the dynamics and close the gaps between experimental observations and microscopic understanding. For this, we choose a well-known 2D Polymer synthesis route shown in Fig. 1 as model system [2]. This computational study gives valuable guidelines and insights for engineering crystalline 2D Polymers.

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FIGURES

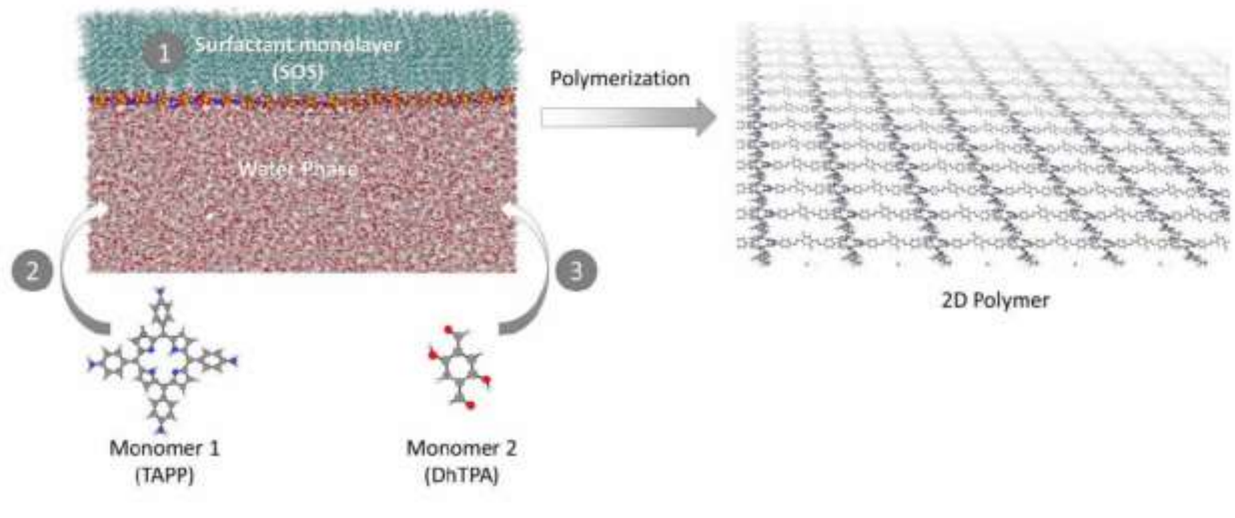

Figure 1: Steps for the polymerization at the water-surfactant monolayer interface, with sodium oleyl-sulfate (SOS) as surfactant, 5,10,15,20-tetrakis(4-aminophenyl)-21H,23H-porphyrin (TAPP) as monomer 1 and 2,5-dihydroxyterephthalaldehyde (DhTPA) as monomer 2.

A Peeling Systematic Study: Holistic Catalyst Design for 2D Material Application

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The homogeneous and repeatable transfer of 2D materials (2DMs) remains a significant bottleneck in the field both for characterization of chemical vapor deposition (CVD) grown materials and the reproducibility of devices made from them. A dry-peeling transfer is thought to be the cleanest and most efficient method of 2DM application, owing to the lack of ionic etchants and catalyst preservation during the transfer process. Specific orientations of metals are often employed for 2D material synthesis due to various growth-based advantages: e.g. reported higher quality, epitaxial or wrinkle-free graphene on Cu(111)[1]. Whilst these catalysts may be ideal for the growth of 2D materials, we show that when integrated into a process chain of device fabrication, there are more ideal choices that result in a higher quality final product.

Here we utilize large scale data acquisition and processing techniques to enable a holistic development route through the copper-oxide-graphene growth and transfer parameter space and demonstrate a clear path that leads to both epitaxially aligned graphene growth and a high propensity for mechanical delamination: maximizing both transfer and quality. We identify the ideal Cu orientation and reproduce it over larger areas utilizing recently developed single-crystal catalyst production methods[2]. We characterize this CVD graphene to show that the quality is comparable to that of exfoliated material, with the added benefit of reproducibility available over much larger areas. Finally we utilise a similar cross-correlative methodology to characterise CVD h-BN growth and application to demonstrate a similar moral: The whole application process must be holistically considered to develop an ideal material synthesis methodology.

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Two Stage Epitaxial Growth of Boron Nitride – Advantages and Prospects

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Sp^2-hybridized boron nitride (BN) is a wide bandgap (about 6 eV) two-dimensional material, very resistant to harsh external conditions [1]. These properties enables its use in a wide range of applications, for example: deep UV light sources, one of the building blocks in van der Waals heterostructures, protective layer etc. [2]. In order for the created structures to be as effective as possible, it is necessary to develop a growth method that will result in the formation of a material with good optical and structural properties on the large scale.

Metal Organic Vapour Phase Epitaxy (MOVPE) is the method that could fulfil all of these requirements. In this technique, the BN growth is carried out on sapphire substrates with triethylboron (TEB) and ammonia as precursors of boron and nitrogen, respectively. The proposed new growth mode - two stage epitaxy - allows to avoid the chaotic nucleation on the substrate, characteristic for Flow-rate Modulation Epitaxy (FME) by introducing a thin (a few nanometers), pre-ordered, Continuous Flow Growth buffer layer [3]. This new growth method leads to the formation of boron nitride with an almost ideal lattice constant and to the reduction of the concentration of point like defects in the structure. Interestingly enough, in depth studies revealed the correlation between the properties and growth conditions of the CFG stage with structural properties and smoothness of the whole two stage sample (Fig. 1). In this communication the influence of the nitridation, temperature, pressure and the growth time on the properties of the two stage samples is discussed.

Our studies show that the high quality, two stage samples may have even better structural and optical properties. Achieving boron nitride comparable to the bulk material on the large scale is within the scope of our possibilities and a further fine tuning of the method brings us closer to practical applications. The proposed growth method shows great potential for the production of high-quality, smooth, epitaxial hBN which is crucial for large scale optoelectronic applications based on 2D materials.

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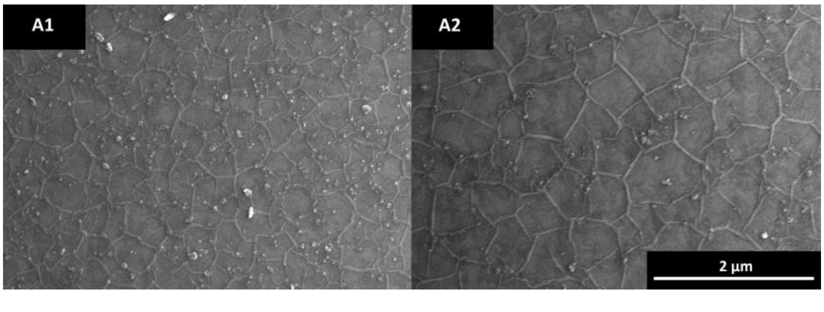

Figure 1: Scanning Electron Microscopy (SEM) image of the two stage samples grown in the same conditions but annealed and stabilized before the growth in nitrogen (A1) and hydrogen (A2).

Acknowledgement: This work has been partially supported by the National Science Centre under grant no. 2019/33/B/ST5/02766

Nanometer-scale Cavities for Mid-infrared Light Based on Acoustic-graphene-plasmons

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Abstract: Acoustic-graphene-plasmons (AGPs) are highly confined electromagnetic modes, which carry extreme momentum and low loss in the Mid-infrared (MIR) to Terahertz (THz) spectra. Here, we demonstrate a new way to excite highly confined AGPs from the far-field, with localized graphene-plasmon-magnetic-resonators (GPMRs). This approach enables the efficient excitation of single AGP resonators, which are able to confine MIR light to ultra-small mode-volumes which are over a billion times smaller than their free-space volume.

In the presented work [1], the GPMRs are formed by depositing specialized metal nanometric cubes on top of graphene capped with monolayer hBN, forming a cavity for AGP's via the generation of magnetic resonances (Fig.1 left pannel). The gate dependent extinction spectra, as measured from a GPMR device in an FTIR spectrometer, is shown in Fig.1 (middle panel). The AGP resonances and their tunable response with the change in the graphene Fermi-level can be clearly seen, together with their well-known hybridization with the surface-optical-phonons of the SiO2 substrate and h-BN layer. The calculated mode-volume normalized to free-space volume, $(\lambda_0)^3$, is shown in Fig.1 (right panel) for different graphene-nanocube distance "d", reaching a huge factor of $\sim 5\cdot 10^{-10}$ at 1nm spacing. We further show that each nanocube acts as an individual GPMR resonator, compressing the AGPs into the nanometer-scale volume between the graphene and nanocube.

Our approach provides direct access to the extremely small mode-volumes of AGPs, enabling a new platform for strong light-matter interaction and efficient AGP-based devices, such as photodetectors and sensors, in the long wavelength spectrum.

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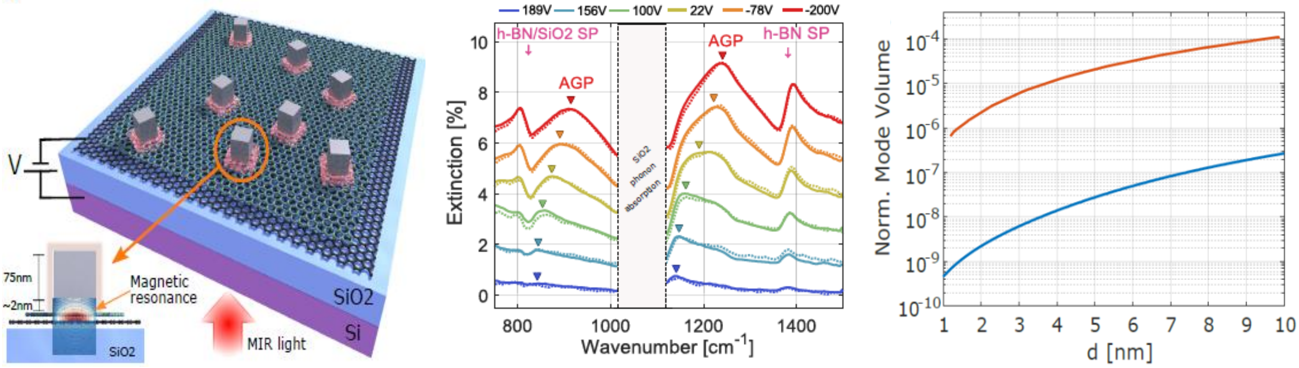

Figure 1: (Left) Configuration of the GPMR device. (Middle) Measured GPMR device extinction spectra for different gate voltages (colors). The triangle marks the AGP peak and the downward arrows mark the location of the h-BN and SiO2 surface-phonons. (Right) Calculated normalized mode volume of the GPMR (blue curve) compared to its equivalent metal-based magnetic resonance in the visible spectrum (red curve), showing several orders of magnitude smaller confinement factor of MIR the GPMR system.

Suitability of NiO-ZnO-rGO sorbents for removal of hydrogen sulphide at intermediate temperatures

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Comprehensive sulfur removal in thermochemical processes is mandatory to comply with the environmental emission limits associated to syngas combustion in boilers, gas engines and turbines, to prevent corrosion of equipment and to avoid poisoning of sulfur sensitive catalysts when upgrading to bio-refinery products. Particularly for syngas, technologies relying on sorbents working in the 300-500°C temperature range are desirable for better process integration. Zinc-oxide based commercial regenerable sorbents, e.g. Z-Sorb™ and S-Zorb™, have demonstrated to provide full removal of hydrogen sulfide from thermochemical conversion processes and specifically from gasification gases [1]. In this work, a new family of NiO-ZnO-rGO sorbents with potential capacity for desulfurization are studied. Synthesis procedure was based on a simple solvothermal process starting from graphene oxide (GO) prepared by the classical Hummers method [2] and the improved Tour method [3]. The morphology and surface properties of sorbents as well as post-reaction products were characterized by XRF, XRD, XPS and N_2 adsorption at -196°C. A commercial sorbent was selected as reference material for comparison studies. The performance of the sorbents for fixed bed desulfurization was studied in a laboratory scale test rig. All graphene–based sorbents performed better than the commercial material studied as reference (Fig. 1). A very good utilization yields degree were attained. Graphene-based materials reached breakthrough times close to the theoretical ones calculated based on their zinc and nickel content.

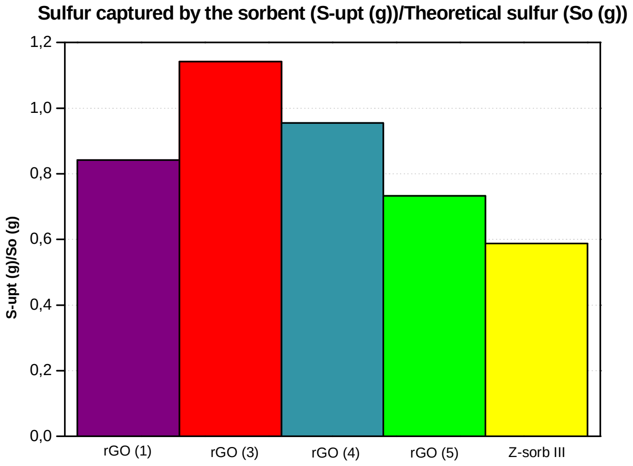

Figure 1: Comparison of the sorbents in terms of utilization yield (T=400°C, P=10 bar, GHSV=3500 h^{-1}, H_2S feed gas= 9000 ppmv, N_2 balance)

Acknowledgements
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Optimized mapping of nanoscale heterogeneity in transition metal dichalcogenides enabled by sample design

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The optoelectronic properties of transition metal dichalcogenides (TMDs) are highly sensitive to a diverse range of internal and external perturbations, such as inhomogeneous dielectric environments [1], structural defects [2], and strain. Non-invasive nanoscale mapping of TMD optical response elucidates the causes of heterogeneity.

We demonstrate scanning-electron-microscope (SEM) cathodoluminescence (CL) hyperspectral mapping of the light emission from hBN-encapsulated TMDs [3] with minimal sample damage [4] and prompt transition between nano- and micro-scale fields of view. Both brightness and spatial resolution in TMD CL depend on the dynamics of electron-hole (e-h) pair generation and diffusion in the hBN encapsulation layers, which are typically significantly thicker than the optically active TMD layers. To date, there is no systematic understanding of hBN carrier dynamics.

Here, we show that hBN thickness controls the CL spatial resolution by acting on the effective diffusion length of the e-h pars generated in hBN. We provide a method to define the optimal working range of hBN thickness to obtain bright signal while maintaining sub-diffraction spatial resolution. We demonstrate the potential of TMD CL with high-resolution hyperspectral CL maps of TMD monolayers (fig. 1a) in which the combination of high spatial and spectral resolution can disentangle different forms of spectral disorder, leading to trion localization and peak energy shifts (fig. 1b).

Our study provides a practical strategy towards the full exploitation of CL to characterize the nanoscale fluctuations of TMD optical properties, which contribute to a robust understanding of TMD optical response for both fundamental and applied physics.

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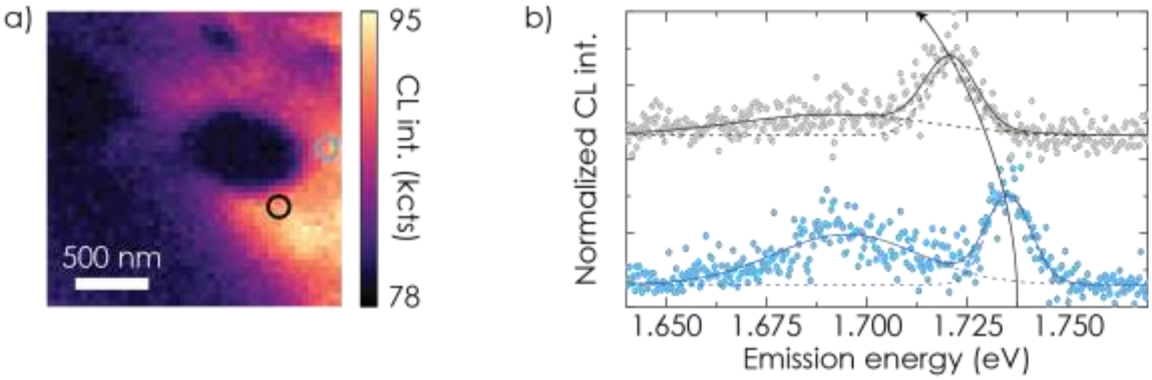

Figure 1: a) Hyperspectral CL map (1.65-1.75 eV shown) of a hBN-encapsulated WS2 monolayer at 15K. b) Spectra from the circled pixels in corresponding colors.

Enhancement of PVDF-based membranes with 2D materials for efficient performance in Membrane Distillation and Membrane Crystallization

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Abstract

Most of membrane transport processes are isothermal and their driving forces are transmembrane hydrostatic pressures, concentrations, electrical or chemical potentials. Membrane Distillation (MD) and Membrane Crystallization (MCr) are non-isothermal processes that actually still needs to be developed for its industrial implementation[1]. These processes are separation technology for treating saline and brine from Reverse osmosis plant such as seawater or brackish water. These operations exploits the hydrophobic nature of the membrane with the possibility to reject 100% of all non-volatiles components contained in the feed solutions[2]. Considered the increasingly demand of fresh and reusable water, our intent is to identify new materials to increase the production and the efficiency of water from desalination with eco-sustainable membrane process. In this direction, graphene and 2D materials are receiving great interest for their additional effect to the host membrane[3]. 2D materials are particular attractive for MD/MCr due to their hydrophobic nature, selective sorption of water vapours and anti-fouling proprieties. In this work Graphene and Bismuth telluride flakes were studied and tested for the enhancement of PVDF membranes in MD and MCr. The flakes were exfoliated with the innovative Wet Jet Mill technique by the colleagues from BeDimensioanl S.P.A[4]. The flakes were incorporated in the membrane during the preparation of the membranes via NIPS. Herein, a summary of the most interesting achievements is given and the behaviour of 2D materials functional membranes is described as a function of chemical composition and salt concentration as well as running conditions selected for membrane operations.

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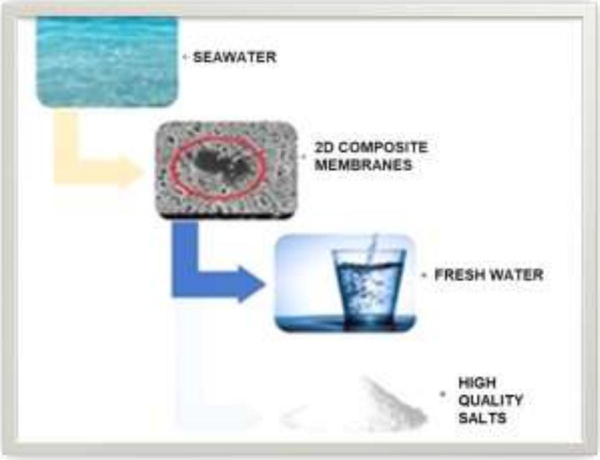

Figure 1: Inclusion of 2D flakes in PVDF-based membrane for desalting highly saline waters and recovery salt crystals

Determining the number of graphene layers based on Raman response of the SiC substrate

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In this presentation we demonstrate a method for direct determination of the number of layers of hydrogen-intercalated quasi-free-standing epitaxial Chemical Vapor Deposition graphene on semiinsulating vanadium-compensated on-axis 6H-SiC(0001). The method anticipates that the intensity of the substrate's Raman-active longitudinal optical *A1* mode at 964 cm^{-1} is attenuated by 2.3% each time the light passes through a single graphene layer. Normalized to its value in a graphene-free region, the A_1 mode relative intensity provides a greatly enhanced topographic image of graphene and points out to the number of its layers within the terraces and step edges, making the technique a reliable diagnostic tool for applied research. Raman spectra of graphene and the underlying SiC substrate were obtained in a backscattering geometry of the Renishaw inVia confocal microscope using the 532-nm (2.33 eV) line of a continuous-wave Nd:YAG laser and the Andor Newton CCD detector. The laser power was kept at 13.5 mW and the spot size was reduced to 0.3 µm. For possibly highest imaging resolution the lateral steps in both *X* and *Y* directions were set at 0.3 µm. In order to extract graphene spectra and the substrate response three types of 4624-point 20 µm × 20 µm maps were recorded. The authors believe that the protocol brings a reliable diagnostic tool for the quantification and comparison of graphene on SiC properties, thus accelerating research and development activities in the field of graphene-based applications.

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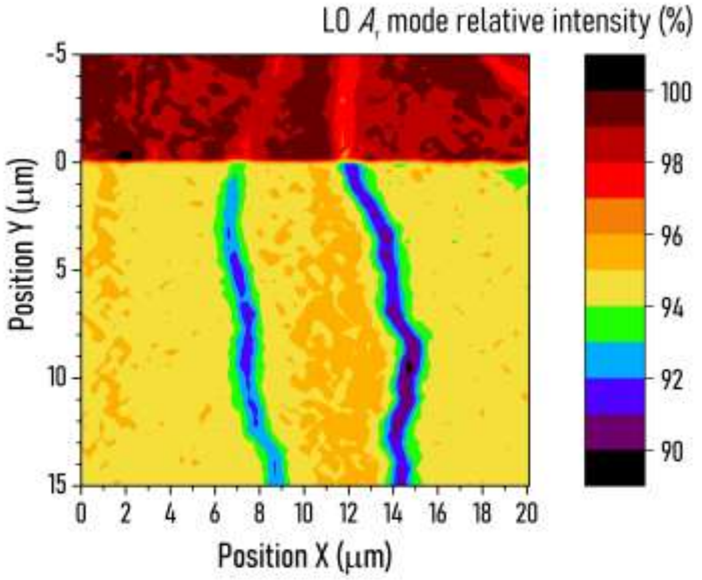

Figure 1: High-resolution Raman map of the 6H-SiC longitudinal optical (LO) A_1 mode relative intensity at 964 cm^{-1}.

Super-Klein tunneling of Dirac fermions through electrostatic gratings in graphene

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Abstract

We use the Wick-rotated time-dependent supersymmetry to construct models of two-dimensional Dirac fermions in presence of an electrostatic grating. We show that there appears omnidirectional perfect transmission through the grating at specific energy. Additionally to being transparent for incoming fermions, the grating hosts strongly localized states.

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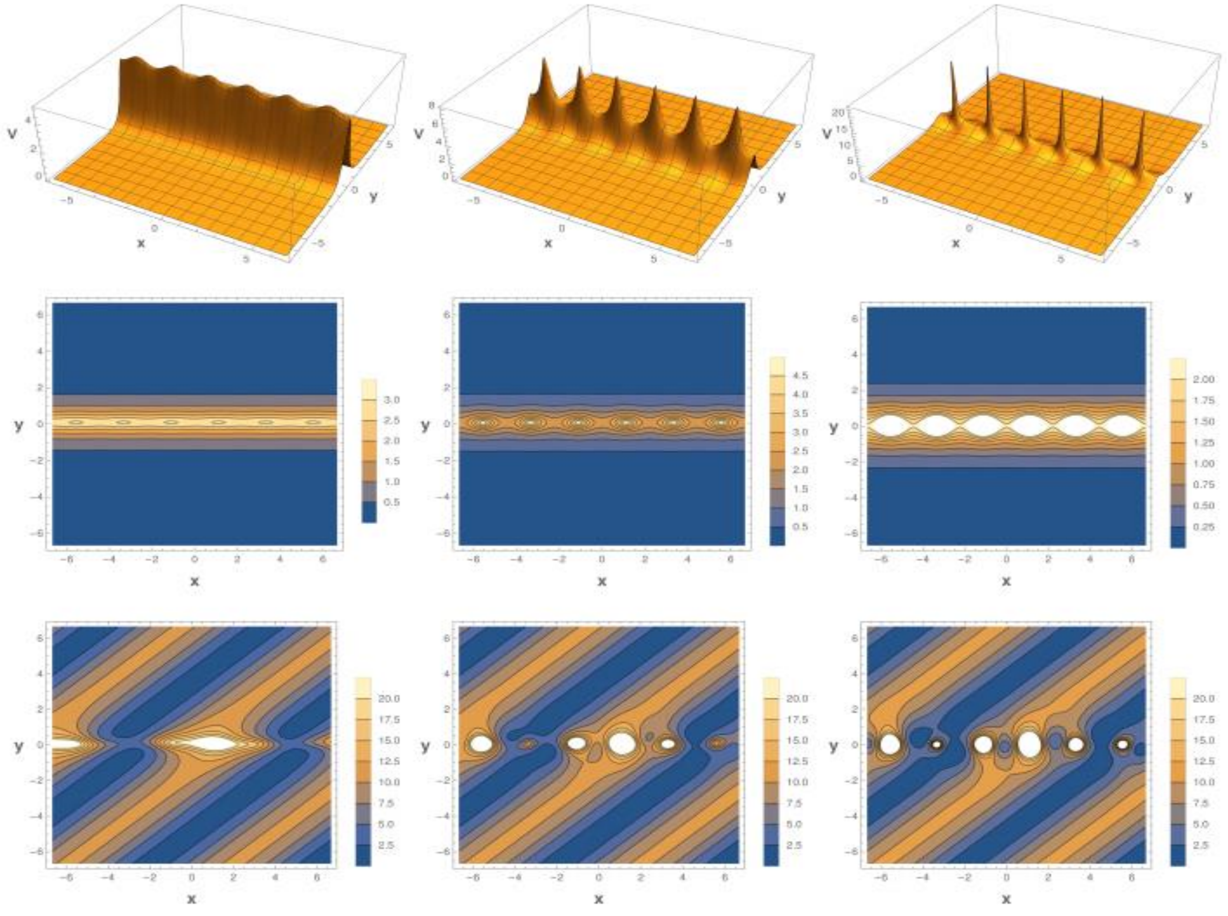

Figure 1: The electrostatic grating (upper row) with density of probability of the confined states (central row) and the density of probability (interference pattern) of a linear combination of the asymptotically plane-waves (lower row). The columns correspond to different choices of the free parameters in the model.

Fast on-site detection of Ochratoxin A by the graphene-based field-effect transistors

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Mycotoxins are a widespread contaminant in food and feed produced as second metabolites of *Asperagillus* and *Penicillium genera* microfungi [1,2]. Ochratoxin A is a mycotoxin that can be found in a wide range of food, from cereals to wine, which is why it has to be regularly monitored by different standardized methods. To date, methods like high-performance liquid chromatography-mass spectrometry or enzyme-linked immunosorbent assay (ELISA) are very prominent tools for Ochratoxin A monitoring, but they require highly trained and qualified staff, as well as controlled laboratory environment, which hinders the in-field use and do not promote low-cost and easy-to-use current and future demands [3,4]. In this research, we report on a specific biosensing tool for the detection of Ochratoxin A, based on lithography-fabricated array of graphene field-effect transistors (G-FETs) on a single silicon chip. G-FETs are assembled with specific aptamers, used as a recognition element on the graphene channel as a transducer deposited via pyrene-based linker (Figure 1). The biosensor showed high sensitivity to Ochratoxin A with the limit of detection of 1.4 pM and a response time of the order of magnitude 10 s. The biosensor is tested on a real red wine samples with a response time of 50 s, showing promising results for future research.

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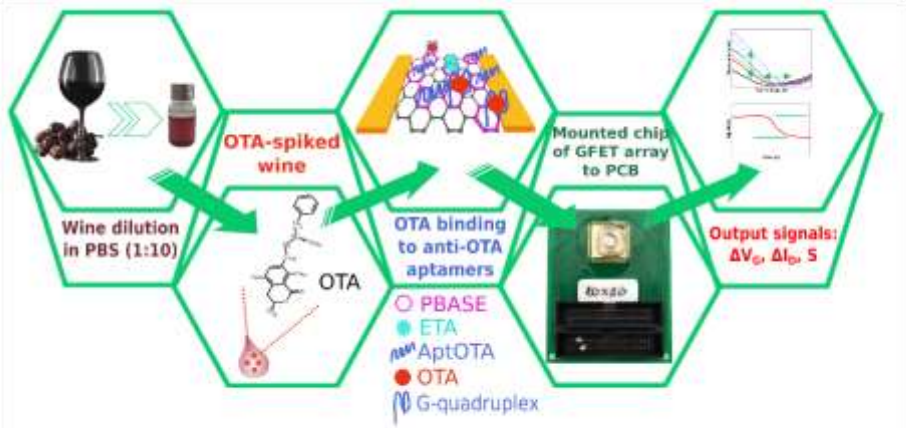

Figure 1: A schematics of G-FET-based biosensor development for Ochratoxin A detection

Ultrasensitive Mercury (II) Detection Platform by Engineering MoS_2-Based Field-Effect Transistors

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Pollution of water with heavy metal ions represents a severe environmental problem associated with societal development [1]. Among the various hazardous compounds, mercury (II) ions (Hg^{2+}) surely belong to the most poisoning ones. Their accumulation in human bodies results in health deterioration, affecting vital organs and eventually leading to chronic illnesses, and, in the worst-case scenario, premature death. Because of this reason, 5-10 nM represents the maximum permitted level of Hg^{2+} in drinkable water [2].

The most common ways of detection of Hg^{2+} in water are based on chromatographic or electrochemical methods [3]. Nevertheless, chemical sensors comprising highly sensitive and selective materials represent more powerful approaches to detect tiny amounts of specific analytes. In particular, low-dimensional materials combine high sensitivity with low limit-of-detection [4]. Among 2D materials, transition metal dichalcogenides (TMDCs) have attracted great attention because of their unique physical and chemical properties.

In this work, we have used MoS_2-based field-effect transistors (FETs) as a platform for Hg^{2+} sensing, relying on the affinity between heavy metal ions and point defects in TMDCs. By XPS characterization on CVD MoS_2, we found a significant reduction on the weight of the defect related peaks as the concentration of Hg^{2+} increased. Low temperature photoluminescence (PL) was also studied. By monitoring the defect contribution in the PL between 1.7 and 1.8 eV, we also confirmed the defect healing, in good agreement with the XPS measurements.

We found that Hg^{2+} acts as a dopant of MoS_2, evidenced by monitoring the transfer characteristics of the MoS_2 FETs. Interestingly, we discovered a strict dependence of the doping with the concentration of Hg^{2+}, following a semi-log tendency. Up to now, we are able to detect concentrations up to 1 pM, way below the health regulations. Electrical characterization showed the sensing platform can be washed and used several times.

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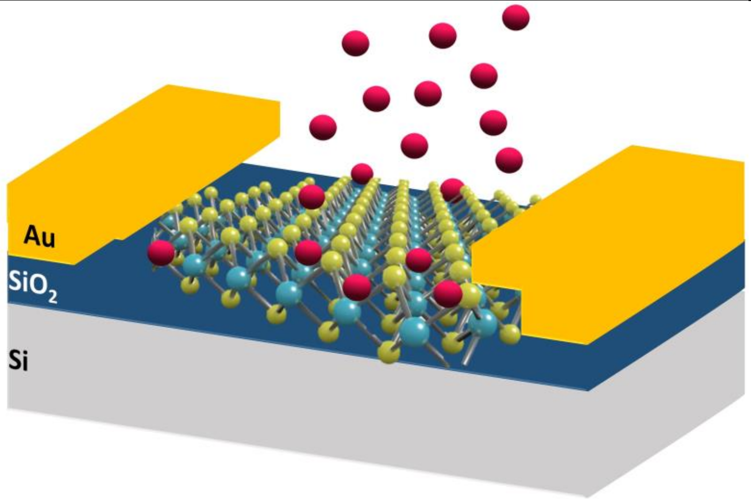

Figure 1: Schematic representation of a MoS_2-based FET interacting with Hg^{2+} ions, represented as red spheres.

Evidence for room temperature quantum spin Hall state in the layered mineral jacutingaite (Pt_2HgSe_3)

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Quantum spin Hall (QSH) insulators are two-dimensional topological materials that have recently attracted tremendous interest, due to the promise of applications from low-power electronics to quantum computing. A major challenge in this field is the identification of large gap QSH materials, which would enable room temperature dissipationless transport in their edge states. Here we show that the layered mineral jacutingaite (Pt_2HgSe_3) realizes the QSH state, within the framework of the Kane-Mele model. Using ultra-high vacuum ($5 * 10^{-11}$Torr) and low temperature (9K) Scanning Tunneling Microscopy (STM), we measure a band gap of 110 meV and identify the hallmark edge states at single layer steps on top of the bulk crystal. We identify the topological nature of the gap by calculating the $\mathbb{Z}_2$ invariant, using density functional theory. By scotch tape exfoliation, we prepare thin flakes of the material and show that it can be incorporated into heterostructures of 2D materials, using well established dry stacking techniques.

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3D-Graphene Based Pressure and Strain Sensor

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Abstract

We demonstrate an ultrasensitive pressure and strain sensor using a conductive and flexible 3D graphene aerogel that enables detecting small pressures/strains and various biological signals from the movement of human skin. The active element of the sensor is composed of a 3D graphene nanoporous framework made of graphene sheets separated with air-filled pores. The 3D graphene aerogel is synthesized using a simple hydrothermal technique followed by freeze-drying and thermal annealing. The resulting graphene aerogel is elastic and exhibits a significant change of electrical resistance with stimuli. It is found that the resistance of the sample is highly sensitive to applied stimuli, enabling the detection of small changes of the sample size down to a few micrometers. The responsivity of the samples allows detecting fast events down to a few milliseconds. We show that the 3D graphene-based sensors can be used as a wearable electronic sensor for human heartbeat monitoring as well as for other kinds of biological motion detection.

Mechanistic Insight to the Chemical Treatments of Monolayer Transition Metal Disulfides for Photoluminescence Enhancement

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Abstract

The discovery of 2D materials based on transition metal dichalcogenides (TMDs), has opened up new interesting possibilities in optoelectronic devices, as monolayer TMDs possess direct bandgaps with absorption in the visible to near-infrared (NIR) spectral region. However, monolayer TMDs often exhibit poor photoluminescence quantum yields (PLQEs) and mobilities, which are signs of poor-quality semiconductor material. While surface passivation by chemical treatment of TMDs has been explored by several groups, thus far only a few methods have been shown to improve a few, but not all of the semiconducting properties. For instance, the use of the 'super-acid treatment' with trifluoromethanesulfonimide (H-TFSI) improves PLQE greatly but gives rise to considerable exciton and charge trapping. At the basis, the chemical mechanisms behind such passivation schemes is unclear, allowing little room for their optimisation and the generation of high-quality materials. Here, I will present new chemical functionalization approaches to greatly enhance the PL intensity of mechanically exfoliated monolayer molybdenum disulphide (MoS_2) and tungsten disulphide (WS_2), while simultaneously enhancing the charge and exciton transport properties.[1] I will also illustrate an unprecedented, detailed understanding of the passivation mechanisms. In addition, I will present a family of ionic salts with superior PL enhancement effect compared to widely discussed "super acid" H-TFSI treatment.[2] More importantly, the ionic salts used in chemical treatments are compatible with a range of greener solvents and are easier to handle compared to super acid, which provides the possibility of directly treating TMDs for device fabrication.

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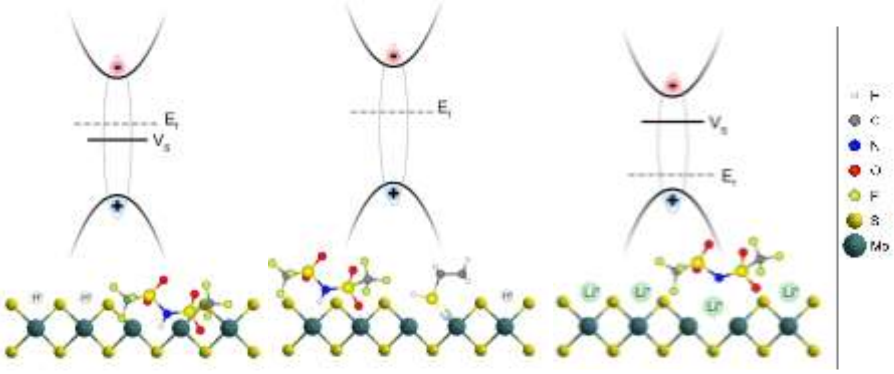

Figure 1: Schematic illustration of different chemical treatments on MoS_2.

Multiscale Charge Transport in van der Waals Thin Films: Reduced Graphene Oxide as a Case Study

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Large area van der Waals (vdW) thin films are assembled materials consisting of a network of randomly stacked nanosheets. The multi-scale structure and the two-dimensional nature of the building block mean that interfaces naturally play a crucial role in the charge transport of such thin films.[1] While single or few stacked nanosheets (i.e. vdW heterostructures) have been the subject of intensive works,[2] little is known about how charges travel through multilayered, more disordered networks. Here we report a comprehensive study of a prototypical system given by networks of randomly stacked reduced graphene oxide 2D nanosheets, whose chemical and geometrical properties can be tuned independently,[3] permitting to explore percolated networks ranging from a single nanosheet to some billions with room temperature resistivity spanning from 10^{-5} to 10^{-1} $\Omega{\cdot}$m. We systematically observe a clear transition between two different regimes at a critical temperature T*: Efros-Shklovskii variable range hopping (ES-VRH) below T* and power law (PL) behavior above. Firstly, we demonstrate that the two regimes are strongly correlated with each other, both depending on the charge localization length ξ, calculated by ES-VRH model,[4] which corresponds to the characteristic size of overlapping sp2 domains belonging to different nanosheets. Thus, we propose a microscopic model describing the charge transport as a geometrical phase transition, given by the metal-insulator transition associated with the percolation of quasi-1D nanofillers with length ξ,[5] showing that the charge transport behaviour of the networks does neither depend on geometry nor on the defects of the nanosheets, ultimately suggesting a generalized description on vdW and disordered thin films.[6]

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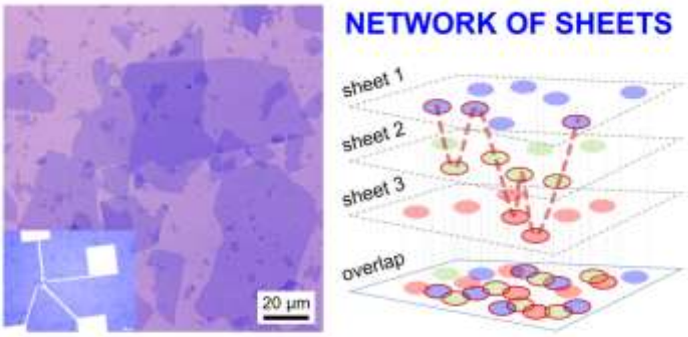

Figure 1: Left) Optical image of a sparse network composed by few 2D RGO sheets in partial contact. Inset: Optical image showing the metal pad geometry used to measure CT in such samples; inset size: 1.7×1.2 mm2.(Right) Three-layer RGO thin film. Each plane is represented as a patchwork of isolated sp2 domains (circles) separated by domain border defects. For sake of clarity, we distinguish each layer with a different colours. Dashed red line corresponds to a random path connecting overlapped disks.

Transfer of Graphene from 200 mm Epitaxial Si/Ge(100) Wafers and it's post-processing

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Since the successful exfoliation of graphene in 2004 the research on graphene gained a lot of attention. The possibility to tune electronic properties of graphene by application of external voltage enables the engineering of Fermi level of graphene. The aim of each research topic is to find the most promising application field materials up to the industrial application level.

In this work, the main technological development and processing steps towards graphene integration in standard Si-technology processes will be presented. The main processing steps includes the graphene growth [1], its transfer by electrochemical delamination on the target wafers [2] and patterning by photolithography followed by reactive ion etching and wet cleaning processes. For the development of test structures (TLM, Hall) and test-devices (capacitors, GFETs) different contacting approaches [3] are under development in order to achieve the low contact resistance values and will be presented as well.

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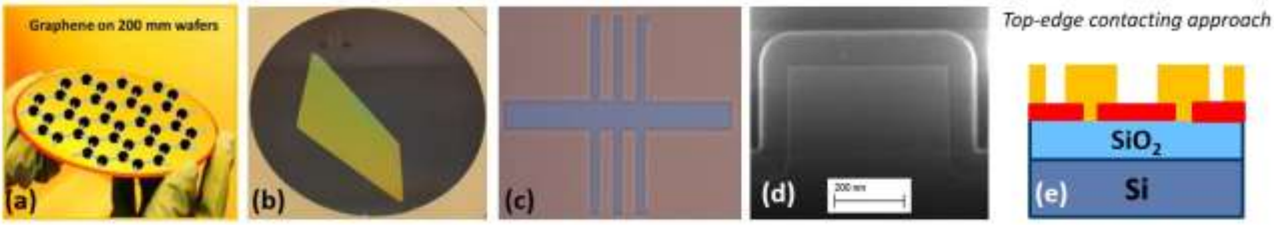

Figure 1: (a) Graphene growth on 200 mm Ge/Si wafers, (b) transferred graphene flake on 200mm SiO2/Si wafers, (c) patterned graphene, (d) passivation of graphene with SiN, (e) graphene contacting approach through top-edge metal contacts.

Acknowledgments: this research was funded by: (1) the Federal Ministry of Education and Research (BMBF) Germany under grant GIMMIK No 03XP0210E; (2) the European Union's Horizon 2020 research and innovation program under Graphene Flagship grant agreement No 952792.

Development of a graphene and fluorographene based gas sensor

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Nowadays the reinforcement of health and environmental standards implies a compact and ppb sensitive air quality monitoring. This can be achieve through graphene ultrasensitive [1] gas sensor as a third way between optical and metal oxides sensors. We have been developing a chemo-sensitive graphene sensor. Our sensor has proven to be ppb sensitive to NO_2 (fig. 1). Nevertheless, we are experiencing low selectivity, high response time and instabilities due to the substrate.

In order to enhance our sensor selectivity and sensitivity to NH_3, we are willing to fluorinate the graphene with an electron beam in order to mute graphene into fluorographene with a high spatial resolution [2]. Indeed, there is a strong binding energy between fluorine and ammonia, which leads to the enhanced sensitivity of the gas sensor. Before performing electrical and gas sensing characterizations with such sensor, we are working to determine the performance over time and temperature of the fluorographene through an X-ray photoelectron spectroscopy (fig. 2.). This technique will support us to investigate the electron affinity between the gases and the graphene or the fluorographene by studying adsorption and desorption mechanisms.

The second step of this work involves the use of a Boron Nitride substrate as it will enhance electron mobility and sensor response time meanwhile reducing substrate effect [3]. We are exploring two leads. Firstly, the processing of an "all-CVD" (Chemical Vapour Deposition) device build with consecutives liquids transfers of commercial CVD BN and CVD graphene (Graphene Supermarket and Graphenea). Secondly, the use of a BN substrate synthesized by CVD in our laboratory, at the ONERA [4]. This BN shows continuous, single crystalline and sp2-hybridized multilayer film on the nickel (111) substrate. (fig. 3). A new approach would be to build the sensor directly on the BN growing substrate of nickel, avoiding the damage induced by the liquid transfer of the BN film.

Lastly, our aim is to combine the use of fluorinated graphene with a BN substrate as an innovative solution for the development of an ultrasensitive NO_2 and NH_3 gas sensor.

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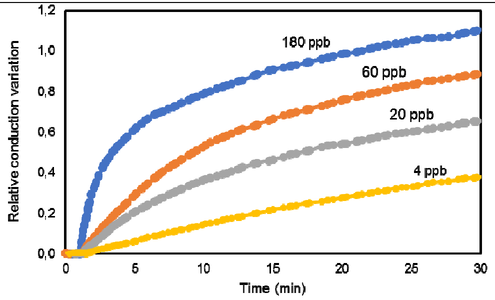

Figure 1: ONERA graphene based gas sensor response to several NO_2 concentration exposure

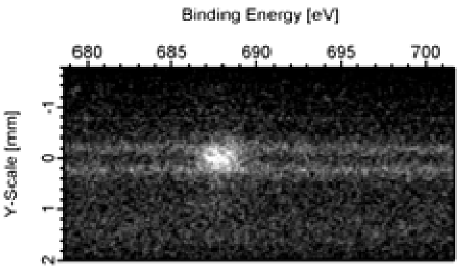

Figure 2: XPS cartography of the fluorinated graphene area after annealing at 450°C

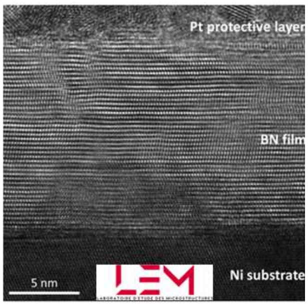

Figure 3: HRTEM analysis of the BN/Ni(111) interface:

The robustness of spin-polarized edge states in a two-dimensional semimetal without inversion symmetry

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Three-dimensional topological gapless phases have attracted significant attention due to their unique electronic properties. One of the flagships is the Weyl semimetal, which requires breaking time-reversal or inversion symmetry in three dimensions. Towards two dimensions, the dimensionality reduction requires imposing an additional symmetry, thereby weakening the phase. Like its three-dimensional counterpart, these “two-dimensional Weyl semimetals” present edge states directly related to the Weyl nodes. Since these edge states strongly resemble those in zigzag-like terminated graphene ribbons[2], it is natural to wonder how robust are.

Here we benchmark the robustness of the edge states in two-dimensional Weyl semimetals with those present in zigzag graphene ribbons. To such end we use a Dirac Hamiltonian model proposed by Young and Kane[1], adding new terms for inducing a two-dimensional Weyl semimetal phase and use a scattering picture for the transport calculation. Our results show that despite having a similar electronic bandstructure, the edge states of two-dimensional Weyl semimetal are more robust against vacancies than graphene ribbons[3]. We attribute this enhanced robustness to a crucial role of the spin degree of freedom in the former case.

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Synthesis of multilayer graphene encapsulated iron nanoparticles using chemical vapor deposition from Fe-sulphate based precursors

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Abstract

Magnetic nanoparticles have been developed for various biomedical applications such as drug or gene delivery, hyperthermia, diseases' detections and imaging [1,2]. Carbon based encapsulations on magnetic nanoparticles improve the biocompatibility and stability, reduce the agglomerations and provide surfaces for drug carrying [3]. Therefore, solvothermal method, sol-gel method, combustion synthesis, plasma and chemical vapor deposition (CVD) are some of methods that used for obtaining graphene coated nanoparticles [2,4]. In the presented study, multilayer graphene encapsulated iron nanoparticles were synthesized via CVD starting from iron sulphate based precursors. Precursor powders prepared from iron sulphate salts that were mixed with fumed silica in ethanol and heated until the ethanol was vaporized. Then, iron sulphate loaded silica powders were placed into CVD system and heated to different temperatures (900, 950 and 1000°C) under 100 ml/min hydrogen (H_2) gas and 100 ml/min methane (CH_4) gas flows. After that, 2 M HF and 3 M HCl solutions were used for leaching to attain purified powders. Remained fumed silica powders were removed with HF acid leaching and uncoated Fe nanoparticles were removed with HCl acid leaching. Synthesized and purified powders were characterized using an X-Ray diffractometer (XRD), Raman spectrometer, scanning electron microscope (SEM), transmission electron microscope (TEM) and vibrating sample magnetometer (VSM) for optimization of synthesized parameters. Representative Raman and VSM results were presented in Figure 1a and 1b prove that nanoparticles with 253.90 Oe coercivity and 91.14 emu/g magnetic saturation have multilayer graphene.

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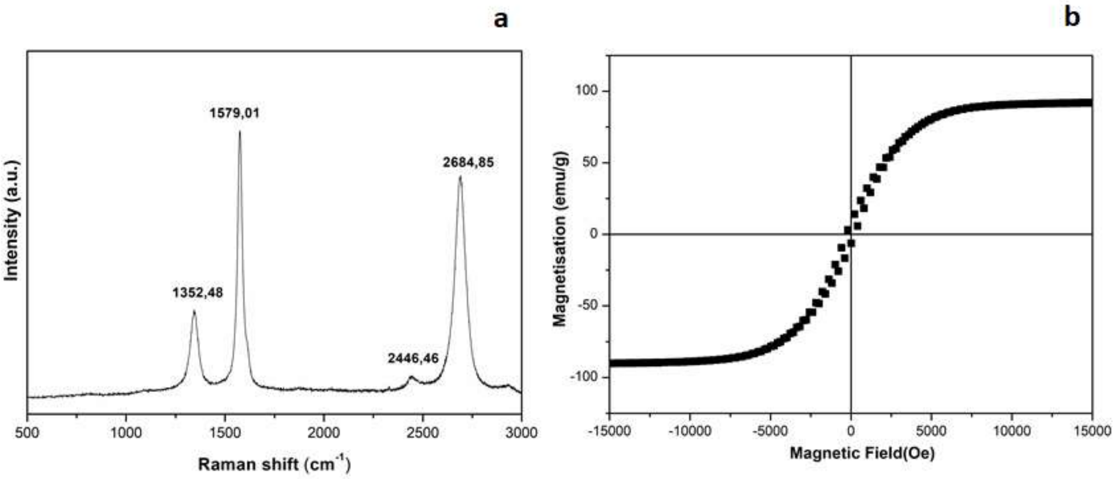

Figure 1: a) Raman shift and b) VSM result of synthesized powders.

Chemical sensing with graphene: A quantum field theory perspective

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Abstract

We studied theoretically the effect of a low concentration of adsorbed polar molecules on the optical conductivity of graphene, within the Kubo linear response approximation[1]. Our analysis is based on a continuum model that includes up to next-to-nearest neighbors in the pristine graphene effective Hamiltonian[2,3]. Our results show that the conductivity can be expressed in terms of renormalized quasiparticle parameters that include the effect of the molecular surface concentration and dipolar moment, thus providing a quantum field theory approach to model a graphene-based chemical sensor[1].

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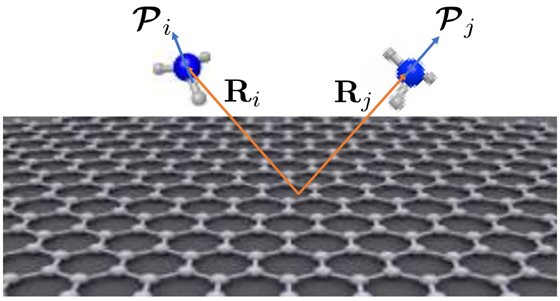

Figure 1: Pictorial (not in actual scale) representation of polar molecules adsorbed at positions **R***i* and **R***j* on the surface of graphene[1].

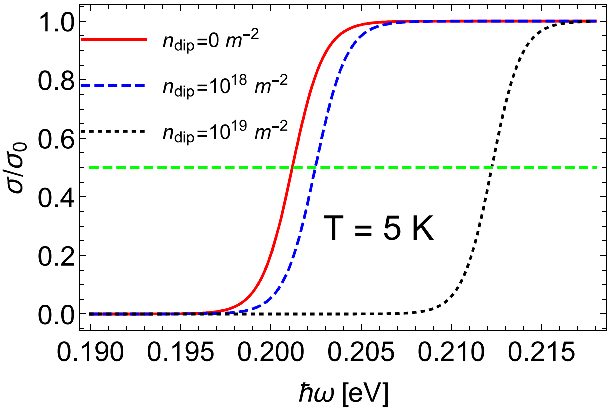

Figure 2: Optical conductivity of graphene, calculated from our theory[1], at different surface concentrations of adsorbed polar molecules.

Real-time monitoring of graphene CVD growth using ultraviolet reflection

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Real-time monitoring is a powerful tool for clarifying growth mechanisms and controlling a material's growth. In the case of graphene growth by chemical vapour deposition (CVD), real-time monitoring has been demonstrated by using environmental scanning election microscopy (SEM) and radiation microscopy [1, 2], but they are available only under limited growth conditions and setups, such as a high-vacuum environment and a cold-wall chamber. Here, we report real-time optical reflection observation with an ultraviolet (UV) light source as a way to monitor graphene growth on a Cu substrate during CVD. Our real-time observation is available for the conventional thermal CVD setup with a hot-wall chamber (over 1000˚C) near atmospheric pressure. Considering the optical reflectance of graphene on Cu and the thermal radiation energy at the growth temperature (around 1050˚C), we choose monitoring wavelengths below 600 nm for clear observation of graphene growth on Cu during CVD. The figure shows images observed during graphene CVD growth at 1060°C using an illumination light source with wavelengths of (a) 265 and (b) 365 nm. As examples, some of the graphene domains are indicated by dotted lines. As the growth progresses, it is clearly observed that graphene domains nucleated on the Cu and their size increased. The formation of graphene domains was also confirmed by ex-situ Raman spectroscopy. The image contrast of graphene on Cu varies with monitoring wavelengths because of their wavelength-dependent refractive index. In particular, the refractive index of graphene largely changes at around 270 nm due to an interband optical transition at the M points in Brillouin zone. Consequently, the contrast inverts: graphene domains are observed to be bright at 265 nm and dark at 365 nm with respect to the Cu surface. We also observed in real time that the nucleation and growth process of graphene changes depending on the CVD conditions. Our method will be helpful in deepening our understanding of the growth mechanism and achieving real-time growth control for high-quality graphene.

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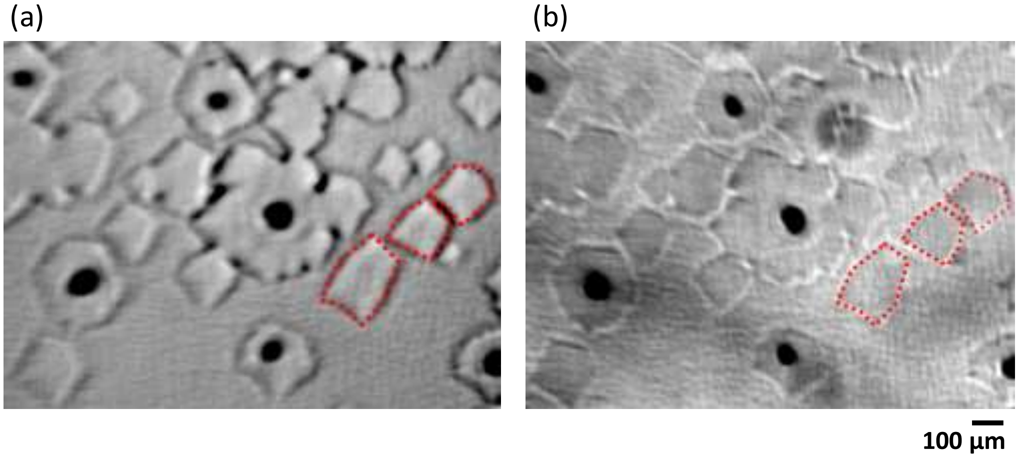

Figure : Reflection optical micrographs of graphene on Cu during CVD growth at 1060˚C with illumination light having peak wavelengths of (a) 265 and (b) 365 nm.

High-quality graphene growth via roll-to-roll chemical vapor deposition

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The investigation on a high throughput manufacturing process is urgently needed in order to enable the mass production of graphene. The roll-to-roll (R2R) production technique has emerged as an economically viable solution since it is easier to automate and more compatible with the subsequent transfer process [1]. So far, the research on R2R process has mainly focused on the reactor design or the loading configuration, and there severely lacks an in-depth understanding of its growth kinetics. In this work, the evolution of graphene growth is comprehensively investigated. In the conventional batch-to-batch (B2B) process, there was no carbon precursor in the heating-up stage [2-3]. In contrast, the substrate was heated up in the early-established reaction atmosphere, and graphene could nucleate and grow at a lower temperature in the R2R process. The graphene domain density grown via the R2R process was apparently larger than that by the B2B process due to different reaction profile. Moreover, the defective graphene could be healed with an elongated reaction time. With our optimized R2R process, graphene film with the quality comparable to that grown by the B2B process could be achieved. Our research will greatly promote the development of the mass-production technique of graphene film.

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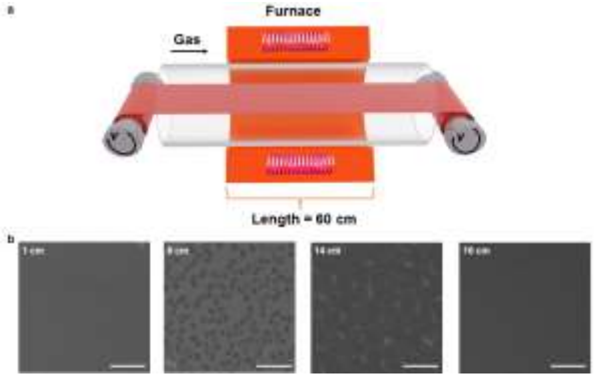

Figure 1: (a) Schematic of the R2R CVD equipment. (b) SEM images of the grown graphene on Cu with a motion speed of 3.5 mm/min and 100 sccm CH_4/Ar. Scale bar is 1 μm. The labels indicates sample positions.

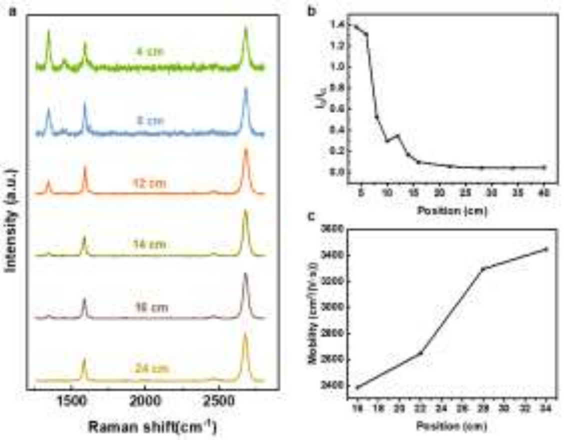

Figure 2: (a) Raman spectra of graphene from different positions with 100 sccm CH_4/Ar. (b) I_D/I_G and (c) the normalized carrier mobilities at the carrier density of 1×10^{12} cm^{-2} v.s. position, respectively.

Predicting the electronic gap of single-layer 2D COFs from their molecular building-blocks

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Two-dimensional Covalent Organic Frameworks (2D COFs) have attracted a lot of interestdue to their large range of potential applications. Bottom-up engineering of theirmolecular building-blocks can lead to novel structures with fine-tuned physical andchemical properties. We have carried out a computational investigation of the electronicproperties of ~350 different 2D COFs with three- and four-arm cores. Four-arm coreswere modeled in 1D-polymer as alternating monomers of the respective 2D-polymer(COF) building units. Specifically, the electronic band structure of the periodic 1D- and2D-polymer, and the HOMO-LUMO difference of the respective molecular building-blockswere calculated. Considering a two-level system and using tight-binding approximation,an analytical model was derived to fit the conduction and valence bands. MachineLearning techniques were employed to find the weight of each variable and predict theelectronic band..

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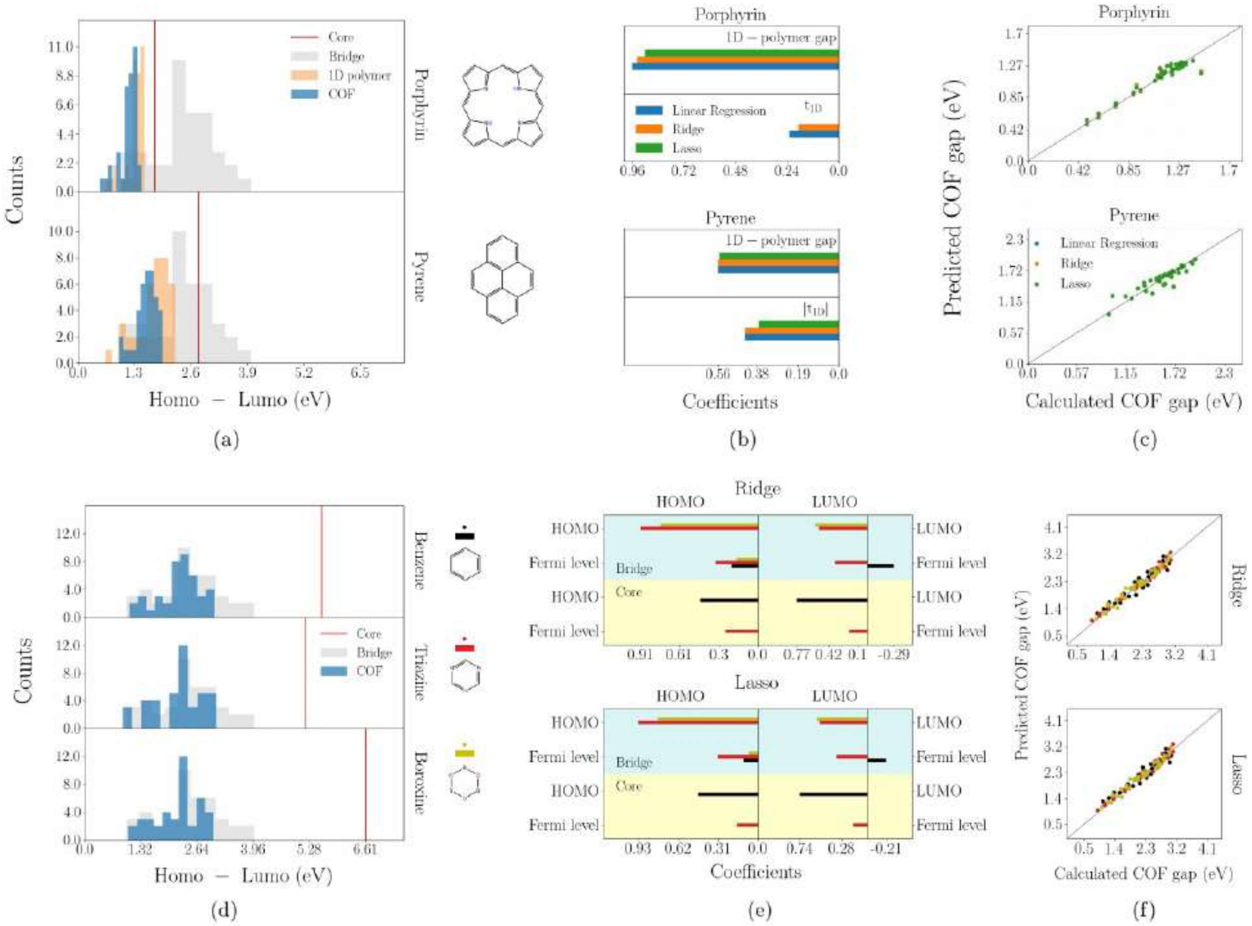

Figure 1: Figure 1: (a), (b) and (c) concern the four-arm cores, whereas (d), (e) and (f) the three arm-cores. (a) and (d) Histograms of HOMO-LUMO difference for the different bridge molecules, core, 1D-polymers and COFs. (b) and (e) Weights of the given variables to the algorithms. (c) and (f) Predicted vs caclulated gap.

Spin-polarized tunable photocurrents

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Circular dichroism, a distinct response to left and right-handed circularly polarized light, is an example of a phenomenon involving light-matter interaction that has been heavily exploited to control valley polarization in two-dimensional materials [1]. In most studies, light-matter interaction enters perturbatively and does not modify the electronic properties. But beyond this weak-coupling regime, Floquet-engineering [2-4] has shown that we can use light to change the band-structure of a material [5-7] and even its topology [2-4, 8], generating a Hall response [9].

Light can also be used to generate directed currents even in the absence of an applied bias voltage, a phenomenon called quantum pumping, and recently it has been shown that by tailoring a selective environment one can take this to the limit of a perfect isolator effect [10], where currents flow in one direction but not the opposite.

Here, we go a step further and show how the rich interplay between electron-photon processes (and the additional synthetic dimension), stacking order, spin-orbit coupling, and the topology of a two-dimensional material can be harnessed to control spin, charge, and valley currents in two-dimensional materials, beyond the weak-coupling regime [11].

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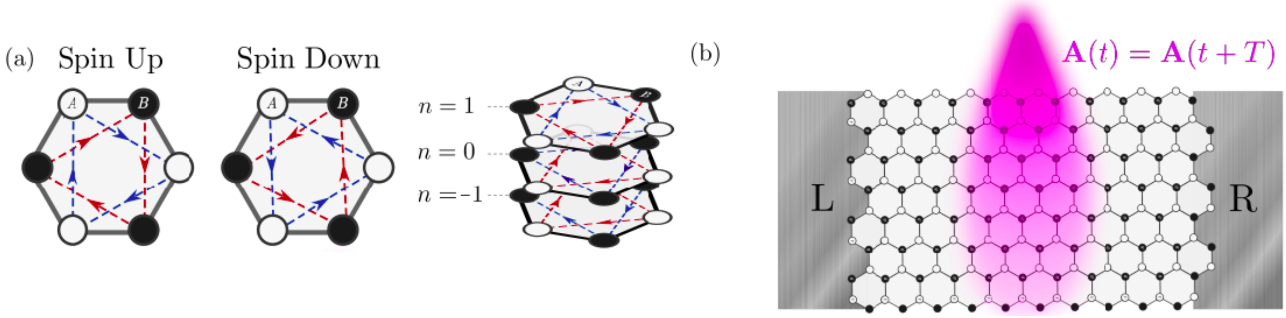

Figure 1: Under the light spot, the system develops the replica scheme unfolding itself into several copies which represent photon dressed processes (a, right). In (b) a schematic representation of the device we will consider in the transport setup. Under particular conditions, the transport of one spin might be suppressed while the remaining is perfectly unaffected.

Atomistic Modelling of Point Defects in Amorphous and Crystalline Phases of Ultra-thin Boron Nitride

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Abstract

Resistive switching architectures are being actively studied for their potential to build the next generation of electronic devices. These architectures are based on a pristine insulator that is sandwiched between two metallic electrodes such that when a voltage difference is applied between both electrodes, a conductive filament is locally formed with a disordered structure. A very strong candidate for this insulator is hexagonal boron nitride (h-BN) due to its large electronic band gap of around 6 eV, among other properties. [1-7] However, the mechanisms for the formation of the conductive filament in h-BN are not yet fully understood. Thus, the goal of this talk is to present our results on the modelling of this conductive filament by evaluating the formation of point defects in hexagonal and amorphous phases. [8] We combine classical molecular dynamics (MD) and density functional theory (DFT) to calculate the formation energy of vacancies in both BN phases. Our calculations with MD indicate that the formation energy for boron vacancies in the crystalline regions is always above 10 eV, a value that reduces to 7.29 and 3.55 eV for the nearest second and third neighbours. On the other hand, the vacancy energy in the amorphous regions shows a much wider stochastic distribution around 4.91 eV and it can reach values down to 0.1 eV. These energies are in very good agreement with the corresponding values of 10.91 and 4.61 eV obtained from DFT calculations on bulk crystalline and amorphous structures. Therefore, the formation of boron vacancies is energetically more favourable in the disordered phase than in its crystalline counterpart. We conclude then that the few-atoms-wide disordered regions in the grown h-BN by chemical vapour deposition represent atomistic loci where electric stress might lead to dielectric breakdown with the resulting creation of conductive channels, in agreement with conductive atomic force microscopy measurements.

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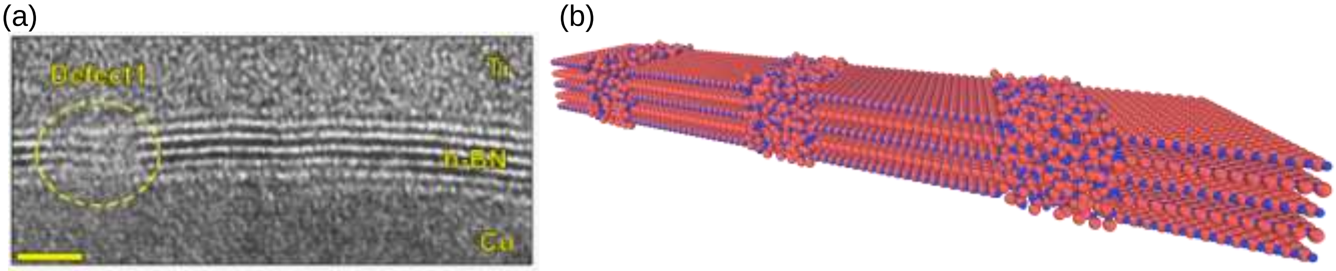

Figure 1: Cross-sectional TEM images of ultra-thin films of hexagonal boron nitride (a) and 3D model of the atomic structure of a multilayer boron nitride.

All-Electrochemical nanofabrication of stacked ternary metal sulfide/graphene electrodes for high performance alkaline batteries

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New approaches are required to create electrode materials with hierarchical and tunable structures to maximize both ion and charge transport for energy storage. These aspects are critical to get practical electrodes with significant mass loading and adequate performance. [1,2]
Here, we demonstrate a versatile two-step approach combining electrophoretic deposition (EPD) and cathodic electrodeposition (CED) to fabricate multilayer hierarchical electrodes made of reduced graphene oxide (rGO) and mixed transition metal sulfides (NiCoMnSx or NCMS) (see Figure 1). The interleaved structure obtained provides an ideal porous network and a continuous conductive path for a facile transport of ions and electrons.[3]
A full Rechargeable Alkaline Battery (RAB) cell with an anthraquinone-based conjugated microporous polymer (IEP-11) as anode and our optimized NCMS-G2 multilayer composite as cathode was assembled with a maximum energy density of 97.2 Wh·kg−1 and a maximum power density of 3.1 W·kg−1, calculated on the total mass of active materials, and outstanding cycling stability (retention 72% after 7000 charge/discharge cycles at 10 A·g−1). When the total electrode mass of the cell is considered, we achieve an unprecedented gravimetric energy density of 68.5 Wh·kg−1, seven-fold higher than that of typical commercial supercapacitors, higher than that of Ni/Cd or Lead-Acid Batteries and similar to Ni-MH Batteries. Our approach can be used to assemble arbitrary, multilayer composite structures on complex electrode shapes.

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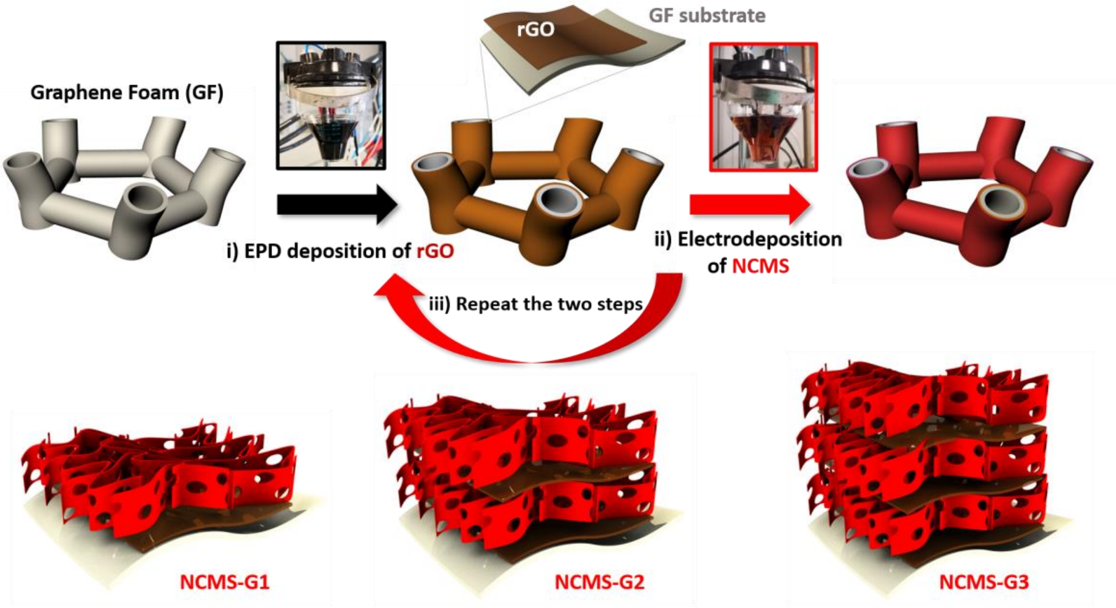

Figure 1: Schematic illustration of the preparation process for multilayer rGO/NCMS graphitic foam architectures.

Steering the current flow in twisted bilayer graphene

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A nanoelectronic device made of twisted bilayer graphene (TBLG) is proposed to steer the direction of the current flow, see Figure 1. The ballistic electron current, injected at one edge of the bottom layer, can be guided predominantly to one of the lateral edges of the top layer. The current is steered to the opposite lateral edge, if either the twist angle is reversed or the electrons are injected in the valence band instead of the conduction band, making it possible to control the current flow by electric gates. When both graphene layers are aligned, the current passes straight through the system without changing its initial direction. The observed steering angle exceeds well the twist angle and emerges for a broad range of experimentally accessible parameters leading to a non-local resistance, see Figure 2. It is explained by the trigonal shape of the energy bands beyond the van Hove singularity due to the Moiré interference pattern. As the shape of the energy bands depends on the valley degree of freedom, the steered current is valley polarized. Our findings show how to control and manipulate the current flow in TBLG. Technologically, they are of relevance for applications in twistronics and valleytronics.

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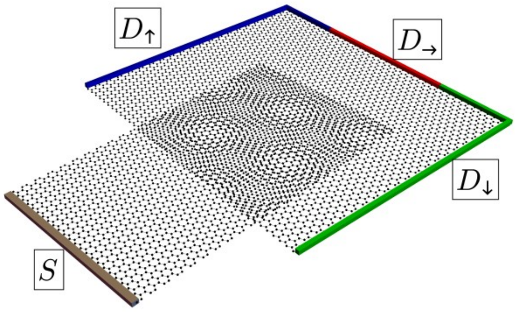

Figure 1: Schematic representation of the studied TBLG device. Electrons are injected through contact *S* at the bottom layer and detected by three drain contacts $D_{\uparrow/\downarrow/\rightarrow}$ at the top layer.

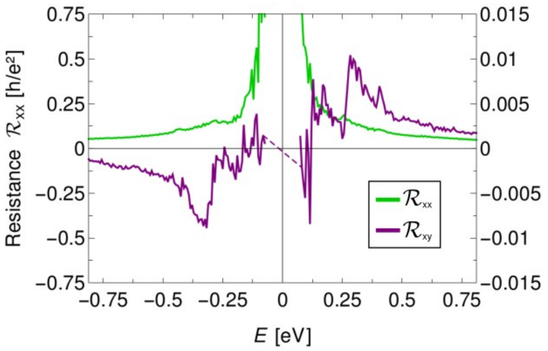

Figure 2: Longitudinal resistance R_{xx} and Hall Resistance R_{xy} as a function of energy for the TBLG device at a twist angle of θ=2.9°. The steering of the current flow to one of the lateral edges generates a non-local Hall resistance.

Pseudo magnetization in twisted bilayer graphene under hydrostatic pressure

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Twisted Bi-Layer Graphene (TBLG) is a rich platform to study novel phenomena, such as unconventional superconductivity, Mott insulating states, orbital magnetism, and spin Hall effect among other interesting phenomena. Despite the great efforts to describe properly the electronic structure of this TBLG at low angles with thousands of atoms through tight-binding calculations or continuum models; these parametrized methodologies tend to overestimate the electronic bandwidths and energy gaps at low energies due to a bad description of relaxation effects in TBLG. Here using density functional theory (DFT) calculations with GGA (PBE) plus an optimized single basis set per orbital, we study several commensurate angles of TBLG under hydrostatic pressure. This is done to achieve flat bands at larger angles, see left panel of Figure 1, and indeed to demonstrate the appearance of pseudomagnetic (B) and potential (V) fields in these graphitic materials generated through in-plane strain by the external pressure, see right panel of Figure 1. We expect these results guide more future experimental and theoretical studies.

Figures

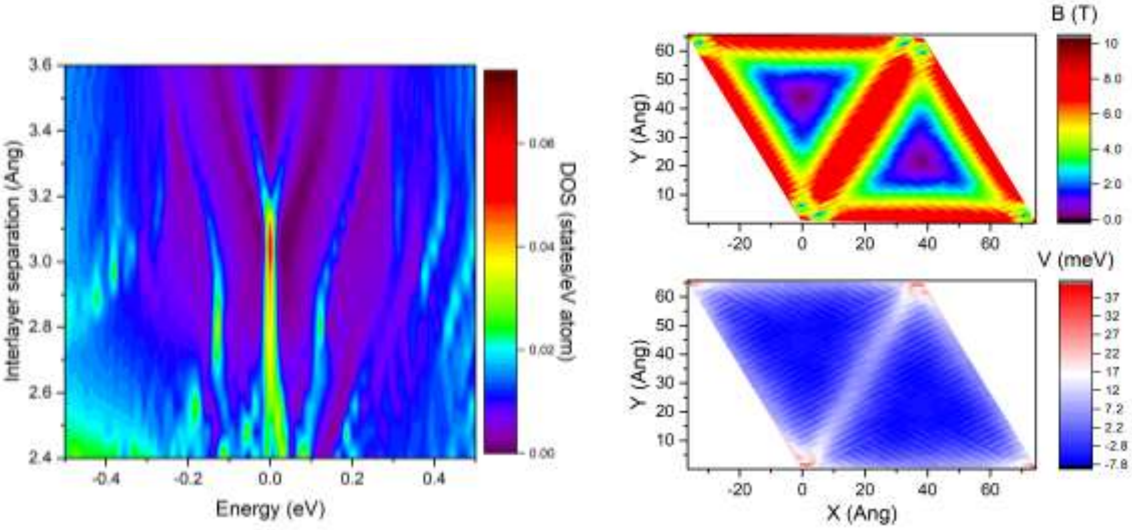

Figure 1: TBLG with θ=1.89° and 3676 atoms. Left panel: density of states (DOS) as a function of interlayer separation and energy. Right panel: Pseudomagnetic (B) and potential (V) fields for the upper graphene layer having an interlayer separation of 2.4 Ang.

Acknowledgements: This work was supported from CONACYT Mexico Grants No. A1-S-14407 and No. 1564464.

Metal-Graphene Composites – Challenges and Opportunities

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Graphene and its related 2D-materials possess outstanding properties, with the potential of having disruptive impact in several industrial segments. Metal-Graphene composites is one such appealing area of interest, considering the global efforts for better and more efficient material utilization. However, harvesting the potential of graphene by combining it with other, conventional materials to render composites with enhanced properties is not straightforward, and requires ample engineering.

Graphmatech is a materials start-up company founded in 2017 that synthesizes, functionalizes, and utilize graphene for manufacturing of graphene-containing composite materials. The company has developed methods for successfully incorporating various grades of graphene and related 2D-materials to metal powders, processes that are under rapid upscaling. While still on a powder level, this yields enhanced flowability and changed optical behaviour. Suitable consolidation methods for the metal-graphene powders includes but is not limited to additive manufacturing (AM) and hot isostatic pressing (HIP), and once consolidated into metal-graphene composites Graphmatech has demonstrated enhanced mechanical, electrical and thermal properties using several different starting elements and alloys.

FIGURES

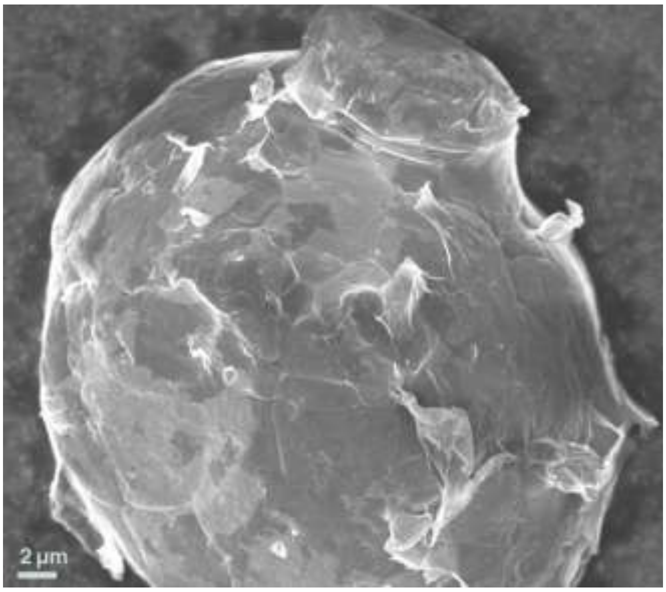

Figure 1: Example of metal-graphene powder with beneficial interactions

Synthesis of Superelastic Graphene Aerogels

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Graphene aerogel is a three-dimensional porous form of graphene with a high surface-to-volume ratio. Graphene aerogels have attracted a significant amount of interest in recent years due to their unique mechanical and electrical properties that show great potential for numerous applications in engineering, electrochemistry, and biology. These unique properties are originating from a clever arrangement of two-dimensional graphene sheets in a three-dimensional porous monolith structure containing air-filled pores. Here, we report the synthesis and investigate the mechanical properties of superelastic graphene aerogels prepared via hydrothermal reduction of graphene oxide. The as-fabricated graphene aerogels, however, contain a lot of defects and oxygen groups which cause poor elastic properties. For this reason, we have thermally annealed the samples in a furnace in an inert gas atmosphere. The high-temperature annealing enabled a complete oxygen removal from the samples, resulting in a significant improvement of the elasticity of the graphene aerogels. The annealed graphene aerogels demonstrate superelastic compression up to a GPa pressure regime. To better understand the deformation mechanism in the samples we have performed in situ SEM measurements that visualized the deformation of individual graphene pores. Based on the observation we developed a model that is able to describe the stress-strain curves of the graphene aerogels. Our study provides new insights into the superelastic behavior and deformation mechanism of the porous graphene aerogels.

PECVD of Graphene on sapphire substrates: A Design of Experiments (DoE) approach

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The use of graphene in the semiconductor industry is not yet widespread because controlling the properties of material and reproducibility of the process is still challenging. In addition, the catalyst-free growth of graphene directly on technologically relevant substrates (such as sapphire) at low temperatures is highly desirable for back end of line integration [1]. By using the plasma enhanced chemical vapour deposition (PECVD) technique, the temperature of the synthesis of graphene on sapphire can be reduced significantly, since the plasma provides the energy to break the molecules from the precursor [2]. Thus, providing a controllable synthesis procedure of catalyst-free graphene on such dielectric substrate will boost the use of graphene in the industry [3].

In this work, the optimization of the PECVD growth of graphene on c-plane sapphire is carried out by means of the statistical Design of Experiments (DoE) method. The quality and defects of the synthesized graphene layers are characterized by means of Raman spectroscopy. Factorial DoE with one central point is performed to evaluate the effect of the growth parameters and the extent of their interactions on the quality of the graphene layers. We found that the main factors affecting the ratio I_{2D}/I_G are the flow of methane and pressure. In addition, we found that a transition from graphene to amorphous carbon can be controlled by tunning the flow of methane, the pressure, and plasma power. Finally, the graphene layers were functionalized using 1-pyrenebutyric acid N-hydroxysuccinimide ester (PBASE), as a molecule that binds to both graphene and to antibodies, demonstrating its potential for future applications in biosensing.

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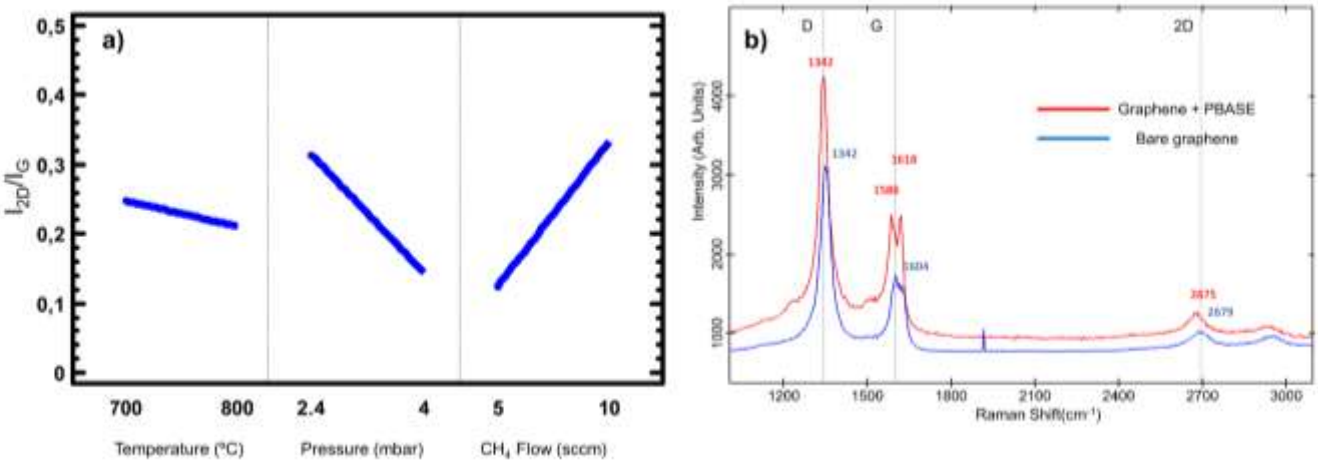

Figure 1a: Main effect plots of the factors temperature, pressure and CH_4 flow for the response I_{2D}/I_G; b) Raman spectra of graphene before and after functionalization with PBASE molecule.

2D carbon-metal frameworks for photochemical reactions promotion

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A wide range of 2D carbon allotropes have been predicted and theoretically explored during the last years [1–5]. It is noteworthy that in recent works there were proposed synthesis methods for production of the allotropes [6], which opens broad prospects for building nanostructures based on them, for example, different metal-carbon frameworks. Such systems exhibit interesting properties due to the presence of metal-carbon bonds like surprisingly stable metallocene molecules [7,8] which consist of metal atoms sandwiched between two cyclopentadienyl anions. In metallocene-like 2D nanostructures the metal atoms are protected by carbon sheets, while the metal atoms are placed in the middle of penta-rings of carbon atoms.

In our work we carried out a theoretical investigation of two 2D metallocene analogs based on graphene allotropes. The first system is a defected graphene monolayer functionalized by metallocene fragments. The second system is a novel 2D nanostructure consisted of two carbon layers and metal atoms (Co or Fe) sandwiched between them, which structure can be represented as metallocene molecules without hydrogen atoms organized into a 2D hybrid structure. By using density functional theory, we examined the stability of proposed structures and studied the features of electronic, magnetic, and optical properties. The Fe-filled structures exhibit semiconducting properties while Co-containing structures show half-metallic properties. Both demonstrate increased absorption spectra in the visible area, which together with changing oxidation degree make them excellent candidates for photoinduced catalytic reactions under sun irradiation. The work was supported by the Russian Science Foundation (№21-73-20183).

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Gradient-index electron optics in graphene p-n junctions

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We investigate the electron transport in smooth graphene p-n junctions, generated by gradually varying electrostatic potentials with or without elastic deformations and calculate numerically coherent current flow patterns. We demostrate phenomena known from light propagating in media with a gradually changing refractive index such as Luneburg or Maxwell lenses. We observe that energetically forbidden regions appear which may increase reflections and generate pronounced interference patterns such as whispering gallery modes. All those patterns can be largely understood in terms of the semiclassical trajectories, obtained from the effective Dirac equation for electronic excitations in graphene, which demonstrates the feasibility of the gradient-index electron optics in graphene p-n junctions. The presented setups and techniques may have technological applications, for example, as electron beam splitters, focusers, or waveguides.

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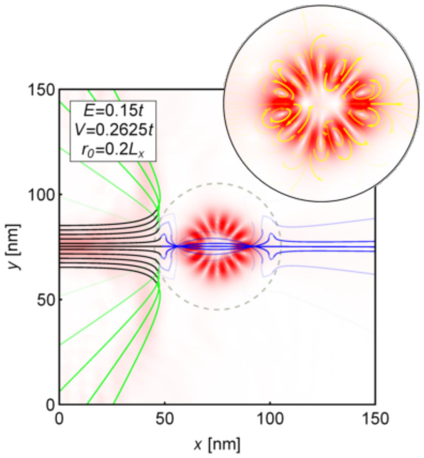

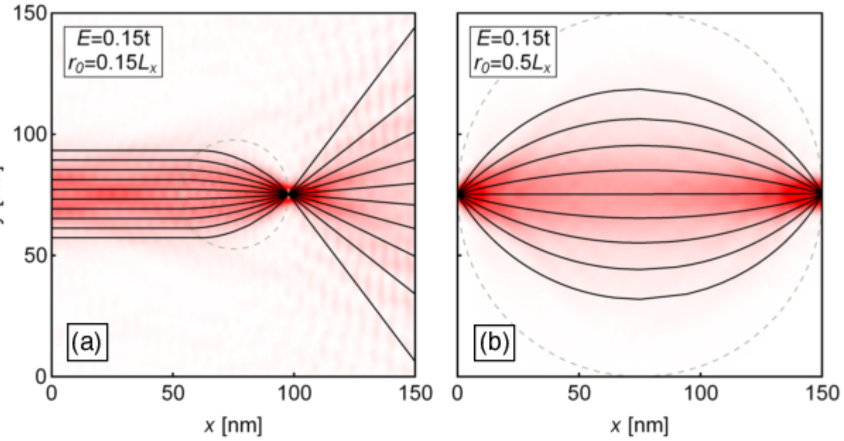

Figure 1 (left): Gradient-index electron optics in smooth circular p-n junctions. Strong interference patterns in the form of whispering gallery modes can be observed for specific parameters.

Figure 2 (right): Current flow in graphene with an electrostatic potential that generates a Luneburg lens (a) and a Maxwell's fish-eye lens (b).

Chemical functionalization of 2D materials

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Abstract

Thanks to their exciting chemical, electrical, optical, mechanical and thermal properties, two-dimensional (2D) materials have attracted great interest in material science research and found interesting applications in energy conversion and storage, optoelectronics, biomedicines, photocatalysis, sensors, etc. 2D materials research has been started after the successive exfoliation of graphene in 2004. The extraordinary physicochemical properties and promising device applications of graphene motivated researchers to develop new atomically thin 2D materials. As a result, a series of 2D layered materials including transition metal dichalcogenides, hexagonal boron nitride, graphitic carbon nitride, layered metal oxides, layered double hydroxides, transition metal carbides or carbonitrides, black phosphorous nanosheets and elemental analogues of graphene have been established within the past few years. Chemical functionalization is found to be an effective way to improve physical and chemical properties of 2D materials. The functionalization can be either through direct covalent bonding or through non-covalent interactions such as van der Waals, electrostatic, π- π and cation- π interactions [1-2]. Herein, I will present the chemical functionalization of 2D materials including graphene, phosphorene and MXene, using our recently synthesized functional organic molecules through covalent and noncovalent approaches. The chemically modified 2D materials have been fully studied using several spectroscopic and microscopic characterization techniques. Finally, relevant potential applications of the chemically modified 2D materials will also be discussed [3-5].

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Bandgap Engineering in strained bulk and monolayer MoS_2

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Abstract

Strain in nanomaterials, especially light emitting 2D materials, is often an important parameter to examine due to its potential for bandgap modulation [1], as well as causing change in photoluminescence efficiency [2]. This study focuses specifically on MoS_2, a layered chalcogenide material with a bandgap which changes from indirect to direct in character when reduced to the monolayer form. Although many properties of MoS_2 are well studied, the effect of strain on band gap has not been investigated in a systematic way. In this study, we performed density functional theory (DFT) calculations using the HSE06 functional including Grimme's D3 corrections for Van der Waals interactions to investigate the effect of both biaxial and uniaxial strains on band gap within this material. calculations were performed for both the bulk and monolayer systems, with strain along several different crystal directions considered for uniaxially strained monolayers. Figure 1 shows the band structure varies more rapidly with biaxially applied strain than for uniaxially applied strain. Variation in band gap was found to be independent of the strain direction; this was characterised by the gradient of the strain-band gap graphs – for both direct and indirect band gaps, see Table 1. Thus crystal orientation with respect to strain direction is not necessary to be considered for strain induced bandgap engineering. These theoretical results provide inspiration for optoelectronic applications based on strain, for example, tunable and highly efficient MoS_2 light emitters.

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Figures

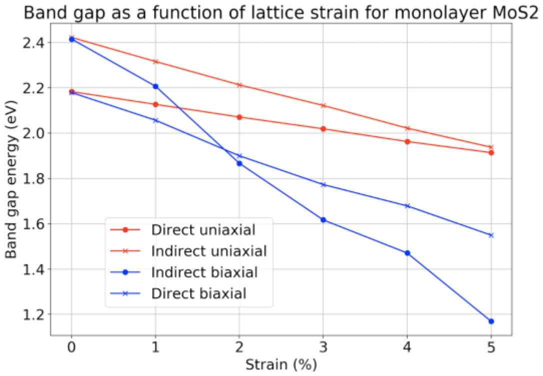

Figure 1: Band gap variation with applied strain for biaxial and uniaxial strain

Table 1: Gradients of the band gap-strain graph for various in plane uniaxial strain directions, with angle measured from one of the in plane lattice vectors

Strain angle (Degrees)	Direct gap Gradient (meV/% strain)	Indirect gap Gradient (meV/% strain)
0	-52.7±0.6	-95.3±0.2
15	-55.1±0.4	-98.9±0.2
60	-53.5±0.4	-96.2±0.1
90	-57.2±0.1	-100.0±0.2

Sputtering Deposition of Antimonene Film

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Antimony (Sb), in the same column of phosphorous in the element table, has a layered crystalline structure. A monolayer of antimony, named as antimonene, is predicted to be a stable semiconductor with a high mobility, and it becomes a semimetal when the thickness increases to bilayer or thicker [1,2]. These properties make antimonene flakes promising for nano-electronic devices and electrochemical applications. In the recent reports, antimonene thin flakes have been prepared by either exfoliation or molecular beam epitaxy [3,4]. However, these flakes are usually so small (less than 1 micrometre) that it is difficult to fabricate devices based on these flakes. The preparation of large size antimonene thin flakes is still challenging. In this work, we explored the deposition of few-layer Sb nanofilms with low-power magnetron sputtering and studied the electrical properties of the deposited films. We found that, with in-situ annealing, the crystalline structure can be greatly improved, and the conductivity much increased. Oxygen evolution reaction (OER) and hydrogen evolution reaction tests also confirm the improved performance of the Sb film deposited at high temperature.

Keywords: antimonene, sputtering deposition, 2D materials, OER, HER

Acknowledgement: This research is supported by Ministry of Education, Singapore, under its Academic Research Fund Tier 1 (MOE2019-T1-001-113).

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FIGURES

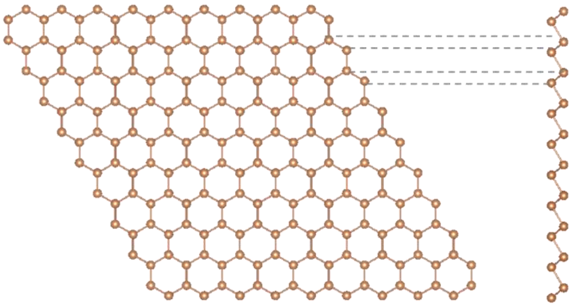

Figure 1: Crystalline structure of antimonene monolayer from top view (left) and side view (right).

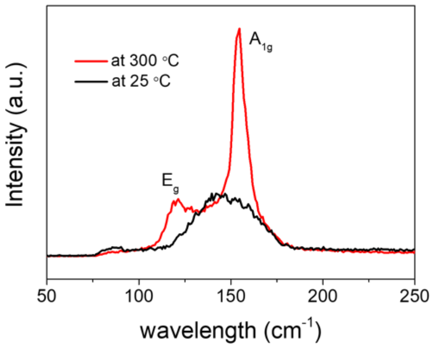

Figure 2: Raman characterization of Sb films deposited at different temperatures. The one deposited at high temperature shows better crystalline structure.

Investigating graphene growth by Plasma-enhanced CVD using various catalyst thicknesses

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Graphene as 2D material with extraordinary properties has attracted the interest of research communities to master the synthesis at a large scale without sacrificing the quality. Plasma-enhanced chemical vapor deposition (PECVD) has attracted more and more attention as a promising method for controllable graphene synthesis. In this research, we report the correlation between the thickness variations of the Nickel as catalyst film and the quality of deposited Graphene using Quartz as substrate. Surface morphology was studied by atomic force microscopy (AFM). Raman spectroscopy was used to investigate the quality of graphene. The results showed that graphene samples deposited on nickel films of 40 and 70 nm thickness possess best quality.

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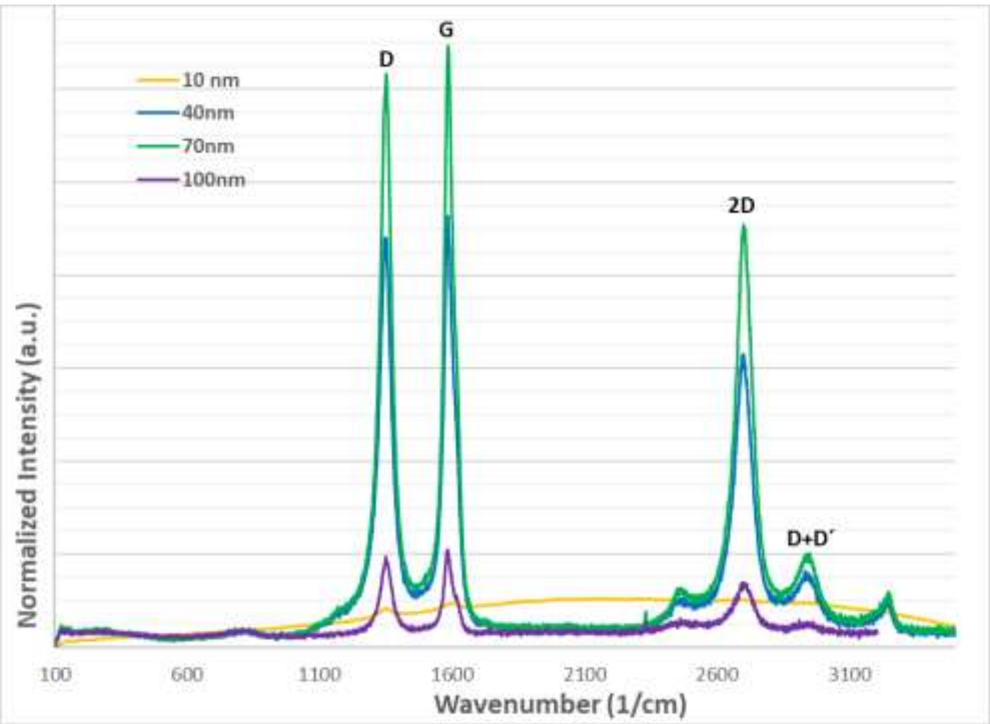


Figure 1: Raman spectra of graphene deposited on nickel of various thicknesses (10,40,70 and 100 nanometer) by PECVD consist of G (1580 cm-1), 2D (2690 cm-1), D (1350 cm-1) and D+D´

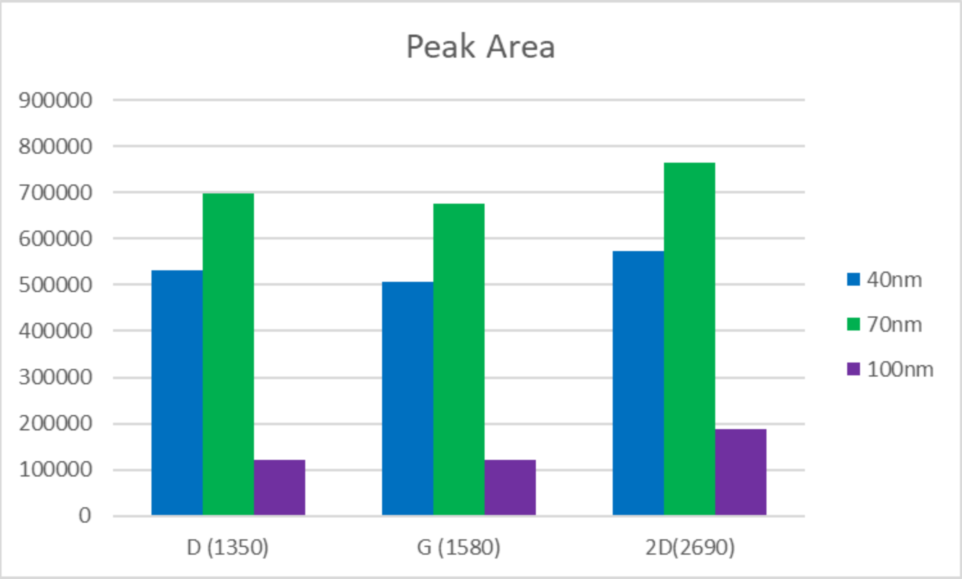


Figure 2: Comparison of area under D, G and 2D peaks of Graphene with different thicknesses

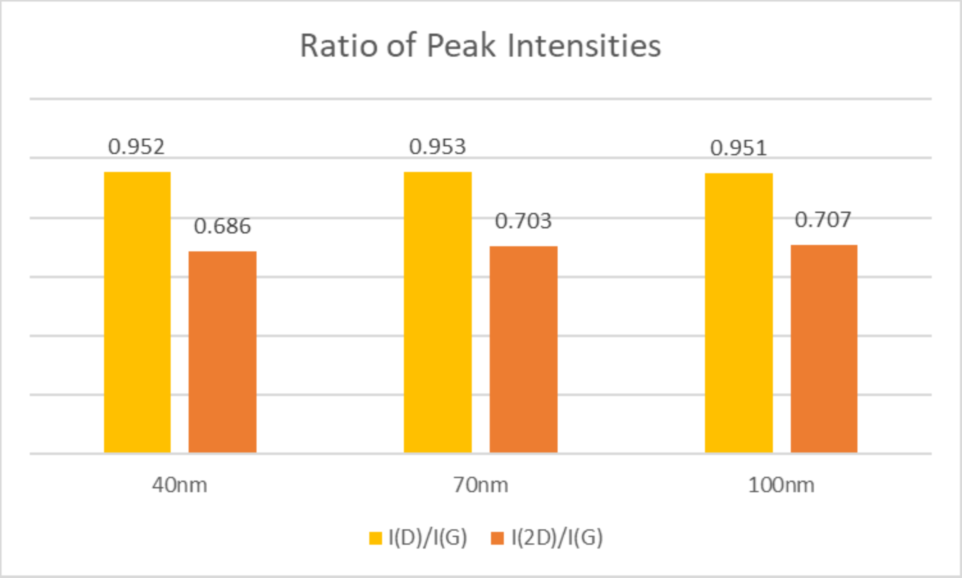
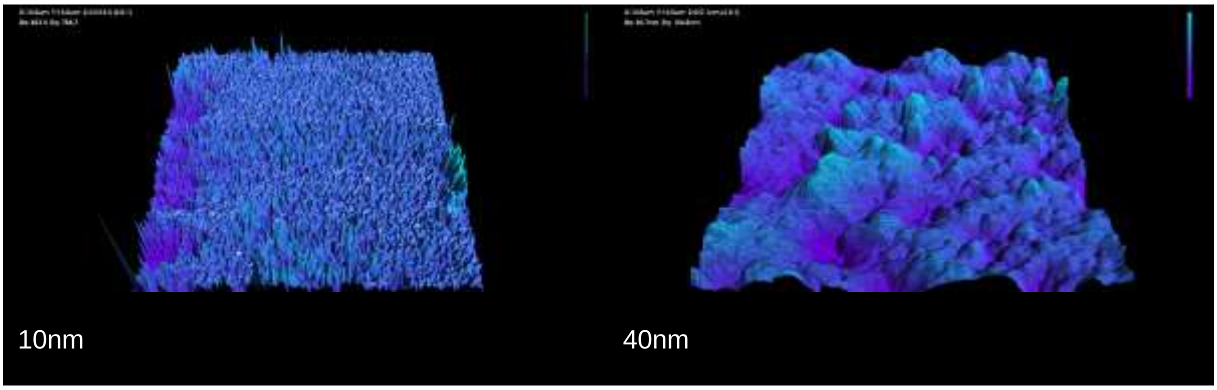


Figure 3: Proportion of intensities (D, G and 2D peak of Graphene growth by PECVD)



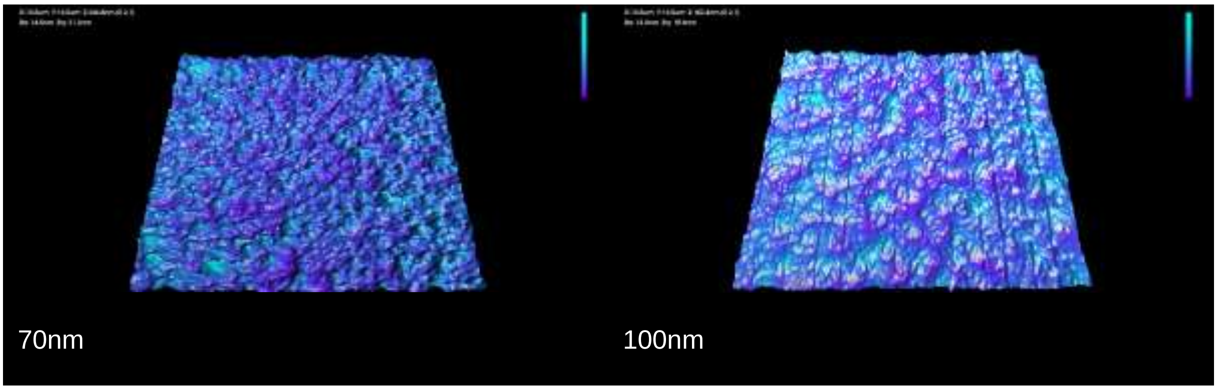


Figure 4: AFM images of graphene after growth on Quartz substrate including nickel (10, 40, 70 and 100) as a catalyst

Twist angle dependent proximity-induced spin-orbit coupling in graphene/WSe$_2$ heterostructures

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In recent years, effects of strong proximity-induced spin-orbit coupling (SOC) in single layer graphene (SLG) on transition metal dichalcogenides (TMDCs) like WSe$_2$ have been detected [1]. Additionally, theoretical calculations predicted a strong dependence of the proximity-induced SOC in relation to the twist angle between graphene and TMDCs [2, 3]. In our work, we fabricated SLG/WSe$_2$/h-BN heterostructures with defined twist angles between SLG and WSe$_2$ layers. The fact that 2D materials like graphene and WSe$_2$ very often break along zigzag or armchair edges was used to align and estimate the rotation angles between the flakes [4]. Since we cannot distinguish between zigzag or armchair edges we consider both cases. Strong SOC causes weak anti-localization [1], which we used to determine the strength of the Rasbha type SOC (λ_R) and the valley-Zeeman type SOC (λ_{VZ}). We found a strong twist angle dependence of the proximity-induced SOC. A sample with an angle around 15° shows a much stronger SOC in both cases, for λ_R as well as for λ_{VZ}, compared to the other samples, with twist angles different to 15°. For those samples with a twist angle near 0° or 30° (zigzag-armchair problem), we found the SOC parameter to be almost equal and much smaller compared to the sample with 15° twist. This is in qualitative agreement with theoretical predictions [2, 3].

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Figures

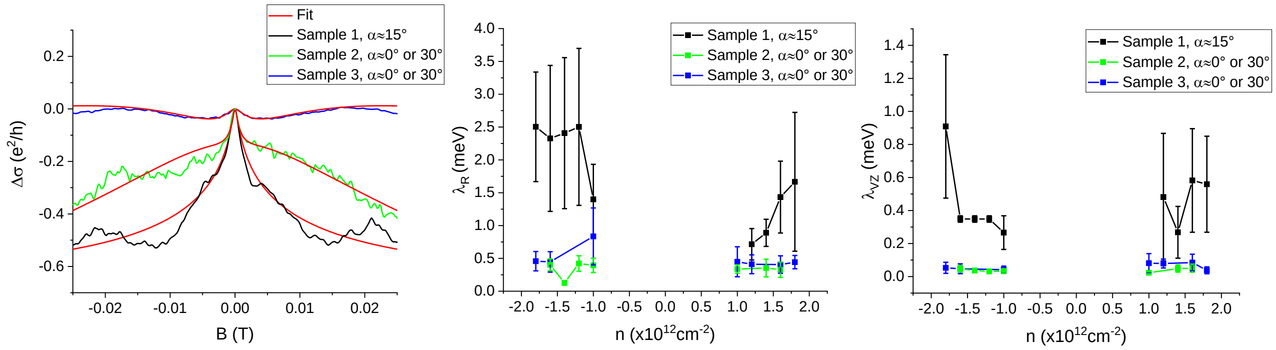

Figure 1: Weak anti-localization effect measured for three different with different twist angles (left). Comparison of λ_R (center) and λ_{VZ} (right) for three different samples with different twist angles.

Investigating topological insulator Bi_2Se_3 and Bi_2Te_3 nanoplatelets with scanning tunneling spectroscopy

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Topological insulators (TIs) have gained much interest in condensed matter physics due to their unique electronic properties. These materials are characterized by an insulating bulk with topological quantum states protected by time reversal symmetry at their surface (3D materials) or edge (2D materials). Their topological properties are related to the inversion of the conduction and valence band as a consequence of strong spin-orbit coupling. Of the many theoretically predicted and experimentally verified TIs, Bi_2Se_3 serves as a model system due to its large inverted bulk bandgap (0.3 eV) and its helical edge state, which manifests as a Dirac cone situated at the Γ point in the Brillouin zone[1-4].

While extended sheets and bulk crystals of Bi_2Se_3 and Bi_2Te_3 have been investigated thoroughly with scanning tunnelling microscopy (STM) and spectroscopy (STS), reports on the electronic properties of Bi_2Se_3 and Bi_2Te_3 nanoplatelets (NPLs) are scarce1. However, the small lateral size of NPLs (~200 nm) and their specific crystal shape provide a unique opportunity to study the effects of quantum confinement and shape on their opto-electronic properties and band inversion. Here, we present a colloidal synthesis method for the preparation of monocrystalline Bi_2Se_3 and Bi_2Te_3 NPLs with hexagonal symmetry. Furthermore, we give an overview of our research plans to use STM/STS to investigate the electronic properties of these highly interesting topological insulator NPLs.

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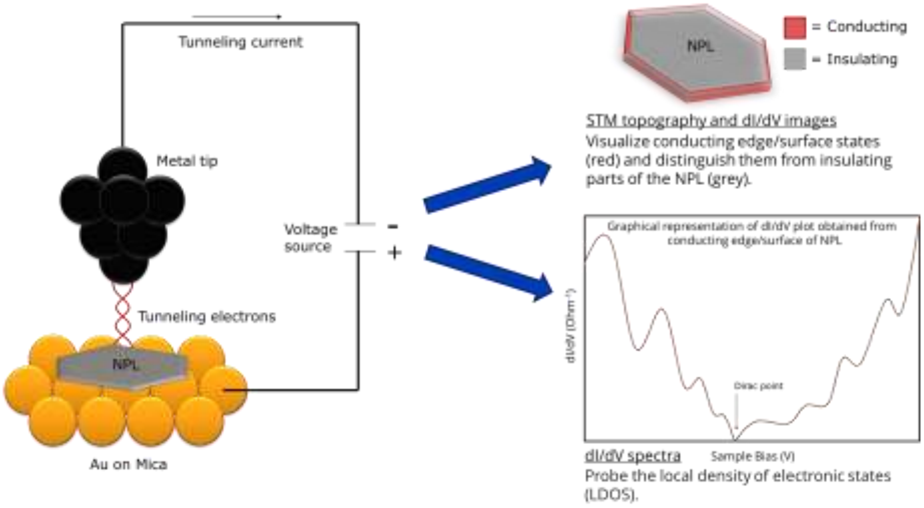

STM topography and dI/dV images
Visualize conducting edge/surface states (red) and distinguish them from insulating parts of the NPL (grey).

dI/dV spectra
Probe the local density of electronic states (LDOS).

Figure 1: Graphical representation of experimental STM set-up and the types of results that can be obtained.

Optical Properties of Sputtered Antimonene Films

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ABSTRACT

Antimonene is an emerging two-dimensional material, which consists of a layer of antimony atoms. Monolayer antimonene is predicted to be a semiconductor with high mobility, while the bilayers and thicker flakes will become metallic.[1,2] In the past reports, the antimonene nanoflakes were prepared by exfoliation, molecular beam epitaxy, and vapor deposition, and demonstrated applications in rechargeable batteries, miRNA detections and Q-switching Pr:YLF lasers, etc.[3-6] In this report, we developed antimonene nanofilms with deposition by ultra-low power magnetron sputtering. We successfully tuned the crystalline quality of the antimonene films from amorphous to polycrystalline and explored their optical properties with ellipsometer.

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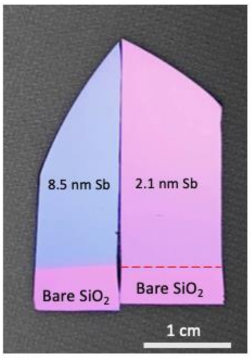

Figure 1: Optical image of as-deposited antimonene (Sb) nanofilms with different thickness.

Graphene functionalization with SARS-CoV-2 antibodies

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Current situation of COVID-19 demands a rapid, reliable, cost-effective, facile detection strategy to break the transmission chain and biosensors have emerged as a feasible solution for this purpose. Among the existing variety of biosensors, photonic biosensors allow real-time detection of infinitesimal quantities (even isolated molecules) of a great variety of biochemical substances, since they measure instantaneous changes in the optical properties of matter. Generally, photonic biosensors are composed by two parts: the photonic part, which is responsible for transducing a biochemical change into a change in the optical response; and the chemical part, a molecular recognition element that ensures that only the targeted analyte adheres to the biosensor and provokes the optical change. In this context, Graphene has demonstrated its potential in the rapid detection of SARS-CoV-2 by its integration in a FET-based biosensor [1].

In this work we have developed a faster, less toxic, and a cost-effective functionalization of graphene with PBASE (- 1-pyrenebutyric acid N-hydroxysuccinimide ester), which is a key molecule to immobilize SARS-CoV-2 spike antibodies onto graphene surfaces (Figure 1a). The PBASE functionalization as well as the SARS-CoV-2 antibody immobilization has been probed in Graphene layers and flakes prepared by means of plasma enhanced chemical vapour deposition and the scotch-tape method. Atomic force microscopy together with Raman spectroscopy confirm all the functionalization steps (Figure 1b).

This demonstration would mean the viability of the chemical part of a graphene-based photonic biosensor for ultra-rapid detection of minimal amounts of the SARS-CoV-2 virus in nano-pharyngeal fluid through the integration of functionalized graphene in a low-cost plasmonic metamaterial photonic biosensor that can be manufactured on a large scale.

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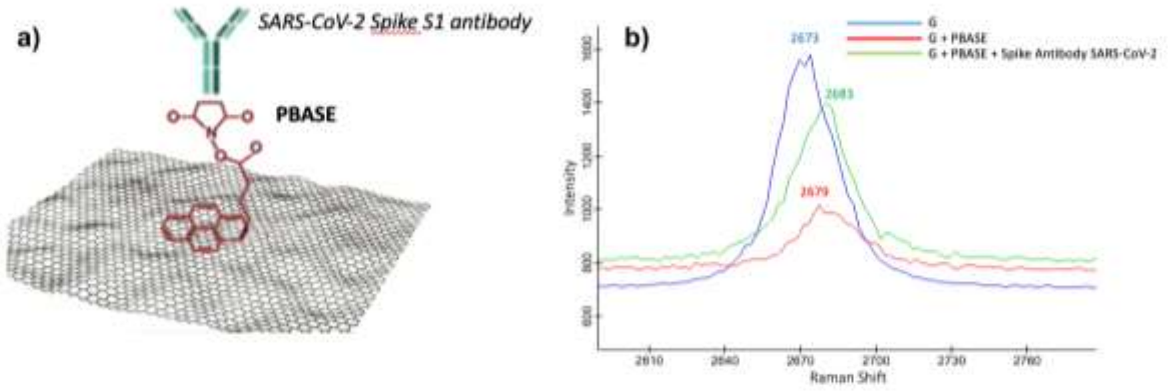
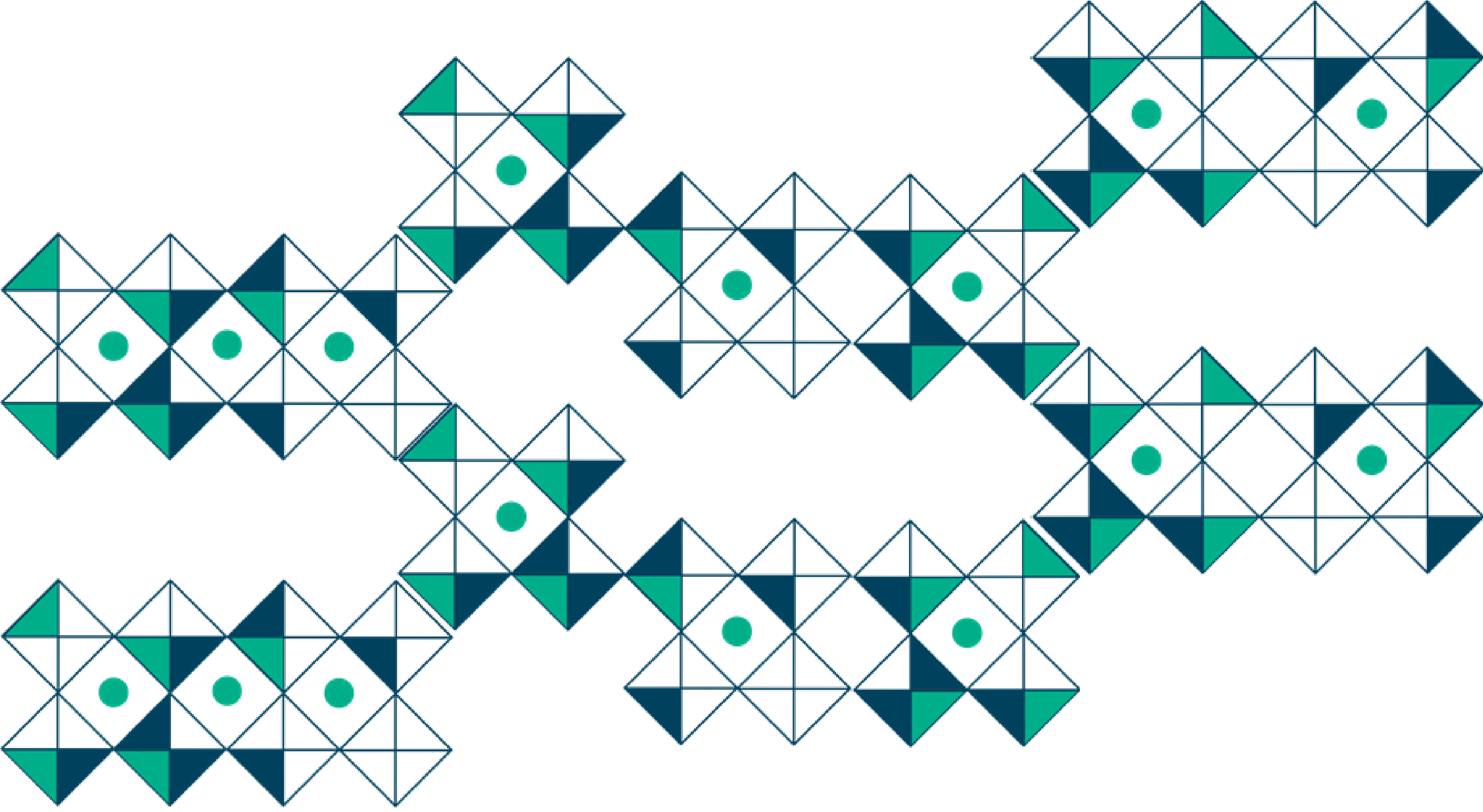


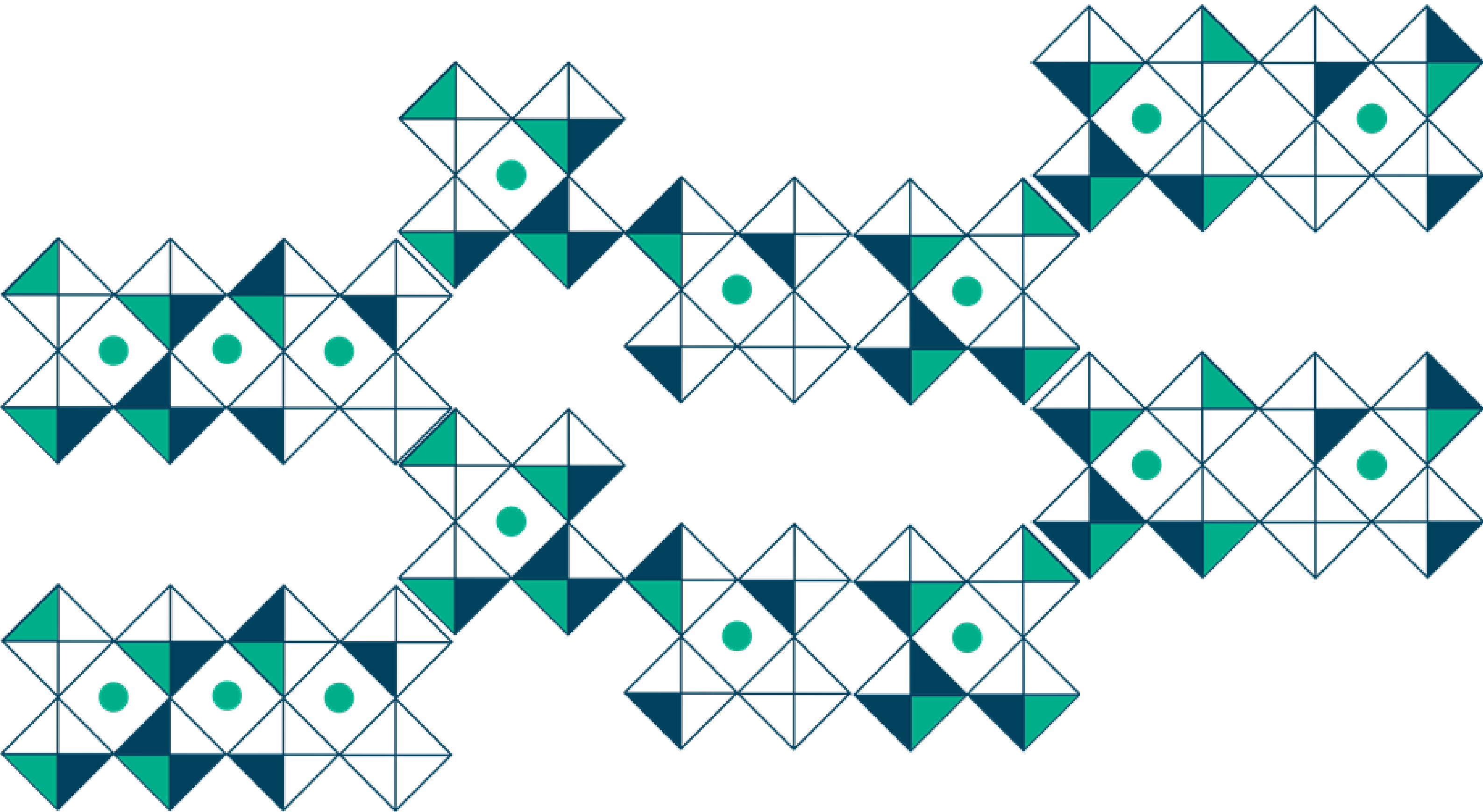
Figure 1: a) Schematic representation of the graphene sheet functionalized with PBASE and SARS-CoV-2 spike antibodies; b) Raman spectra of bare graphene, functionalized with PBASE and with PBASE and SARS-CoV-2 spike antibodies.



2D-HAPES2021

2D Halide Perovskites from basic science to applications

November 3-4, 2021



Perovskite Tandem Solar Cells

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ABSTRACT

In this presentation I will discuss the multiple ways how monolithic perovskite/silicon tandem solar cells, built from textured silicon heterojunction solar cells, with high performance can be fabricated. For the perovskite deposition on such micron-scale, complex surfaces, adequate methods include hybrid deposition (via a 2-step combination of evaporation and solution processing), and solution-processing, resulting either in conformal or non-conformal perovskite films, respectively. Generally, key to successful tandem devices is the absence of pinholes in the perovskite films, which otherwise would lead to device shunting. For the solution-processed perovskites, this mandates the deposition of relatively thick perovskites [1]. However, efficient charge-collection from such perovskites requires adequate defect passivation, for example via passivation of the NiO_x/perovskite interface with dyes [2], as well as concurrent cationic and anionic defect passivation strategies via molecules such as phenformin [3] or carbazole [4]. Overall, this resulted in certified power conversion efficiencies > 28.2%.

Next, with the developed high-efficiency tandems, I will the discuss their outdoor performance, with specific attention to the impact of the operational temperature on current matching [5], as well as general reliability aspects. I will conclude my talk with arguing how bifacial perovskite/silicon tandems aid further improving device performance and stability, thanks to their reliance on narrow-bandgap perovskites for optimal performance.

BIO

Stefaan De Wolf received his Ph.D. degree in 2005 from the Katholieke Universiteit Leuven in Belgium, during which time he was also affiliated with imec in Belgium, working on crystalline silicon solar cells. From 2005 to 2008, he was with the National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan. In 2008, he joined the Photovoltaics and Thin-Film Electronics Laboratory, Ecole Polytechnique Federale de Lausanne (EPFL), Neuchatel, Switzerland, as a team leader working on high-efficiency solar cells. Since September 2016 he is an associate professor at the King Abdullah University of Science and Technology (KAUST) in Saudi Arabia, working on high-efficiency silicon and perovskite solar cells, and combinations thereof.

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Understanding and Optimizing Interface Energetics and Processes: an essential step towards efficient and stable perovskite solar cells

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Engineering interfaces in perovskite solar cells is nowadays paramount in the optimization of multilayer perovskite device stack. This stem true for multi-dimensional (2D/3D) perovskite based solar cells, where high efficiency can be combined with promising device durability. However, the exact function of the 2D/3D interface in controlling the device behaviour and the interface physics therein are still vague.

Here I will discuss the 2D/3D functions which can simultaneously act as surface passivant, electron blocking layer, and driving efficient and selective charge extraction. In particular, I will demonstrate that the exact knowledge on the interface energetics is crucial to obtain for a smart interface engineering. As an example, I will discuss the case of thiophene-based 2D perovskite/ 3D perovskite interfaces forming a p-n junction. This leads to a reduction of the electron density at the hole transport layer interface and ultimately suppress the interfacial recombination. As a consequence, we demonstrate that photovoltaic devices with enhanced fill factor (FF) and open-circuit voltage (VOC) of 1.19V which approaches the potential internal Quasi-Fermi Level Splitting (QFLS) voltage of the perovskite absorber, nullifying the interfacial losses. We thus identify the essential parameters and energetic alignment scenario required for 2D/3D perovskite systems in order to surpass the current limitations of hybrid perovskite solar cell performances. This knowledge turns fundamental for device design, opening a new avenue for perovskite interface optimization.

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I acknowledge the HY-NANO project that has received funding from the European Research Council (ERC) Starting Grant 2018 under the European Union's Horizon 2020 research and innovation programme (Grant agreement No. 802862).

Brighter Metal Halide Perovskite Light Emitting Diodes Via Heat Management

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Abstract:

Hybrid organic-inorganic halide perovskite materials are promising for light emitting applications. In this talk, I will discuss our recent work on perovskite-based LEDs, where we have established a general protocol for preparing ultrathin, smooth, passivated, and pinhole free films of metal halide perovskites with various compositions, by incorporating bulky organoammonium halide additives to the stoichiometric 3D perovskite precursors [1-7]. In addition, we have found that a major factor contributing to roll-off of perovskite LEDs is heating [8-11]. By avoiding heating through multiple strategies, we are able to reduce roll-off and report record-bright perovskite LEDs, pushing toward display, lighting, and even lasing-relevant current densities.

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The use of 2D materials for perovskite photovoltaics: graphene and beyond.

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Hybrid perovskite solar cells (PSCs) are one of the most promising technologies for new-generation photovoltaics due to outstanding semiconductor properties and low-cost solution processing methods for the fabrication. Indeed, PSCs dominated the PV scientific research in the last decade, by developing efficient and stable devices, produced by employing scalable and low-cost printing techniques, easily embedded in roll2roll or sheet2sheet production lines. However, PSC technology still requires to demonstrate the transfer from lab to fab, pushing the scientific community in finding brilliant solution for drawing a feasible and reliable route toward its commercialization. Indeed, the use of perovskite crystallization processes from the liquid phase tends to the formation of imperfections and defects in the bulk and surfaces that could give rise to non-radiative charge recombination. Moreover, energy levels in halide perovskite semiconductors and materials for the transporting layers cannot be simply controlled by chemical doping as for Si and III-V semiconductors. Here, the use of interface engineering based on bi-dimensional (2D) materials is proposed as an efficient tool for trap passivation and energy level alignment, by mitigating the performance losses induced by the scaling-up process.[1] In particular, the successful application of 2D materials, i.e., graphene,[2] functionalized MoS_2,[3] and MXenes [4,5] in perovskite solar modules (PSMs) allowed to achieve PCE overcoming 17% and 14.5% over 121 and 210 cm^2 substrate area respectively. Moreover, an ad-hoc lamination procedure employing low temperature cross linking EVA (at 80°C-85°C) allowed to fabricate several 0.5 m^2 panels, finally assembled in Crete Island, in the first worldwide fully operating 2D material-perovskite solar farm.

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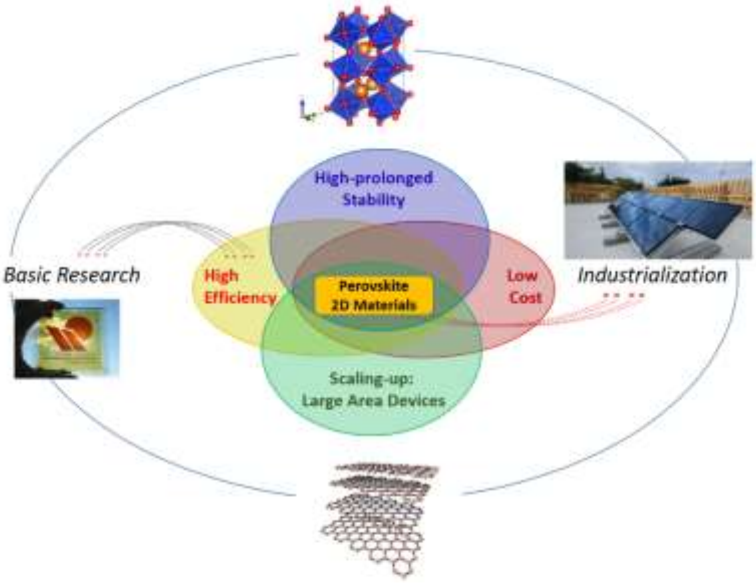

Figure 1: The use of 2D materials as inter or intra layer in perovskite solar cells is a winning strategy to boost perovskite photovoltaics in term of power conversion efficiency and stability under real working conditions, allowing the low cost production of large area solar module and panels.

Perovskite On-Chip Lasers for Photonic Integrated Circuits

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An on-chip laser that can be monolithically integrated into silicon substrates is the final missing component for integrated photonics, the applications of which span from telecommunication [1] to retinal projection systems [2]. Metal-halide perovskites are semiconductors gaining momentum as laser gain materials as they can be deposited on silicon or amorphous substrates by low-cost, low-temperature methods such as spin coating [3]. These materials are ionic crystals and therefore are incompatible with standard patterning methods used by semiconductor based on photolithography.
We have developed such photolithography-based process and used it to fabricate perovskite disc lasers (Fig. 1a-b). These devices have the lowest lasing threshold of 4.7 µJcm^{-2} ever reported for any monolithically integrated laser compatible with back-end-of-line of CMOS [4]. When pumped with femtosecond pulses multiple modes are lasing in the discs, even at an excitation slightly above the lasing threshold. When pumped with 700 ps long pulses, which are much longer than stimulated emission lifetime of 20 ps, the lasers work in a quasi-steady-state and show a single mode operation (Fig. 2). The measured output intensity vs. excitation curve can be fitted with the rate equation for semiconductor lasers [5].

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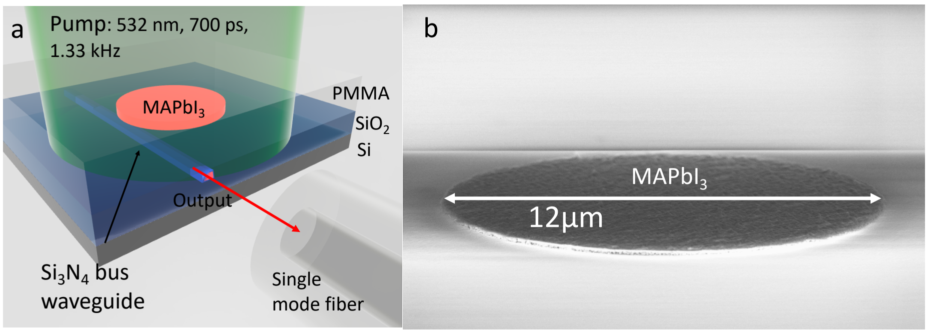

Figure 1: a) Schematic of optically pumped perovskite waveguide integrated disc later b) SEM image of top-down patterned perovskite disc

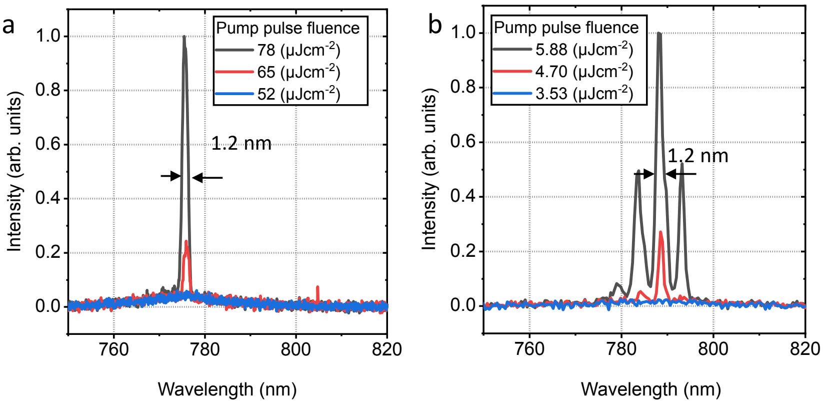

Figure 2: a) Laser spectrum obtained by pumping with 700 ps pulses at 532 nm wavelength b) Laser spectrum obtained by pumping with 120 fs pulses at 630 nm wavelength

Perovskite solar cells based on layered materials

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Metal halide perovskite solar cells (PSCs) are promising for low-cost (~50% price compared to Si-based PV) [1] solar power generation, due to their high efficiencies (~25%) [2] and their solution processability [3]. However, these highly efficient PSCs have low (<1000hours) continuous operational lifetimes in high temperature/humidity conditions (e.g. 85 ^{o}C and 85% R.H.) [4] and rely on metal current collectors (CCs) and expensive hole transporting layers (HTMs) [5]. Replacing the metal CCs with a solution processed material and avoiding the use of expensive HTMs can increase stability and throughput and further reduce cost and manufacturing complexity. In the first part of the talk, I will summarize the state of the art reports on the development of fully printable Carbon-based PSCs (CPSCs), while in the second part I will present our recent progress on fully printable CPSCs where we first reported the use of graphene ink based current collectors in CPSCs. We report a low temperature (<80 oC) curable perovskite-compatible high-pressure homogenized graphene ink with sheet resistance, R_S<5 Ohm/sq at 10μm and long-term stability in ambient conditions (>12 months). Fully printed PSCs are fabricated using this ink to print the CC. By optimizing the halide perovskite/HTMs/CC interface we get PSCs with average power conversion efficiency~16% %. Our devices satisfy ISOS-D1 and ISOS-D2 [6] long-term stability tests for >100 hours without any encapsulation layer to prevent oxygen/moisture diffusion, outperforming PSCs based on metallic CC [5,7]. This demonstrates that low-cost (due to the replacement of metallic CC and use of low cost HTMs and passivation layers), efficient, stable and fully printable devices can be achieved using high-pressure homogenized graphene.

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Visualizing Exciton Transport in 2D Metal-Halide Perovskites.

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Metal-halide perovskites are a versatile material platform for light-harvesting and light-emitting applications as their variable chemical composition allows the optoelectronic properties to be tailored to specific applications. However, the reduced dimensionality can significantly impact the spatial dynamics of the excitonic excited state within the two-dimensional plane. To study these effects, we employ Transient Microscopy techniques which allow for a direct visualization of the excited state transport.[1] I will start the talk by giving an overview of some of the surprising effects that can be observed, particularly regarding the relationship between lattice softness and the exciton transport properties.[2,3,4]

In the second part of the talk, I will focus on very recent results on exciton transport mixed-halide 2D perovskites.[5] Halide mixing is one of the most powerful techniques to tune the optical bandgap of metal-halide perovskites across wide spectral ranges. However, halide mixing has commonly been observed to result in phase segregation, which reduces excited-state transport and limits device performance. While the current emphasis lies on the development of strategies to prevent phase segregation, it remains unclear how halide mixing may affect excited-state transport even if phase purity is maintained. To try and answer this question, we study the specific case of 2D metal-halide perovskites, in which phase segregation is absent. We show that, despite phase purity, halide mixing inhibits exciton transport in these materials. We find a significant reduction even for relatively low alloying concentrations, with bromide-rich perovskites being particularly sensitive to the introduction of iodide ions. Performing Brownian dynamics simulations, we are able to reproduce our experimental results and attribute the decrease in diffusivity to the energetically disordered potential landscape that arises due to the intrinsic random distribution of alloying sites. Our results show that even in the absence of phase segregation, halide mixing may still impact carrier transport due to the local intrinsic inhomogeneities in the energy landscape.

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Simultaneous Interfacial and Grain-Boundary Passivation for Highly Efficient Inverted Methylammonium-Free Perovskite Solar Cells

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Inverted p-i-n perovskite solar cells (PSCs) have proven their potential for fabricating high-performance perovskite-based tandem photovoltaics [1]. However, severe non-radiative recombination at the perovskite/electron transport layer and at the grain boundaries (GBs) still limits their open-circuit voltage (V_{OC}) and fill factor (FF) as compared to their n-i-p counterparts. We introduce a novel dual passivation approach using phenethylammonium chloride (PEACl) to simultaneously passivate the GBs and the perovskite/C_{60} interface by using PEACl:$PbCl_2$ as the additive and PEACl for surface treatment, respectively. Thereby, we achieve a substantial enhancement in charge carrier lifetime and quasi-Fermi level splitting compared to reference devices. Thereby, we achieve a substantial enhancement in charge carrier lifetime and quasi-Fermi level splitting compared to either of the individual passivation strategies or reference devices. By analyzing cathodoluminescence, scanning electron microscopy, X-ray/ultraviolet photoelectron spectroscopy and Kelvin probe force microscopy measurements, we attribute the positive effects to the formation of a heterogeneous 2D Ruddlesden-Popper perovskite at the film surface and GBs, which leads to efficient chemical passivation of GB and surface defects as well as additional electronic passivation at the perovskite/C_{60} interface. This results in one of the highest reported PCEs for p-i-n PSCs of 22.7% with a remarkable V_{OC} and FF of 1.162 V and 83.2%, respectively. Our study researches the advanced use of dual passivation as key mechanism to manage the detrimental defects both in the GBs and the surface of the perovskite layer to achieve highly efficient p-i-n PSCs. The work paves the way for the development of high-efficiency two-terminal perovskite-based tandems photovoltaics.

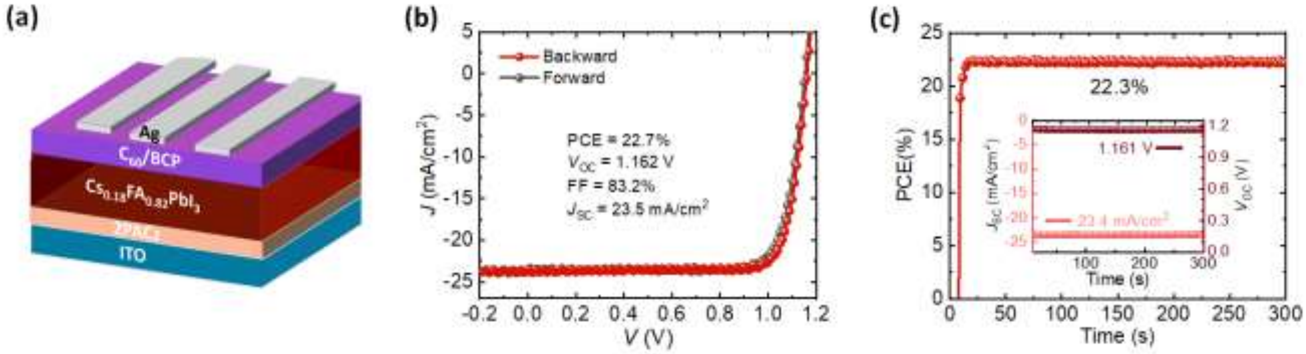

Figure 1: (a) Schematic of the employed perovskite solar cell configuration with a layer stack sequence of ITO/2PACz/perovskite/C_{60}/BCP/Ag. (b) *J-V* characteristics and (c) maximum power point (MPP) tracking of the best-performing dual passivation perovskite solar cell, demonstrating a stabilized PCE of 22.3%. The inset shows the stabilized J_{SC} and V_{OC}.

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Hybrid Organic-Inorganic Halide Post-Perovskite 3-Cyanopyridinium Lead Tribromide

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To date, the most studied families 2D halide perovskites are Ruddlesden−Popper, Dion-Jacobson and other phases that can be derived from 3D halide perovskites by slicing along different crystallographic directions. This leads to the spatially isotropic corner-sharing connectivity type of metal-halide octahedra in the 2D layer plane.

We introduce a new family of hybrid organic-inorganic 2D lead-halides: hybrid organic-inorganic post-perovskites. The first member of this family - 3-cyanopyridinium lead tribromide (3cp)PbBr3 is reported [1]. Post-perovskites have unique octahedra connectivity type in the layer plane: typical “perovskite-like” corner-sharing in one direction, and the rare edge-sharing connectivity pattern in the other [2]. Such connectivity leads to a significant anisotropy in the material properties within the inorganic layer plane. The (3cp)PbBr3 clearly shows the 2D quantum size effect with a band gap around 3.2 eV and typical broadband self-trapped excitonic photoluminescence at temperature below 200 K.

This study was supported by the RFBR project 19-03-00836, SPbU Grant ID 73032813, “NANO-TANDEM” (MIS 5029191), SARF UoC grant KA 10652. This work was carried out on the equipment of SPbU Resource center “Nanophotonics”.

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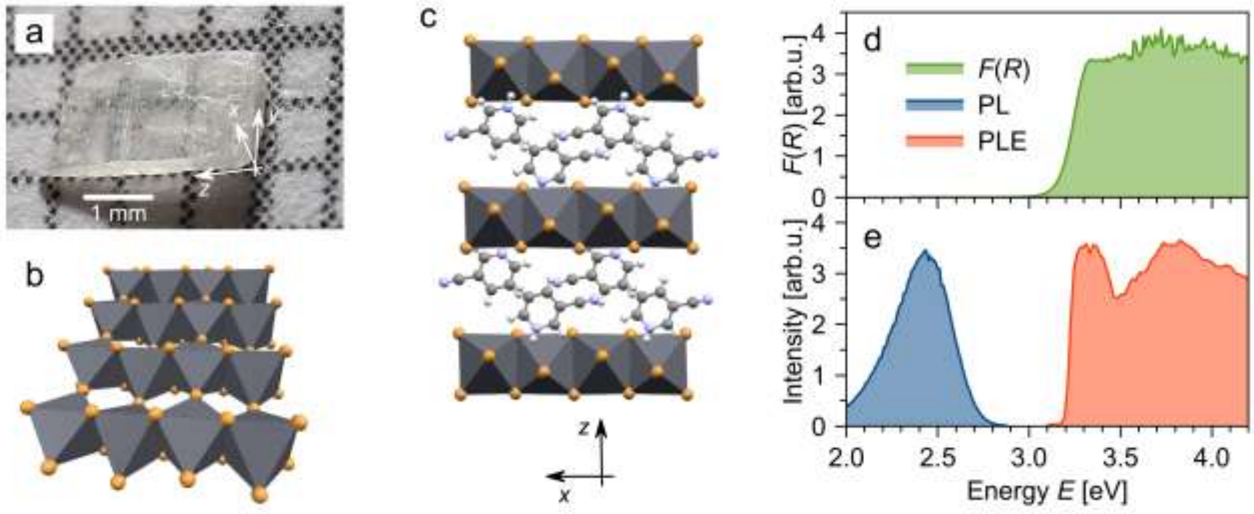

Figure 1: The photo (a) and the crystal structure (c) of (3cp)PbBr3 crystal. (b) Single inorganic layer with post-perovskite-type connectivity of $[PbBr_6]$ octahedra. (d) Kubelka-Munk function F(R) at T = 300 K. (e) PL (E_{ex} = 3.31 eV) and PLE (E_{em} = 2.45 eV) spectra at T = 77 K.

Photoluminescence and Amplified Spontaneous Emission in Quasi-2D and 3D Perovskite: Influences of Excitonic Versus Free Carrier Emission

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Quasi-two-dimensional (2D) perovskites are promising optoelectronic materials for display and lighting technologies due to their excellent luminescent properties [1]. Light-emitting diodes (LEDs) based on quasi-2D emitters have demonstrated external quantum efficiencies over 20% [2]. Meanwhile, the recent demonstration of optically pumped continuous wave lasing at room temperature [3], giving quasi-2D perovskites front-runner status for realizing electrically driven lasers.

We investigate the photoluminescence (PL) and amplified spontaneous emission (ASE) of the quasi-2D emitter ($CsPbBr_3$ with 80% butylammonium bromide), and its 3D analogous formed by thermal removing the organic spacer (Fig 1a). Although the PL from the quasi-2D films is much brighter at low excitation power (Fig 1a), the ASE thresholds (600 μJ cm^{-2}) of the quasi-2D materials tend to be higher than the 3D counterparts (130 μJ cm^{-2}). This counter-intuitive behaviour is investigated through time-resolved photophysical studies, which reveal the emission in quasi-2D perovskite originated from the excitonic emission (Fig 1b). This accounts for its superior PL at low fluence, as the excitonic emission is efficient at low excited-state densities (Fig 1c). However, the 2nd order exciton–exciton annihilation of quasi-2D perovskite starts to take over the exciton dynamics at a low exciton density (<10^{16} cm^{-3}), resulting in a low radiative efficiency at around transparency carrier density (10^{18} cm^{-3}). Hence, to achieve the ASE in quasi-2D film, a much higher excitation fluence is necessary to increase the photon density in this low radiative efficiency regime. In contrast, the 2nd order free-carrier radiative recombination in 3D film leads to a high radiative efficiency steadily increasing to the transparency carrier density, which explains its lower ASE threshold. Through further examining the ASE thresholds of a series of quasi-2D perovskites with different 2D spacer content and type (i.e. 2-phenylethylammonium bromide and 1-naphthylmethylamine bromide), we highlight that quasi-2D perovskite gain materials should target fast free carrier recombination by engineering the thickness and size of QW, but not maximum PL quantum yields under low power excitation.

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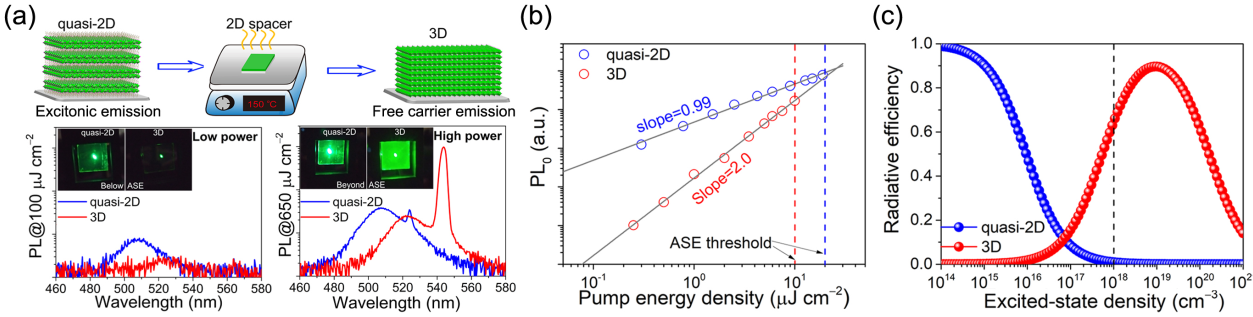

Figure 1: (a) Transform from the quasi-2D into a 3D perovskite film through an annealing step (top). PL/ASE spectra of quasi-2D and 3D perovskite films (bottom). (b) Plots of PL_0 versus the pump energy densities. (c) Calculated radiative efficiency. The dash line indicates the transparency carrier density.

Broad emission from the structural distortions induced by substituting trivalent element Sb^{3+} in low dimensional halide perovskites

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Abstract

Hybrid lead halide perovskites [$APbX_3$] have attracted a great deal of attention due to their outstanding tuneable broad-band emission and charge transport properties. The toxicity of lead hinders their further application in the photoelectric field. Here, we report tuneable broadband emission obtained in lead-free vacancy ordered triple halide perovskites [$A_3M_2X_9$] due to self-trapped excitons (STE) by tuning the M^{3+} cation.[1],[2] In this work, we have systematically prepared $Cs_3Sb_aBi_{2-a}X_9$ (X=Cl, Br, I) with x between 0 and 2, where at $x \neq 0$ & 2 we obtain mixed trivalent cations in the triple perovskites. We explored the distortion in these materials using a combination of Raman and FT-far-IR spectroscopic measurements. Finally, we investigated the effect of distortion of these materials on the photoluminescence properties.

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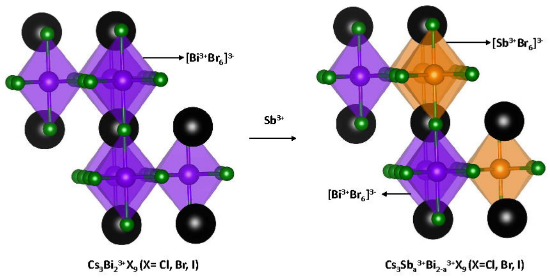

Figure 1: Method of doping Sb^{3+} in Bi^{3+} based lead-free halide perovskites.

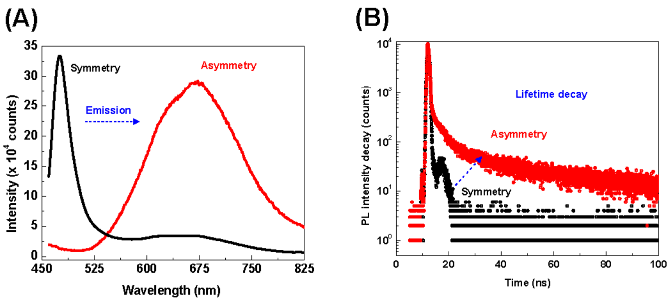

Figure 2: A & B are Emission and lifetime of undoped (symmetry) and doped (asymmetry) of $Cs_3Sb_aBi_{2-a}X_9$ (a=0, 0.5, X=Br) perovskite materials.

Tetrazine-incorporating layered halide perovskites featuring type II electronic interface: a small cation with several optical and electronic resonances

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2D-layered perovskites form assembled natural quantum well structures, where the perovskite layer is separated by large organic cations. They have been known for decades, but they are attracting growing interest, for their strong photoluminescence properties, their chemical versatility and their low sensitivity to external degradation mechanisms due to UV light and moisture. In particular, the chemical versatility of the organic part is a decisive advantage compared to their 3D counterparts.

Energy matching and band alignment engineering between the organic/inorganic parts can either be done by tuning the halide composition, by modifying the number of haloplumbate layers or by adjusting the HOMO/LUMO gap and/or levels of the organic spacer, that is to say by incorporating optically active molecules in the perovskite structure. In this case, instead of playing a simple passive barrier role, the organic part can be used to engineer the optoelectronic properties to these materials. Depending on the optical matching, defined for hybrid perovskites as the spectral overlap between the perovskite and organic absorbers optical transitions, along with the type I/II of interface, charge and/or energy transfers can be induced between the inorganic and organic moieties

We have synthesised two novel layered perovskites containing optically active s-tetrazine (R-C_2N_4-R) as sole included organic spacer. Thanks to the various energy resonances between the inorganic and organic components, both at the level of the single particle electronic states and at the level of many-body exciton states, this system represents the ideal test case to discuss in the detail charge and energy transfer processes at the type II interface. Furthermore, the incorporation of this novel chromophore as spacer is based on a new design concept, which exploits heterocycles with large fraction of nitrogen, rather than extending the size of carbon-based p-core. We further performed extensive optical characterization supported by computational studies, in order to gain a complete picture of all potential charge and energy transfer processes ongoing in this complex perovskite-luminophore system. More specifically, both excited states as well as band alignment were studied to rationalize the complete quenching of the perovskites light-emission. We conclude that several decay channels may coexist between the s-tetrazine and the perovskite frame, and highlight the necessity of depicting these materials at the level of both excitonic and monoelectronic states.

REFERENCE: F. Lédée et al, ***Mater. Horiz.***, 2021,**8**, 1547-1560,https://doi.org/10.1039/D0MH01904F

Layered perovskites and chalcogen semiconductor materials for solar cell applications

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Layered semiconducting materials have gained attention because of their remarkable property of tuneable bandgap and also excellent stability in the ambient conditions. 2D perovskites and transition metal di-chalcogenides (TMDs) comes under this category. The photo absorption and emission properties of a dimensional perovskite vary with the number of octahedral layers where with the increase in octahedral layers, the bandgap of the material decreases because of which there will be an increase in photo absorption. Utilizing these properties, these materials were used in photovoltaics application. My work demonstrates the fabrication of a single junction solar cell with layered materials as photo absorbers. solar Along with the applications, research on fundamental properties like photoluminescence, life time, and absorption were carried out.

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FIGURES

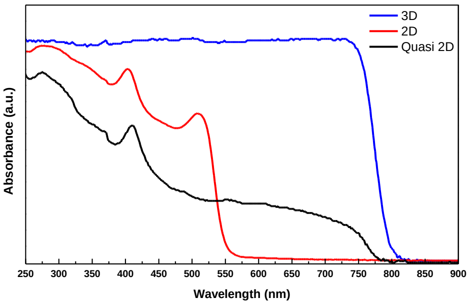

Figure 1: Absorption spectra of layered perovskites

Figure 2: Picture of fabricated solar cell device

Organic Cation Engineering and its Effect on Distortion in 2D Halide Perovskites

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Abstract: Engineering of organic cation in 2D perovskite halide has gained attention in search of highly stable material with better structural tunability and optoelectronic properties. Degree of octahedral distortion is one such criteria that needs to be taken in account for better understanding of these properties.

The present work will show a systematic study of degree of distortion with increase in organic cation chain length. With the introduction of organic cation in a non-distorted 3D perovskite $Cs_2AgBiBr_6$, the single crystal XRD of $A'_4AgBiBr_8$ (Where A' is PA-Propylammonium, BA-Butylammonium and HA-Heptylammonium) showed dimensional reduction to 2D perovskite and significant inter and intra octahedral distortion. This degree of distortion has been quantified as a measure of bond length and bond angle variations.[1][2] Furthermore the impact of this distortion on optoelectronic properties and applications has been studied which will help the research community to choose the desired organic cation for their research.

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FIGURES

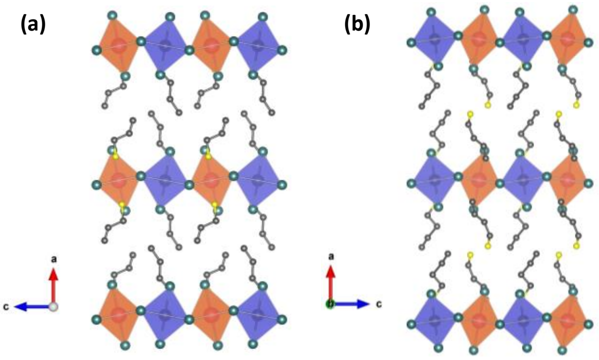

Figure 1: Crystal structure of 2D double perovskite (a) $PA_4AgBiBr_8$[3] at 293 K and (b) $BA_4AgBiBr_8$ at 298 K.

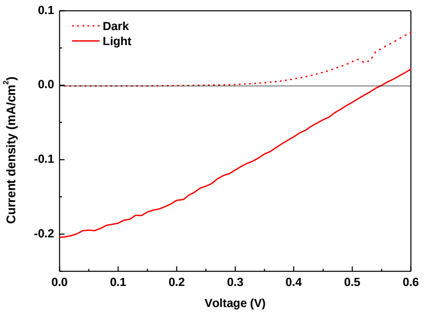

Figure 2: J-V curves of a $BA_4AgBiBr_8$ cell measured in the dark and light conditions.

A New Class of Low Dimensional Organic-Inorganic Hybrid Halides for Optoelectronic Applications

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Abstract: In the world of perovskite halides, the lower dimensionality is showing high structural tunability and more stability with the introduction of hydrophobic organic cations by blocking the moisture penetration in comparison to 3D structure. This result in attractive optoelectronic properties for different field of applications such as solar cells, lasers, photodetectors, memory devices and LEDs[1],[2],[3]. The progress and field of applications of perovskite halides in the last decade is tremendous, however they contain toxic lead which is restricting the applications due to stability, health and ecological concerns. So, there is an urgent need to include the non-toxic elements[4].

Here, we are reporting a new photoluminescent lead-free class of materials, BZA_3BiX_6 [BZA is benzylamine, Bi is bismuth and X is bromine and iodine]. They have been synthesized by a solution-based approach with a monoclinic structure that has isolated MX_6 octahedra surrounded by the organic cations. The powder morphology of the grown crystals is analysed by HR-SEM which concluded the layered growth. BZA_3BiBr_6 and BZA_3BiI_6 exhibits semiconducting behaviour with a bandgap of 2.7eV and 2.2eV respectively. Upon 350 nm excitation, BZA_3BiBr_6 exhibits broad emission centered at 415 nm and 450 nm with a long tail. On the other hand, BZA_3BiI_6 is not an emitter. We consider them as 0D perovskite halides as the octahedral cations are completely surrounded by the organic cations[5]. In this work we are doing a systematic study of the crystal structure, degree of distortion and its purity using the single crystal X-ray diffraction, powder X-ray diffraction and Fourier-transform infrared spectroscopy. The thermal stability of the sample has been examined by TGA/DTA analysis. The optical studies have been thoroughly studied on UV-spectrophotometer and spectrofluorometer. This study will open the doors for a new type of materials by exploring the individual sites in the structure.

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Figure 1: Powder samples of BZA_3BiBr_6 (left) and BZA_3BiI_6 (right).

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