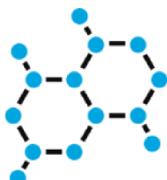European conference on chemistry of two-dimensional materials

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foreword

On behalf of the Organising Committee we take great pleasure in welcoming you to Bologna (Italy) for the 4th edition of the European Conference on Chemistry of Two-Dimensional Materials (chem2Dmat2023).

During the last years, the chemistry of graphene has played an ever-increasing role in the large-scale production, chemical functionalization and processing as well as in numerous applications of such material, and it has been expanded to various new 2D inorganic and organic materials. This conference aims at providing a forum to the rapidly growing community of scientists mastering the chemical approaches to 2D materials in order to fabricate systems and devices exhibiting tunable performance. The chemical approach offers absolute control over the structure of 2D materials at the atomic- or molecular-level and will thus serve as enabling strategy to develop unprecedented multifunctional systems, of different complexity, featuring exceptional physical or chemical properties.

The 4th edition of chem2Dmat will cover all areas related to 2D materials' chemistry spanning their synthesis as well as their functionalization, using covalent and non-covalent approaches, for composites, foams and coatings, membranes, (bio-)sensing, (electro- and photo-)catalysis, energy conversion, harvesting & storage, electronics, nanomedicine and biomaterials.

chem2Dmat2023 Highlights:
- Expected attendance: 140 participants
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- 1/2-day Innovation Forum to get an updated understanding of Graphene based technologies
- 5 Awards to PhD students

chem2Dmat2023 is now an established event, attracting global participant's intent on sharing, exchanging and exploring new avenues of graphene-related scientific and commercial developments.

We also would like to thank all the sponsors, exhibitors, speakers and participants that join us this year. In addition, thanks must be given to the staff of all the organizing institutions whose hard work has helped planning this conference.

We truly hope that chem2Dmat2023 serves as an international platform for communication between science and business.

Hope to see you again in the next edition of chem2Dmat, to be held in 2025 in Valencia (Spain).

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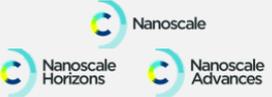**Roberta Chiodini** (Italian National Research Council (CNR), Italy)
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GRAPHENE FACTORY is the CNR web portal born with the aim to show and promote the research on graphene and bi-dimensional materials performed within the CNR network. It also offers contents and information about "graphene" to the scientific community, to the media, to SMEs, Industry and general public.

The National Research Council (CNR) is the largest public Research Institution in Italy. CNR is strongly involved in the research activities on graphene and two-dimensional materials beyond graphene, both on the fundamental research, and on future applications and technological innovation. On a national basis, is the institution with the largest number of researcher involved on these topics and the largest scientific production

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speakers

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Growth and Applications of Hexagonal Boron Nitride

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Hexagonal boron nitride (hBN) is a promising two-dimensional (2D) material owing to its unique optical properties in the deep-UV region, mechanical robustness, thermal stability, and chemical inertness. hBN thin films have gained significant attention for various applications, including nanoelectronics, photonics, single photon emission, anti-corrosion, and membranes. Thus, wafer-scale growth of hBN films is crucial to enable their industrial-scale applications. In this regard, chemical vapor deposition (CVD) is a promising method for scalable high-quality films. To date, considerable efforts have been made to develop continuous hBN thin films with high crystallinity, from those with large grains to single-crystal ones, and to realize thickness control of hBN films by CVD. However, the growth of wafer-scale high crystalline hBN films with precise thickness control has not been reported yet. The hBN growth is significantly affected by substrate, in particular the type of metals, because the intrinsic solubilities of boron and nitrogen depend on the type of metal. In this talk, state-of-the-art strategies adopted for growing wafer-scale, highly crystalline hBN are summarized, followed by the proposed mechanisms of hBN growth on catalytic substrates [1]. Furthermore, various applications of the hBN thin films are demonstrated, including a dielectric layer, an encapsulation layer, a wrapping layer of gold nanoparticles for surface enhanced Raman scattering, a proton-exchange membrane, a template for growth of other 2D materials or nanomaterials, and a platform of fabricating in-plane heterostructures [2]. Finally, the inherent challenges are summarized, and future research directions for the facile CVD-based growth of single-crystal hBN are proposed.

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chem2Dmat

European conference on chemistry of two-dimensional materials

Hexagonal hybrid bismuthene by molecular interface engineering

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High-quality devices based on layered heterostructures typically require materials obtained through complex solid-state physical approaches or laborious mechanical exfoliation and transfer. Wet-chemically synthesized materials are not commonly used due to their surface residuals and intrinsic defects. Here, we introduce a new two-dimensional (2D) member to the pnictogen family (group 15 of the Periodic Table), synthetized by a colloidal approach [1,2], that consists of a coherent sandwich of beta-bismuth, encapsulated by sulfur-alkyl-functionalized flat bismuthene interfaces [3,4]. While an unprecedented degree of structural quality is demonstrated, an altered atomic arrangement of the outermost, functionalized bismuthene layers leads to a drastic change in the chemical reactivity and electronic structure especially when compared to other heavy pnictogen: antimonene[5–7]. The metallic behaviour of the hybrid is supported by *ab initio* predictions and room temperature transport measurements of individual nanoflakes. Our findings indicate how surface reconstructions in 2D systems can promote unexpected properties that can pave the way to new functionalities and devices. Moreover, this scalable synthetic process opens new avenues for applications in plasmonics or electronic (and spintronic) device fabrication. Beyond electronics, this 2D hybrid material may be of interest in organic catalysis[8], biomedicine, or energy storage and conversion[2]. Last but not least, a large-scale production strategy will be introduced.[9]

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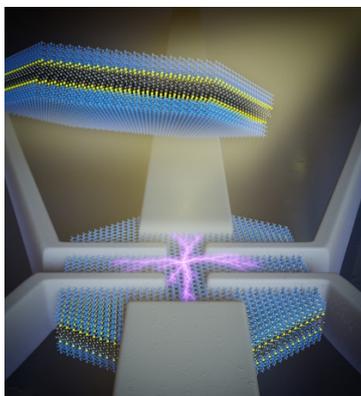
Figure 1: The illustration shows the synthesis of a few-layer bismuth hybrid with electronic grade structural quality and unique surface reconstruction.

Graphene & related Aeromaterial Devices by chemistry only

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Assembly of actuators, sensors, or energy devices typically involves complex structuring methods based on lithographic microstructuring processes or electromechanical assembly. In this talk, a class of ultralightweight and open porous materials known as aeromaterials will be reviewed, that can fulfill these functions without any of those microstructuring techniques. These materials can be created through wet or gas phase chemistry and directed self-assembly steps using 2D materials like graphene variants, TMDC's, h-BN, or MXCENE. This allows them to be shaped and assembled into 3D aeromaterials either by a gas phase process or from wet chemical inks that can be used directly as functional devices, such as a pneumatic actuator [1] capable of lifting more than 10,000 times its own weight (see figure 1).

To achieve the desired shape with the right porosity and enhanced surface area, a template process based on a flame transport synthesis is used. This process enables the massive growth of tetrapodal shaped ZnO microcrystals, which can be arranged in a 3-dimensional, continuously connected network spanning macroscopic dimensions. The gas phase process has already been demonstrated with the Aerographite process, which was introduced 11 years ago [2]. In this process, thin 2D layers are formed, and the ZnO network [3] is simultaneously decomposed. The CVD can be used to form 2D materials, such as graphene layers, surprisingly directly on the surface of the ZnO. A variant based on ammonia found by Schütt [4] can even synthesize h-BN layers on the ZnO, creating a strong light-scattering material. Nanoscale GaN [5] is capable of growing even epitaxially on the ZnO. In the wet chemical infiltration procedure, basically every 2D material ink can be utilized, including variants such as carbon nanotubes [6].

Finally, examples of fully functional devices made from these 2D materials will be presented and discussed.

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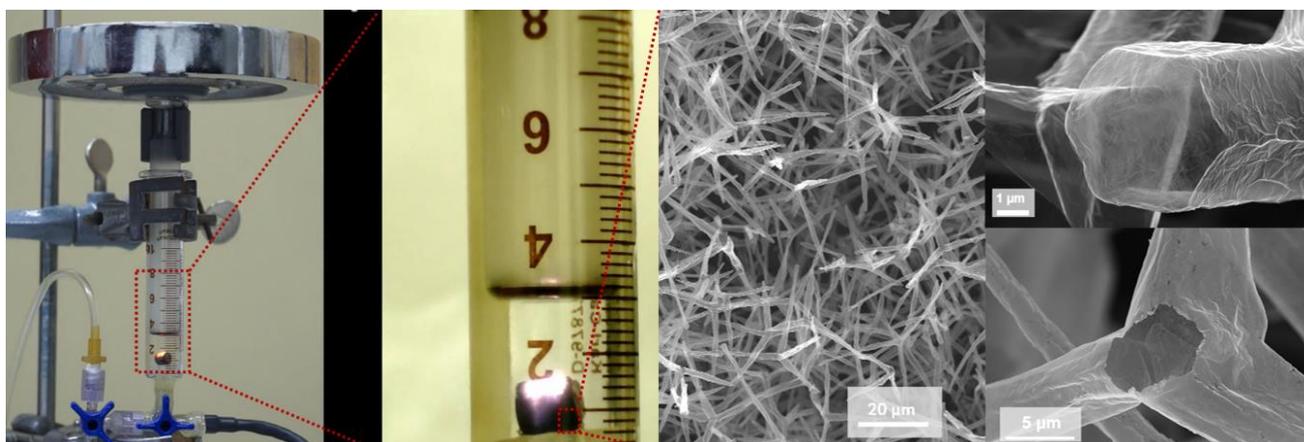
Figure 1: Graphene based pneumatic actuator of ~1mg lifting 2 kg and magnification into its microstructure

Low temperature growth of MoS₂ on III-V compound semiconductor

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Abstract

Heterogeneous integration of transition-metal chalcogenides such as MoS₂ on III-V compound semiconductors offers a wide variety of opportunities for developing new optoelectronic devices. In this talk, we present a novel approach for heterogeneous integration of MoS₂ on III-V epitaxial wafers. A thin film of MoS₂ was directly synthesized on a GaN-based epitaxial wafer through the MOCVD technique and fabricated as the TFT array. Subsequently, the MoS₂ based TFT was monolithically integrated with micro-LED devices to produce an active matrix micro-LED display. In addition, we demonstrate a simple approach to obtain red and green colors through the printing of quantum dots on a blue micro-LED, which allows for the scalable fabrication of full-color micro-LED displays. This strategy represents a promising route to attain heterogeneous integration, which is essential for high-performance optoelectronic systems that can incorporate the established semiconductor technology and emerging 2D materials.

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Figures
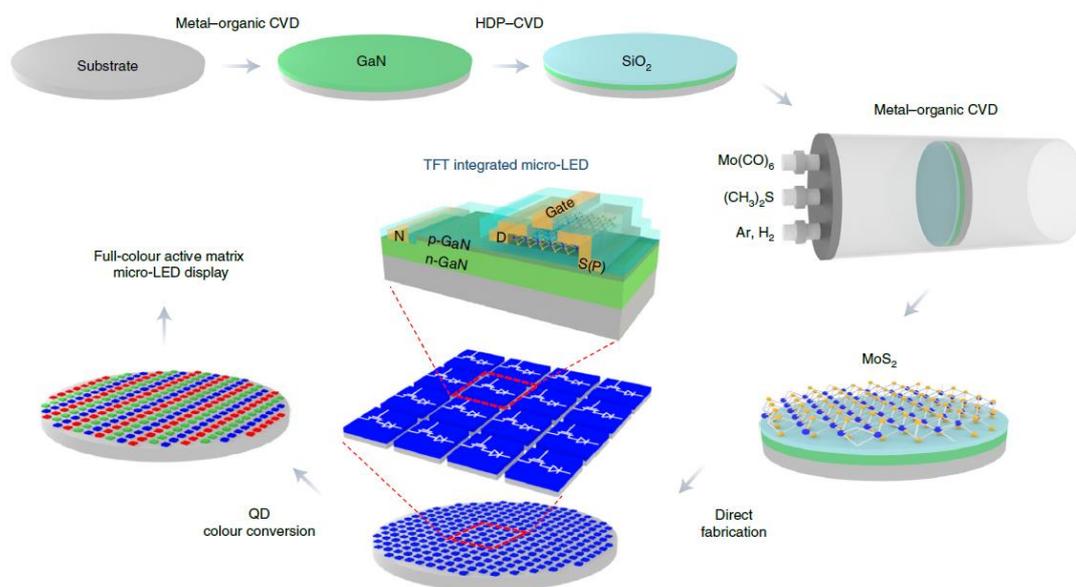
Figure 1: Monolithic integration of MoS2 transistor and GaN-based full-colour micro-LED display

Design of biofunctional nanostructures for theraregenerative medicine

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The implementation of a personalized therapy together a less invasive surgery for the restoration of human tissues is becoming an appropriate strategy to mitigate costs of the modern health care system and the maintenance of health and quality of life.

The design biomaterials endowed with therapeutic and regenerative (theraregenerative) properties are recently of particular interest. The selection of a suitable injectable technique is often based on material characteristics (including mechanical properties, drug release kinetics and degradation) that serve for the specific treatment function.

Micro or nano-structured materials in the form of gels, nanoparticles and nanocomposites have gained increasing interest in regenerative medicine because they are able to mimic the physical features of natural extracellular matrix (ECM) at the sub-micro and nano-scale levels [1]. 2D materials such as graphene oxide (GO) and exfoliated black phosphorus (2D BP) show important therapeutic and regenerative activities due to their physicochemical properties. Recent studies have shown the effectiveness of 2D BP and GO as photodynamic therapy (PDT) agents for cancer treatment [2]. This activity has been ascribed to their capability of generating singlet oxygen and acting as photosensitizers that, in presence of reactive oxygen species (ROS) and infrared light irradiation, constitute an essential component of PDT therapy. On the other hand, the oxygen-containing functional groups of GO and the phosphates ions (PO_4^{3-}) [3,4] derived by BP decomposition act as anionic ligands for positive calcium ions (Ca^{2+}), enhancing the attraction, binding, and aggregation of free Ca^{2+} in bone tissue, ultimately leading to the formation of calcium phosphate (CaP). In this way, GO and 2D BP represent bioactive signals able to promote osteogenesis. Here, we propose the *in vitro* use of 2D substrates (GO and 2D BP) to inhibit cancer cell proliferation and migration and at the same time to preserve the healthy cells [5]. Furthermore, we offer an overview of how these 2D materials may be used to develop nanostructured hybrid materials (*e.g.,* gels, nanoparticles) as a theraregenerative platform for bone tissue engineering in terms of bone cancer therapy and regeneration.

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Assessing Degradation of Liquid-Exfoliated Nanosheets

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An established, widely applied technique to produce 2D materials is liquid phase exfoliation (LPE) which relies on breaking down layered crystals through mechanical forces, e.g. sonication, and subsequent stabilization in liquid media to form colloidal nanoplatelets. To date, this process has been applied to ~60 layered van der Waals crystals. However, for some materials, the 2D nanosheets are considerably more reactive than the parent crystals so that oxidative degradation can occur. While this can also be the case for micromechanically-exfoliated nanosheets, it will be more crucial for LPE materials, as the harsh exfoliation conditions not only result in delamination, but also in-plane tearing [1] creating more reactive edge sites. It is thus crucial to investigate potential degradation under external stimuli which will define the framework for further processing.

In this talk, I will review our work on assessing the degradation of LPE nanosheets. This is achieved by measuring extinction, absorbance or emission as function of time under external stimuli (e.g. temperature, addition of water) using ensembles of size-selected nanosheets in liquid media. Typically, we find first order decay kinetics which allow us to extract half lives and portion of reacted material after infinite time. This is extremely powerful, as it allows for a comparison across materials ($NiPS_3$,[2] $FePS_3$,[3] $MnPS_3$,[3] $RuCl_3$,[4] $CrTe_3$,[5] TiS_2, InSe) with black phosphorus [6] being the original benchmark. Through the variation of the nanosheet size or changes in the spectroscopic profile, it is possible to infer whether degradation preferably occurs on edge or basal plane. Addition of water to nanosheets exfoliated under inert gas conditions can also be useful to investigate the degradation mechanism. [5,6]

Through the measurement of the spectroscopic signature as function of time and temperature, it is possible to extract macroscopic, average activation energies of the degradation as shown for transition metal phosphorus trisulfides [3], $RuCl_3$ [4] and monolayered WS_2 [7]. Here, one can find peculiarities, such as a combination of slow decay kinetics and low activation energies in the case of $RuCl_3$ [4]. This is an indication of relatively complex nanoscale kinetics in solution that can be dominated by the solvent environment.

In a first comprehensive study to demonstrate this, we focused on WS_2 monolayers measured through luminescence in aqueous surfactant solution [7] and were able to show a significant effect of the surfactant on the degradation. For example, in sodium cholate we observe a protection of the basal plane and an edge-centered photo-induced degradation, whereas an additional thermal basal plane degradation is observed with sodium dodecyl sulfate.

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In vivo lung fate and biotransformation of MoS₂ nanosheets

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Among the different 2D nanomaterials and graphene, MoS₂ have received tremendous attention in many fields, including (opto)electronics and nanomedicine [1, 2]. We have recently applied an integrated approach to follow the fate and biotransformation of MoS₂ nanosheets at the nanoscale and their impact on the lung inflammation status over one month after a single inhalation in mice. The analysis of the immune cells, the alveolar macrophages, the extracellular vesicles, and the cytokine profile showed that MoS₂ nanosheets can induce an initial phase of lung inflammation that is rapidly resolved despite the persistence of various biotransformed molybdenum-containing nanostructures in alveolar macrophages and extracellular vesicles up to one month (Figure 1). Using *in situ* liquid phase transmission electron microscopy, we evidenced the dynamics of MoS₂ nanosheet transformation triggered by reactive oxygen species. Three main alteration mechanisms were observed: 1) scrolling of the dispersed sheets leading to the formation of nanoscrolls and folded patches, 2) etching releasing soluble MoO_4^-, and 3) oxidation generating oxidized sheet fragments. Extracellular vesicles were also identified as a potential shuttle of MoS₂ nanostructures and their degradation products and more importantly as mediators of inflammation resolution [3].

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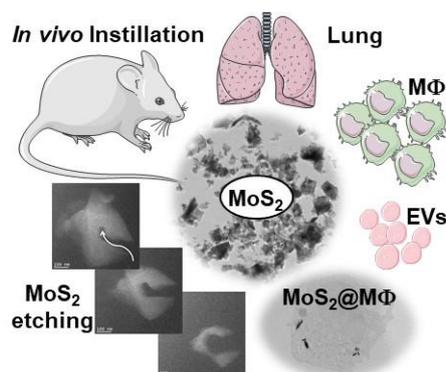
Figure 1: Degradation, fate and impact on lungs of MoS₂ nanosheets.

2D Materials in Space

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We are at a crucial point for human and robotic space exploration, with the International Space Station coming to the end of its lifetime, commercial space stations being built to replace it, and the Artemis programme set to take humans back to the Moon for the first time since the 1970s. The European Space Agency has set out a strategy [1] for the next 10 years, with the following main objectives:

1. to create new opportunities in Low Earth Orbit for a sustained European presence in the post-ISS era,
2. to enable the first European to explore the Moon's surface by 2030 as a step towards sustainable lunar exploration in the 2030's,
3. to prepare the horizon goal of Europe being part of the first human mission to Mars.

In this talk, ongoing and upcoming scientific and exploration programmes will be discussed including LEO, Moon, and Mars, with particular regard to their enabling technologies and how 2D materials may be used to enhance them or how 2D materials research could benefit from them.

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Figures
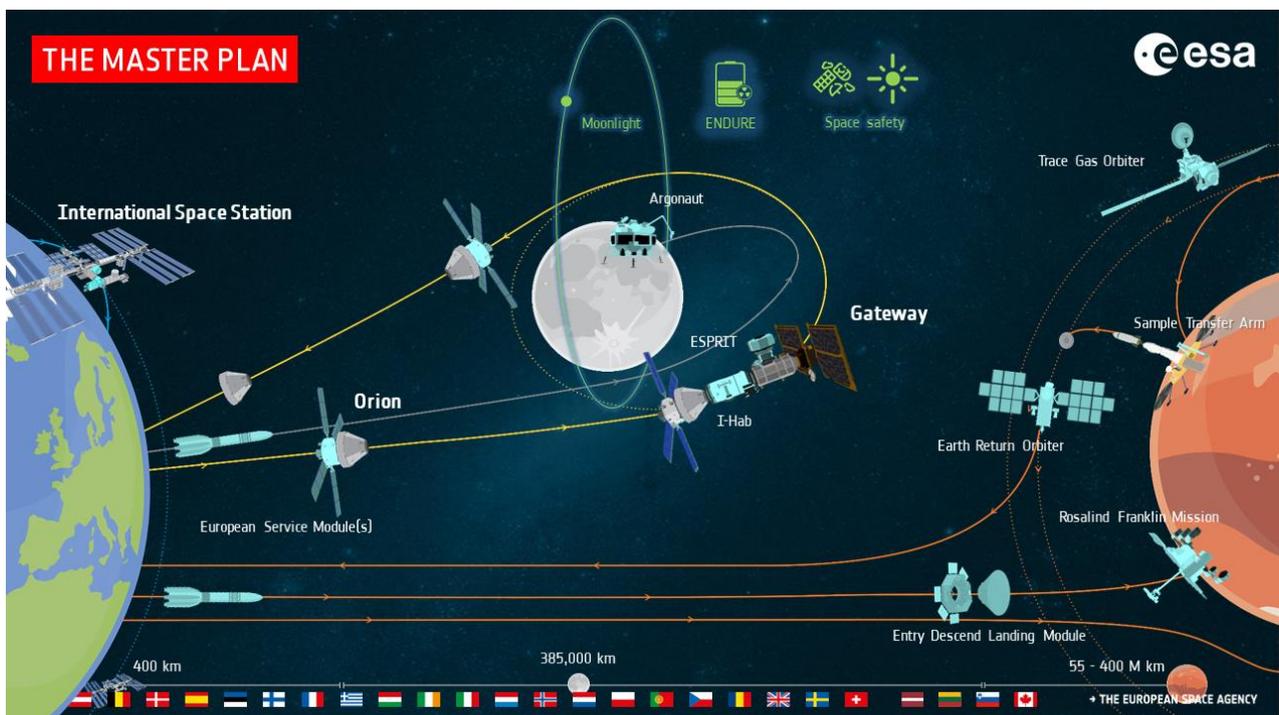
Figure 1: The European Space Agency's Terrae Novae 2030+ strategy [2]

Moving from fundamental studies to industrial applications with CVD-grown 2D materials

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To make 2D materials appealing for several applications at high technology readiness levels, requirements such as high-quality, scalability and contamination control have to be satisfied. In this talk, I will discuss scalable growth of high-quality graphene and transition metal dichalcogenides via chemical vapor deposition (CVD) [1-3] and discuss how these scalable 2D materials can be adopted in industrial applications, from integrated optical photonics [4], to power distribution [5].

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Leveraging 2D Materials to Boost Perovskite Photovoltaic Performance and Durability

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The vast library of two-dimensional materials presents a unique opportunity to optimize the interface properties of perovskite solar cells. In this presentation, we will discuss the implementation of 2D materials in perovskite cells, modules, and panels, with a specific emphasis on a novel class of 2D materials called Titanium Carbide MXenes (e.g., Ti3C2). These MXenes not only possess outstanding chemical and mechanical properties but also provide a broad range of work function (WF) tunability based on their surface termination. The WF can vary from approximately 2 eV for OH-termination to around 6 eV for O-termination.

By fabricating well-exfoliated Ti3C2Tx MXenes with a relatively low WF (~3.7 eV), we demonstrate the ability to modify both the perovskite absorber and electron transporting layer (ETL) WFs. This approach has been applied to both nip [1] and pin [2] cell structures, as well as large-area modules.[3] We reveal that MXene interface engineering employed on the n-side of the pin cell (NiO/perovskite/C60/BCP/Cu) significantly enhances the cell's stability, with a T90 exceeding 2000 hours under continuous light soaking at the Maximum Power Point (in ambient conditions) and a T80 exceeding 1000 hours under thermal stress (85 °C).[4]

This strategy of leveraging a combination of 2D materials to boost the performance and stability of perovskite technology has been extended to panels (nine panels of 0.5 sqm each) tested for over a year in a Solar Farm in Crete. The outcomes of this outdoor trial in a real-world environment will be presented, and the performance and stability will be thoroughly examined. [5]

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Mattermorphosis

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The properties of a material are defined by their composition and structure. This principle of chemistry is well-known for decades and the basis for the development of molecules and materials. In my talk, I will show some factors that define materials properties beyond their intrinsic characteristics: In the first part, I will show how the edge structure in graphene nanoribbons determines the band gap (including metallic state!) and electronic topology of these all-carbon materials. In the second, I will discuss superlattice states in transition metal dichalcogenide bilayers, which can form flat bands, Dirac or kagome features depending on the twist angle. In the final part, I will discuss how the underlying lattice topology can define the properties of a 2D framework material, such as a 2D polymer, covalent-organic framework or metal-organic framework.

Some of the introductory literature are given below (if you don't have access, they are also available on arXiv or chemRXiv.

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In-situ Electrical Characterization of Atomic Layer Deposition of Top Gate Dielectrics for 2D TMD Transistors

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Abstract

Atomic layer deposition (ALD) is one of the most practical thin film deposition techniques for gate dielectrics for advanced CMOS technology since year 2007 when Hf based gate dielectrics were introduced. When ALD is applied to deposit on top of 2D materials, it is commonly reported that a surface treatment is introduced to modify surface characteristics and then followed by top gate dielectric deposition or passivation layer formation using ALD. Those surface treatment and ALD process directly impacts on backgated 2D field-effect-transistor (FET)'s transfer characteristics as shown in Fig. 1. Although it is critical to understand the effects of processes on 2D FETs performance, there are not many reports on effects of individual process steps, such as surface treatment, a half-cycle of ALD, particularly initial cycles.

In this presentation, I will introduce a new UHV clustered system connected both ALD and plasma treatment chamber to a probe station under vacuum for in-situ electrical measurement as shown in below figure. I will also discuss effects of nitrogen radical treatment and consecutive ALD process with tri-methyl Al and ozone on MoS_2 backgated FET's transfer characteristics.

Figures

(a)　　　　　　　　　　　(b)
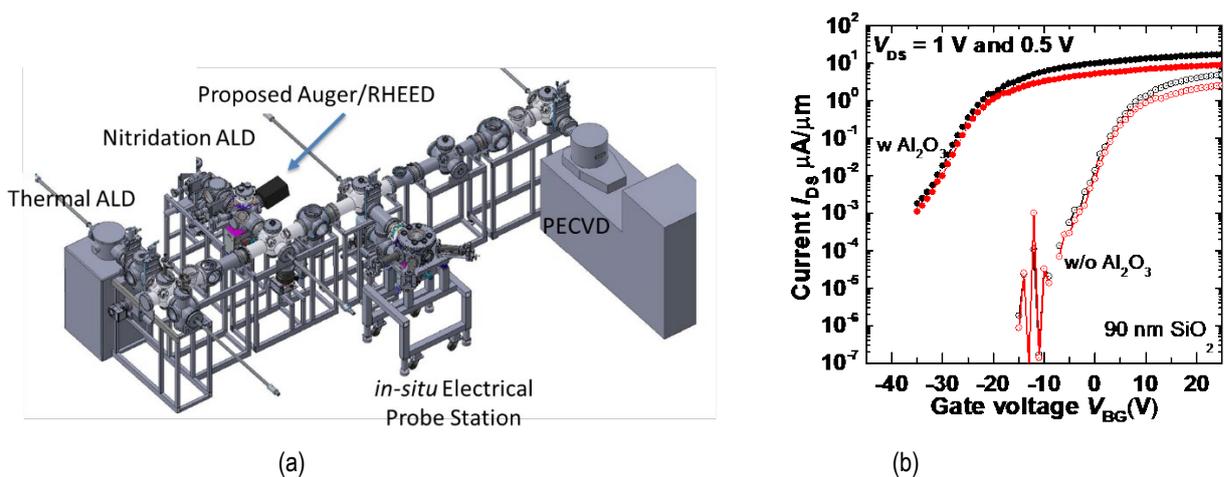
Figure 1: (a) Schematics of in-situ electrical characterization system clustered with thermal ALD and plasma treatment chambers (b) back-gate transfer characteristics of MoS_2 transistors with and without ALD Al_2O_3

Graphene based materials and technologies for advanced drinking water monitoring and treatment

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The last few years have seen the increasing occurrence of water contamination, including drinking water, by pharmaceuticals, personal care products, plastic and their additives among the other, that are not satisfyingly removed by conventional drinking water treatment technologies. [1] In some cases, as for the endocrine disrupting agents such as per and polyfluoroalkyl substances (PFAS) and bisphenol A (BPA), the eco and human toxicity has been demonstrated,[2] calling for the urgent development of new technologies for detection, early warning, and remediation of those contaminants.

I will report our recent results on the development of advanced graphene materials and technologies for drinking water monitoring and treatment.

Graphene based materials and approaches with high removal performances toward several classes of contaminants, including PFAS and outperforming in most cases, [3] granular activated carbon (GAC) the industrial sorbent benchmark, will be presented.

In addition, I will introduce chemically modified graphenes and related electrochemical sensors for fast and high sensitivity detection of molecular contaminants in drinking water through simultaneous capture and transduction enabled by the graphenic layer.

An overview of graphene chemical modification approaches,[4] processing into composites [5] and membranes, [6] applications in real environment and safety related aspects will be presented.

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Figures
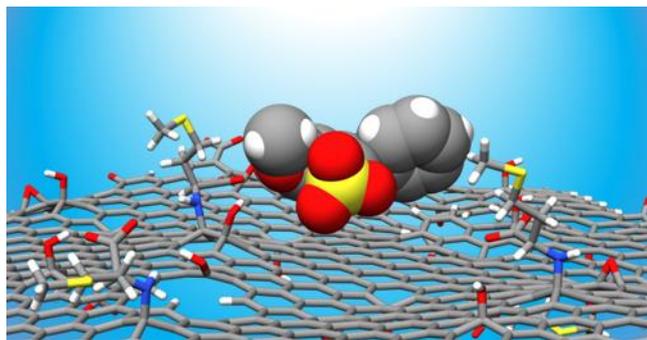
Figure 1: Recognition and capture of molecular contaminants in water by chemically modified graphenes.

An Insider's view of Nature journals

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In my talk, I'll try to provide a glimpse of what goes on behind the doors of an elite scientific journal. I will discuss the role of journals and journal editors in the scholarly publishing landscape: what motivates us, what service we offer, what are the forces shaping our industry. I will also introduce Nature Nanotechnology and our interest in the chemistry of 2D materials field. I will then reflect in the past 10 years of Nature journals and will touch a bit on the transition to open access. I'll then move from open access to open science.

2D materials-based intelligent membranes

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Permeation through nanometre-pore materials has been attracting unwavering interest due to fundamental differences in governing mechanisms at macroscopic and molecular scales, the importance of water permeation in living systems, and relevance for filtration and separation techniques. Latest advances in the fabrication of artificial channels and membranes using two-dimensional (2D) materials have enabled the prospect of understanding the nanoscale and sub-nm scale permeation behavior of water and ions extensively. In particular, several laminate membranes made up of 2D materials show unique permeation properties such as ultrafast permeation of water and molecular sieving. In my talk, I will discuss our recent results on controlling molecular transport through various 2D materials-based membranes by an external parameter and will discuss the prospect of developing next-generation intelligent membranes based on 2D materials.

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Electrochemical oxidation and reduction of graphite by continuous flow system

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Exfoliation of graphite through functionalization is a promising technique to produce two-dimensional (2D) nanocarbons on a large scale. Due to the high stability of graphite, a conventional functionalization of graphite has been performed in harsh conditions. Therefore, environmental and safety have been problems for scaling up the operation. In contrast, the electrochemical functionalization of a graphite electrode has recently attracted considerable attention because it does not require oxidants or acid. However, 2D carbons produced through the existing electrochemical method are generally lacking in quality, due to the non-uniform destruction of the intermediately functionalized graphite. We discovered a method for the non-destructive functionalization of graphite using HBF_4 as an electrolyte. This electrochemical method is also applicable to a continuous flow system, thus promising the mass production of 2D carbons for future industrialization. Further, successive electrochemical oxidation and reduction was achieved. Thus, the method provides facile access to high-quality two-dimensional carbon materials in a manner that has the potential for mass production.

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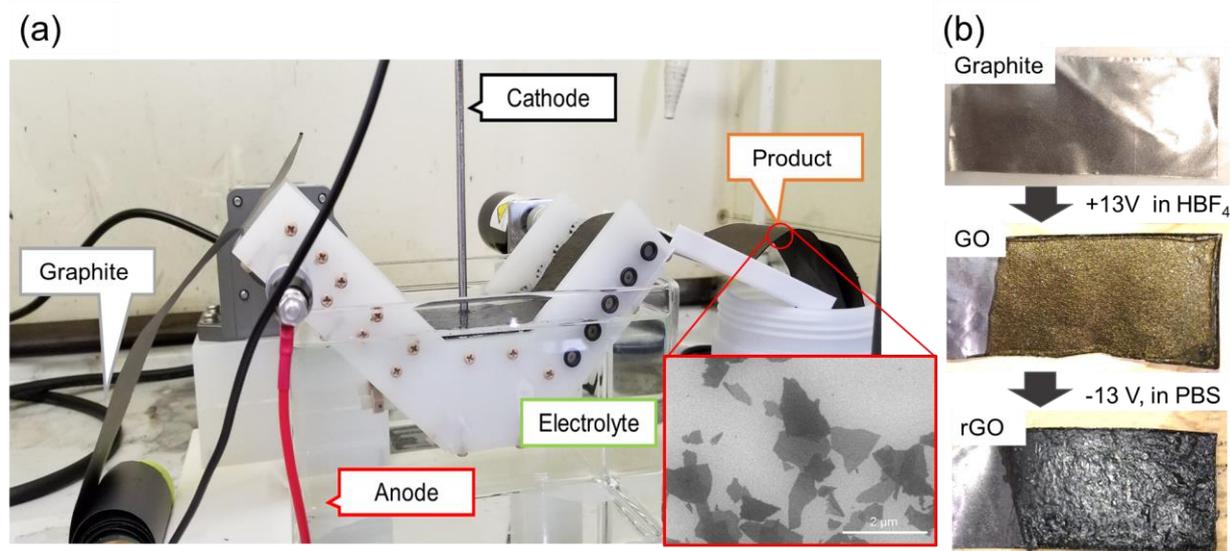
Figure 1: (a) Continuous-flow electrochemical oxidation system. Inset is SEM image of the product. (b) Successive electrochemical oxidation and reduction of graphite sheet.

Understanding thermal transport in Transition Metal Dichalcogenides: from the monolayer to the bulk

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Layered Transition Metal Dichalcogenides (TMDs) have received significant attention in the past years because of their exceptional properties, which differ from those of 3D-bonded materials. Reaching an understanding of their thermal properties is crucial for many applications e.g., in electronics and thermoelectrics. We present a theoretical study of the phonon heat transport properties of WS_2, WSe_2, MoS_2 and $MoSe_2$, from the monolayer to the bulk. We calculate the thermal conductivity of TMDs by solving the Boltzmann Transport Equation for phonons, using input from first principles calculations. We use the SIESTA method, based on Density Functional Theory, to compute ab-initio energies and forces from which we obtain the phonon structure and the phonon-phonon interactions using the Temperature Dependent Effective Potential package for finite temperature lattice dynamics calculations. We compute the thermal properties for the TMDs at room temperature and compare the results with experiments on a full range of thicknesses, which demonstrates the reliability and efficiency of our computational method [3]. We compare the results for different TMDs and reach a unifying picture of heat transport in 2D-bonded semiconductors, which will be useful for future technologies.

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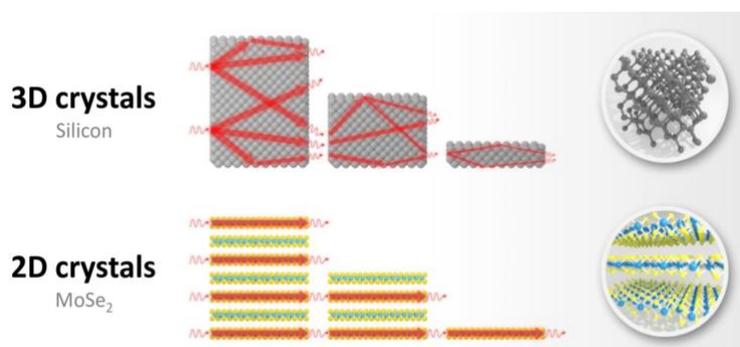
Figure 1: Schematic view of the heat transport mechanism in 3D materials compared to layered materials composed of 2D sheets. In the latter case, thermal conductivity is quite unsensitive to the thickness, as heat is transported within each layer.

Amorphous 2D Materials for Applications in Nanoelectronics and Neuromorphic Computing

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Abstract

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

The excellent physical properties of the mentioned materials derive from the nature and degree of their disorder which, controlled at the fabrication level, represents the key ingredient to tune their physical/chemical properties for specific target applications. In this respect, new fabrication strategies to modify the degree of disorder and a systematic theoretical characterization of the impact of the material structural quality on the ultimate performance is urgent. Even more importantly, the search for new disordered materials for novel applications appears as an extremely promising way. In this talk we present a systematic analysis of the structural, vibrational and electronic properties of amorphous carbon monolayers as a function of the structural quality of the material. We show how disorder results in a tunable electrical conductivity and thermal properties [3]. Finally, we present the results of the newly demonstrated synthesis of a thin film of amorphous Boron Nitride showing extremely low dielectric characteristics: high breakdown voltage and likely superior metal barrier properties [4]. The fabricated material aims at replacing current interconnect insulators in the next generation of electronic circuits. We discuss the experimental setup and present the results of our calculations which have contributed to the understanding of the structural morphology of the amorphous material, as well as addressing the issue of dielectric properties in highly disordered sp^2-dominant materials. We conclude discussing the resulting thermal and electronic properties [5,6] and the applications in neuromorphic computing.

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chem2Dmat
EUROPEAN CONFERENCE ON CHEMISTRY OF TWO-DIMENSIONAL MATERIALS

From polycyclic aromatic hydrocarbons to two dimensional nanopores, nanogaps and energy devices

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Starting at the smallest scale, with polycyclic aromatic hydrocarbons, we investigate the conformational preference of propeller-shaped polycyclic aromatic hydrocarbons to design propellerene molecules as building blocks of millimeter to centimeter scale devices. We design and synthesize polyaromatic hydrocarbon based macromonomers capable of self-assembling into 2D materials, which we integrate in fuel cells, electrolyzers, electro-osmosis and desalination devices. Zooming out a little bit more, we use as-prepared membranes like graphene to tailor nanopores tiny and functional enough to – we hope – will only allow the passage of a proton. We are currently looking into time-dependent diazonium solution treatment to obtain leak-tight graphene selective ion channels. At the device level, we use chemistry to tailor graphene devices. We designed graphene field-effect transistors that can electrically probe the molecular state of spin crossover crystals using chemo-electrical gating. As an electrode, we use graphene as a model carbon-based electrode and systematically introduce nitrogen and oxygen dopants, together with vacancy defects, to study ORR. The latter work not only indicates a non-negligible contribution of oxygen and especially oxygenated vacancy defects for the catalytic activity of nitrogen-doped graphene, but also provides important insights into the fundamental understanding of activity-structure correlations for tailoring the catalytic performance of carbon-based, most particularly graphene-based electrode materials. Importantly, graphene edges offer interesting chemical opportunities for sensing. The inability to systematically characterize covalently functionalized graphene edges however, could still potentially limit the use of graphene in nanogap constructs for single molecule detection and recognition. We develop now parallel routes for edge functionalization that will allow the in situ spectroscopic characterization of edge functionality. On the other side of the spectrum, our knowledge of graphene handling and graphene transfer allows now a high-yield graphene liquid cell fabrication, which will enable – we believe – the progression of the liquid phase electron microscopy field with 2D materials. Chemistry has a lot to bring to the research field of graphene and 2D materials in general, from the smallest molecular scale to the device level: graphene instrisic's hydrophilicity in water, edge reactivity in devices, chemical routes for the alignment of tunneling junction in nanoporous nanofluidic devices for single molecule detection, graphene devices in water, on ice and on hydrogels, 2D functional membranes, to name a few.

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Chemistry and applications of monoelemental 2D materials beyond graphene

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Beyond carbon with most explored 2D material, graphene, are in the 14th group of elements also silicon, germanium, tin and lead. In comparison to carbon, the stable allotropes of these elements posses three-dimensional structures like cubic for silicon and germanium or tetragonal for tin. In order to get these elements in layered structure new top-down and bottom-up approach must be applied. For the bottom-up methods the UHV deposition is most broadly used providing one atom thick isolated island on various substrates. On the other hand, top-down methods offering scalability and access to free standing isolated sheets of two dimensional silicon and germanium (silicene and germanene) and their derivatives. The main approach for silicene and germanene and their derivatives is topochemical exfoliation of Zintl phases containing layers of silicon and germanium atoms stacked in between germanium atoms. Various methods of exfoliation and functionalization of germanene and silicene derivatives will be shown. The methods showing different approach to functionalize silicene and germane are show on Figure 1. The synthesis approaches can be based on direct chemical exfoliation of parent Zintl phase ($CaSi_2$, $CaGe_2$) as well as multi-step functionalization using hydrogenated counterpart (silicane, germanane). In addition, the chemical exfoliation of other Zintl phases producing 2D structures of silicene-germanene solid solution and complex structures like AlGe layers will be shown.

Figures
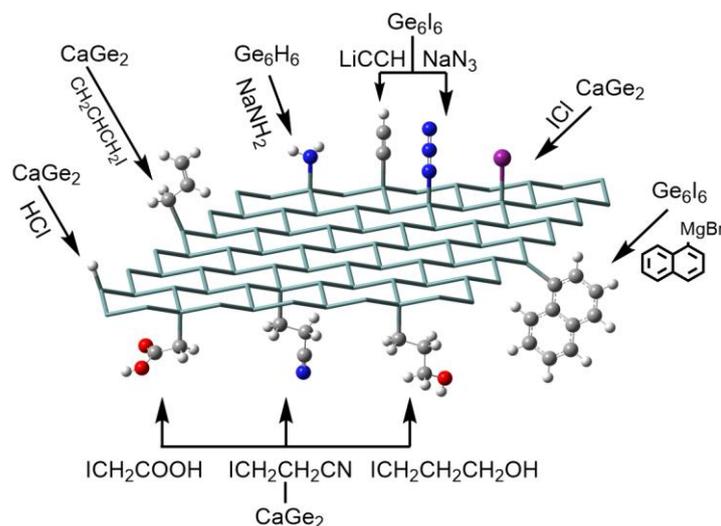
Figure 1: Figure(s) caption(s) (Calibri 11)

Graphene oxide in 2D and 3D: structures, defects and applications.

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Abstract

Graphene oxide (GO) is a material studied for over 150 years and still providing many intriguing questions. I fact, GO is not one material but a family of materials with properties strongly depending on methods of synthesis. GO synthesized using Hummers and Brodie methods demonstrate major differences in swelling, thermal exfoliation, mechanical strength of individual flakes, sorption of polar solvents and heavy metals. Dispersing GO and re-depositing individual sheets into multilayered 3D structures (e.g. membranes) provide new set of materials distinctly different from precursor graphite oxides. Moreover, the defects (holes and vacancies) are an essential part of the GO structure affecting e.g. permeation of GO membranes and providing additional sorption sites for heavy metals. High abundance of hole defects in Hummers GO was demonstrated by many methods and can be compared semi-quantitatively using analysis of XPS data. In other hand, Brodie graphene oxide is preferable in applications, which require less defects. The difference in defect state of Brodie GO and Hummers GO was recently demonstrated using direct AFM imaging of bi-layered flakes exposed to water and ethanol vapors.[1] Recent studies demonstrated also that an increased number of defects and carboxylic groups in GO is correlated with the improvement of its sorption capacity for several radionuclides.[2] This trend led us to the synthesis of extremely defect-rich GO (dGO), which demonstrated up to a 15-fold increase in sorption capacity towards U(VI) compared to standard GO.[3] The material was also demonstrated as promising for the sorption of organic pollutants.[4] However, both GO and dGO need to be dispersed in water in order to make their high surface area accessible for sorption. Therefore, we designed an alternative approach to prepare carbon sorbents with similar to GO oxidation state but rigid 3D structure using high surface area porous carbon materials as precursors. Porous carbons demonstrate very high surface area (up to ~3000 m^2/g for "activated graphene") which is available for oxidation directly without the need for lattice expansion. The surface oxidation methods are sufficient to convert porous carbons into GO-like 3D architectures. Surface oxidation of "activated graphene" is demonstrated to result in a materials with oxidation degree similar to that of graphene oxide while preserving relatively high BET surface area. "Super-oxidized activated graphene" showed extremely high sorption capacity for U(VI) removal. Notably, the bulk "3D GO" can be used as a sorbent directly without dispersing, the step required for GO to make its surface area accessible for removal of pollutants.[5]

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The path toward mass production of high quality 2D materials

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We will provide an overview on the BeDimensional strategy in the development of industrial-scale, reliable, inexpensive production processes of graphene and related two-dimensional materials (GRMs).[1-3] This is a key requirement for their widespread use in several application areas,[1-8] providing a balance between ease of fabrication and final product quality. We will show the effectiveness of the production of GRMs by wet-jet milling [3] and the route towards future Industrial scale up, maintaining the high-quality production ruled by the ISO standard.

Afterward, we will focus on some key applications of the as-produced GRMs, with particular emphasis on the energy sector. In this context, the production of GRMs in liquid phase by wet-jet milling [2,3] represents a simple and cost-effective pathway towards the development of GRMs-based energy devices, presenting huge integration flexibility compared to other production methods. We will provide an insight into some application areas such as anticorrosion coatings and energy conversion and storage devices. [4-12]

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From Invention to Innovation: the challenge of the Technology Transfer

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Creativity, invention and innovation are the key words to pursue technological progresses in our society. The invention is considered the materialization of ideas generated by the creativity that lead to new discoveries. However, the process that take innovative ideas from their inception to implementation is very complex involving several steps (Fig. 1) with multi actors and multi-competences from fabrication processes implementation and sustainability to market and regulation [1].

In the modern world, organizations are encouraged to support the process of invention and conversion to innovation. Several initiatives have been adopted either at European level (i.e. European Innovation Council (EIC) [2]) or national level (i.e. Proof -of Concept (POC) [3]) to push a process of technology transfer that targets to achieve prototypes that can be industrialized and sold starting from ideas demonstrated at lab level.

In this contribution, we describe the main features and requirements of a typical technology transfer applicated to some specific case studies related to biochips technologies using 2D biolayers [4,5].

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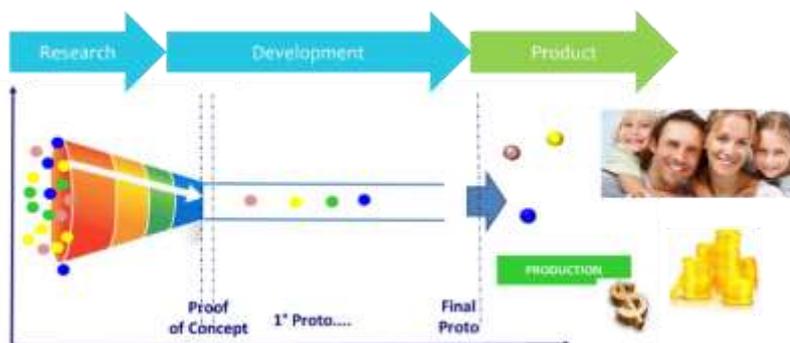
Figure 1: Scheme of process steps from Research to Innovation

New paradigms for automotive innovative materials

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Automotive sector is moving to a new era. Electrification, autonomous driving, carbon zero and green global policies lead to new car paradigms, that needs to be addressed also at material level. Material innovation is mandatory to reach such goals, but also industrial factors as possibility of scaling up at multinational level, quality over time and overall costs must be taken into account to move from R&D level to market. Motivations, new paradigms and the needs of the automotive industry about innovative and multifunctional materials will be treated in this challenging momentum.

Graphene Oxide Industrialization: Technical & Economic Challenges

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Graphene oxide (GO) is an effective material alternative to graphene for driving industrialization and commercialization of graphene materials. It is no longer a question of whether graphene oxide (GO) can transform industries, but a question of when. The answer comes down to when GO can be industrialized and produced on an industrial scale, at low cost and with controllable quality. LayerOne is a leading GO manufacturer in Europe, with a capacity of up to 2.0 ton / y. We aim to provide the highest quality graphene oxide materials at larger industrial scales globally. Several technical and economic challenges must be considered for large-scale GO production and commercialization.

How to deal with big industries?
Highlights for Tec-developers

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Innovation is one of the greatest forms to make the word a better place. Being a technology developer or a start up owner it is so great and unlock ideas and possibilities. But why so many fails? The idea is the beginning. The journey is: the team, business model, timing, agility, and adaptability means the most. The big Tec-customer is the true reality.

Tetra Pak is a food packaging company leading innovation: we are a big Tec-customer. Managing product development to meet sustainability transformation demands is a must and material technology is a key to drive this change. From small collaborations to partnerships & ecosystems: example of successful integration between different realities like small graphene companies.

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Figures

Figure 1: Example of Sustainable material development @Tetra Pak

General

Dry to touch lubricant graphene as new paradigm in lubrication

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Global lubricant market in 2020 was around 126 billion $ (1). Despite the maturity of the market, numerous innovations are directed to the reduction of harmful carbon emissions and to the enhancement of efficiency performance. In Europe, eco-labeling norms and increasing use of environmentally friendly oils is a key driving force towards the growth. In this context, solid dry lubricants represent a small percentage of the market but are gaining wider acceptance as improvements in performance and lifetime are being achieved. Such materials are non-toxic and usually they do not require a costly relubrication system, cost of lubrication/cooling systems vary from 7 to 20% of the total manufacturing cost, compared to only 4 to 7% of the utensil costs. Compared to oil or grease lubricants, solid dry lubricants maintain low COFs even in severe contact conditions, such as high temperature, high pressure or aggressive chemicals. The uses are expected to further increase in coming years, mainly because the operating conditions of future tribosystems are becoming more demanding and liquid and grease-type lubricants are undesirable due to environmental concerns. They are in fact normally mixed with solvents and primers, which are often laden with VOCs and other potentially toxic components, also the decomposition at temperatures beyond 300 °C making them not a suitable for high temperature application. On top of this, such lubricants percolate in the work environment and during transport as well as leaving the piece dirty especially in very dusty environments. Graphene can play a key role on the transition from oil to dry lubrication system, due to it's astonish lubricant properties even at very low coating thickness.

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Figure 1: Aluminum foil with and without graphene.

A comparative study on the application of synthetic 2D MOFs as active materials in hybrid supercapacitors

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Two-dimensional (2D) conjugated metal-organic frameworks (c-MOFs) composed of metal ions and organic ligands have emerged as promising active nanostructured materials for electrochemical energy storage devices.[1] Their unique 2D structure made of regular open channels, large surface area, and abundant redox-active sites of the 2D c-MOFs make them a promising active material for the development of next-generation supercapacitors (SCs).[2] We designed and produced SC electrodes based on nanoscale hexahydroxybenzene-Cu (HHB-Cu), a representative example of $M_3(C_6X_6)_2$ (X = N, S, O) c-MOF family. While c-MOFs with porous structures have been extensively studied in SCs, there is limited research on the electrochemical properties of their counterparts with non-porous structures. The comparison between 2D c-MOFs sharing the same chemistry but different structural properties can provide novel insights into their rational design for electrochemical applications. In this study, we investigate the electrochemical behavior of HHB-Cu with porous and non-porous structures (p-MOF and np-MOF, respectively) in the organic electrolyte (Lithium hexafluorophosphate solution in ethylene carbonate and dimethyl carbonate, 1.0 M $LiPF_6$ in EC/DMC=50/50 (v/v)) in a 3-electrode system by cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), and electrochemical impedance spectroscopy. Our CV and GCD data indicated that the p-MOF electrode shows capacities larger than the np-MOF, implying that porosity plays a crucial role in the Li-ion intercalation mechanisms.[3] The p-MOF yields a specific capacity of 63 mAh g^{-1} at 0.02 A g^{-1}, a capacity retention of 15% at 10 A g^{-1}, and moderate cyclic stability (66% after 1000 cycles). The specific capacity of the np-MOF was 44.7 mAh g^{-1} at 0.02 A g^{-1}, which was lower than p-MOF, even though the rate capability (capacitance retention of 25% at 10 A g^{-1}) and cyclic stability (75% after 1000 cycles) were higher than p-MOF. To validate np-MOF and p-MOF electrodes in practical applications, hybrid supercapacitors (HSC) were constructed by using np-MOF/p-MOF as the negative electrode materials and activated carbon (AC) as the positive electrode materials. The hybrid devices have shown a specific capacity of 24.1 mAh g^{-1} for AC//p-MOF and 19.5 mAh g^{-1} for AC//np-MOF at a specific current of 0.05 A g^{-1}. Moreover, AC//p-MOF and AC//np-MOF devices demonstrated capacity retention of 55.5 % and 60.6% at 10 A g^{-1}, respectively, which is +40% and +45%, respectively compared to the pristine c-MOF electrodes. After 1000 GCD cycles, AC//np-MOF and AC//p-MOF retained more than 85% and 80%, respectively, of their initial specific capacities. The results of this study can provide insights into the electrochemical behavior of 2D c-MOFs for their use in electrochemical energy storage devices.

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Spin waves engineering in 2D van der Waals materials

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The recent isolation of two-dimensional (2D) magnets offers tantalizing opportunities for spintronics and magnonics at the limit of miniaturization.[1] Among the key advantages of atomically-thin materials are their flexibility, which provides an exciting avenue to control their properties by strain engineering, and the more efficient tuning of their properties with respect to their bulk counterparts. In this presentation we will provide an overview of our recent results on this fascinating topic. First, we will focus on the magnetic properties, magnon dispersion and spin dynamics of the air-stable 2D magnetic semiconductor CrSBr (T_C = 146 K)[2] and will investigate their evolution under mechanical strain and Coulomb screening using first-principles.[3] Our results provide a deep microscopic analysis of the competing interactions that stabilize the long-range ferromagnetic order and the orientation of the spin in the monolayer.[4]

Then, we will apply our approach to some of the derivatives of the family of transition-metal phosphorus trichalcogenides and we will show the possibility of tuning spin wave transport by atomic-layer substitution, building a so-called Janus single-layer.[5] Finally, we will introduce novel hybrid molecular/2D heterostructures using sublimable organic molecules to show, as a proof-of-concept, the potential of a chemical approach for magnon spintronics applications.

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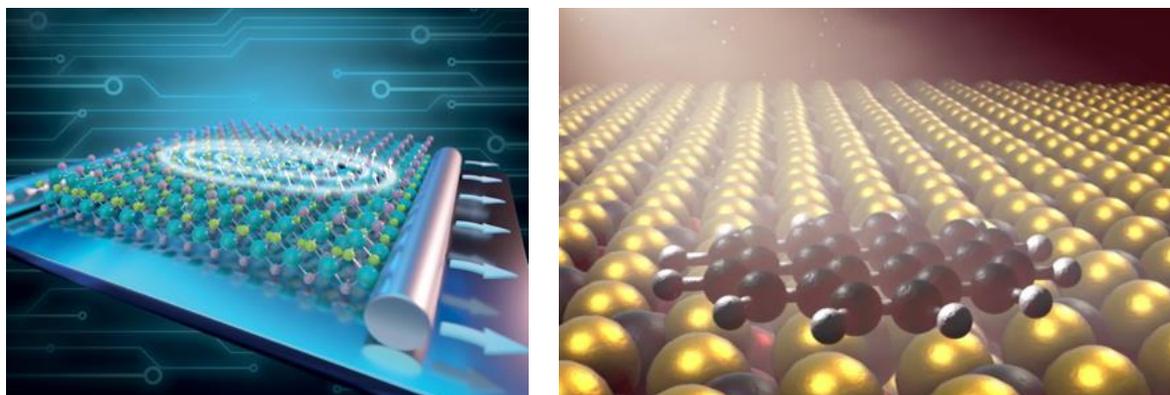
Figure 1: *Artistic representation of (left) strain-engineering of spin waves in single-layer CrSBr and (right) a coronene molecule on the surface of a 2D magnetic material.*

Hydrogel platforms for strain-free and homogeneous 2D materials and devices

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Applying mechanical strain in two-dimensional (2D) materials alters the interactions between photons, electrons and phonons and, consequently, the electronic, magnetic and optical properties of the 2D materials. Examples of phenomena induced or affected by extrinsic strain in 2D materials include modification of the charge carrier and exciton properties in graphene, alternation of vibrational properties and optical characteristics of quantum emitters in hexagonal boron nitride (h-BN), modification of magnetic properties, moiré potentials, excitons and phase transitions in van der Waals heterostructures of 2D materials. Both tensile and compressive strain in graphene cause degradation of graphene field effect transistor (GFET) performances by reducing the charge carrier mobilities in comparison to unstrained graphene. Moreover, even when no strain is applied intentionally, random strain fluctuations are still ubiquitously present across the surface of a 2D material, originating from the inhomogeneities and imperfections of the 2D material-substrate interface, particularly from the inherent substrate roughness, lattice mismatch and fabrication-induced impurities and corrugations. These inhomogeneous strains introduce variations of electrostatic potential, centers for charge carrier scattering and exciton recombination, local modifications of the band structure and random effective magnetic fields in the sheets of 2D materials, and ultimately – degraded performances and large device-to-device variations in 2D materials-based devices. Although strain fluctuations have been successfully reduced in graphene and MoS_2 by encapsulating them between atomically flat h-BN layers, their presence is still substantial even in the most state-of-the-art samples. This indicates a fundamental limit in strain reduction that can be achieved with flattening of the substrate. On the other hand, suspending graphene over the surface of water at water/air or water/nonpolar liquid interfaces was shown to reduce strain in CVD (chemical vapor deposition) graphene to nearly zero, achieving the uniformity level superior to that observed with graphene on solid substrates. As opposed to solid surfaces, in liquids fast diffusion is constantly compensating occurring inhomogeneities and gradients, making the surface of a liquid a superiorly uniform, adaptable and molecularly smooth support for 2D materials. However, a free-floating graphene sheet cannot be immobilized on the liquid surface and integrated into devices, hence this phenomena has not been practically incorporated, despite its potential promise. In this work we propose hydrogels as substrates for 2D materials and devices, which harness the strain relaxation and unification effects of liquids for practical applications. Hydrogels are water-infused polymeric matrices, in which liquid content typically exceeds 90%, but on which nonetheless monolayer materials can be immobilized and probed. We demonstrate that graphene sheets deposited on hydrogel slabs show the lowest mean value (zero) and the most uniform distribution of strain, compared to graphene on other state-of-the-art substrates, including h-BN and liquid water. The strain relaxation and unification effect was observed with both tested types of hydrogels - agarose- and acryl amide(AAm)-based hydrogels. Furthermore, this strategy was also proven to work on monolayer h-BN, and can, in principle, be used as a general approach for achieving uniform untrained sheets of any 2D material grown on metals. Finally, we propose how such graphene/hydrogel platforms can be integrated into devices by demonstrating a graphene/hydrogel-based field effect transistor (FET) with superior charge carrier mobilities.

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Chemical, electrical, and thermal characterization of metal-organic coordination polymer multilayers produced by sequential in situ self-assembly.

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Graphene, being the pioneer, has initiated the discovery of new classes of 2D materials with promising chemical and physical properties. Among those materials are the coordination polymers [1] which exhibit intrinsic porosity, thermal stability, and electrical conductivity and therefore are considered suitable candidates for numerous applications.

In this work, we studied different configurations of metal-organic coordination polymer thin films prepared by Shear coating technique (Fig. 1), a fast and versatile synthesis technique that allows the preparation of many different film configurations. Scanning Probe Microscopy (SPM) techniques were utilized to characterize the electrical properties of these films. More specifically, we employed Kelvin probe force microscopy (KPFM), a technique used for measuring the work function of materials under different experimental conditions [2]. In our study, KPFM is used to monitor the changes in the work function of the films with respect to the main metallic element and reaction time (Fig.2). In addition, the conductivity and thermal stability of these films have been investigated via conductive AFM and XPS spectroscopy respectively.

Our work suggests the exciting possibility to tune the electrical properties of the studied films not only by the synthesis but also by using different stacking configurations.

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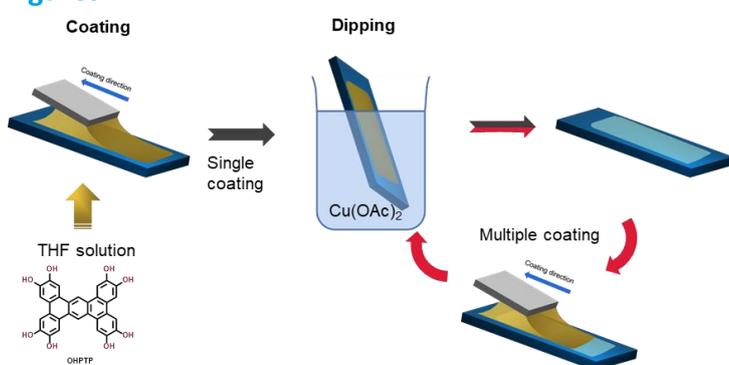
Figure 1: Shear coating technique
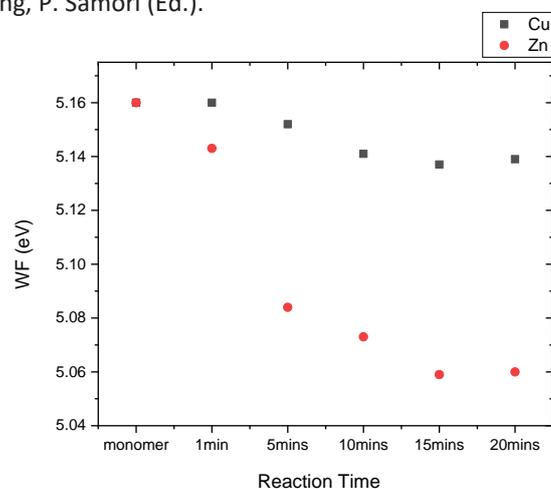
Figure 2: Summary graph of the work function dependence on reaction time.

Graphene-based printed reference electrodes for next-generation lithium-ion batteries

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Reference electrodes are conceived to investigate the electrochemical characteristics of Li-ion battery (LIB) electrodes. The type, size, geometry, and position of a reference electrode in LIB play a key role causes measurement artifacts by geometric and electrochemical asymmetries, complicating a detailed impedance spectra analysis. In this work, novel flat and flexible printed reference electrodes based on lithium salts, namely lithium titanate and lithium iron phosphate, and single-/few-layer graphene (SLG/FLG) flakes are produced to reduce high-frequency measurement artifacts in mesh-like geometry and accurate monitoring of anode and cathode potentials separately in both static and dynamic (operando) conditions. The SLG/FLG flakes were preferred to other graphene-based materials (*e.g.* reduced graphene oxide) because of their excellent chemical purity (percentage atomic content of C > 95%), high electrical conductivity (e.g., carbon-paste with conductivity approaching 100 S cm^{-1}) and superior mechanical properties corresponding to an electrically conductive paste with low electrical resistivity (on the order of 0.01 Ω·cm).[1,2] The influence of the reference electrode coated on the separator together with an additional uncoated separator is analyzed using galvanostatic charge-discharge cycling and electrochemical impedance spectroscopy (EIS). The electrochemical characterizations of two- and three-electrode pouch cells were compared to demonstrate that the insertion of a printed reference electrode does not affect the performance of the full cell. The printed reference electrode on the battery separator (Celgard 2500) is placed in the proper placement (between symmetrical electrodes) in the three-electrode pouch cell configuration. Pre-conditioning treatments are recommended also for these types of reference electrodes to obtain phases corresponding to their 50% of the state of charge, at which the change of potential with state of charge variation is approximately minimized. Plateau potentials in charge-discharge cycling curves were coincident with reported values (3.4-3.5 V for LFP and 1.5-1.6 V for LTO) in the literature.[3] The produced reference electrode shows long-term stability (more than 400 hours) because of graphene flakes' superior electrical and mechanical properties. The impedance contribution of the reference electrodes was properly modelled through a mesh-like electrical equivalent circuit. The obtained electrical modelling data confirm that all produced reference electrodes exhibit characteristic frequencies of more than 100 kHz, meeting the specifications requested for the EIS analysis of LIB half cells. The measured impedance of the whole cell exactly matched the sum of the measured impedances of the positive and the negative electrodes by the produced printed reference electrode.

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From Molecular Radicals to 2D Quantum materials: 2D Covalent Organic Radical Frameworks (CORFs)

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A few years ago, we proposed using stable triarylmethyl radicals as novel open-shell building blocks for 2D covalent organic *radical* frameworks (2D CORFs) [1,2]. When forming a hexagonal lattice, we calculated that 2D hex-CORFs would exhibit antiferromagnetic (AF) ground states and would have energetically close lying closed-shell quinoidal and graphene-like semimetallic states [2]. Soon after this prediction, the first 2D hex-CORF was synthesised and was indeed found to show an AF state [3]. The AF state in 2D hex-CORFs is associated with a parent correlated Mott insulating phase in which unpaired spin-carrying electrons are localised on the radical nodes of the framework [2]. From this parent AF state, graphene-like semimetallic and closed-shell quinoidal/dimerised states should be accessible by modest out-of-plane compression [4] or in-plane strain [5], respectively. Recently, we have studied partial chemical substitution of the spin-carrying C centres in 2D hex-CORFs by B or N. The resulting materials can be viewed as 2D extensions of neutral mixed valence compounds and exhibit emergent spin-frustrated triangular lattices which have the potential to host a range of exotic quantum states (e.g. superconductivity, spin-liquid, novel magnetic ordering) [6].

Overall, our findings establish 2D hex-CORFs as a new class of 2D multifunctional quantum materials that can be tuned by stress/strain/substitution for potential future technological applications.

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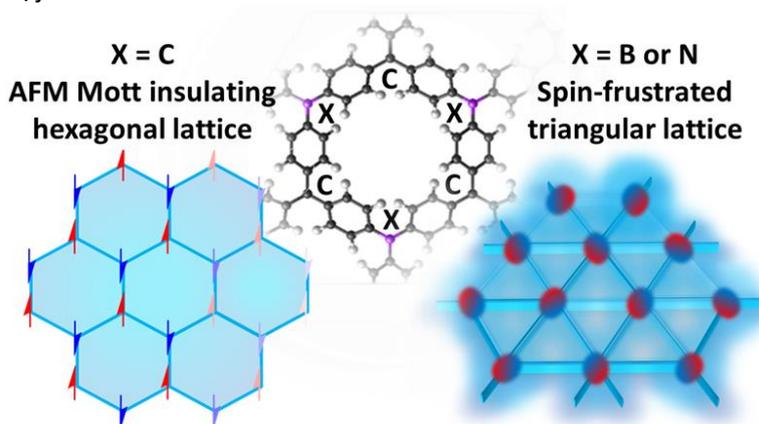
Figure 1: All-carbon 2D hex-CORFs tend to be half-filled correlated Mott insulators (left). Substituting half the carbon centres with B or N leads to emergent 2D spin-frustrated triangular lattices having promise as a platform for exotic quantum materials (right).

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Covalent benzenesulfonic functionalization of graphene and graphene nanopore for enhanced and selective proton transport

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A fundamental understanding of the proton transport through a graphene and graphene nanopore is essential for developing innovative two-dimensional proton exchange membranes. We computationally explore ways to enhance proton transport using a combination of ReaxFF Molecular Dynamics, Metadynamics, and Density Functional Theory (DFT). We identified consistent improvements in proton permeability, in terms of activation barrier and selectivity, for the benzenesulfonic functionalized graphene (incl. nanopores) compared to other functional moieties such as -OH and COOH for example. The benzenesulfonic functionality dynamically acts as proton-shuttle by establishing a favorable hydrogen-bond network, resulting in an effective proton transport channel. The discovered optimal balance between the proton permeability and selectivity is a key ingredient for efficient proton exchange membrane applications. Both the benzenesulfonic functionalized graphene and graphene nanopore exhibits a theoretically estimated areal proton conductivity that surpasses even the state-of-the-art Nafion. Ergo, these models exhibit formidable potential as candidates for the future advancement of graphene-based membranes in energy conversion devices.

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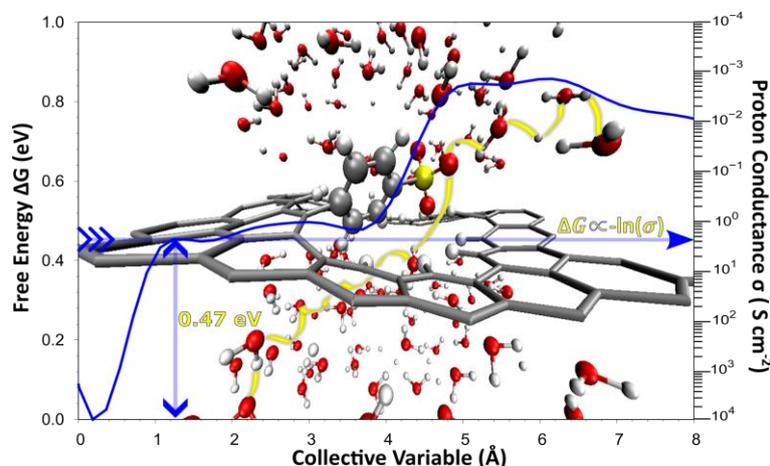
Figure 1: Free energy ΔG profile (eV) along the Collective Variable (Å) for the proton transport through a benzenesulfonic functionalized graphene nanopore solvated in water, over 1 ns of ReaxFF-MD Metadynamics simulation. Estimated proton conductance σ (S cm^{-2}), in logarithmic scale, is proportional to the Gibbs free energy barrier ΔG (eV) for proton diffusion, using the Nernst-Einstein equation.

Emerging field of few-layered intercalated 2D materials

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Abstract

Intercalation is an effective way to tune the physical and chemical properties of 2D materials, thereby facilitating the development of next-generation energy storage and optoelectronic devices, including batteries, sensors, transistors, and electromotive adjustable displays. Among all the 2D materials intercalation compounds, $FeCl_3$ intercalation compounds are most investigated owing to their stability under ambient conditions.[1] However, high uniformity and a high degree of intercalation are critical to the properties and applications of $FeCl_3$ intercalation compounds. In our recent work, we successfully prepare a homogeneous stage-1 $FeCl_3$-bilayer (2L) graphene intercalation compound by inserting a few layers of hBN as protective layer on top of 2L graphene, which are good prototype materials for property investigations and further exploratory studies. In addition to the traditional intercalation methods, we expand the term intercalation beyond the traditional process of atoms or ions penetrating the channels of layered compounds. We propose artificial assembly, a structure that can also be called a van der Waals (vdW) structure. The structure to be fabricated is not limited to certain ions or small molecules but any guest embedded in a specific host, such as a three-dimensional intercalant fullerene or a layer of 2D materials inserted between the layers of other 2D materials.[1] In our recent works, we fabricate graphene/functional groups/MoS_2 (F-G/MoS_2) intercalated structures. The functional groups between graphene basal plane and MoS_2 act as intercalants, which not only introduces the p-doping effect to MoS_2 but also effectively enlarges the interlayer distance and weakens the vdW interaction of the two single layers, thus enhancing the photoluminescence of MoS_2.[2] Hence, artificial assembly has the opportunity to integrate novel building blocks for the fabrication of few-layer intercalation compounds and gain more control over the chemistry that can be induced close to the surface.

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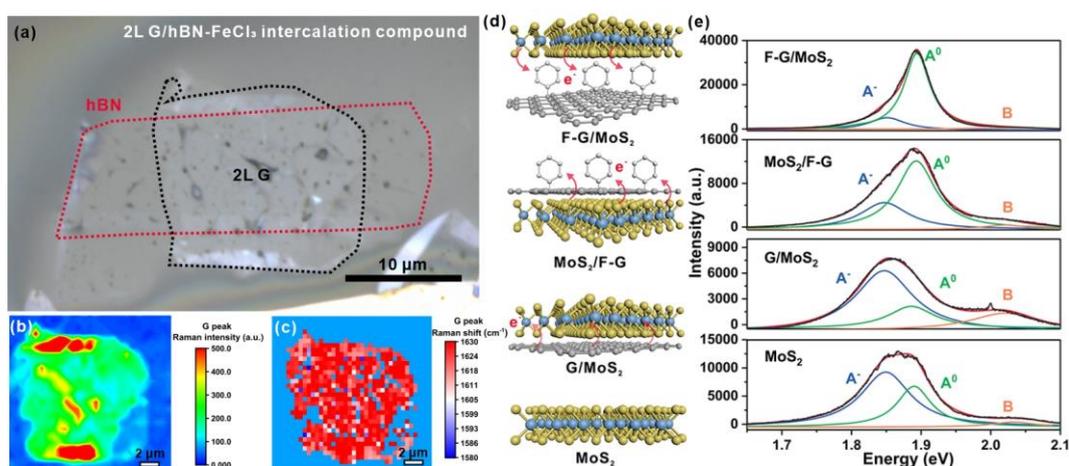
Figure 1: (a) Microscope image, (b) G peak Raman intensity mapping, and (c) G peak Raman shift mapping of 2L G/hBN-$FeCl_3$ intercalation compound. (d) Interfacial interaction mechanism in the structures: F-G/MoS_2, MoS_2/F-G, G/MoS_2, and MoS_2. (e) Peak fittings using Lorentz functions for the above structures.

Interactions of Graphene Oxide and Few-Layer Graphene with the Blood–Brain Barrier

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The blood-brain barrier (BBB) is an essential regulatory layer at the neural interface with the brain vasculature, which acts as a selective barrier. The tight junctions forming between adjacent cells prevent molecules from moving paracellularly, forcing them to take a transcellular route for their translocation.[1, 2]

Graphene, either in the form of colloidal suspension or planar substrate, has been considered an exciting biomaterial for biological applications, and its interactions with the central nervous system (CNS) have been widely investigated in the past decade.[3-8] Like all other nano/micro materials, graphene-based materials, when administered systemically, must cross the blood-brain barrier (BBB) in order to access the brain. Thanks to their biocompatibility and high cargo capability, graphene-based materials (GRMs) might represent an ideal brain delivery system. The capability of GRMs to reach the brain was mainly investigated *in vivo*, and has highlighted some controversy.

Herein, we employed two in vitro BBB models of increasing complexity to investigate the bionano interactions with graphene oxide (GO) and few-layer graphene (FLG), so far overlooked. We employed a 2D murine Transwell model, followed by a 3D human multicellular assembloid, to better mimic the complexity of the *in vivo* architecture and inter-cellular crosstalk. We developed specific methodologies to assess the translocation of GO and FLG in a label-free fashion and a methodological platform widely applicable to any nanomaterial type. Overall our results show good biocompatibility of the two GRMs, which did not impact the integrity and functionality of the barrier. Sufficiently dispersed subpopulations of GO and FLG were actively uptaken by the endothelial layer; however, the translocation was identified as a rare event.
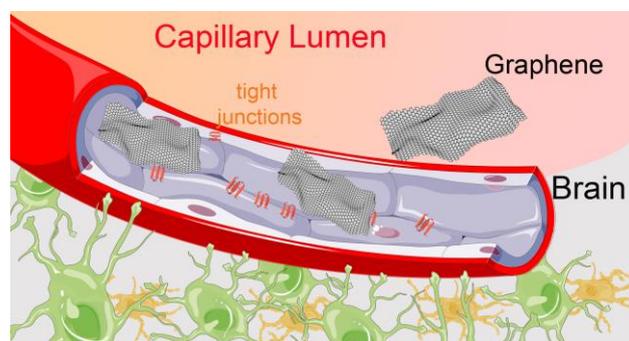
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Preparation of graphene-based all-carbon hybrids based on fluorographene chemistry

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Fluorographene (FG) is a stoichiometric (C_1F_1) and well-defined graphene derivative,[1] which has been employed as an alternative precursor for the preparation of covalently modified graphene derivatives.[2] The reaction mechanism stems from FG electrophilicity and can be simplified as a nucleophilic substitution (S_N) mechanism initiated by radical point defects.[3] Owing to their bonding with the highly electronegative fluorine atoms, carbons of FG behave as electrophiles and hence, are susceptible to attack by nucleophiles.[4] Simultaneously with their substitution, nucleophiles cause reductive defluorination through promoting the heretolytic cleavage of the C-F bonds, which results in the formation of the extended π-network of graphene. Thus, practically fluorine-free graphene derivatives are prepared.[2] In this frame, a fullerene derivative bearing a primary amine unit as nucleophile reacted with the electrophilic FG, resulting in the synthesis of the first all-carbon hybrid based on the chemistry of FG.[5] Recently, going one step further and taking into account that F atoms of FG have been replaced by two different functionalities through tuning the equivalents of reagents,[6] first the covalent linking of FG with a carbon allotrope was performed and next, the remaining F atoms were employed for the grafting of another nucleophile, thus providing a selective – in respect with the other carbon allotrope – post modification.

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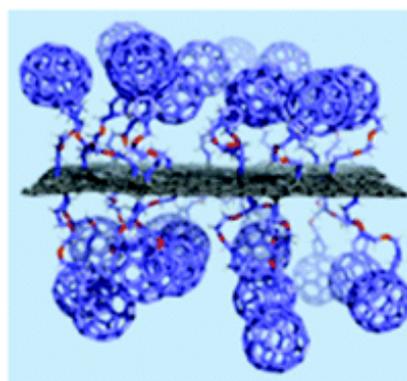
Figure 1: Covalently linked fullerene moieties onto graphene lattice *via* the chemistry of FG.

Investigation of correlation between rigidity of graphene-based hybrid materials and responsiveness of sensors device

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Abstract

Graphene is one of the most promising 2D material and it becomes central for many research fields organic electronics, sensing and energy storage.[1] Nevertheless, in some applications graphene oxide (GO), an oxidized form of graphene is more beneficial as the presence of organic moieties enables non-covalent interactions with the target molecules and serves as anchoring point in various reactions allowing formation of functionalized graphene oxide. Since, the presence of oxygen groups decreases of electrical properties such as: conductivity, capacitance, electron transfer in comparison with pristine graphene,[2, 3] to obtain material which combines electrical properties of graphene and ability to form supramolecular interactions the GO is chemically reduced yielding reduced graphene oxide (rGO).

This research aims at developing new generation of piezoelectric pressure sensors based on two-dimensional materials (non-)covalently functionalized with organic molecules and their application in proof-of-concept devices. The study involves the design of a high-efficiency method of graphene oxide (GO) reduction using various reductors, preparation of graphene hybrids material with organic molecules featuring variable rigidity and their processing into thin-films onto flexible surfaces by layer-by-layer method. The schematic illustration for preparation of devices is presented in Figure 1. The combination of different rigidity of molecular pillars and conductivity of rGO will allow to investigate impact on responsiveness of piezoelectric sensors.

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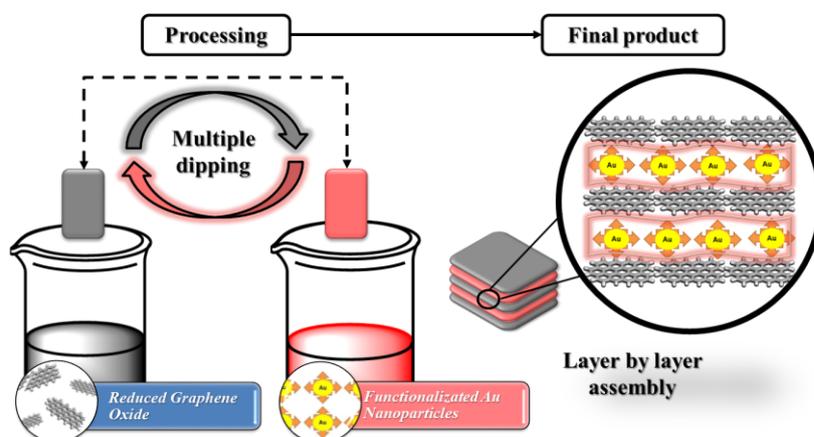
Figure 1: Schematic illustration of layer-by-layer processing.

Acknowledgements

Simple Low-Cost Fabrication of Laser-Induced Graphene-Based Electrochemical Sensors

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Graphene-based materials are of interest in electrochemical sensing due to their unique properties, such as high surface areas, high conductivity, and electrocatalytic behavior [1]. In this scenario, Laser-Induced Graphene (LIG) has emerged as an exciting material. LIG can be patterned on flexible substrates in ambient conditions using a fast and facile laser irradiation process. Based on that, we are addressing a simple low-cost fabrication of an electrochemical sensor based on laser-induced graphene for the detection of nicotinamide adenine dinucleotide (NADH) at low potential (50 mV vs Ag/AgCl). By using mild laser power conditions (1.5 W laser power at 405 nm), it was possible to obtain electrically conductive graphene (with a sheet resistance of 24.38± 2.19 $\Omega/\square$), on polyimide substrate, displaying a porous 3D morphology rich in defects, as shown in the scanning electron microscopy image (SEM) and Raman spectrum (with high 2D band intensity at 1350 cm^{-1}) respectively in Figure 1. A massive number of electrochemical sensors based on LIG was easily fabricated as shown in Figure 2. The pseudo reference electrodes based on Ag/AgCl were obtained by a simple chlorination approach on a deposited silver layer, using a commercial bleach solution, resulting in a stable potential, showing a potential difference of less than 2.5 mV vs Ag/AgCl (3 mol L^{-1} KCl) commercial electrode. The electrochemical sensors based on LIG were employed to detect NADH, an important essential coenzyme for neurotransmitter activities, with a linear range of 0.05-10 mmol L^{-1}. The presence of residual oxygenated functional groups (C-O/C=O) on LIG structure is essential for the electrocatalytic activity towards the electrooxidation of NADH at low potential [2].

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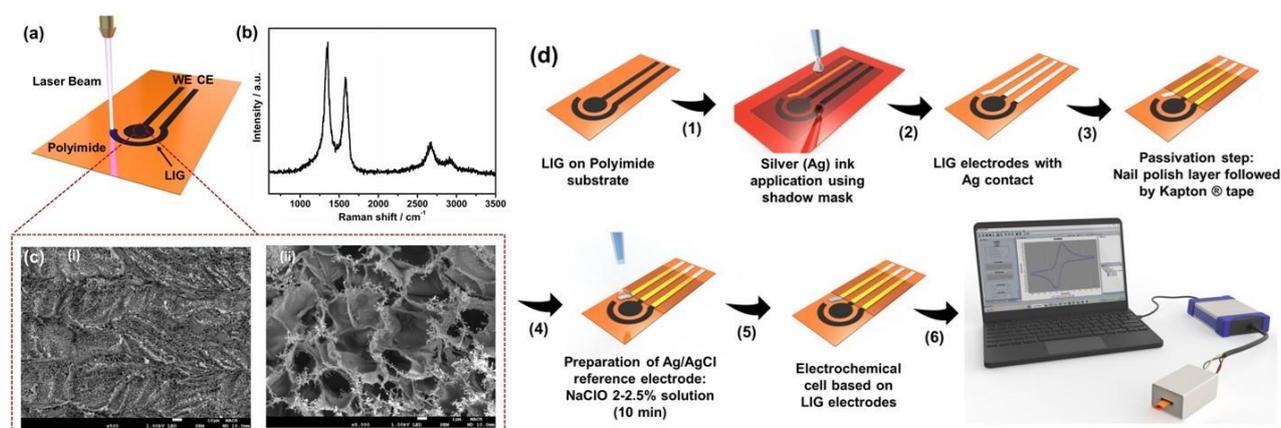
Figure 1: Schematic representation of the preparation of LIG on polyimide substrate (a). Raman spectrum of LIG (b) and SEM images low (i) and high (ii) magnification of LIG surface showing the porous structure (c). Representation of each experimental step of fabrication of LIG-based electrochemical sensors.

Molecular Permeation in 2D Silicon Dioxide

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2D silicon dioxide or bilayer silica was discovered in 2010 and since then has been thoroughly characterized in a supported form by surface-sensitive techniques. It is composed of corner-sharing [SiO$_4$] tetrahedra that organize into either a hexagonal lattice or a vitreous network of four- to nine-membered rings. Unlike graphene and similar single-layer structures, the pores in bilayer silica appear large enough for the translocation of small molecules. In this work, we for the first time isolate free-standing sheets of 2D SiO$_2$ and carry out direct mass transfer experiments [1-3]. The material preparation is done by atomic layer deposition (ALD), and sensitive gas permeation measurements are combined with quantitative adsorption studies. It is shown that regular gases do not permeate through the vitreous polymorph whereas vaporous substances like water readily cross its natural openings. The passage of the vapors is understood in terms of the surface-mediated flow, and the membrane selectivity is demonstrated to depend on the strength of gas-surface interactions. As illustrated in Figure 1, bilayer silica further enables size exclusion for chemically alike species which is associated with distinct energy barriers for entering the structure. Thus, 2D silicon dioxide proves to be an inherently open material with a high areal density of well-defined pores.

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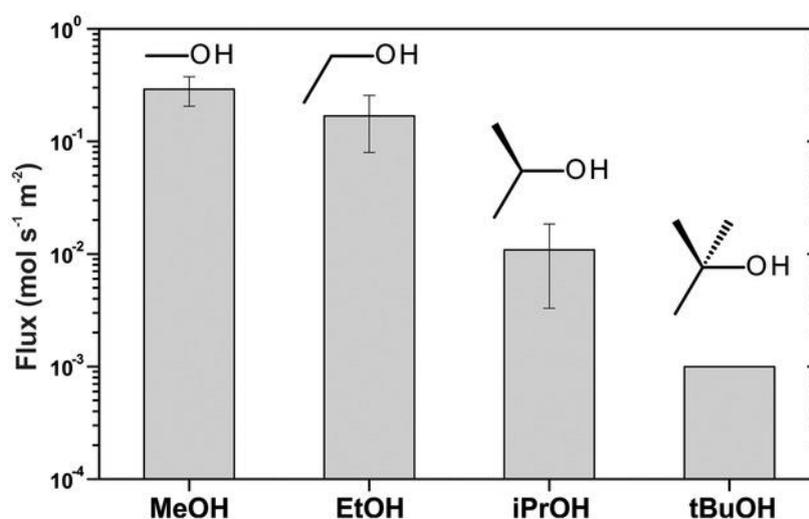
Figure 1: Transmembrane flux of alcohol molecules in vitreous bilayer silica. Adopted from ref. [1].

Synthesis and nanomechanical assessment of ultrathin carbon nanomembranes targeted for permeation applications

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Carbon nanomembranes (CNMs) are a type of two-dimensional material created by using low-energy electron irradiation to cross-link self-assembled monolayers (SAMs) of aromatic precursor molecules [1]. The thickness and porosity of CNMs can be adjusted according on the precursor molecules and the preparation circumstances, from which they also inherit their terminal functionality [2]. This tunability renders them the ideal candidates for permeation applications such as water separation. Pressure-driven membrane processes rely a great deal on the mechanical integrity of the material, as these carry the mechanical loads generated by the flow of liquids. The membranes may be subjected to substantial physical compression at high working pressures, which can diminish or even destroy their performance [3]. In order to guarantee the structural stability of the membrane during operation, the goal of this work was to investigate and analyze the mechanical properties of CNMs and their substrates. Unlike macro-materials, measuring the mechanical characteristics of nanometer-thick membranes is a daunting task. For that reason, Atomic force microscopy (AFM) was used to measure the membranes' inherent mechanical properties as they were suspended over patterned substrates but also supported on atomically flat substrates. CNMs were tested with Quantitative nanomechanical mapping, nanoindentation and fatigue experiments which highlighted the ability of the membranes to withstand flow related mechanical loads.
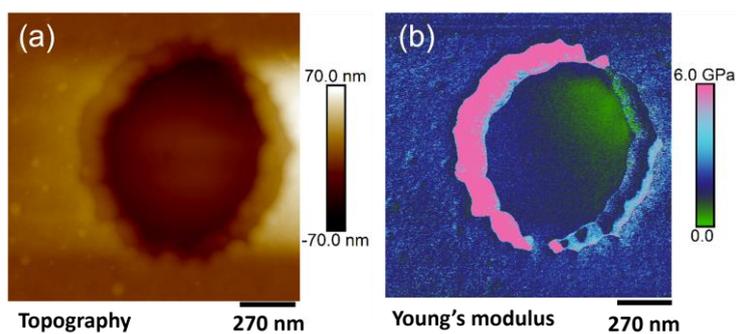
Figure: (a) Topography and (b) Young's modulus mapping of a suspended CNM.

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Hybrid hydrogels based on 2D MoS$_2$ for applications in wearable devices

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The continuous research on electronics, biocompatible materials and nanomaterials has led to the design of a new generation of wearable devices that can be employed in direct contact with the body of the user, which is attractive for real-time, non-invasive health monitoring[1]. For the satisfaction of such requirements, hydrogel-based conductive devices are often proposed as promising candidates for these applications, thanks to their softness, flexibility, and biocompatibility. Here we report the synthesis of conductive hybrid hydrogels containing two-dimensional (2D) MoS$_2$. The nanoflakes are integrated in the polymeric matrix creating an anisotropic structure, which helps to generate mismatch stress for a strain sensing under a certain stimulus[2], thus allowing the gel to give an electrical response to pressure. 2D MoS$_2$ nanoflakes were produced *via* top-down chemical exfoliation[3] and were incorporated in the hydrogel through a covalent grafting to the polymeric building blocks by exploiting the prior surface functionalization of the flakes[4]. The conductivity of the hydrogels was increased with the further incorporation of *in-situ* polyaniline (PANI), which is a widely used material in biomedical applications as a biocompatible conductive polymer[5]. The as-obtained hydrogels are characterized through a combination of techniques, whereas their electromechanical properties are investigated via a home-made setup to prove that compression causes an increase in current due to the piezoresistive properties introduced with the incorporation of 2D MoS$_2$ and PANI.

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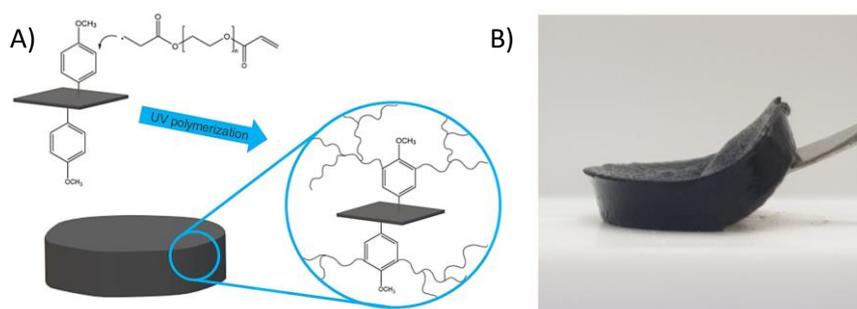
Figure 1: A) Grafting of PEGDA onto functionalized MoS$_2$ surface. B) MoS$_2$/PEGDA soft hybrid hydrogel.
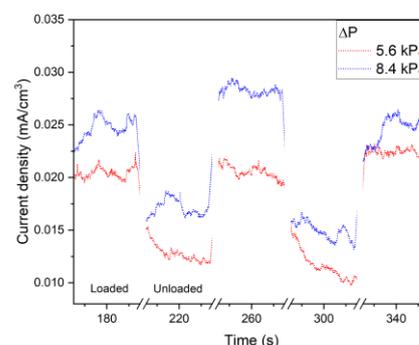
Figure 2: Compressive electromechanical tests of MoS$_2$/PEGDA/PANI hydrogel.

Photocatalytic-triggered nanopores across multilayer graphene for high-permeation membranes

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2D nanoporous graphene nanomaterials have been considered for the development of high permeability membranes, compared to dense laminate architectures. Current perforation technologies, however, have struggled to deliver a membrane for practical use due to a lack of scalability and increased related complexity/costs over commercial membranes. Herein, the perforation of ultrathin graphene membranes, with thicknesses ranging from 50 to 200 nm were performed via a triggered and site-selective photocatalytic etching process. The perforated graphene membranes exhibited a narrow distribution of in-plane nanopores with sizes ranging from 20 and up to 100 nm, depending on irradiation durations. The surface pore density across porous graphene can be tuned, achieving a maximum surface density of 1011 cm^{-2}, depending on the amounts of pore-mediators i.e. nano-catalysts loaded to multilayer graphitic assemblies. The perforated membranes exhibited a water permeation of 85 LMH/bar, 3.5 times higher compared to unperforated membrane analogues though a decrease in dye removal (~20% for the methylene blue organic dye) was noted over the extended permeation duration (2-hour). The synergetic characteristics between inherent nanochannels between graphite planes and incorporated nanopores across such ultrathin perforated graphene membranes promise improvements in water treatment using such architectures of high permeability graphene membranes.

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Graphene multilayers for gas sieving

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Climate change combined with current geopolitical upsets are seriously demanding a conversion of our energy supply chain. Hydrogen is a carbon-free energy vector that can be prepared from a vast series of resources, even renewable, [1] but a low-cost strategy to isolate it is still challenging. Indeed, independently from the production approach, hydrogen is obtained in gas mixtures, mainly coupled with CO_2. [2,3] Membrane-based separation can be a suitable solution to prepare pure hydrogen, [4] but perm-selectivity performances of conventional materials are limited by the permeability/selectivity trade-off, named Robeson upper bound. [5] Nanosized composite membranes, fabricated using 2D materials, offer possibility to efficiently size-sieve gas molecules. Graphene-based self-assembled multilayers represent a tunable platform that allows to tailor final molecular architectures and resulting sieving performances, eventually surpassing current Robeson upper bound. Presented multilayers are prepared by an electrostatically ruled Layer-by-Layer self-assembled technique, alternatively exposing a polymeric substrate to a polyelectrolyte solution and a graphenic suspension. Each dipping step is followed by a rinsing in pH=7 water, to remove excess of deposited material (**Figure 1**, left). All perm-selectivities of prepared multilayers are determined by a standard manometric technique. In an attempt to improve poor level of permeability, the properties of the prepared multilayers are modified by post-fabrication modifications or by tuning process parameters of the self-assembly, such as annealing of the self-assembled multilayers or change in the concentration of solution/suspension used for the self-assembly (**Figure 1**, right). All prepared multilayers are extensively characterized in terms of morphology (SEM), elemental composition (XPS) and molecular architecture (XRD).
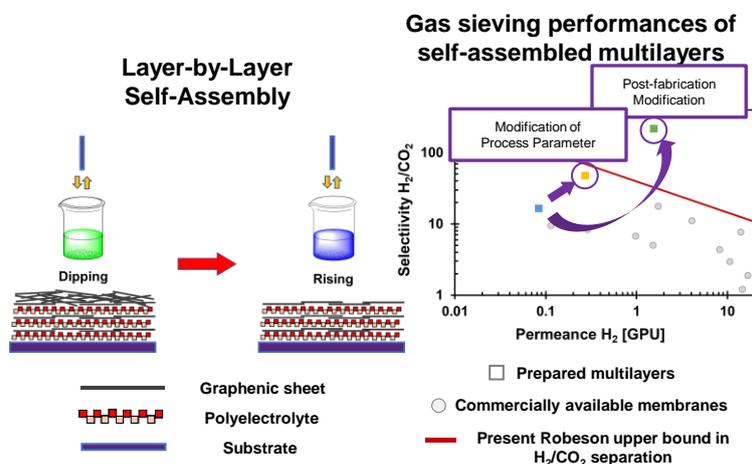
Figure 1: On the left, schematic representation of layer-by-layer self-assembly; on the right, perm-selectivity performances in H_2/CO_2 separation of some prepared multilayers compared with currently commercially available membranes (present Robeson upper bound in reported, red line).

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GrapheNet: A Novel Deep Learning Model for Predicting Physical and Electronic Properties of 2D Materials Using Images

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The quest to represent complex materials structures and nanostructures has been a persistent challenge in the field of chemistry and materials science. Traditional methods of representing small molecules, such as SMILES, have proven to be insufficient to represent more complex systems. In recent years, the use of 2D images to represent the structure of materials has gained popularity, especially with the development of artificial intelligence (AI) tools and deep learning algorithms [1]. In this study, we present a novel approach to represent the structure of 2D based materials, such as graphene [2] and graphene oxide nanosystems [3], and an advanced predictive AI-based framework. Our proposed deep learning model, GrapheNet, is based on an Inception-ResNet architecture consisting of multiple blocks of convolutional layers with different kernel sizes. The GrapheNet model can be trained to make predictions about the physical and electronic properties of graphene-based systems using PNG images as structural representations. The efficacy of the approach was tested on datasets of graphene oxide and defected graphene systems, built starting from repositories of computed structure/property data. Structural data of the nanosystems in the dataset, encoded in standard structural formats, are transformed into three-dimensional (graphene oxide) or two-dimensional (defected graphene) tensors, converted into RGB (graphene oxide) or grayscale (defected graphene) PNG images and pre-processed (cropping, resizing, recentering, padding). Upon training, the GrapheNet framework yielded very accurate results in predicting phyisico-chemical properties of graphene oxide and graphene nanostructures, with low mean prediction errors for all target properties considered, also exhibiting a significant computational efficiency. Being based on highly-efficient frameworks borrowed from state-of-art computer vision technologies, the approach proposed demonstrates the potential of using image-like representations of 2D and low-dimensional nanostructures in connection with deep learning predictive models, predicting the chemico-physical properties of nanographenes with great accuracy and outperforming the computational efficiency of current methods.

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Discovering Two-Dimensional Non-van der Waals Materials

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While two-dimensional (2D) materials are traditionally associated with bulk layered compounds bonded by weak van der Waals (vdW) interactions, the recent surprising experimental realization of *non*-vdW 2D compounds obtained from non-layered crystals [1,2] opens up a new direction in 2D systems research. These materials show several distinct differences to traditional 2D sheets as their surface was revealed to be terminated by cations rather than anions. Here, we outline several dozens of candidates of this novel materials class derived from employing data-driven research principles in conjunction with autonomous *ab initio* calculations [3,4] (Figure 1). The oxidation state of the surface cations of the 2D sheets turns out to be an enabling descriptor regarding the manufacturing of these systems as it determines their exfoliation energy: small oxidation states promote easy peel off [3]. When extending the set from oxides to sulfides and chlorides, the exfoliation energy becomes ultra low due to strong surface relaxations [4]. The materials also pass several tests validating their vibrational and dynamic stability. The candidates exhibit a wide range of appealing electronic, optical and in particular magnetic properties making these systems an attractive platform for fundamental and applied nanoscience.

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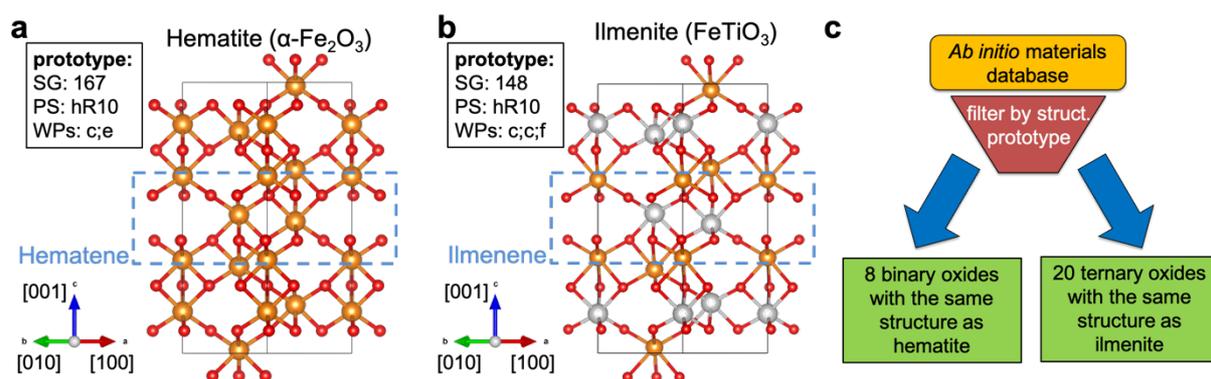
Figure 1: **2D materials from non-vdW systems**. Atomic structure of (**a**) hematite (α-Fe_2O_3) and (**b**) ilmenite ($FeTiO_3$), the first non-vdW bulk materials with 2D analogues [1, 2]. For both prototypes, space group (SG), Pearson symbol (PS), and Wyckoff positions (WPs) are indicated in the respective boxes. In each case, the exfoliable [001] facet (monolayer) is indicated in the blue dashed frame leading to hematene and ilmenene 2D materials. Colors: Fe orange, O red, and Ti light gray. The black line denotes the conventional unit cell. (**c**) Schematic workflow illustrating how the candidate systems were obtained from the *ab initio* materials database using structural information as input.

Sensitive Piezoresistive sensors made of Graphene/PDMS 3D porous structures for wearable electronics

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The excellent properties of graphene have made it the best candidate for the next generation of flexible electronics applications [1]. Wearable sensors require several properties, such as high flexibility, stretchability, lightweight, and inexpensive fabrication, and they have to be suitable for integration with electrical components. One solution is the combination of nanostructures that act as sensors and polymers that guarantee the flexibility of the device. Different methods have been proposed in the literature to achieve these essential properties [2]. However, all techniques develop a flexible sensor entirely enclosed by the polymer, which reduces the effect of external stimuli, limiting the graphene sensitivity. In order to improve the sensitivity of the piezoresistive system, here we present a device in which the 3D polymer skeleton is covered by graphene layers grown by the CVD method, as shown in figure 1a.

Sensors based on piezoresistivity rely on transducing external mechanical loading into resistance change signal. Based on this principle, we investigated the electrical and mechanical properties of the graphene/polymer 3D structures by measuring their electrical resistance variation as a function of compressive and tensile strain. The optimized methodology to produce these materials will be presented and discussed as the results obtained.

The realization of a piezoelectric sensor with an exposed graphene surface would be exploitable for several applications, such as biosensing, where the device will also be sensitive to external analytes.

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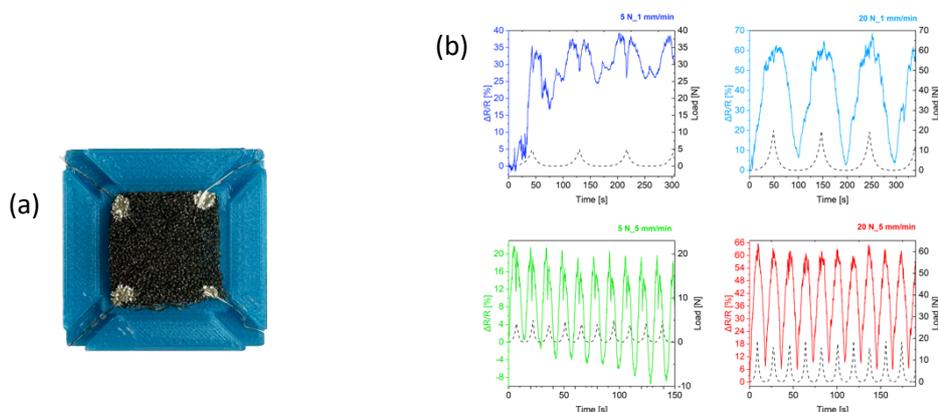
Figure 1: (a) 3D Graphene/PDMS foam contacted with silver paste. (b) Electrical-resistance variation of the composite as a function of compressive strain

Industrial exfoliation of 2D graphene analogues for functional coatings

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This research focuses on the development of a top-down approach for the production of exfoliated hexagonal boron nitride (h-BN) as a 2D analogue of graphene. 2D materials have gained considerable attention in recent years due to their potential applications in various fields, such as semiconductors, biomedicine, and catalysis. In particular, h-BN presents the outstanding properties of graphene such as mechanical strength and thermal conductivity but is electrically insulating. However, the production of these materials has been mainly based on lab-scale methods, which are sometimes difficult to scale up for industrial production at moderate costs [1].

To overcome this challenge, the research proposes a top-down method for the production of exfoliated h-BN, which involves increasing the production from lab scale to semi-industrial scale using standard industrial methods such as ball milling [2][3]. A screening method was used to select the best surfactants, which could stabilize exfoliated h-BN flakes to a concentration above 1 mg/mL, the minimum concentration needed for standard deposition techniques.

The solutions containing h-BN flakes and surfactants were then used to coat different surfaces such as aluminium and polyethylene terephthalate, to create thin layers of h-BN nanoflakes with the minimum presence of polymers, avoiding the use of composites or binders. These thin-layered h-BN systems are studied for their potential applications in thermal management systems and as protective coatings.

The results of this study demonstrate the feasibility of a top-down approach for the large-scale production of exfoliated h-BN. The surfactant selection process, combined with ball milling, proved to be an efficient method for producing stable dispersions of h-BN flakes. Thin layer h-BN coatings showed promising results for the potential of h-BN as a versatile 2D material for various applications.

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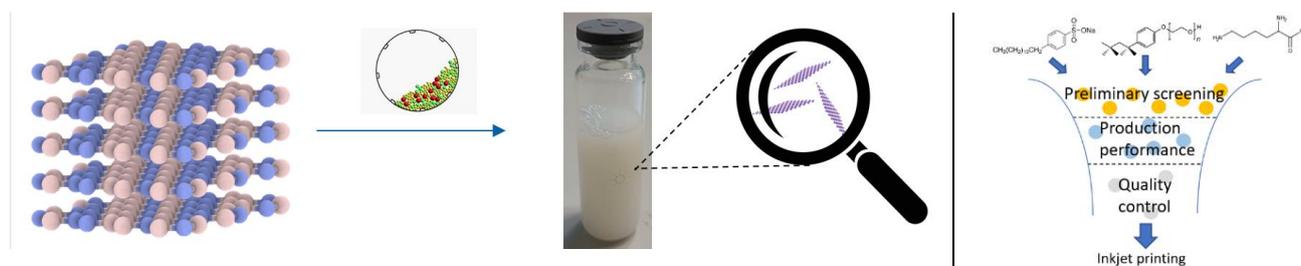
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Figure 1: Schemes of h-BN exfoliation from raw powder up to h-BN stabilized in solution (left) and screening method to select the best h-BN/surfactant combination (right).

Investigation of the Ionic Conductivity and Relaxation of COF/polymer Composite Solid Electrolytes

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With the ever-growing issue of fossil fuels scarcity, the development of clean and renewable energy resources has become the most important global challenge. Proton exchange membrane fuel cells (PEMFCs) are a clean technology employing hydrogen as fuel and yielding only water and heat as byproducts of the electrochemical reaction. Their efficiency mostly depends on the proton conductivity (σ) of the solid polymer electrolyte (SPE) in the membrane electrode assembly (MEA). In a PEMFC operating at 60-80 °C, the ideal SPE should possess high σ also at low relative humidity (RH), apart from being insoluble in water and stable in acids or bases. Indeed, the main challenge in the development of PEMFCs consists in the water management: although σ usually depends on the SPE's hydration, the latter is detrimental for the cell stability and performance, since condensation, followed by flooding, is inevitable when the operating temperature is around 80 °C. A common and simple activation strategy in real-life use of FCs is to steam or boil the MEA prior to use, but SPEs exhibiting good σ preservation at low RH are still lacking. Although covalent organic frameworks (COFs) do not usually exhibit high intrinsic proton conductivity (σ), they have been recently proposed as SPEs in PEMFCs, thanks to their high crystallinity and stability to acids and bases. [1]

Here, a simple strategy to improve the performance of poor COF-based proton conductors through addition of sodium polyacrylate (PANa) superadsorbent polymer is presented. Electrochemical impedance spectroscopy (EIS) investigations after activation at high temperature and RH provide insights into the role of PANa, whose presence is key to preserve high σ at low RH. For the first time a humidity-dependent X-ray diffraction analysis was performed to support the EIS data, revealing a strengthening of the stacking interaction along the COF (100) plane direction via H-bonding, thereby promoting the proton hopping. Furthermore, an extensive investigation of the relaxation mechanism as a function of PANa content enabled us to determine a Debye relaxation regime for the COF/PANa blends with the maximum relaxation frequency increasing with the PANa content, resulting in a more efficient charge carrier transport. [2]

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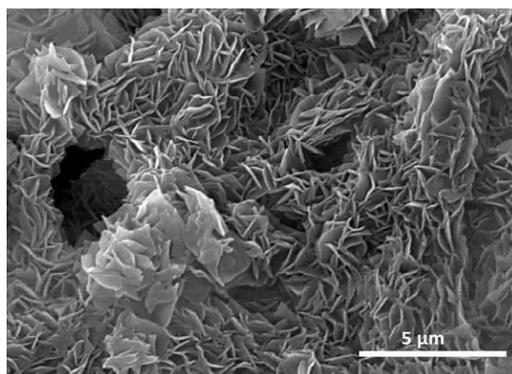
Figures

Figure 1: Scanning electron microscopy image of the investigated COF/PANa blend.

Chemically Functionalized Top-contact Electrodes: Boosting the Performance of MoS₂ Field-Effect Transistors by Tuning the Charge Injection

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The interface between electrodes and semiconductors plays a critical role in the (opto-)electronic performance of devices based on ultrathin two-dimensional layered materials. Unfortunately, a lack of interfacial modulation in the top-contact configuration impedes the performance of these devices. Here, we propose a contact engineering method to functionalize the electrodes of top-contact field-effect transistors (FETs) by transferring chemically pre-modified electrodes. We systematically tuned the electrodes of molybdenum disulfide (MoS₂)-based FETs using conventional thiol molecules with different dipoles. Notably, we observed significant improvements in device performance when we modified the Au electrode with electron-donating molecules. Using this facile approach, we fabricated a high-performance Schottky diode with asymmetrically functionalized electrodes by utilizing dipole-opposed molecules on two electrodes, resulting in a rectification ratio of ~10³. Our results demonstrate a powerful and unprecedented strategy for tuning the interfacial properties in top-contact MoS2 FETs and tailoring device performance on demand.

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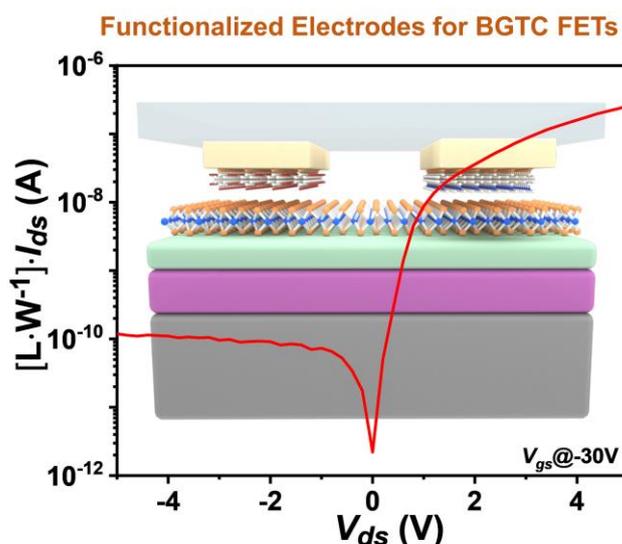
Figure 1: Schematic diagram and the output curve of asymmetric MoS₂ FETs device with electrodes functionalized by PFBT and DABT respectively.

Covalent surface functionalization of graphene based materials controlled by blue light

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We present an unprecedented methodology for the covalent functionalization [1] (arylation) of different sp^2 carbon-based materials with arylazo sulfones: i) Chemical Vapor Deposited Graphene on Cu (CVD-G), ii) Graphene Oxide, iii) reduced Graphene Oxide (rGO), iv) considering also the highly oriented pyrolytic graphite (HOPG) as ideal 100% sp^2 substrate.

The reaction can be activated by commercial blue led (461 nm). Mild reaction conditions, absence of photosensitizers, functional group tolerance and high atomic fractions (XPS analysis) represent some of the salient features characterizing the present methodology. The study was completed by a mechanistic proposal based on both experimental as well as spectroscopic analyses, in particular n Raman analysis on HOPG [2] and CVD-G, where D peak was observed after functionalization. The quantitative analytical determination of the tagged aryl units via XPS, represent a unique combination of factors electing the present methodology as a valuable synthetic alternative to the known protocols based on electrochemical charge transfer [3,4] for the covalent modification of a wide range of graphene based materials.

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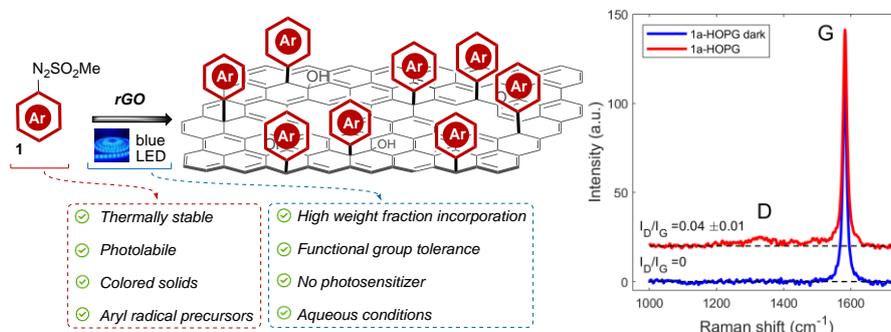
Figure 1: left: schematic representation of the present visible-light assisted covalent arylation of rGO with arylazo sulfones. Right: Raman spectrum of 1a-HOPG dark and 1a-HOPG. Linear background was subtracted, and spectra were shifted for clarity.

Dye-sensitized 2D materials composites for photocatalytic hydrogen production

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Photocatalysis is a an appealing strategy to exploit solar energy for fuel production. Innovative 2D materials with unique layered structures are expected to enhance photocatalytic activity due to excellent mobility of charge carriers and extremely high specific surface area.

In our work we explored the correlation between the photocatalytic activity and graphene oxide morphology (size and thickness) [1]. Our results clearly demonstrated that both size and thickness of GO flakes do matter for the photocatalytic hydrogen production. Subsequently by integrating two types of functional materials: graphene oxide and Co-MOF we designed a stable system with enhanced charge-separation properties which ultimately boost their photocatalytic activity. The activity of our Co-BDC in the presence of graphene oxide was found to be remarkable (33,300 μmol $g^{-1} h^{-1}$ per gram of MOF) in comparison to other MOF systems (Fig. 1) [2].
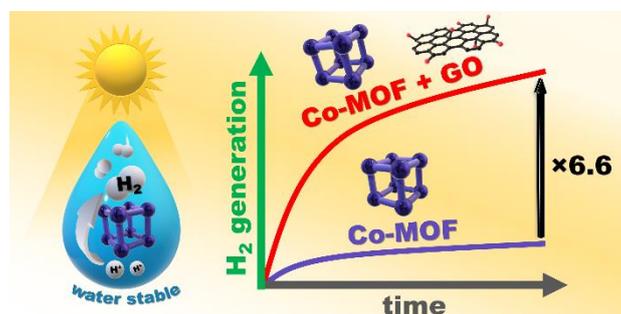
Figure 1. Boosting photocatalytic hydrogen generation by integrating Co-MOF and graphene oxide.

Recently we explored the hydrogen production by functionalizing non-covalently eosin Y to $Ti_3C_2T_x$ or Nb_2C. For example it was found that a Nb_2C sample obtained by chemical etching and 4 h sonication (Nb_2C-4h) with a high specific surface area in aqueous suspension of 161 $m^2 g^{-1}$ showed the highest hydrogen generation rate (10,290 μmol $h^{-1}g^{-1}$), 3.2 times higher than that of Nb_2C obtained by chemical etching without post-synthetic sonication that has 55 $m^2 g^{-1}$ of specific surface area in suspension. The increased performance of Nb_2C-4h surpassing many reported photocatalysts was attributed to the beneficial influence of the exposed surface area and level of exfoliation of the MXene sheets [3].

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Dye-sorption in liquid for surface area analysis

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Materials interact with their surrounding through their surfaces. Thus, several physical properties of solids, such as adsorption, degradation, thermal stability, etc. as well as its role in chemical reactions as a reagent or catalyst is also governed by the surface. Thus, the characterization of the surface is essential to predict the properties of the materials and their potential applications. The SA measurement is extremely important as it provides a measure of the exposure that a solid has towards the surrounding environment. One of the most used technique to measure SA is based on gas-sorption, where the gas penetrates into the pores, sit on the inner surface and measuring the amount of gas used up in covering the surface, the surface area of a particular solid can be measured with greater accuracy. Gas adsorption is usually described by isotherms (BET model),[1] i.e. the amount of adsorbate on the adsorbent as a function of its pressure at constant temperature. Although it is widely used to measure the SA of granulates, powders micro-fibers and metallic foams,[ISO 9277-2010] such technique is affected by several limitations, such as dimensions of solid objects of a few mm and minimum surface area (SA_{min}) of 4 m^2.[2] Moreover, the measurement procedures require vacuum-gas cycles and can cause mechanical stress in soft or fragile samples, closing the pores. Here, we present a protocol for SA measurement technique based on the adsorption of commercial dye (Methylene Blue) in green solvents (water, IPA) where isotherms are described in term of BET-modified model.[3] The protocol has been successfully tested on a wide range of materials: such as single layer graphene oxide nanosheet in water, graphite micro-powders, granular activated carbons, polymeric micro-fibers used as tap water filters, polymeric fabrics, metallic foams, ZnO ans Si nanobrushes.[4] In particular, the proposed protocol allows to measure the SA of atomic-flat surface as 1x1 cm^2 Si(111) substrate proving that the SA_{min} is about 4 orders of magnitude better than that achievable with gas-sorption BET.

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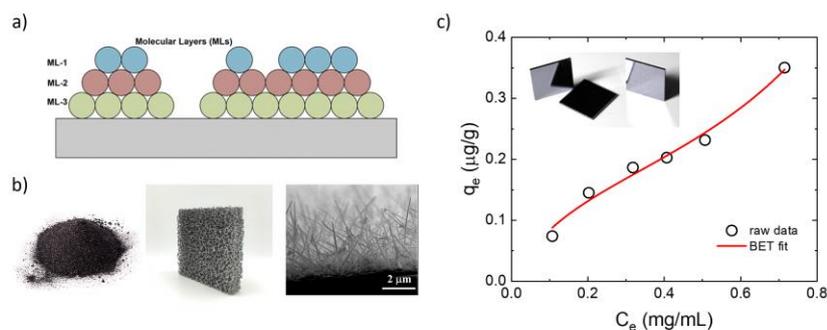
Figure 1: The process of BET multilayer adsorption, b) list of materials tested and c) isotherm measured on Si substrate

Solid-State NMR Investigations of 2D Materials

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Almost 20 years have passed since the first successful synthesis of graphene. Since then, related materials have attracted increasing interest due to promising physical, electrical, chemical, and optical properties of two-dimensional materials (2DM). 2DMs are ultrathin nanomaterials and exhibit unique characteristics such as high surface-to-volume ratio, surface charge, shape, high degree of anisotropy and adjustable chemical functionality. [1]

Solid-state NMR spectroscopy has emerged as a powerful technique for investigating the atomic-level structure and dynamics of solid materials. [2] One of the key advantages of NMR, its ability to provide detailed information about the local atomic structure of materials, is particularly important for 2D materials, which often have highly anisotropic structures that can be difficult to characterize using other techniques. In this contribution, we investigated two types of 2DMs: transition metal carbides/nitrides (MXenes)[3] and covalent organic frameworks (COFs), using various solid-state NMR experiments.

The structure of 2D COFs and MXenes was investigated with solid-state NMR MAS spectroscopy detecting ^{1}H, ^{11}B, ^{13}C nuclei by employing techniques like cross polarization (CP), heteronuclear correlation spectroscopy (HETCOR) and the back-to-back (BABA) NMR multiple pulse sequence. Fast-spinning ^{1}H MAS NMR spectroscopy could be established as a powerful method to visualize and quantify defect and edge sites in 2D COFs.[4] ^{11}B MAS NMR spectroscopy at variable field strength was applied in order to study the coordination state of surface-exposed ^{11}B nuclei in MXenes.

Future research in this field could focus on developing new methods for enhancing the sensitivity and resolution of solid-state NMR spectra, as well as combinations of solid-state NMR spectroscopy with other analytical techniques to provide a more comprehensive understanding of 2D materials.

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UV-C driven reduction of nanographene oxide opens path for new applications in phototherapy

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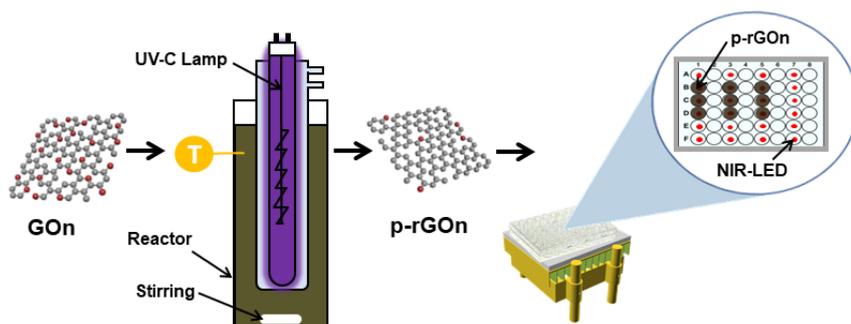
- **New nanosized, water stable and biocompatible PTT agent**
- **New NIR-LED system to evaluate PTT agents efficacy *in vitro***

The main challenges associated to the application of graphene-based materials (GBM) in phototherapy are obtaining particles with lateral nanoscale dimensions and water stability that present high near-infrared (NIR) absorption. Nanosized graphene oxide (GOn) is stable in aqueous dispersion, due to the oxygen functionalities on its surface, but possesses low photothermal efficiency in NIR region. GOn total reduction originates reduced nanographene oxide (rGOn) that presents high NIR absorption, but poor water stability. [1] In this work, partially reduced nanographene oxide (p-rGOn) has been produced by GOn UV-C photoreduction. Different irradiation times (2–12 h) were tested to determine the optimal point for obtaining a partially reduced material that is still water-stable, but displays the ability to convert NIR light into heat. 8 h of UV-C irradiation was identified as the optimal value, yielding a p-rGOn that remains well dispersed in water for at least 6 months and possesses strong photothermal efficiency. After 30 min of NIR irradiation, an aqueous p-rGOn 8 h dispersion (250 µg mL^{-1}) attains 57.2 °C, corresponding to a temperature increase of 26.4 °C. Its mean lateral nanoparticle size was 188 ± 99 nm, measured by TEM. Finally, after 24h incubation with p-rGOn 8 h (150–250 µg mL^{-1}) no significant effects have been observed in human skin fibroblasts (HFF-1) cell viability, demonstrating its high potential for use in the biomedical field, namely in photothermal therapy. Furthermore, an innovative custom-built NIR LED-system has been successfully developed for *in vitro* tests.

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Functionalizing 2D transition metal dichalcogenides with electron-accepting phthalocyanines

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Due to the unique properties of 2D transition metal dichalcogenides (TMDs) the preparation of these materials has attracted immense interest, in particular the liquid phase exfoliation and subsequent liquid cascade centrifugation, obtaining size selected TMDs in their semiconducting 2H-phase [1]. This opens up possibilities in tuning the electronic properties though functionalization, particularly pyridyl-zinc phthalocyanines (Pcs) with variable electron accepting strengths [2] awarded positively doped TMD nano-hybrids. We herein report on non-covalent functionalized TMDs with Pcs immobilized onto the basal plane of the exfoliated material [3], which exhibit distinct steady-state absorption and emission spectra. Furthermore, this nano-hybrids present charge transfer character where the electron donor is the 2D-TMD and the acceptor is the Pc which was assessed through steady-state Raman spectroscopy. Furthermore, charge separation was corroborated by femtosecond transient absorption spectroscopy [4] when contrasting to steady-state spectroelectrochemistry.

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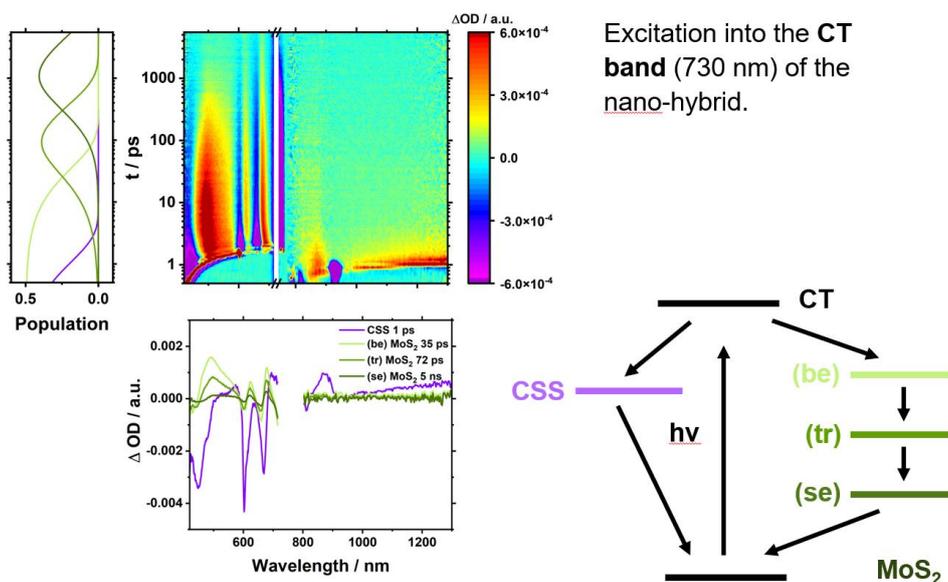
Figure 1: Excited state dynamics of the Pc-MoS$_2$ nano-hybrid where distinct spectral features of the radical anion appear around 850nm.

In the crib: how Graphyne cradles the natural amino acids

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Graphene is widely heralded for extensive applications in distinct, but converging, areas that include nano and regenerative medicine, anticancer/antibacterial approaches, and drug delivery. It can also be the active material for bioimaging, biosensing and photo-therapies (both photodynamic, PDT, and photothermic, PTT).

Graphane is its hydrogen-saturated counterpart, graphyne its acetylene-based 2D analogue. Both of these carbon allotropes are endowed with physico-chemical properties that in some cases improve those of graphene. In biomedicine, graphane and graphyne have generated interest for biosensing and for PTT anticancer therapy. Much of the theranostic potential of these 2D materials relies on their ability to interact with biological targets, which are largely proteins and peptides. [1,2]

A deep knowledge of the interaction underlying the affinity of graphane, graphene and graphyne for proteins is therefore crucial for their nanotechnological and nanomedical applicability.

Here, we investigated the atomistic details of the interaction between amino acids and graphane, graphene, and graphyne. We determined the binding energies of all twenty natural amino acids for these materials by means of Molecular Dynamics (MD) simulations and Molecular Mechanics/Generalized Born Surface Area (MM-GBSA) method.

Aromatic amino acids, such as tryptophan, phenylalanine, and tyrosine, but also arginine with its guanidinium group, show the highest affinity for graphane, graphene and graphyne (Figure 1). This trend is readily understood on the basis of $\pi - \pi$ interactions, which drive the binding.

The "corrugated" surface of graphane displays the lowest affinity towards the amino acids because of the presence of protons that shove the amino acid away from the carbonaceous basal plane. Graphyne has the highest affinity for the amino acids. This 2D material is able to cradle the amino acid increasing the number of interactions.

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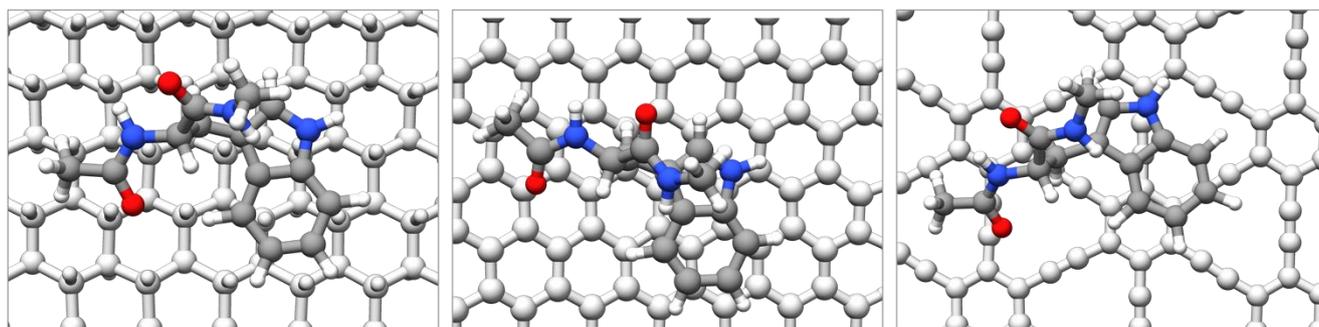
Figure 1: Representation of the interaction of tryptophan with graphane (left panel), graphene (central panel) and graphyne (right panel).

Graphene vs. carbon black supports for Pt nanoparticles: towards next-generation cathodes for advanced alkaline electrolyzers

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The development of efficient and cost-effective water splitting electrolyzers is fundamental toward the path to reach climate neutrality by using renewable energy sources to produce green H^2 as a form of clean fuel. Here, we investigated Pt-based nanostructured cathodes for high-performance alkaline electrolyzers (AELs), showing the beneficial effect of graphene, over traditional carbon black, as nanocatalysts support. Surface-cleaned Pt nanoparticles were produced in aqueous environment and strongly anchored to defect-free graphene flakes, the latter produced through wet-jet milling exfoliation of graphite.[1,2] Pt/graphene catalysts outperform traditional Pt on Vulcan (Pt/C) in terms of hydrogen evolution reaction (HER) activity and performance durability.[3] The 2D morphology of graphene flakes strongly retains the catalysts in the electrode even in the absence of any binder, allowing the exposure of the catalytic sites for the HER. By using commercially available cost-effective anodes, our AELs reached current densities of 1 A cm^{-2} at a voltage of as low as 1.71 V and can even operate up to more than 2 A cm^{-2} (*e.g.*, 2.2 A cm^{-2} at 1.90 V), with stable performance during accelerated stress tests. Our study discloses two main aspects: 1) graphene is an effective conductive support[4,5] for nanocatalysts for the development of nanostructured cathodes, ensuting endurance performance; 2) the use of efficient nanostructured cathodes can boost the AEL's performance to state-of-the-art values reported for proton-exchange membrane electrolyzers, avoiding the use of expensive anodes (*e.g.*, Ir-based ones).

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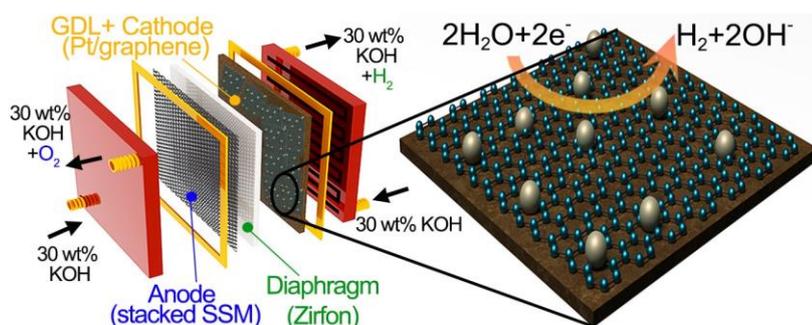
Figure 1: Sketch of our AEL, with Pt/graphene or Pt/C cathode, stacked SSMs anode and Zirfon UTP 220 diaphragm. Operating conditions: 30 wt% KOH electrolyte; atmospheric pressure (1 bar); 80 °C temperature.

Hierarchical Nanocarbon Aerogel Catalysts

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Directed self-assembly of graphene derivatives into structured aerogels and foams is explored as route to create unique, porous catalyst systems with highly-tailored materials characteristics, including hierarchical porosity, mechanical durability, and electro-thermal responsiveness. Here, template-based assembly approaches are explored to produce sponge-like nanocarbon aerogels with a wide range of well-controlled hierarchical microstructures. Different gas-phase and wet-chemical methodologies are developed to enable uniform and structure-preserving aerogel functionalisation with catalyst nanoparticles (anionic clays, mixed metal oxides, precious metals).[1,2] Advanced X-ray micro-CT and FIB-SEM-EDX techniques are employed to characterise the aerogels' three-dimensional microstructure and surface chemistry. Embedding nanoparticles within the aerogels is shown to provide remarkable improvements in functional performance (activity, selectivity, kinetics, recyclability) across a range of chemical applications, including high-pressure CO_2 capture,[1] fine-chemical catalysis,[2] and fuel desulfurisation.[3] Beyond this boost in functional nanoparticle performance, graphene-derived aerogels also provide valuable additional functionality. For example, the electrical conductivity of the interconnected 3D nanocarbon network can be utilised for energy-efficient and very fast direct electrical heating.[4] Ultrafast and ultrahot resistive aerogel heating (>2000°C) is exploited for highly controlled nano-catalyst synthesis and rapid thermal catalyst recycling. Nanoparticle-decorated aerogels are also explored as flow-through catalysts within chemical flow processes, an area of increasing interest due to substantial benefits in process control and sustainability. Specifically, the performance of aerogel catalysts in fine-chemical flow reactions and potential for controlling the chemical reaction profile through aerogel microstructure are explored.

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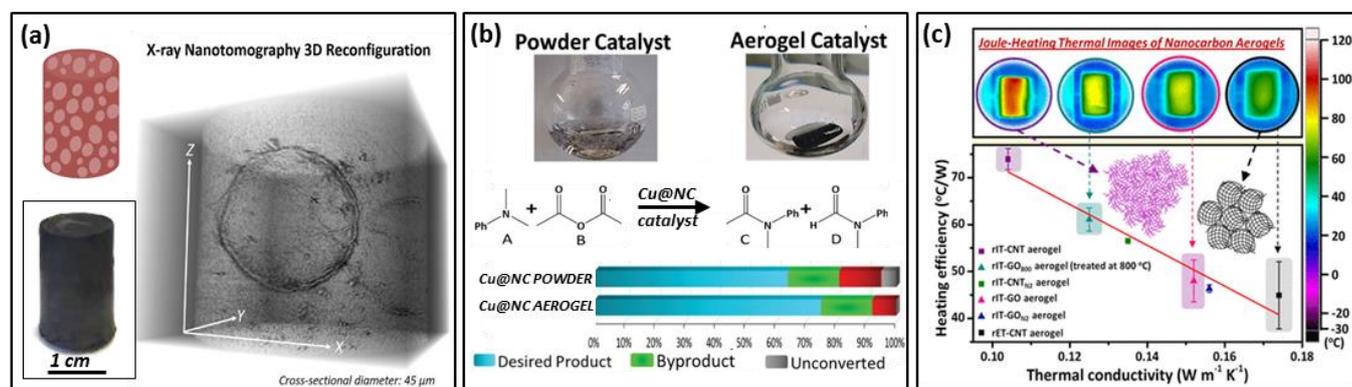
Figure 1: (a) X-ray nanotomography of an emulsion-templated nanocarbon aerogel catalyst; (b) Catalytic performance of metal-decorated nanocarbons in powder and aerogel form; (c) Thermo-electric structure-property relationship study of different nanocarbon aerogels.

DoE-Assisted Development of a 2H-MoS$_2$-Catalyzed Approach for the Production of Indole Derivatives

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Transition metal dichalcogenides (TMDCs) represent a large family of solid compounds with unique electrical, mechanical, and optical properties.[1] Within this group of materials, 2H-MoS$_2$ is an appealing semiconductor material due to its earth-abundant nature, cheapness, and low toxicity.[2] Although 2H-MoS$_2$ has shown promising catalytic activity for various energy-related processes, its use in the catalysis of C-C bond forming reactions to yield useful organic compounds is still largely unexplored. The lack of examples in organic synthesis is mostly a consequence of the intrinsic difficulties of using bulk 2H-MoS$_2$ (*e.g.*, low surface area), which implies the use of high catalytic loadings for obtaining acceptable yields.[3] This aspect renders the overall optimization process more expensive, difficult, and tedious. In our research, we have focused on the development of a 2H-MoS$_2$-mediated synthesis of valuable bisindolylmethane (BIM) derivatives (**3**),[4] using indoles (**1**) and benzaldehydes (**2**) as starting materials. Notably, with the aid of Design of Experiments (DoE) method, we have effectively established the optimal reaction conditions while also identifying the critical parameters affecting the catalytic performance of commercial 2H-MoS$_2$ powder (Figure 1).[5] Lastly, we have demonstrated that the catalytic system has large versatility and good tolerance towards functional group variations of the reagents. M. Morant thanks Margarita Salas grant (MS21-041) from the Universitat de València

Lewis Acid Sites: Unsaturated "Mo" atoms
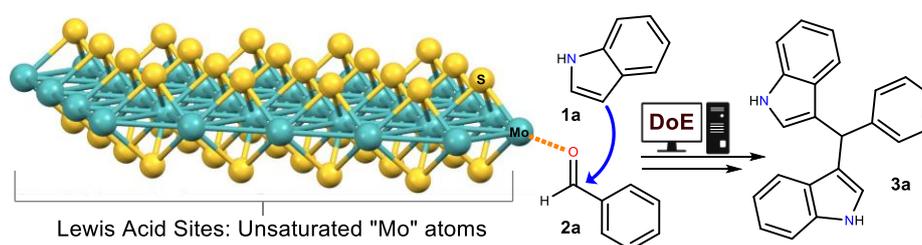
Figure 1: Schematic representation of the reaction between 1a and 2a to give 3a catalysed by bulk 2H-MoS$_2$.

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Graphene derivatives for electrochemical sensing

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Graphene equipped with specific chemical groups would be a wonder material for sensing applications. Synthesis of such graphene derivatives directly from graphene is, however, hampered by its low reactivity. Graphene oxide and its reduced forms are chemically complex materials. Chemistry of fluorographene represents a promising strategy for obtaining controllable and well-defined graphene derivatives. [1] Our lab introduced a wide portfolio of graphene derivatives via this approach and demonstrated their potential in wide range of applications including sensing,[2-5] catalysis [6-8] and energy storage. [9-11] A two-step synthesis leads to graphene acid, i.e., graphene bearing ~10-15% of covalently grafted carboxyl groups on both sides [12]. Graphene acid is perfectly water dispersible, biocompatible, and conductive (~25 S/m) material. These features predispose it as an electrode material for electrochemical sensing applications. Graphene acid can be further conjugated with other molecules,[12] enzymes [13] and nucleic acids [4,5] via carbodiime or click chemistry.[5] Using click chemistry, a selective aptamer can be immobilized and used as a successful platform for the selective determination of ampicillin in real samples in the presence of interfering molecules. The constructed electrochemical aptasensor displays a detection limit of 1.36 nM, high selectivity among other antibiotics, storage stability of 4 weeks and is effective in real samples. This strategy enables fast and simple construction of various (bio)sensors.

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Superconductivity in Organic-Ion Intercalated MoS_2

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MoS_2 exhibits degenerate semiconductor behavior characterized by exotic phenomena such as charge density waves (CDWs) or superconductivity when doped within a specific range of charge carrier concentrations.[1] Achieving this carrier doping level typically involves ionic-liquid gating or alkali-ion intercalation.[2,3] However, the potential of organic intercalation of transition metal dichalcogenide to reach similar milestones remains largely unexplored. Organic chemistry offers an extensive range of intercalating compounds, potentially capable of inducing novel, exotic electronic behaviors that would otherwise be unachievable with inorganic intercalates. Here, we present the first observation of superconductivity and a CDW state emerging in MoS_2 intercalated using Cetyltrimethylammonium Bromide (CTABr) and tetraethylammonium Bromide (TEABr). We demonstrate that these correlated electronic phases depend significantly on the intercalated cation. A fully developed zero-resistance state is only observed in bulk crystals, but not in thin flakes of TEA-intercalated MoS_2. We attribute this effect to the presence of 3D superconductive paths, which are severed upon mechanical exfoliation of the crystals. Our results establish organic-ion intercalated MoS_2 as a platform to study the emergence and modulation of correlated electronic phases.[4]

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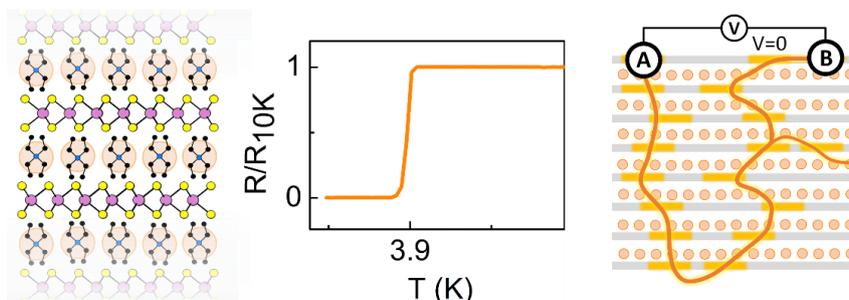
Figure 1: The intercalation of TEA^+ cations in MoS_2 leads to the emergence of superconductivity in bulk MoS_2 due to the formation of percolating path resulting from the alignment of nanoscale-sized highly doped regions located in contiguous layers.

2D-Layered Amorphous Metal Oxide Gas Sensors (LAMOS): perspectives and gas sensing properties

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The intrinsic thermodynamic instability ($\Delta G < 0$) of 2D exfoliated TMDs/MCs/TMTHs (Transition Metal Dichalcogenides/Metal Chalcogenides/Transition Metal Trihalides), demonstrated by their spontaneous oxidation in dry/wet air laboratory conditions [1], represents a great opportunity to grow, by suitable thermal treatment, template-self-assembled, amorphous-metal-oxides (a-MO_x) skin-layers over crystalline 2D exfoliated TMDs/MCs/TMTH.

Departing from liquid phase exfoliated TMDs/MCs/TMTHs, annealing in air at temperatures below the crystallization temperature of the native oxide, either amorphous/crystalline 2D-heterostructures a-MO/TMDs [2-3], or fully oxidized amorphous 2D a-MO_x interfaces can be prepared [4] with unexploited surface properties.

Herein we demonstrate that the oxidation/amorphization process can be applied to a large variety of exfoliated TMDs (WS_2), MCs ($SnSe_2$) and TMTH ($CrCl_3$) where sulfur, selenium or chlorine atoms can be easily displaced by O_2 atoms under controlled oxidation conditions, producing 2D layered n-type a-WO_3, a-SnO_2 and p-type a-Cr_2O_3 2D-flakes spin coated as thin film, with excellent sensing properties to H_2, NH_3, H_2S, NO_2 gases and long term stability properties. LAMOS, preserving all the surface to volume advantages of their 2D precursors, open new perspectives for a novel generation of layered amorphous semiconductors with unexplored interaction mechanisms with the environment.

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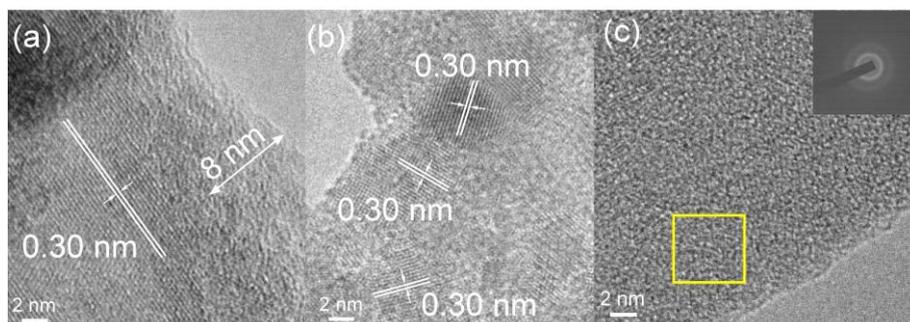
Figure 1: HRTEM pictures of (a) Liquid phase exfoliated $SnSe_2$ flakes displaying the presence of an amorphous oxidized edge (a-SnO_2) over crystalline of $SnSe_2$; (b) $SnSe_2$ flakes annealed in air at 250 °C for 1 week displaying a patchwork of amorphous/crystalline a-SnO_2/$SnSe_2$ phases; (c) $SnSe_2$ flakes annealed in air at 250 °C for 2 weeks displaying a fully oxidized amorphous 2D a-SnO_2 phase (SAED patterns in the inset) [4].

PEC based Self powered Photodetector and sensors using Hydrogen-terminated 2D Germananes and silicene

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The last two decades have belonged to various 2D materials such as graphene, black phosphorus (BP), and transition metal compounds. These 2D materials offer a wide range of applications ranging from sensors, photodetectors, energy storage, catalysis, to health monitoring.[1-3] Recently, 2D monoelement materials (Si, Ge, Sn, and other group 14 elements), also referred to as "Xen", have attracted great scientific and technological interest and have become recent favourites of scientific research thanks to their structure comparable to graphene, band opening by spin-orbit coupling, tunable band gap, and 2D quantum confinement effect, and offer great future potential.[4] In particular, germanane silicane (the single layer of germanium and silicon), [5] which exhibits mixed sp^2/sp^3 hybridization with a predicted compatible band gap of about 1.65 eV (GeH) for optoelectronic applications , shows excellent carrier mobility and quantum Hall effect. Here, we have successfully exfoliated a layer with hydrogen terminated germanene and silicene composition (Ge-H, $Ge_{0.75}Si_{0.25}H$ and $Ge_{0.5}Si_{0.5}H$) of alloyed $Ca(Si_{1-x}Ge_x)_2$. The monoelement photoelectrochemical (PEC) device exhibited self-powered broadband photodetection in the range of 385 to 940 nm with unprecedented responsivity and detectivity on the order of 168 μAW^{-1} and 3.45×10^8 cm $Hz^{1/2}$ W^{-1}, respectively, under the illumination of 420 nm LED light. In addition, 2D germanene and silicene showed excellent sensing capability for organic vapours with ultrafast response and recovery time of less than 1 s. Finally, the photocatalytic activity in the form of hydrogen evolution reaction was investigated due to the suitable band alignment and catalytic activity. This novel material with the mentioned fascinating phenomenon will pave the way for practical future applications in optoelectronics and sensing.

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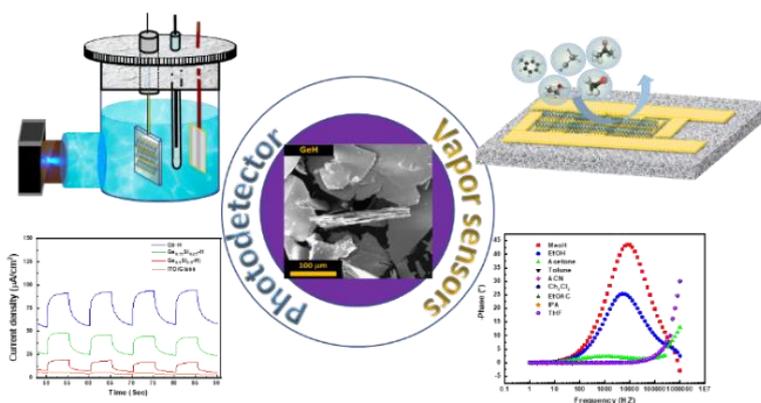
Figure 1: Hydrogen terminated two-dimensional germanane/silicane composites, a self-powered, ultra-sensitive and ultra-fast broadband photodetector, and sensors

Modulation of charge carriers in TMDs using covalent chemistry

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2D materials belong to a class of nanomaterials characterized by extreme thinness down to the nanometer regime and thus often do not have a bulk phase. Apart from this peculiar physical nature, these materials also display a wide variety of interesting electronic and optical properties that are sought in various nanoelectronic applications. One of the representative examples of 2D materials is the subclass of layered materials known as transition metal dichalcogenides (TMD) like molybdenum disulfide (MoS_2). Single layer (sl) MoS_2 in its 1H phase is semiconducting and fluorescent. It also may exist in a metastable metallic phase termed 1T-MoS_2. Due to its ultrathin nature, the properties of sl-MoS_2 are influenced by various external and internal factors.[1] Chemical functionalization can be a promising means for controlled modulation of properties in these materials.[2] A large number of molecular functionalization approaches have focused on the more reactive, metallic 1T-phase to modulate its sensing and catalytic properties.[2,3] The functionalization on 1H-MoS_2 is less explored, but given its distinctive optoelectronic properties, will also be equally important going forward.

In this contribution, I will present results on the covalent functionalization of CVD grown sl-MoS_2 and using diazonium chemistry. Attachment of aryl groups carrying different functional groups with varying electronic nature ranging from strongly electron donating to strongly electron withdrawing was studied using Raman and photoluminescence spectroscopies. We observe that the changes in the property correlate well with the electronic nature of the functionalization layer.

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Figures

Factor change in PL: 0.74 ± 0.02   Factor change in PL: 1.40 ± 0.15   Factor change in PL: 1.59 ± 0.11
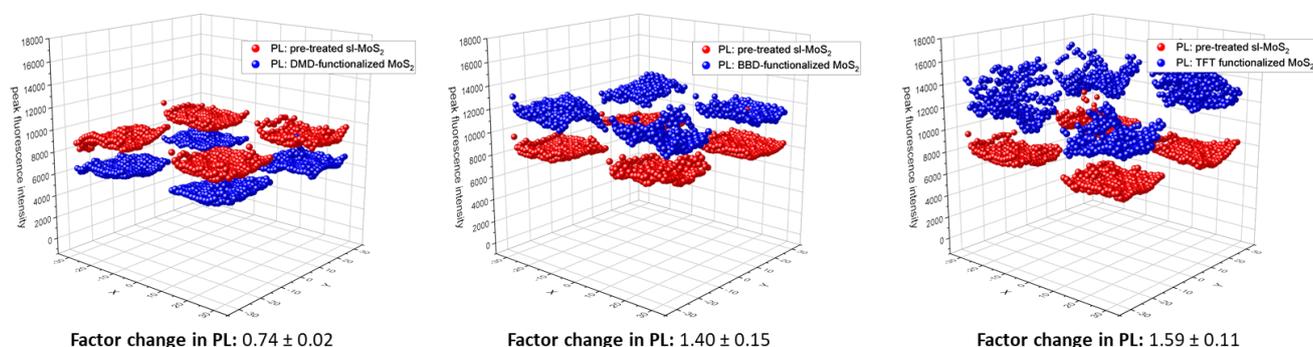
Figure 1: Spatial maps of photoluminescence intensity of single layer 1H-MoS_2 before and after covalent attachment of a functionalized aryl group.

Graphene/MXene based self-assembling structures for energy storage applications

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Abstract

The morphology of nanomaterials has significant influence on their properties and the performance of the devices made of such materials. Creating 3D structures by self-assembling 2D nanomaterials could dramatically improve the overall performance of 2D materials for energy storage and conversion, especially where high surface area and porous structure are needed. Template-assisted methods are the most popular way to fabricate 3D structure. Freeze-casting using ice as template is considered as an environmental-friendly and simple method. However, it is still challenging to achieve the desirable 3D structures due to the uncontrollable ice crystals growth and the limitation of 2D materials dispersion in the system. I will present an innovative method that we developed recently based on self-assembling 2D materials, as example graphene and MXenes, into 3D hollow spheres (Fig. 1). Differently from the 3D porous network obtained from conventional freeze-drying method,[1] such innovative and simple method allow us to prepare uniform graphene/MXene hollow spheres with controllable size and spherical structure. In this way, we produced a series of graphene hollow spheres with different size and 3D structure. Advanced *in-situ* characterization methods were used to understand the formation of the 3D hollow structures.[2] Used as electrode materials, the 3D hollow spheres exhibited superior electrochemical performance in terms of specific capacitance and rate capability thanks to their spherical structure. Our method is very simple and can be scaled up for industrial synthesis, with great potential for practical applications.

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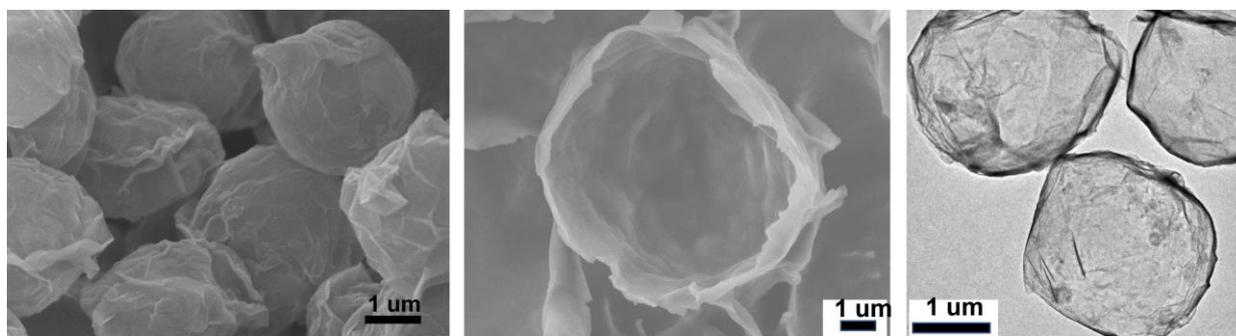
Figure 1: The SEM and TEM images of as-prepared graphene/MXene hollow spheres.

Tuning the magnetism of NiPS₃ and MnPS₃ through organic ion intercalation

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Organic ion intercalation is a powerful tool to tailor the physical properties of layered materials [1-3]. Here, we report on the tuning of the magnetic properties of antiferromagnetic NiPS₃ (T_N = 155 K) through electrochemical intercalation of tetrabutylammonium ions (TBA⁺), followed by cobaltocenium ($Co(Cp)_2^+$) – TBA⁺ exchange in solution (Figure 1a)[4]. On the other hand, MnPS₃ was processed in aqueous solutions of four alkylammonium bromide salts (R_4NBr, with R_4 = tetramethyl, tetraethyl, tetrabutyl, cetyltrimethyl), leading to the corresponding hybrid intercalates via direct cation exchange. X-ray diffraction, Raman, and gravimetric studies were carried out for structural characterizations. Finally, magnetometry measurements revealed the suppression of pristine antiferromagnetism and the emergence of molecular-dependent ferrimagnetism for both intercalated host materials. We found that $TBA_{0.25}NiPS_3$ (T_C = 78 K) and $[Co(Cp)_2]_{0.25}NiPS_3$ (T_C = 98 K) show doping-induced magnetizations in the order of 10^{-2} μB/atom (Figure 1b) [4]; conversely, the four R_4N-MnPS₃ intercalates (T_C ~ 45-55 K) display a guest's size-dependent magnetism with saturation magnetization reaching up almost 1 μB/atom. Our results establish organic ion intercalation as an effective tool to control the magnetism of layered magnetic materials.

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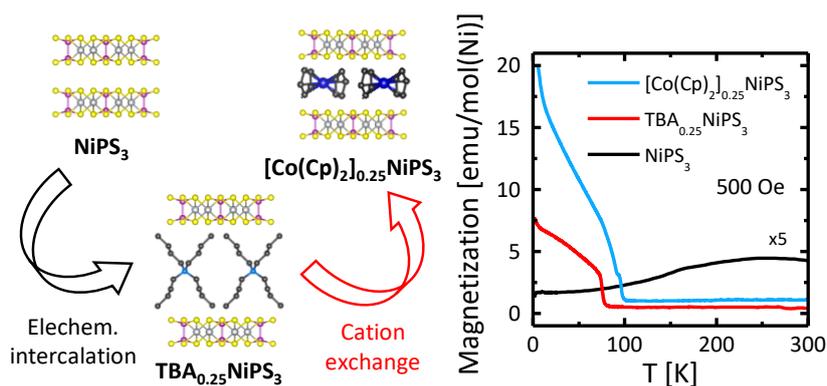
Figure 1: a) Schematic of the two-step intercalation process for NiPS₃: electrochemical intercalation of TBA⁺ ions is followed by a TBA⁺/Co(Cp)₂⁺ exchange; **b)** Molar magnetization vs. temperature of pristine NiPS₃, $TBA_{0.25}NiPS_3$ and $[Co(Cp)_2]_{0.25}NiPS_3$.

Electrodeposition of Transition Metal Dichalcogenide Thin-films from Non-aqueous Solvents

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Transition metal dichalcogenides (TMDCs) are an interesting group of 2D materials characterised with a layered structure analogous to graphene and they possess unique electronic and optical properties, especially when in the few- and mono-layer form. Developing scalable techniques for depositing TMDCs is a major challenge which needs to be overcome to fabricate functional devices with these materials. Electrodeposition is an industrially relevant technique that has some key advantages over other conventional deposition methods. It is a low cost and easily scalable technique and could be used for obtaining complex nanoscale features and for depositing over topologically demanding surfaces. Even though the electrodeposition of MoS_2 has been achieved both in aqueous and non-aqueous electrolytes, not much progress has been made in the deposition of other TMDC materials. Tungsten based TMDCs such as WS_2 and WSe_2 are shown to be very promising materials in different applications, however electrodepositing them remains extremely challenging. One of the major obstacles here is developing electrochemically active precursors which are compatible with the electrolyte system and able to deliver both the tungsten and chalcogens to the electrolyte. Controlling and optimizing the deposition process to obtain few- and mono-layer TMDCs is another challenge. In addition, the choice of substrates for deposition is very important, especially for direct growth of ultra-thin TMDCs. Electrodeposition, being a bottom-up deposition method, would benefit from an atomically thin and smooth substrate such as graphene for depositing few- and mono-layer TMDCs.

Here we present non-aqueous electroplating as a scalable alternative technique for tungsten-based TMDC deposition, with WS_2 and WSe_2 as examples. Tailored single source precursors were developed to use in non-aqueous electrolytes. WS_2 was electrodeposited from dichloromethane (CH_2Cl_2) using the $[NEt_4]_2[WS_2Cl_4]$ precursor. WSe_2 was then electrodeposited from acetonitrile (CH_3CN) electrolyte using $[WSeCl_4]$ as the precursor. Electrochemical quartz crystal microbalance (EQCM) studies were performed to optimize the deposition process and to probe the mechanism of precursor electrochemistry. Electrochemical deposition parameters were then carefully adjusted to obtain few- and mono-layer TMDCs. Patterned graphene electrodes were used as an atomically thin and smooth platform for the deposition of few- and mono-layer WS_2. Few-layer TMDC films obtained on graphene were found to be much smoother than films deposited on other standard substrates such as titanium nitride (TiN) or Pt. These TMDC/graphene structures gave interesting 2D heterostructures which are technologically important for different applications.

Solution approach for smart asymmetric 2D heterostructures

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Asymmetrically decorated nanoparticles (NPs), also known as Janus NPs, possess two or more differently functionalised surfaces and this biphasic morphology gives rise to a complex coexistence of properties within one particle [1]. The general synthetic routes commonly designed for spherical NPs could also be extended towards less studied Janus two-dimensional (2D) monolayers. In general, asymmetric functionalisation of 2D materials is achieved through exposing their faces to different local environments, most commonly, by masking one of the surfaces with a substrate [2]. During past few years, considerable attention has been drawn towards asymmetric decoration of molybdenum disulfide (MoS_2) widely known for its appealing optoelectronic properties [3]. These properties can be finely tuned by designing heterostructures on the basis of semiconductive MoS_2 and switchable bistable molecular systems, such as spin-crossover (SCO) complexes. So far, the heterostructure reported by R. Torres Cavanillas et al. [4], based on SCO NPs covalently grafted on semiconductive MoS_2, was demonstrated to experience controllable modulation of its optoelectronic properties upon application of external stimuli. Meanwhile such symmetric hybrids had been successfully processed in solution, their asymmetric analogues are commonly prepared *via* physical deposition on a solid substrate [5]. In this work we aim to address this gap and explore the possibility of creating Janus-hybrid composed by SCO NPs covalently anchored onto semiconducting MoS_2 using solution approach assisted by easily removable polystyrene microspheres.

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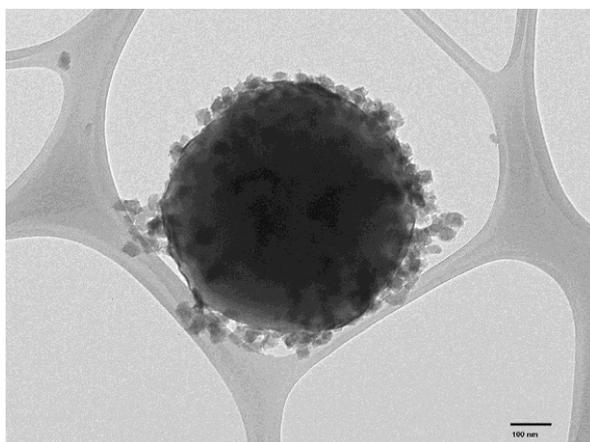
Figure 1: TEM image of SCO NPs grafted on exposed surface of MoS_2 deposited on polystyrene microsphere

Ionic Liquids – Graphene Interface: Effect of ions of Ionic liquids on the Fermi Level

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Electrochemical energy storage devices receive significant attention due to their sustainability and reliability. In order to meet the energy demand, it is imperative to fabricate high-energy and high power-density electrochemical energy storage devices.

Graphene-based supercapacitors using ionic liquids (ILs) as electrolytes are an important class of energy storage devices.[1] The research activities in this field focus on the energy density of these devices. Since energy storage and conversion take place at the graphene – ILs interface, it is important to develop experimental and theoretical procedures to understand the interfacial nanostructure in graphene-based supercapacitors where ILs are used as electrolytes.

In the first part, we will focus on how the adsorption of a homologous series of 1-alkyl-3-methylimidazolium tetrafluoroborate (C_nMIM BF_4, n = 2, 4, 6, 8 and 10) ionic liquids (cation size) influences the interfacial nanostructure and its impact on graphene electronic structure using experimental and theoretical studies. Raman spectroscopy showed that adsorption of the ILs led to n-type doping of graphene and the magnitude of such doping increased as the length of the alkyl chain attached to the cation increased (cation size).[2]

In a second part, we will focus on the interfacial nanostructure of 1-butyl-3-methylimidazolium-based ILs with different anions (X = SCN, BF_4, DCA, PF_6, TFO and TFSI) and its impact on the electronic structure of graphene using molecular dynamics (MD) simulations and Raman spectroscopy. The latter reveals that small anions cause n-type doping of graphene and the magnitude of such doping decreases as the size of the anion increases. This contrasts the trend observed for cations. MD simulations provide insight in these opposing trends.

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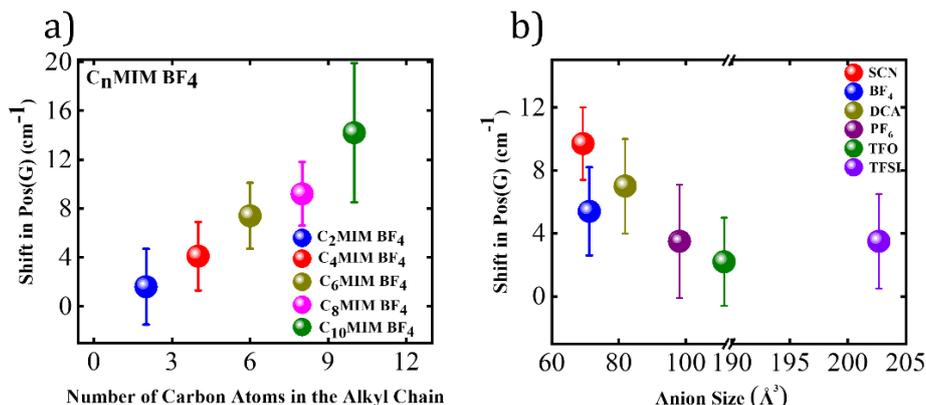
Figure 1: (a) Shift in Pos(G) versus the number of carbon atoms present in the alkyl chain on the imidazolium cation. (b) Shift in Pos(G) versus anion size.

On-Water Surface Synthesis of Two-Dimensional Polymer Membranes toward Effective Ion Transport

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Synthetic two-dimensional polymers (2DPs) are an emerging class of structurally-defined crystalline materials that comprise covalent networks with topologically planar repeat units. Yet, synthesizing 2DP single crystals via irreversible reactions remains challenging. Herein, utilizing the surfactant-monolayer-assisted interfacial synthesis (SMAIS) method, few-layer, large-area, skeleton-charged 2DP (C2DP) single crystals were successfully synthesized through irreversible Katritzky reaction, under pH control. The resultant periodically ordered 2DPs comprise aromatic pyridinium cations and counter BF_4^- anions. The representative C2DP-Por crystals display a tunable thickness of 2-30 nm and a lateral size of up to 120 μm^2. Using imaging and diffraction methods, a highly uniform square-patterned structure with the in-plane lattice of a = b = 30.5 Å was resolved with near-atomic precision. Significantly, the C2DP-Por crystals with cationic polymer skeleton and columnar-like pore arrays offer a high chloride ion selectivity with a coefficient up to 0.9, thus ensuring the integration as the anion-selective membrane for the osmotic energy generation. In addition, as the graphite electrode skin, we demonstrate that C2DP enables to prevent the cation/solvent co-intercalation into the graphite electrode and suppress the consequent structure collapse, leading to enhanced durability of Li battery. Our studies reveal a route to synthesize 2DP single crystals using a kinetically controlled irreversible reaction and will propel the development of membrane-based energy-conversion and storage technologies.

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Figures

1) Skeleton-charged framework
2) Irreversible linkage

1) Large-sized single crystal
2) Columnar-like pore arrays

As membrane for osmotic power generator

As the artificial skin for the graphite cathode in Li battery
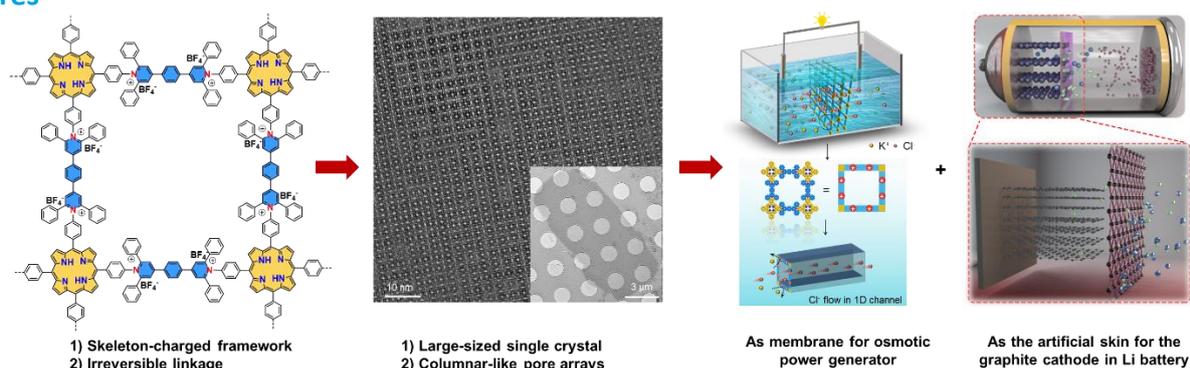
Figure 1: On-water surface synthesis of charged 2DP single crystal as the membrane for osmotic power generation, and electrode skin for Li battery.

Electrochemical synthesis of metal sulfide/3D-graphene composites for energy storage applications

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Electrochemical synthesis is a powerful tool for the fabrication of nanostructured materials such as metal/alloy plating and oxide/sulfide semiconductors. Especially, direct electrodepositing functional materials on conductive substrates has attracted intensive attention for battery, supercapacitor and electrocatalysis application. In this work, we report a two-step approach combining electrophoretic deposition (EPD) and cathodic electrodeposition (CED), to fabricate multilayer hierarchical electrodes (Figure 1) of reduced graphene oxide (rGO) and mixed transition metal sulfides ($NiCoMnS_x$, NCMS) [1,2]. The process is performed directly on conductive electrodes applying a small electric bias to electro-deposit rGO and NCMS in alternated cycles, yielding an ideal porous network and a continuous path for transport of ions and electrons. A fully rechargeable alkaline battery (RAB) assembled with such electrodes gives maximum energy density of 97.2 Wh kg^{-1} and maximum power density of 3.1 kW 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}). The approach can be used to assemble multilayer composite structures on arbitrary electrode shapes.

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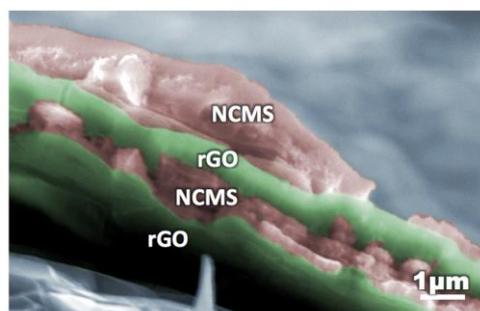
Figure 1: SEM image of the multilayer rGO/NCMS structure.

In situ x-ray quantitative investigation of the grown of 2D TiS$_2$ transition metal dichalcogenide prepared by hybrid ALD/MLD

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Transition metal dichalcogenides (TMD) are receiving great interest in the past few years due to their future applications in super-capacitors, batteries, electronics and optoelectronics etc [1]. Lamellar titanium disulfide TiS$_2$, which consists of S-Ti-S layers separated by van der Walls gaps, is also considered to be integrated into emerging energy devices such as rechargeable batteries [2]. Ultra-thin films of TiS$_2$ are equally technologically challenging to prepare in large-scale production for device application. Among the various growth methods, atomic layer deposition (ALD) is the technique that could produce a high-quality ultra-thin film of TiS$_2$ in a controlled manner [3]. Recently, our group has demonstrated the controlled growth of TiS$_2$ ultra-thin films by a two-step process composed of (i) ALD/MLD step using inorganic and organic precursors (tetrakis-dimethylamido titanium and 1,2-ethanedithiol); (ii) annealing under Ar/H$_2$ atmosphere [4]. This work aims to understand both steps, i.e. the reaction of precursors with the substrate and subsequent growth cycles using *in situ* monitoring by X-ray. The growth of ultra-thin films has been carried out on thermal SiO$_2$ on Si substrate in a custom-built portable reactor designed to be installed on the 6-axis diffractometer of beamline SIRIUS at SOLEIL Synchrotron for in situ characterization [4]. X-ray fluorescence (XRF), X-ray reflectivity (XRR) and X-ray absorption spectroscopy (XAS) have been performed *in situ* during the sample growth and the subsequent

Figure: Experimental and simulated XANES spectra at Ti K-edge for the first half cycle. Insets show experimental setup and possible bonding with surface.

annealing, to understand and control the growth mechanism. The XAS measurements have been performed at both the Ti and S K-edges.

To understand the initial growth process, Density Functional Theory (DFT) calculations have been performed to obtain the best suitable model structure. The DFT-optimized structures are used to simulate the XANES spectra, and the initial model is revised until the best matching. The analysis gives an atomistic view of the mechanism underlying the initial growth cycles with a quantitative approach (*in situ* XAS and DFT). The quantitative analysis of S K-edge data gives stronger evidence of the formation of TiS$_2$ ultrathin layers at the final stage.

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Amino acid modified graphene as smart material for glyphosate capture and electrochemical detection

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Analytical tools to assess the presence of organic pollutants in water are urgently required to map, prevent and, eventually, reduce the risks related to drinking water consumptions. The integration of sensor systems in the water distribution plans is attracting great interest due to the possibility of performing a continuous water monitoring. Although electrochemical sensors seem to be the most suitable solution for this application, the use of such analytical devices is limited by the fairly high concentration levels which they can detect. This prompted us to focalize our efforts in the development of materials capable to transduce the recognition event only after a massive adsorption of the target. Due to the recognized adsorption capability of graphene oxide (GO) derivatives[1] and the advantages relying in the use of these materials in electrochemical sensing,[2] we direct our attention in the synthesis and application of GO derivatives bearing aminoacidic residues (GO-AA), which are capable to strongly interact with selected organic contaminants.[3] Glyphosate (GLY) was chosen, among various organic contaminants, as a case of study for this study, due to the concerns related to its occurrence in several water compartments.

Figure 1: Schematic representation of the double role of GO-AA: adsorption, i.e. pre-concentration, and following electrochemical detection of chemical pollutants

Adsorption and electrochemical tests demonstrated that GO-AA outperform the pristine unmodified material for GLY detection in water. Molecular dynamic simulations allowed us to ascribe the origin of this enhanced performance to the chemical interactions arising between the AA residues and GLY. Preliminary tests of the applicability of GO-AA for the real time monitoring of GLY in water are also reported.

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Highly sensitive and selective chemical sensing with functionalized 2D MoS₂: a supramolecular approach

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The relentless escalation of industrial and agricultural activities has resulted in a dramatic increase in diverse pollutants released into the environment worldwide.[1] To address such an environmental challenge, the development of new robust chemical sensors allowing the monitoring of the water composition efficiently and rapidly is highly sought after. Liquid-phase exfoliated two-dimensional (2D) transition metal dichalcogenides (TMDs) are suitable candidates for chemical sensing thanks to their high surface-to-volume ratio, sensitivity to the environment, unique electrical characteristics, and scalable processing.[2] However, pristine TMDs lack selectivity due to non-specific analyte-nanosheet interactions. To overcome this drawback, defect engineering enables controlled functionalization of 2D TMDs. Here, we develop ultrasensitive and selective MoS₂-based sensors for heavy metal Co^{2+} ions via the covalent functionalization of defect-rich MoS₂ flakes with a specific receptor, i.e. 2,2':6',2''-terpyridine-4'-thiol. A continuous network is assembled by the healing of MoS₂ sulfur vacancies in a tailored microfluidic approach, which guarantees high control over the assembly of thin and large hybrid films. The Co^{2+} cations complexation represents a powerful gauge for low concentrations of cationic species which can be best monitored in a chemiresisitive ion sensor, featuring a 1 pM limit of detection, sensing in a broad concentration range, high sensitivity combined with high selectivity towards Co^{2+} over K^+, Ca^{2+}, Mn^{2+}, Cu^{2+}, Cr^{3+} and Fe^{3+} cations. This supramolecular approach based on highly specific recognition events can be adapted for sensing other analytes such as ions and (bio)molecules through the ad-hoc design of the specific receptor.[3]

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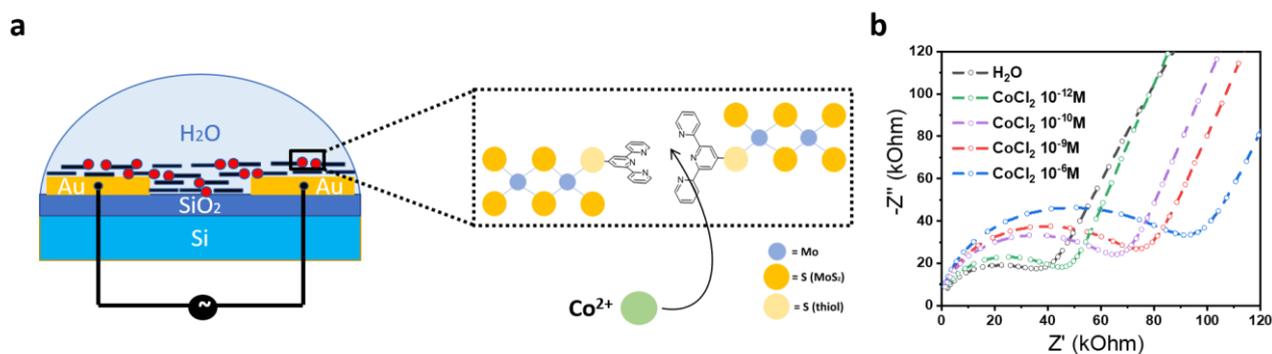
Figures

Figure 1: (a) Schematic representation of the device architecture. (b) EIS signal evolution upon Co^{2+} concentration increase.

Cation-controlled wetting properties of vermiculite membranes and its promise for fouling resistant oil–water separation

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Abstract

Oil/water separation has attracted great interest as it has direct practical application for resolving the problem of industrial oily wastewater1-4. Therefore, the development of novel materials for efficient oil-water polluted waste treatment is imperative. Engineering surface chemistry to precisely control interfacial interactions for fabricating superior antifouling separation membranes is important. Here we present super wetting surface, lithium-exchanged vermiculite laminate. We find that vermiculite laminates can be tuned from superhydrophilic to hydrophobic by exchanging the cations on the surface and in the interlamellar space; hydrophilicity decreases with increasing cation hydration free energy, except for lithium. Based on these findings we address a major challenge for oil–water separation technology.

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Colloidal Synthesis of 2D-Pnictogens: Antimonene and Bismuthene

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The mono elemental 2D-materials based on allotropes from group 15, called *Pnictogens* (P, As, Sb, and Bi) have emerged as one of the most promising families of 2D-materials beyond graphene. 2D-Pnictogens have been highlighted as excellent candidates in a great variety of applications due to the outstanding properties that they exhibit, including layer-dependent bandgap, pronounced chemical reactivity, and strong spin-orbit coupling, to name a few. These 2D-materials can be isolated using top-down approaches, for instance, micromechanical and liquid-phase exfoliation. However, the utilization of top-down methods yielded unsatisfactory outcomes because of the challenging interlayer interactions present in the bulk material, hindering the large-scale production of high-quality material. [1,2] To overcome this challenge, a new bottom-up approach has been recently reported, involving a solution phase synthesis of well-defined hexagonal few-layer antimonene via anisotropic growth,[2] which has facilitated large-scale production of this material. In this context, we optimized the synthetic parameters for producing high-quality few-layer antimonene hexagons, and their implementation in a scalable process under continuous-flow conditions to pave the way for optoelectronic device fabrication.[3] Furthermore, we have recently developed a novel synthesis of anisotropic few-layer bismuthene hexagons based on colloidal chemistry showing outstanding electronic properties.[4,5] In this contribution, we will show the potential of the colloidal synthesis approach for the preparation of electronic-grade high-quality heavy 2D-Pnictogens.

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Aerosol-Assisted Chemical Vapor Deposition of MoS$_2$ and ZnS Thin Films

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Transition metal dichalcogenides (TMDCs) are versatile two-dimensional (2D) materials that have unique optical and electronic properties. Amongst them, molybdenum disulfide (MoS$_2$) and zinc sulfide (ZnS) have attracted attention due to their semiconductor nature. Remarkably, MoS$_2$ shows a thickness-dependent bandgap that ranges from 1.2 eV for bulk (indirect bandgap) to 1.9 eV for monolayer (direct bandgap). Furthermore, ZnS exhibits a similar property with a large bandgap from 3.26 eV to 3.7 eV. The band gap of these materials laying from the near-infrared to the visible and ultraviolet range of the electromagnetic spectrum potentially makes them suitable for photodetectors and photovoltaics [1]. Various deposition techniques such as physical vapor deposition (PVD) and chemical vapor deposition (CVD) have been successful growth methods of monolayer MoS$_2$ [2]. However, these methods have had limited success in the synthesis of crystalline 2D ZnS thin films. Moreover, there are still great challenges on scalable production in terms of large-area uniform growth. Here we demonstrate that the epitaxial growth, by an Aerosol-Assisted Chemical Vapor Deposition (AACVD) method, [3] results in large area coverage (~1 cm^2) of MoS$_2$ on different substrates (Si, SiO2, glass, hBN, and HOPG). The morphology and thickness of MoS$_2$ can be tuned by precursor concentration and/or growth temperature allowing for the engineering of different structures such as nanorods, snowflake-like structures, and 2D layers as thin as 40 nm (see Figure 1). The AACVD method is also successful in the synthesis of ZnS thin films of 400 nm thickness. The growth of 2H-MoS$_2$ and Wurtzite ZnS was confirmed by X-ray diffraction (XRD), Raman, and electron-dispersive X-ray (EDX) spectroscopies. Raman analysis indicates that the grown MoS$_2$ structures show a substrate-dependent strain. On the other hand, ZnS crystalline growth can only be successfully achieved on smooth surfaces such as glass and exfoliated Indium selenide layers on SiO$_2$ indicating substrate dependency [3]. The successful growth of 2H-MoS$_2$ and Wurtzite ZnS offer the prospect for large-area device fabrication that exploit distinctive optical and electronic properties.

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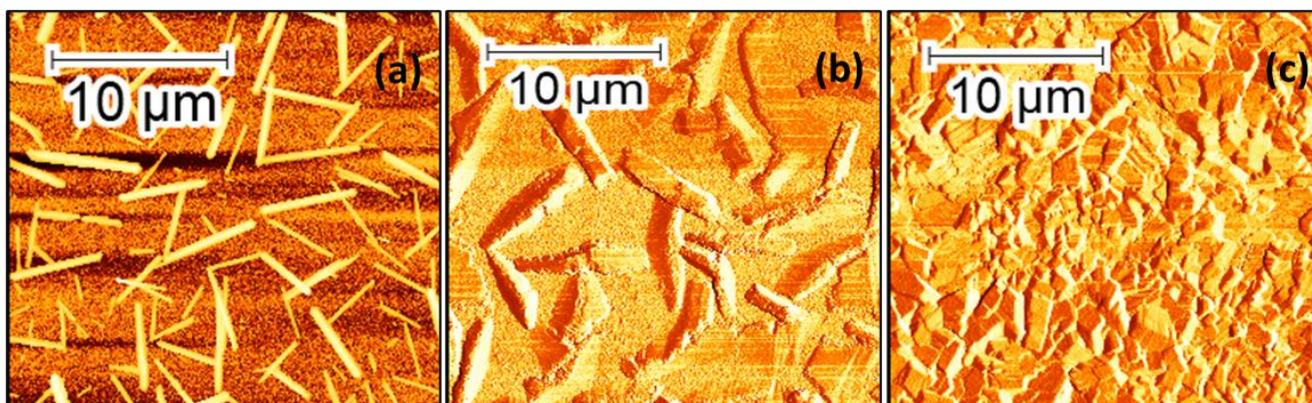
Figure 1: AFM image of MoS$_2$ nanorods (a), snowflake-like structures (b), and 2D layers (c) on glass substrates.

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Bipolar electrochemistry for functionalization of 2D materials

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After the isolation of graphene monolayer graphene 2D materials have garnered great attention for their theoretically predicted exceptional properties. Covalent functionalization strategies are used to further finetune and improve these properties, which allow to integrate these materials into a wide range of applications. However, these strategies need highly reactive conditions, which do not guarantee a control over the degree and homogeneity of functionalization of the surface. Moreover, existing methods do not allow the functionalization of non-conductive surfaces and not much work has been done on 2D materials besides graphene. Additionally, there is a need in obtaining these 2D materials in a scalable fashion to be viable for industrial application. In this work we propose a scalable, low cost, facile method to achieve both exfoliation and functionalization in one-pot using bipolar electrochemistry for the production of 2D material in dispersions. Bipolar electrochemistry applies a high voltage to the electrolyte cell, and a gradient of the electric field occurs over the cell which induces the polarization of material placed between two electrodes. The polarization drives simultaneous reduction and oxidation reactions at the opposite poles of the placed material. This opens possibilities of functionalization of inert and semiconductor materials. The material is characterized with a range of techniques including Raman, AFM and TEM.

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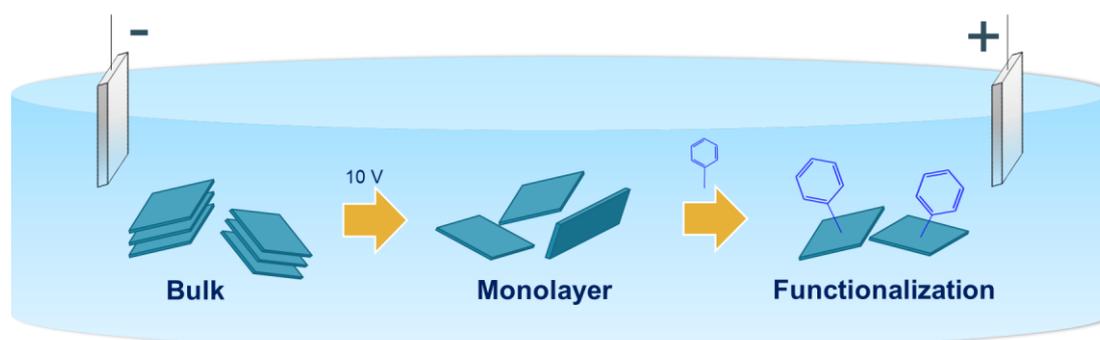
Figure 1: Schematic of the one-pot exfoliation and functionalization bipolar approach.

Polysulfone-Graphene Oxide Hollow Fiber Membranes for Advanced Water Remediation

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Water sources are increasingly affected by chemical contamination by emerging contaminants, e.g. chemicals for industrial uses, pharmaceuticals, personal care products, heavy metals, and perfluoroalkyl substances. Standard water purification technologies are inefficient or ineffective in the removal these pollutants from water, thus they represent a severe risk for the health of humans and the ecosystem. Nanomaterials, in particular graphene related materials, represent a promising source of technologies for the selective and highly efficient removal of such substances and ions from water. Here, we report on composite polysulfone-graphene oxide (PSU-GO) membranes showing synergic ultrafiltration and adsorption capabilities, and on their application for drinking water purification from emerging contaminants. Doping with amount lower than 5% w/w of GO resulted in membranes with porosity lower than 6 nm and related filtration modules with permeability of 300 L/h/bar*m^2 (as the standard PSU ones). These modules showed an adsorption efficiency of up to 14 µg/g toward a mixture of PFAS, to >1000 µg/g toward some heavy metals. These results outperform those of granular activated carbon, the industrial sorbent benchmark, in the same conditions (2 µg/g and 100 µg/g, respectively). No release of GO from the modules was proved by surface enhanced Raman spectroscopy (SERS), at the current state of the art detection limit for GO nanosheets in water (0.1 µg/L). [1-3]

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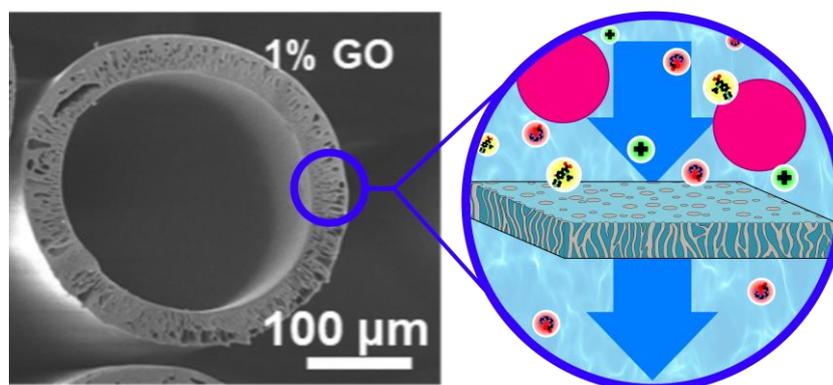
Figure 1: SEM image of a polysulfone-graphene oxide (PSU-GO) hollow fiber, and scheme of its functions.

Functionalized Graphene Oxide as sensing element for the amperometric detection of Na$^+$ and K$^+$ in sweat

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Recent events have shown the need to develop new wearable sensing devices for continuous monitoring of biomarkers present in sweat or saliva, as well as of giving early detection of specific diseases. However, the detection of biomolecules in complex biological fluids is not trivial, due to low concentrations, the presence of a huge number of interfering species and of the great variability of the composition of the matrix. Conventional electrochemical biosensors base their detection in the selective recognition of specific analytes, and this limits their reliability. For this reason, we are focusing our attention on the realization of a **multisensor platform** which achieves quantitative detection of the analytes by combining the responses from different sensors and elaborating them using a deep learning approach (Fig. 1).

As work in progress, we describe here a multisensor platform for the quantification of Na$^+$ and K$^+$, which are main electrolytes present in sweat. The detection of these species, generally performed by a potentiometric transduction, is here demonstrated for the first time with an amperometric approach combined with a deep-learning algorithm. The sensing strategy takes advantage of the peculiar properties of graphene oxide when acting as the sensing element in amperometric sensors: the versatility of this material is here exploited for the stable anchoring of selected receptors, namely metal hexacyanoferrates [1] and crown ethers [2], involved in the recognition of Na$^+$ and K$^+$.

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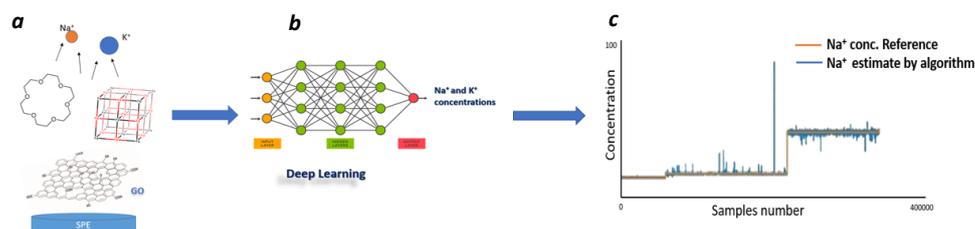
Figure 1: sensing strategy by deep learning involving *a)* development of screen-printed electrodes (SPE) involving functionalized graphene oxide, *b)* elaboration of the amperometric responses by artificial neural network, *c)* verification of the accuracy of the prediction models.

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Hybrid Spinterfaces for Organic Antiferromagnetic Spintronics

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Spinterfaces, i.e. interfaces between an organic semiconductor (OS) and a ferromagnetic (FM) substrate, have been raising an ever increasing interest in the last two decades, first through the realization of organic spintronics prototypical devices, then by showing new intriguing phenomena related to the formation of hybridized interface states [1]. As a promising development of the spinterface approach within the rapidly developing fields of *Antiferromagnetic (AF) Spintronics* and *AF Magnonics* [2], we have been extending those concepts to OS/AF interfaces, within an ongoing EU-FET project [3], during which we have been investigating different combinations of AF oxides, in particular Cr_2O_3, NiO and CoO, interfaced to various organic molecules, in particular belonging to the families of Metal-Tetra Phenyl Porphyrins (MTPP; e.g., CoTPP) and Metal Phthalocyanines (MPc; e.g., FePc) [4]. Both kind of molecules are ideal candidates for building spinterfaces, since their ion core can have its own magnetic moment, due to the presence of unpaired spins [5].

Here, we are going to present the concept of our project, where the spinterface represents a true 2D magnetic nanosystem, along with a series of results related to the growth and characterization (including crystalline, morphologic, electronic and magnetic properties) of selected spinterfaces. An example of the surface morphology of a molecular 2D layer of CoTPP on FeO/Fe is reported in the Figure. In many cases, those properties can be compared to computational results based on first-principle theoretical approaches (see, e.g., Ref. 6), which will also be briefly introduced.

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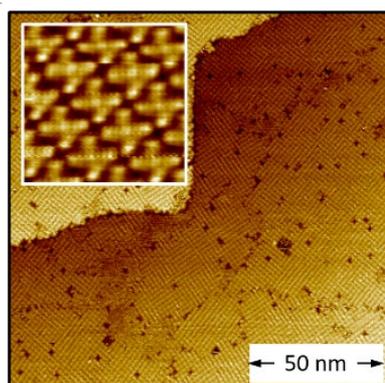
Figure 1: STM image of 1 ML Co-TPP on Fe(001)-*p*(1x1)O. Inset: high resolution scan 5.3x5.3 nm^2.

A scanning probe view on the photoreactivity of all-organic Core@Shell Nanoparticles: the effect of photoinduced charge separation from enhanced neuronal photostimulation to in vivo tunable ROS production

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Thiophene-based core@shell nanoparticles are characterized by a core made of P3HT polymer, surrounded by its oxydized form, namely P3HT@PTDO NPs. Photo chemical and physical characterizations show that such nanoarchitecture results in a quite unique all-organic type II interface, which, in addition to the soft and biocompatible nature, makes the material a promising platform of a variety of applications, particularly in biological fields.

Here, using scanning probe techniques and, more specifically, an extensive use of microscopic and macroscopic Kelvin Force Probe (KPFM and KP), we demonstrate that the surface of core@shell NPs becomes rich in negative charges under light illumination, due to the promotion of photogenerated electrons from the inner P3HT core to the outer oxidized PTDO shell, making them more reactive to the environment (air dopants, water, substrate, etc...).

Combing our results with complementary analysis -including time-resolved photoluminescence (TRPL), femtosecond transient absorption (TA) and electron paramagnetic resonance (EPR)- we show that such peculiar photoreactivity properties can be exploited for: i) efficient photostimulation of retinal neurons[1] and ii) the modulation of ROS generation depending on the shell's oxygenation degree, both in vitro and in vivo[2].

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Single-molecule study of Heck cross-coupling on surface

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The interaction of organic molecules with metallic structures is particularly important in heterogeneous catalysis where metallic particles or surfaces help to overcome energy barriers of chemical reactions. This concept is specifically important for Heck cross-coupling, which relies on a palladium catalyst to form a carbon-carbon bond between two different reagents [1]. Model heterogeneous catalysis reactions can be investigated by scanning tunneling microscopy (STM) on metal single crystals. The role of active sites could be determined [2, 3], and Heck coupling could be induced thermally [4].

We studied firstly the cross-coupling between vinyl-naphthalene (VN) and different halogenated molecules on a Cu(111) surface by STM at low temperatures (7 K). We analyzed the bond of the de-halogenated molecules to different atomic structures of the copper surface. Then, we investigated the manipulation of a single metal-organic intermediate, and analyzed the products obtained from the thermally induced reaction. In this way we obtained insight into the catalytic activity of the copper surface, and the dependence on the surface morphology.

Subsequently, we deposited palladium nano-islands on a relatively inert Au(111) surface. Thus, the same reaction can be studied on this second substrate, and compared with the performance of the copper substrate. The fundamental understanding obtained with this study might allow a rational design of catalyst materials with controlled stability, activity and selectivity, which operate toward specific cross-coupling.

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Bilayer Networks of TTF Derivatives at the Solid-Liquid Interface

Presenting Catarina L. Delfino[1], Yansong Hao[2], Kunal S. Mali[1] and Steven De Feyter[1]

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Abstract

The current work is an endeavour to explore the complementary fields of substrate-induced phases and 2D crystallization, in order to attain a fundamental understanding of the role of interfaces and surfaces upon crystallization. This study strives to further our insight into how the first stages of crystallization occur, i.e. from the moment the first layer of molecules assembles onto the surface, subsequently the second and the third, and so on. Scanning tunneling microscopy (STM) has been employed to investigate the growth and organisation of the self-assembly of tetrakis-(octadecylthio)-tetrathiafulvalene at the solid-liquid interface. The impact of temperature, concentration, solvent solubility over the organisation of networks from the monolayer to the multilayer system is addressed.

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A low cost and rapid approach for producing a conductive graphene oxide-based polycaprolactone composite

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Since the discovery of graphene, diverse graphene-based materials have been extensively studied, for many different applications. One of the most relevant areas aims at obtaining new polymeric composites, in order to strategically unite the unique advantages of graphene, such as its high electrical conductivity, incorporating it to the polymeric matrix [1,2]. However, one of the main challenges in this field is to consolidate a low cost, nontoxic and large scale manufacturing route. This project proposes a new manufacturing route to produce a reduced graphene oxide (rGO) based polycaprolactone (PCL) fibrous membranes. PCL is a biodegradable and biocompatible polymer commonly used in implants and tissue engineering. The GO was synthesized by the modified Hummers' method, being dip-coated on the PCL membranes produced via rotary jet spinning [3], a low cost and high production technique. The obtained PCL-GO presented a poor electrical performance, with high electrical resistance (2-3 MΩ). Then, a thermal reduction of GO was studied, using a hot plate under ambient condition, which is a fast and green reduction route, in order to evaluate the effect of the reduction time and the temperature in terms of electrical resistance variation. The samples were characterized through the X-Ray diffraction, Raman and XPS spectroscopies, thermogravimetric analysis, scanning electron microscopy, and four-point probe for the electrical measurements. The overview of the manufacturing process is shown in the figure 1. The electrical resistance dropped up to 3 orders of magnitude. The results are promising for applying this composite as a biosensor or a scaffold.

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Figures
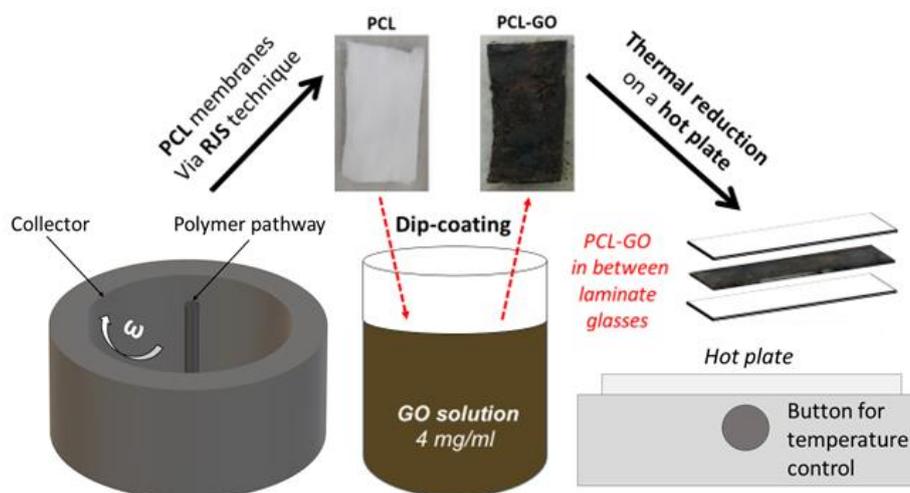
Figure 1: Manufacturing process overview

2D Antimony Oxide by Deintercalation of $K_2(Sb_2O_3)_2Te$

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Perspectives and research on free-standing 2D materials, especially functional materials, promises new chemical and physical properties but also comes with challenges regarding the control of dimensions, minimization of defects, handling, mechanical and chemical damage prevention and many more factors. Utilizing hydroflux synthesizes [1-2] in an equimolar mixture of KOH and water in an autoclave, shiny green platelet crystals of the layered material $K_2(Sb_2O_3)_2Te$ were synthesized. Similar to Sb_2O_3, but unlike K_2Te, the compound is insensitive to air and water. By using ion extraction techniques in presence of crown-ethers under mild conditions, both potassium and tellurium ions can be deintercalated. The crystal morphology does not change significantly, but the platelets are now silvery and mica-like. The composition is Sb_2O_3, but the 3D crystallinity has been lost. We assume that the ferroelectric Sb_2O_3 layers of the initial compound have been preserved and form a metastable polymorph. Since the dipoles of adjacent layers are opposite, it is a repulsive van-der-Waals stack that is prone to delamination.

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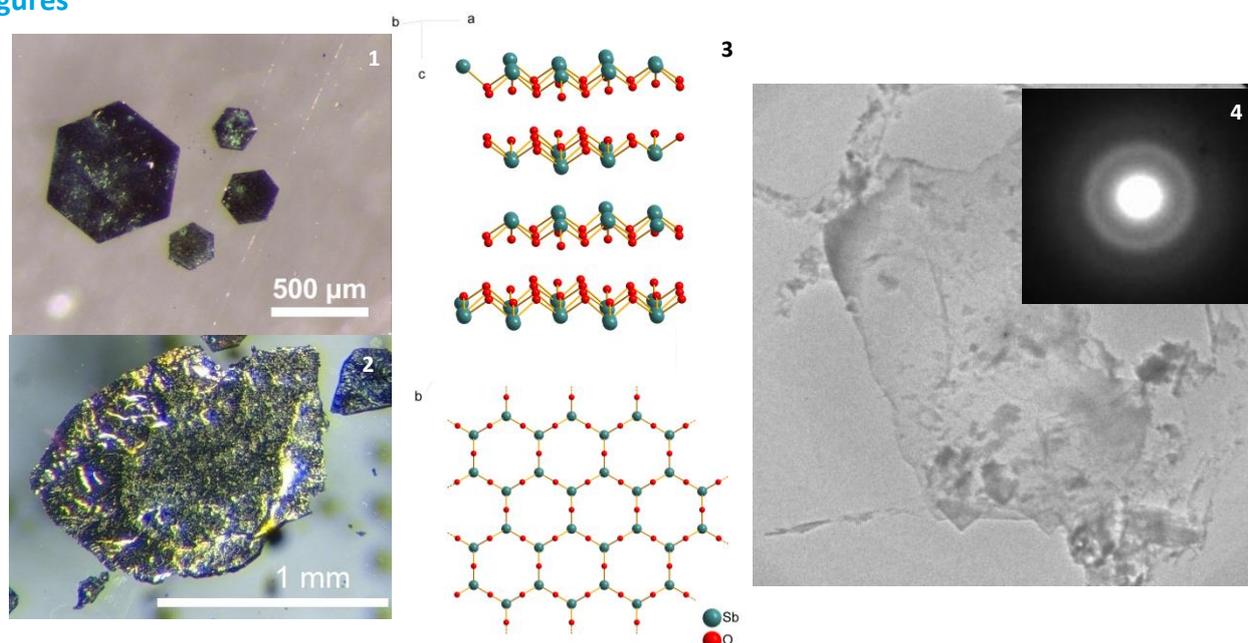
Figure 1: Cystals of $K_2(Sb_2O_3)_2Te$ (1) and layered Sb_2O_3 (2). Sb_2O_3 partial structure in $K_2(Sb_2O_3)_2Te$ (3) and TEM image of exfoliated flakes of metastable Sb_2O_3 (4).

Understanding hydrogen diffusion in between layers of 2D materials

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In 2018, the group of Geim from Manchester performed very interesting experiments, in which hydrogen atoms were transported inside the interstitial space of layered materials, such as hexagonal boron nitride or MoS_2, showing a good sieving of deuterium from protium.[1] We later showed theoretically that indeed hydrogen atoms rather than ions are transported between the layers and reported their diffusion coefficients.[2] We also showed that the transport is assisted by the layer shearing modes. In present work, we investigated the hydrogen diffusion between layers of different transition-metal dichalcogenides (TMDCs), where we studied the influence of possible stackings, stoichiometry, and exemplary twist angles between layers on the self-diffusion coefficients. The calculations were performed using well-tempered metadynamics simulations as implemented in CP2K package,[3] which gives us access to the free energy surface. We found that TMDCs with Se or Mo atoms have lower free energy barriers than these with S or W. Furthermore, structural stackings of MoS_2 (H_h^h(2H), R_h^X (3R), R_h^h, H_h^M, H_h^X) also result in different free energy barriers, varying between 50 and 150 meV, meaning that the corresponding self-diffusion coefficients are in the range of $3.3 - 0.3 \times 10^{-3}$ cm^2 s^{-1}. This study is the first step to understand whether stacking-induced self-diffusion, which most likely depends on the twist angle between layers and the resulting moiré potential, can be optimized to be more directional.

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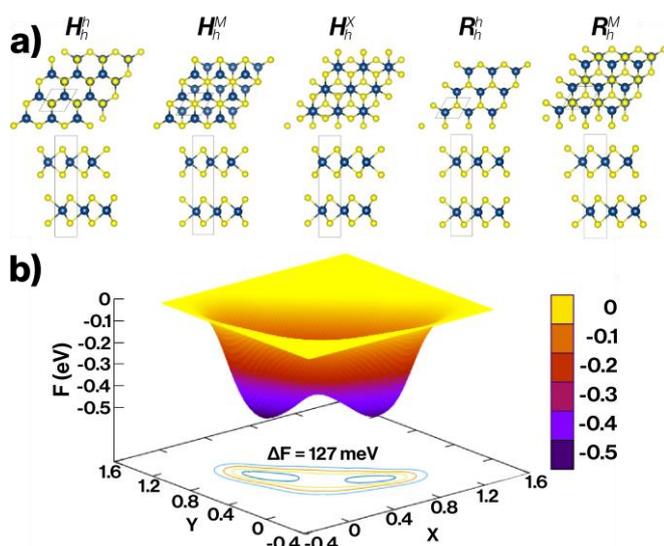
Figure 1: (a) Top and side views of all considered structural high-symmetry stackings. Unit cells are marked with black lines. Blue - Mo, yellow - S.

(b) Free-energy surface (F) of the H transport through interstitial space (also named as collective variables (CV1: X- CV2: y-axis) obtained from well-tempered metadynamics simulations for WS_2.

Graphene-Glial interfaces for the selective modulation of brain signaling

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Abstract

Among 2D nanomaterials, Graphene has emerged as biomaterial interface due to its outstanding properties, including electrical conductivity, mechanical flexibility and biocompatibility. It is now established that implant devices and electrodes for brain stimulation and recording interact apart from neurons, also with glial cells, called astrocytes. However, evidence is lacking on the possibility to use graphene as electrode interface to modulate the functionality of brain astrocytes. Astrocyte Ca^{2+} signaling is important for the regulation of cognitive and vascular functions, and results compromised in many neurological disorders, such as stroke, epilepsy and spreading depression. In this view, understanding the biophysical mechanisms behind the cell/material interaction has remained a critical challenge. Here, we investigate the unique combination of Graphene-oxide (GO) and reduced GO (rGO) coated electrodes to modulate Ca^{2+} signaling in astrocytes by electrical stimulation. Our results indicate that GO/rGO films are biocompatible coating interfaces, promoting the cell growth with no adverse gliotic reactivity [1]. We found that the electrical stimulation can trigger distinct intracellular Ca^{2+} responses in astrocytes, in vitro and in brain slices, depending on the electrical properties of rGO/GO interfaces. Astrocytes stimulated by conductive rGO electrodes show rapid Ca^{2+} response with oscillating peaks, exclusively mediated by Ca^{2+} release from intracellular stores. Conversely, electrical stimulation delivered by insulating GO electrodes causes slower, sustained Ca^{2+} response, mainly due to external Ca^{2+} influx through membrane channels [2]. We propose a bioelectrical model, hypothesizing that the different conductivity of the substrate influences the electric field at the cell/material or cell/electrolyte interfaces, inducing, respectively, the extracellular Ca^{2+} influx or the intracellular Ca^{2+} release. Graphene-glial interfaces might be extremely promising for neural engineering and neuroscience investigation, offering a new way to dialogue and selectively interact with glial cells in the Nervous System [3].

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Ultrasensitive Rapid Cytokine Sensors Based on Asymmetric Geometry MoS₂ Diodes

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Cytokines are small immune system signaling proteins found in body fluids such as blood, saliva, and sweat, that are considered as biomarkers for numerous health conditions and diseases. An abnormal variation in cytokine concentrations is an indicator of uncontrolled inflammatory reactions that has been associated with diseases such as cancer, diabetes, and Alzheimer's. Most diseases, particularly cancers, can often be cured if they are detected at an early stage. Thus, the ability to monitor and detect a slight change in cytokine levels is of great significance for early clinical diagnosis.

In our recently published work [1], we reported the development of biosensors based on asymmetric MoS₂ diodes for rapid, label-free, highly sensitive and specific detection of tumor nercosis factor-α (TNF-α), a representative inflammatory cytokine biomarker.

Our biosensors employ mechanically exfoliated multilayer MoS₂ flakes with asymmetric geometry as the sensing channel, and aptamers (short single-stranded nucleic segments) as the bioreceptors. The sensing area is passivated with a thin aluminum oxide layer (around 5 nm) using atomic layer deposition technique (ALD) to provide available sites for facile functionalization with bioreceptors. Interactions between the immobilized aptamers and TNF-α at the sensor surface induce a change in surface energy that alters the current-voltage rectification behavior of the MoS₂ diode, which can be read out using a two-electrode configuration.

The key advantages of this diode sensor are the simple fabrication process and electrical readout, and therefore, the potential to be applied in a rapid and easy-to-use, point-of-care, diagnostic tool.

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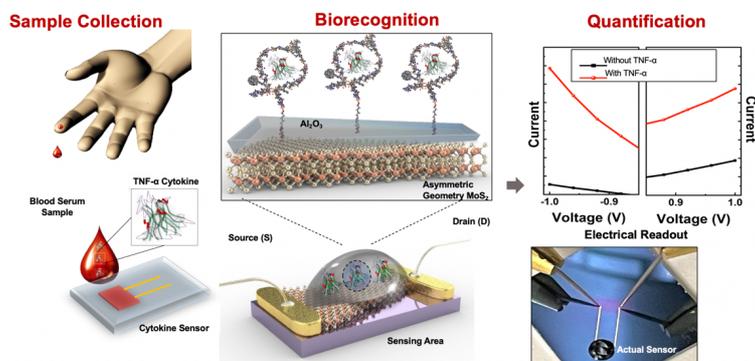
Figure 1: A schematic illustration of the concept of the cytokine sensor operation.

Laser-induced Graphene *in vitro* cytotoxicity

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Laser-induced graphene (LIG) is a versatile and promising material with a wide range of potential applications, and research in this area is ongoing to explore new ways to use this innovative material [1]. The method of LIG synthesis is considered fast, low-cost, and scalable since it can be synthesized by using a laser to burn a pattern onto a substrate (i.e., polymers or paper) [2]. Laser-induced graphene has many potential applications, including energy storage devices, sensors, and biomedical applications [3]. However, little is known about LIG toxicity, which is extremally necessary for medical devices, tissue engineering, wearable sensors, or regenerative medicine applications. For biocompatibility assessment, *in vitro* testing is an essential tool providing valuable information about the potential risks associated with using chemicals and materials in biological systems. In particular, cytotoxicity and proliferation assays are commonly used to assess the potential toxicity of graphene-based materials on living cells. Herein, we reported the *in vitro* study about LIG toxicity in mice fibroblasts (L929) and osteoblast precursor cells (MC3T3).

The cell viability was tested using polyimide discs (PI) and LIG discs through a direct contact test. The LIG was obtained by the direct irradiation of a laser (1.5 W laser power at 405 nm) on PI substrates. The presence of LIG was confirmed by scanning electron microscope images and Raman spectroscopy. For the experiment, the cells were seeded in 96-well plates (10^4 cells per well), and 24h later, the discs were carefully placed on the cell layer. After 48 hours, the cell viability was tested with the XTT protocol. For the cell proliferation assay, cells were cultured at the bottom of each well (6 discs per sample). This way, the cells would grow on top of the discs, and the growth would be compared with cells grown on the plate substrate (Control cells). The cells were cultured for 5 days; then, the cell viability was performed with an XTT assay. The direct contact cytotoxicity test results of both PI and LIG means are statistically different from control cells in terms of cell viability. Still, they are not different from each other. Although the cell viability is lower than the controls, it remained over 70% in both scaffolds, which is considered non-cytotoxicity. While in the proliferation assay, both platforms led to a lower cell proliferation than controls (cells grown on a substrate specifically modified for cell growth). The cell growth on top of LIG scaffolds was even lower (p<0.05), probably due to LIG's surface effect not giving rise to the most favorable conditions for efficient cell adhesion, growth, and proliferation.

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Flexible and electrically conductive polymeric composites for wearable electronics

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Electrospinning of fibers from solution (Figure 1) is the most studied method to produce polymeric nanofibers, because it offers a good compromise between morphology control and scalability. Several polymers can be electrospun obtaining lightweight, flexible textile mats composed by randomly-oriented or aligned nanofibers with nanometric (< 100 nm) or sub-micrometric (from 100 to 500 nm) diameters.

Nanosheets made of Graphene correlated materials can have a lateral size comparable to the nanofiber dimensions, and are an interesting filler for the production of polymeric composites. Electrospun GRMs composites possess enhanced mechanical properties[1] and their nanofibrous morphology confers them a high surface-to-volume ratio, which can lead to a faster response to external stimuli[2]. Nonetheless, the choice of an appropriate technique for the production of the polymeric composite is crucial for the improvement of the electrical conductivity of the material.

In this research activity, we study and optimize the electrospinning of PA6 nanofibrous mats to obtain nanofibers with a controlled diameter in the 300-500 nm range. Previous work[3] showed that co-electrospinning hinders the possibility to obtain electrically conductive GRM-based composites. For this reason, we produced novel materials by coating pristine polymer mats with GO exploiting a sonication-assisted dip coating technique. These coated composites were afterwards reduced both chemically, using Vitamin C, and thermally.

Characterization of these materials confirmed the effectiveness of the electrospinning and coating processes (Figure 2). Electrospun composites showed considerable electrical properties while preserving the mechanical flexibility and the surface morphology conferred by the electrospinning process. Thanks to these unique features, these materials are interesting for wearable electronics and smart textiles, as they can be exploited in different applications (e.g. sensors).

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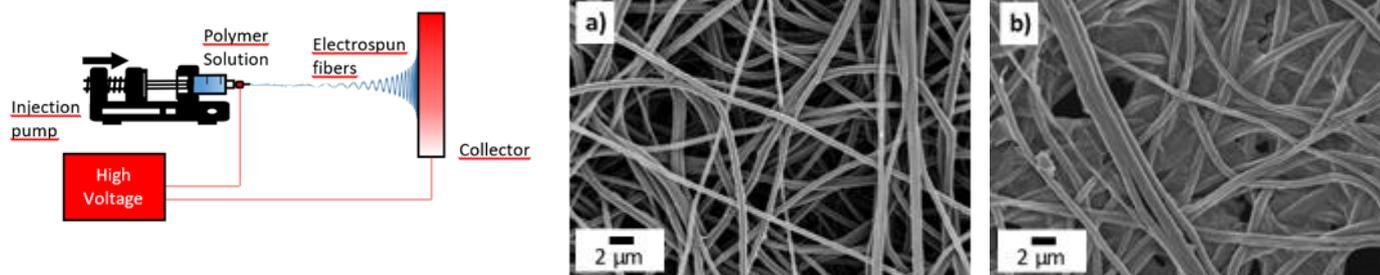
Figure 1: Electrospinning setup schematization
Figure 2: SEM images of pristine electrospun PA6 (a) and rGO-coated PA6 composite (b)

Dipolar linkers as electric field responsive switches for magnetic 2D organic materials

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 A 2D-covalent organic radical framework (2D-CORF) has been chemical-designed from polychlorotriphenylmethyl (PTM) spin-localized radical nodes joined by difluorobenzene dipolar linkers. Density functional theory (DFT) calculations have shown that the linker conformation with respect to the material plane modifies the exchange spin coupling between PTMs, achieving a maximum J coupling variation of 75 cm^{-1}. A set of moderate electric fields have been applied to an isolated diradical excised from the extended 2D-network, revealing significant conformational changes of the linker with respect to the zero-field case, due to the coupling of the linker dipole moment and the electric field. These variations enable electric field induced conformational control [1]. Consequently, the proposed 2D-CORF is a responsive material with intrinsic switches in its structure. Extended 2D-material DFT calculations reveal flat bands whose low dispersion is independent of the linker conformation, a signature of its Mott insulator behaviour. The high spin-localization in the extended 2D-CORF system leads to it having very similar zero field behaviour to the isolated diradical. The strong analogy between molecular and extended system mean that the properties of the latter can largely be understood by relatively computationally inexpensive calculations of the former.

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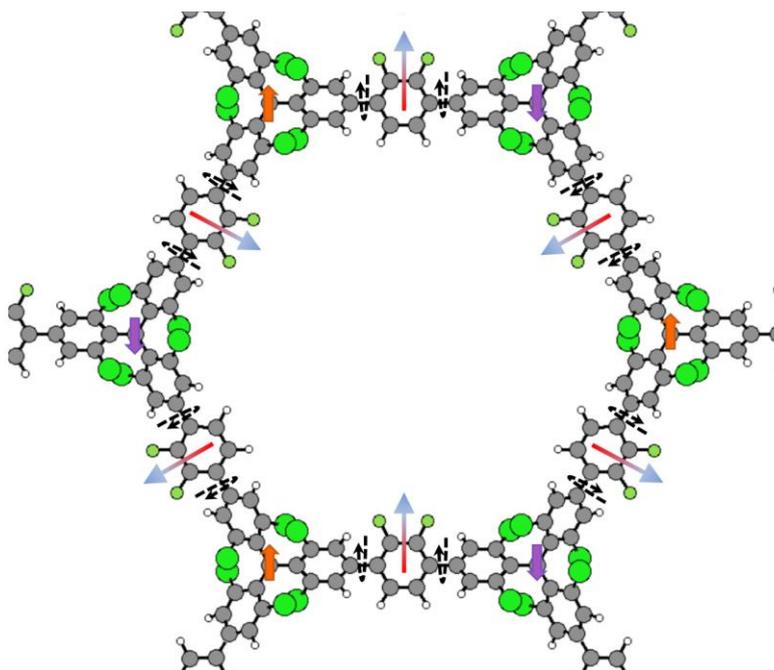
Figure 1: 2D-CORF made of PTM spin centers and dipolar difluorobenzene linkers.

Light-mediated degrafting of covalently anchored moieties from the graphene surface

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Light-mediated controlled covalent grafting and degrafting of functional moieties on the basal plane of graphene have become increasingly popular for devising different graphene substrates for future high-performance devices.[1] The photo-cleavage (degrafting) results in the removal of the addend from the graphene and will yield the re-establishment of the pristine structure (sp^3 to sp^2) without even a point defect. However, we observe that a structural modification occurs during the photo-cleavage of covalently anchored phenyl derivatives from a single layer of graphene sheet at ambient conditions.[2] The modification has been characterized by confocal micro-Raman spectroscopy and AFM technique. The time-dependent Raman spectrum reveals two distinct features during the photo-cleavage especially when the intensity crosses a threshold of 6 MW/cm^2: an unusual broadening of the D band together with the enhancement of G band intensity at the initial stages, while the redistribution of these intensities occurs at later timescale. The combined time-dependent Raman and AFM measurements suggest that laser-induced damage occurs at the highly irradiated region, which subsequently generates amorphous carbon through carbonization of the aryl functional group and graphene.[3,4] On the other hand, molecular desorption dominates in the surrounding less irradiated area. These observation has been validated with different excitation wavelength, power, and time. Furthermore, the AFM analysis also manifests how the heat is being transported to the surrounding area in a single-layer graphene sheet.

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Graphene related materials nanosheets and technologies for drinking water treatment

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Standard Water treatment technologies based on both adsorption and filtration do not allow complete removal of drinking water contaminants. For example, Granular activated carbon (GAC), the benchmark industrials sorbent, fails on metal contaminants and on short chain perfluoroalkyl substances (PFAS), just to mention a few. New materials, approaches and technologies are urgently required to the face the increasing occurrence of Emerging contaminants (EC's) in ground and surface water, ultimately affecting drinking water safety. Graphene-related materials (GRM) have shown great potential in water purification due to the high surface area and multiple interactions pathways with organic molecules. [1] Despite the high number of papers published on GRM promoted adsorption of contaminants, comparison between these materials and standard technologies is not always possible due to the different experimental conditions used. Here we report the comparison of the adsorption properties (kinetics, selectivity, adsorption capacities) of different GRM nanosheets including graphene oxide (GO), reduced GO (rGO), graphene nanoplatelets (GNP) and chemically modified nanosheets.[2][3] A mixture of contaminants of concern (i.e. PFAS, pharmaceuticals and dyes) is considered and the performance are compared to that of GAC through standardized protocol. Molecular dynamic simulations are also exploited for unraveling the interactions driving the adsorption. Finally, in order to overcome secondary contamination, we also describe a scalable and automatized procedure for water purification based on tandem adsorption on GO nanosheets and microfiltration Recovery and reuse of both GO and microfiltration modules is described.[4]

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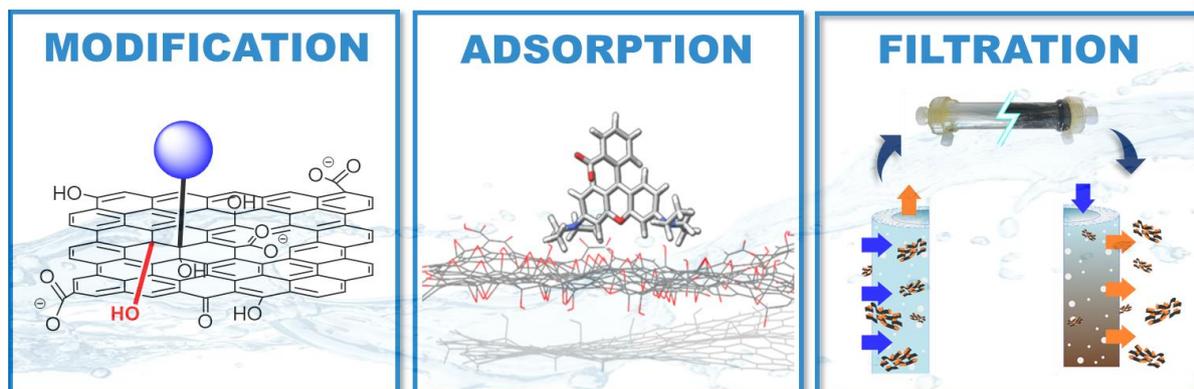
Figure 1: Graphene oxide and modified graphene oxide used as sorbent for drinking water purification.

Conversion of CO2 into valuable chemicals and fuels via photocatalytic reduction reaction by using MoS_2/MoO_3 nanocomposite heterostructure as catalyst.

The conversion of CO_2 towards hydrocarbon fuels via photocatalytic reaction, to solve the environment and energy problem, is a current topic under thorough investigation. The main phenomenon that enables CO_2 reduction is the bending, upon adsorption to a surface, of the molecule in a partially charged CO_2^- molecule with a lower LUMO and, therefore, a lower reduction energy. The most challenging part of the CO_2 reduction reaction is the selectivity due to the multielectron-transfer process, thus the photocatalysts used in CO_2 reduction reaction are of utmost importance. Among those already used as catalysts or co-catalysts, 2D materials such as MoS_2 have shown promising results for photocatalytic reaction of CO_2.

Here, we will show our recent work on 2D material-based nanocomposite for photocatalysis of CO_2 reduction reaction. In this study, 2D MoS_2 has been prepared by Chemical Vapor Deposition (CVD). Then, the MoO_3 powder is spin coated with different parameters, e.g., temperatures, times, etc. on top of the MoS_2 nanoflakes. The heterostructure MoS_2/MoO_3 was used as catalyst for CO_2 reduction to chemicals. The prepared material has been characterized for structural, optical, chemical, electrochemical, and photocatalytic properties towards the selective reduction of CO_2 to chemical fuel.

Solvothermal synthesis of 2D titanium carbo-oxide: High selective gas-sensing and supercapacitor evaluations

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Abstract

Owing to the ever-increasing world population, energy shortage and environmental pollution issues have become hot topics. Therefore, research for innovative new materials to sort out such issues are urgent [1]. Among the known conventional nanostructured materials, two-dimensional (2D) nanomaterials have attracted increased interest due to their outstanding electrical, magnetic, and mechanical properties; make them highly suitable for supercapacitor (energy storage) and gas sensor (environmental monitoring) applications[2,3]. However, the commonly synthesis method of some of these 2D material such as MXene are not simple and involves the etching step of MAX phase via highly concentrated hydrofluoric acid, which, in addition to be highly toxic, generally leads to a high content of -F termination groups on the surface of the material, thus negatively affecting its performances. In this work, we are developing for the first time, to the best of our knowledge, a highly pure new 2D titanium carbo-oxide layered structure, via simple and eco-friendly solvothermal method using MAX phase and tetramethylammonium hydroxide (Figure 1). The full characterizations using XRD, Raman, SEM, HRTEM and XPS confirm the formation of the crystalline 2D titanium carbo-oxide layered structure. The prepared new 2D nanomaterial (which is not MXene usually obtained from MAX Phase) has a very good selective methanol vapor sensing properties at room temperature, which may be useful for environmental monitoring as well as for the non-invasive assessment of gut bacterial activity by measuring methanol in exhaled breath. The evaluation of its supercapacitor in three different basic (KOH), neutral (Na_2SO_4) and acidic (H_2SO_4) electrolytes demonstrates that KOH is the most effective solution to obtain high electrochemical performance. This material is very promising to be applied for some other high-tech applications.

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Figures

Ti_3AlC_2 + TMAOH

After stirring for 15 mins

Hydrothermal, 170 °C, 12 h

Autoclave
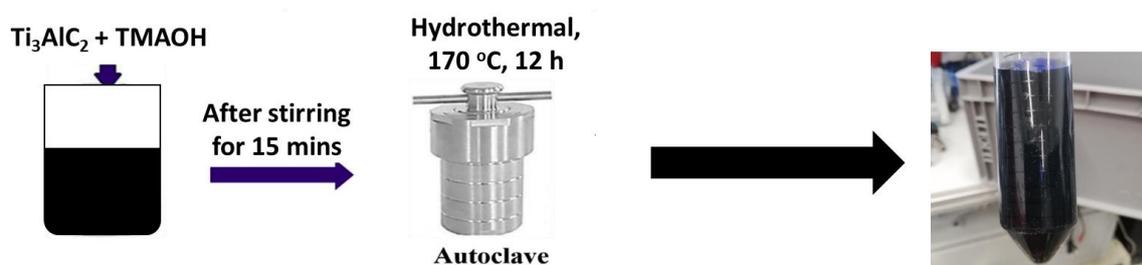
Figure 1: Synthesis route

Preparation of visible light excitable phosphorescent carbon dots and their optical applications

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Room temperature phosphorescent (RTP) materials are attracting more and more the attention thanks to their advantages. Recently, researchers are looking for cost-effective, facile preparation and high performance RTP materials, and carbon dots are one of the targets. However, to synthesize carbon dots with RTP emission is still very challenging, especially for carbon dots to be excited by visible light.[1] So far, dozens of substrates have been applied in preparing RTP carbon dots, such as H_3BO_3, SiO_2, PVA and others.[2] Here, we present a novel strategy to manufacture phosphorescent carbon dots by calcinating the composites which mix green carbon dots (g-CDs) with aluminium hydroxide ($Al(OH)_3$). The processed hybrid materials (g-CDs@Al_2O_3) reveal remarkable properties, showing blue fluorescence and green RTP in an on/off irradiation process at 365 nm. It is noteworthy that, g-CD@Al_2O_3 can also emit yellow RTP after switch off the white light. Besides, this hybrid shows strong resistance in strong basic and acidic condition for 30 days. Finally, this multicolor emissive hybrid has been applied in anti-counterfeiting and encryption successfully. Our method of preparation provides a universal and facile option to obtain RTP carbon dots.[3]

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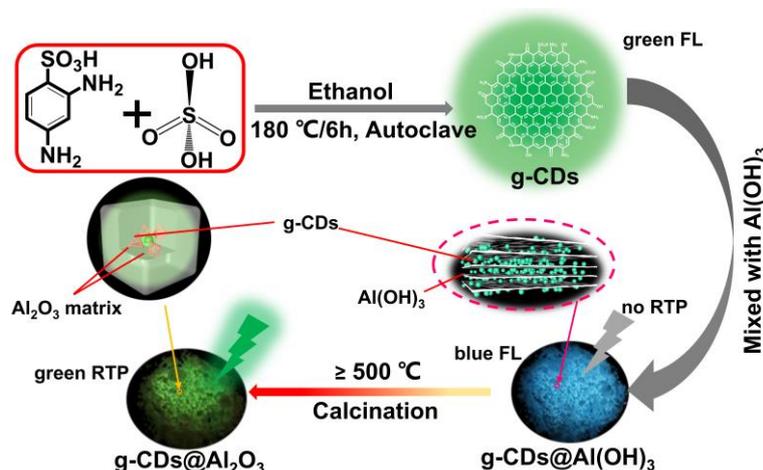
Figure 1: Flow chart illustrating the synthesis of g-CDs@Al(OH)$_3$ and g-CDs@Al$_2$O$_3$ composites.

Spectroscopic insight into single step growth of atomically thin h-BN-graphene heterostuctures on top of curved crystals

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Two-dimensional materials lately attract increasing attention due to their excellent physicochemical properties. Current innovations based on 2D materials are focused on the design of hybrid layers and heterostructures, which allow obtaining new, emerging properties. Simply when considering the advantages offered by each of the 2D materials used, the functional needs in a variety of fields (electrical, photoelectric, biosensing, etc.) can be satisfied. The combination of hexagonal boron nitride (h-BN) and graphene (Gr) is among the most attractive alternatives. On the one hand, the hybrid h-BNC material enables the development of bandgap-engineered applications in electronics and optics, and generally leads to properties that are distinct from those of Gr and h-BN [1]. On the other hand, the interface between Gr and h-BN domains exhibits promising properties, e.g., its unique catalytic behaviour that drives the electrochemical production of H_2O_2 [2]. Finally, in-plane h-BN-Gr heterostructures, consisting of alternating strips of h-BN and Gr, may provide a feasible material platform to realize electrocatalytically switchable high-capacity CO_2 capture [3].

Effective growth of h-BN-Gr in-plane heterostructures can be achieved via chemical vapor deposition (CVD) on transition metal substrates by either using a mixture of chemicals [4], or single molecular precursors [5]. The substrate plays a crucial role in determining the morphology, crystal orientation, domain size, wrinkles etc., thereby defining the physicochemical properties of the emerging material. Real surfaces or nanoparticles contain not only low-index planes, but also steps, defects or additional facets. Therefore, for technological applications it is of high importance to study surfaces containing non-trivial topography. The simplest realization of a non-trivial substrate is a curved crystal, namely a cylindrical section cut and polished around a high-symmetry plane. This geometry allows one to span a full set of vicinal planes featuring arrays of atomic steps. Taking advantage of the smooth variation of the density of steps, one can systematically study their influence on the growth and properties of the resulting 2D material.

Within present study, we have investigated the influence of the density of steps on the number and type of h-BN-Gr boundaries, as well as on the dopant density and character in the h-BN-C monolayer. Moreover, here we compare different substrates: those characterising by weak and strong bonding with h-BN-Gr layers, e.g. c-Ni(111), c-Pt(111) and c-Pd(111).

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High-performance synthesis of amino acids modified graphene oxide for adsorption of emerging contaminants in water

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Chemical modification of surface groups of graphene oxide (GO) has been recently exploited for promoting selective adsorption capability toward several classes of water pollutants, including emerging concern contaminants (ECs)[1]. Here we discuss a family of GO nanosheets covalently modified with different amino acids (Fig 1) and the study of their adsorption properties toward a mixture of selected contaminants, including pharmaceuticals, additives, and dyes. L-glutamic acid, L-methionine and L-lysine (GO-Glu, GO-Met and GO-Lys) were grafted on GO by epoxide ring opening reaction and purified by a scalable and fast synthetic and purification procedure based on microfiltration [2,3]. The obtained materials shows adsorption capacities toward bisphenol A (BPA), benzophenone-4 (BP4), and carbamazepine (CBZ) than those of standard GO and rGO, from 14 mg/g for pristine GO/BPA to 295 mg/g for GO-Lys/BPA. Molecular dynamics simulations highlighted higher interaction energies (-11.9 kcal/mol for GO/BP4 and -22.0 for GO-Met/BP4) for the modified GOs than unmodified GO, as a result of higher van der Waals and hydrophobic interactions between the contaminants and the amino acid side chains on the nanosheet surface4.

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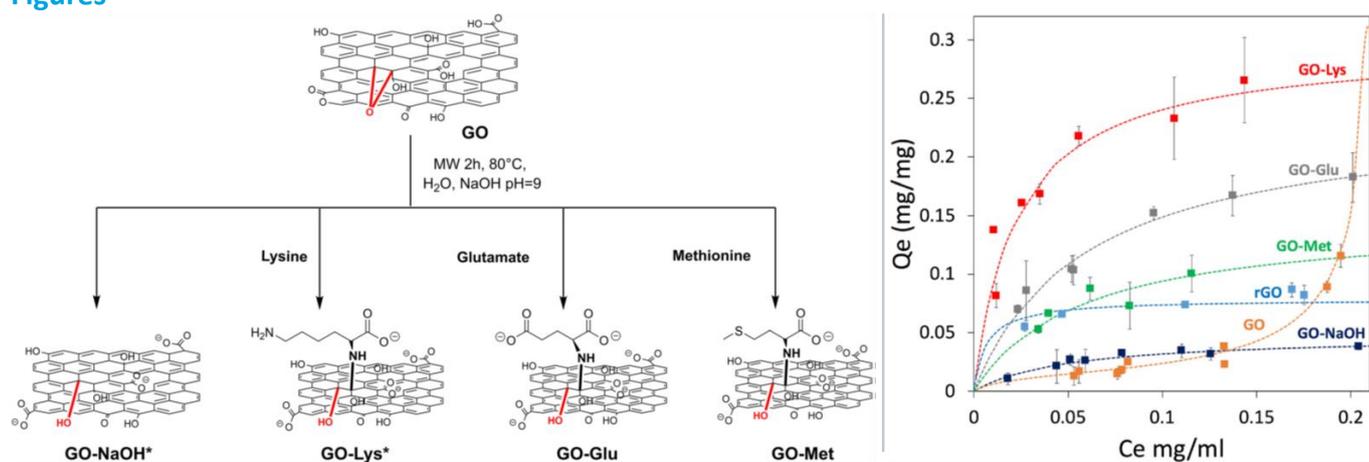
Figure 1: Synthetic pathway to amino acid-modified GOs (left) and adsorption isotherms toward BPA, BP4 and CBZ (right).

Boosting the Electrocatalytic Activity of Chemically Exfoliated MoS₂ by Surface Functionalization

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The vibrant research area on ultrathin two-dimensional (2D) layered materials has continually shown that the unique and superlative properties firstly observed for graphene find a significant equivalence in other 2D materials as the transition metal dichalcogenides (TMDs). The MoS_2 is an important example which has triggered broad and intense investigations. The 2H-to-1T phase conversion is a semiconductor-to-(semi)metal transition with huge impact on its applications, mainly for electrochemical technologies. The surface functionalization of MoS_2 with a wide variety of species such as metal atoms, organic molecules, metallic nanoparticles, and polymers has been explored as an efficient strategy to modify its intrinsic properties [1,2], for multiple purposes and applications, including phase engineering. In this study, by an experimental-theoretical approach, we show how the chemical functionalization of 1T'-MoS2 with iodoacetic acid molecules improves both the structural stability and the electrocatalytic properties of the metallic nanosheets for the hydrogen evolution reaction (HER) (Figure 1). The presence of -CH_2COOH groups on the MoS_2 surface boosts the electrocatalytic effects for the hydrogen evolution reaction, reducing the charge transfer resistance of the interface and preventing the oxidation and deactivation of the active sites.

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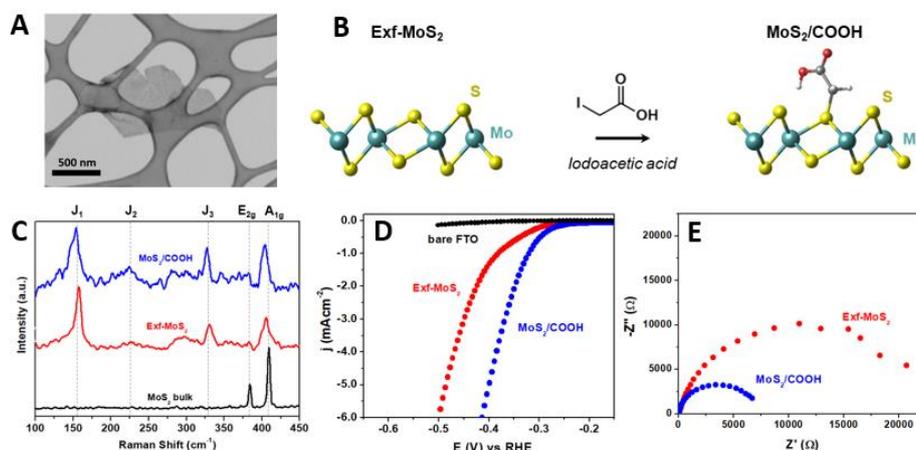
Figure 1: (A) STEM image of chemically exfoliated MoS₂; (B) schematic illustration of the functionalization of MoS₂ nanosheets; (C) Raman spectra of pristine and functionalized MoS₂ and (D-E) electrochemical HER studies of MoS₂ and MoS₂/COOH samples.

Covalent functionalization of photoluminescent liquid-exfoliated WS_2 nanosheets

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Transition metal dichalcogenides (TMDs), such as WS_2, turn from indirect into direct semiconductors when exfoliated to monolayer thickness. For applications in (opto-)electronics, enhancement of the intrinsically low photoluminescence quantum yield of TMD nanosheets would be required. One potential approach to tackle this task, is the introduction of new types of defects to the nanosheet surface. In this project the covalent aryl functionalization of liquid-phase exfoliated WS_2 nanosheets (f–WS_2) and effects upon optical properties were investigated. Since first results pointed towards an improved nanosheet-nanosheet separation in thin films from functionalized monolayer-enriched dispersions, the material was embedded in cavities and reflectivity experiments were performed, to learn whether strong-coupling can be achieved from our largely liquid-based processing protocols. Liquid-phase exfoliated WS_2 nanosheets in water/surfactant dispersions were size selected, according to literature known centrifugation protocols.[1] Dispersions with high monolayer content were treated with aryl diazonium salts in different concentrations to achieve functionalization. By performing solvent transfer to IPA, colloidal stable dispersions were obtained, which were used for further film fabrication. Extinction, Raman and photoluminescence (PL) spectroscopy suggest reduced nanosheet aggregation due to functionalization. In thin films spectral features typical of individual TMD monolayers, such as A exciton PL, are largely maintained. Characterization of films, assembled at liquid-liquid interfaces and deposited via a Langmuir based method, suggests that functionalization leads to improved high film homogeneities and increased hydrophobicity of surfaces. Such films embedded in cavities allow for the detection of exciton-polaritons, which might represent a further step towards polaritonic devices from liquid-phase processed TMDs.

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Synthesize Lewis Acid and Base Containing 2D Material

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Lewis acid- and base-containing materials attract much interest as multifunctional catalysts. The previous example of such 2D materials is graphene co-doped with nitrogen and boron.[1] However, this material have problems of randomness and uncontrollability of structure. It is difficult to control the bonding state of this material because of the annealing process. To solve these problems, we try to synthesize the 2D carbon skeletons using monomers with Lewis acid-base moieties and controlling their alignment at the molecular level.

In this study, we use alkyne (triethynylborane) with Lewis acid and aryl halide (tris(4-bromophenyl) amine) with Lewis base moieties in the Sonogashira-Hagihara coupling polymerization (**B-N Polymer,** Scheme 1). In general, the three-coordinate boron molecules are difficult to handle because of their high reactivity. Therefore, we use pyridine for protecting the boron moiety to inhabit the acid-base reaction between triethynylborane and tris(4-bromophenyl) amine before cross-coupling.

We analyzed product structure with SEM, IR, TG-MS, and XPS (Figure 1).

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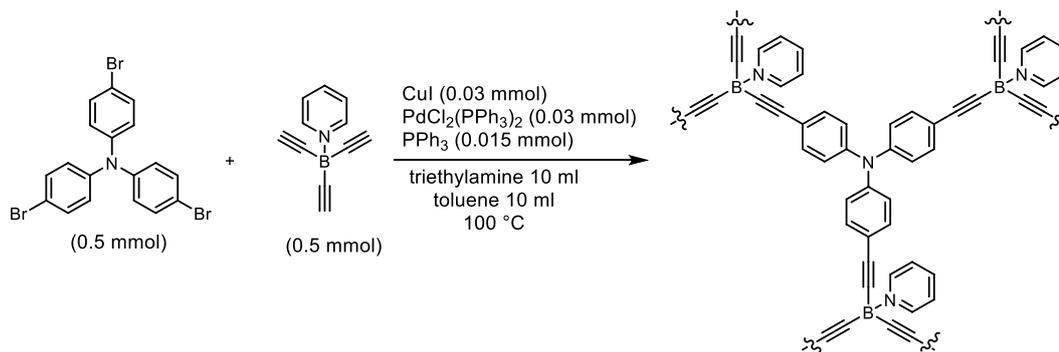
Scheme 1: Reaction scheme
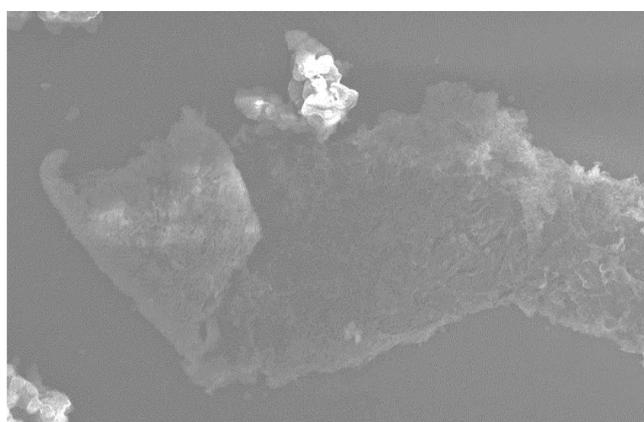
Figure 1: SEM image
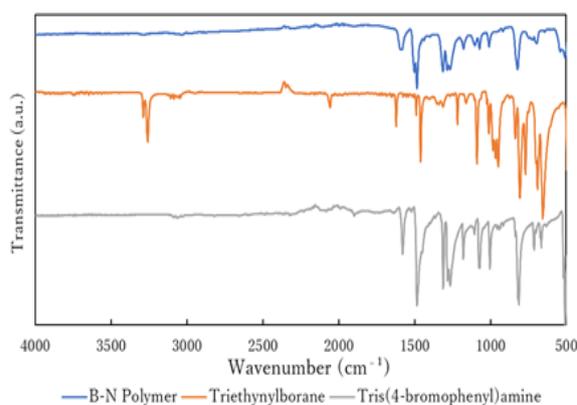
Figure 2: IR spectrum

High surface area reduced graphene oxide via L-ascorbic acid treatment

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Graphene has attracted significant attention due to its excellent chemical and physical characteristics. Graphene materials prepared from graphene oxide (GO) by reduction have been investigated because of their potential to scale up. There are diverse physicochemical methods to reduce GO such as UV-light irradiation,[1] thermal,[2] hydrazine,[3] sodium bisulfate,[4] and L-ascorbic acid (AA) treatments.[5] Unfortunately, the reduction of GO generally accompanies the stacking of graphene sheets, which results in a lower surface area than is desired for graphene structures (2,630 m^2/g).[2,6]

In this research, we investigated the reduction process while suppressing the stacking of graphene sheets using AA. We synthesized reduced graphene oxides (rGOs) fixing the mass ratio in 1:5 (GO:AA) at 25 (**rGO$_{5-25}$**), 35 (**rGO$_{5-35}$**), 50 (**rGO$_{5-50}$**), and 80 °C (**rGO$_{5-80}$**), reaching specific surface areas as higher as 403 m^2/g. All rGOs showed similar morphology and Raman spectra; however, they showed different oxygen contents, physisorption performances (Figure 1a), surface areas (Table 1), and XRD patters (Figure 1b). Our experiments demonstrate that AA not only acts as a reducing agent, but also as a spacer that prevent the stacking of graphene sheets. Besides, by carrying out a time-course mechanistic study on **rGO$_{5-25}$**, we can propose a successive grafting-reduction mechanism.

Table 1.- Surface area of rGOs.

Material	S_{BET} (m^2/g)
rGO$_{5-25}$	403
rGO$_{5-35}$	253
rGO$_{5-50}$	69
rGO$_{5-80}$	44
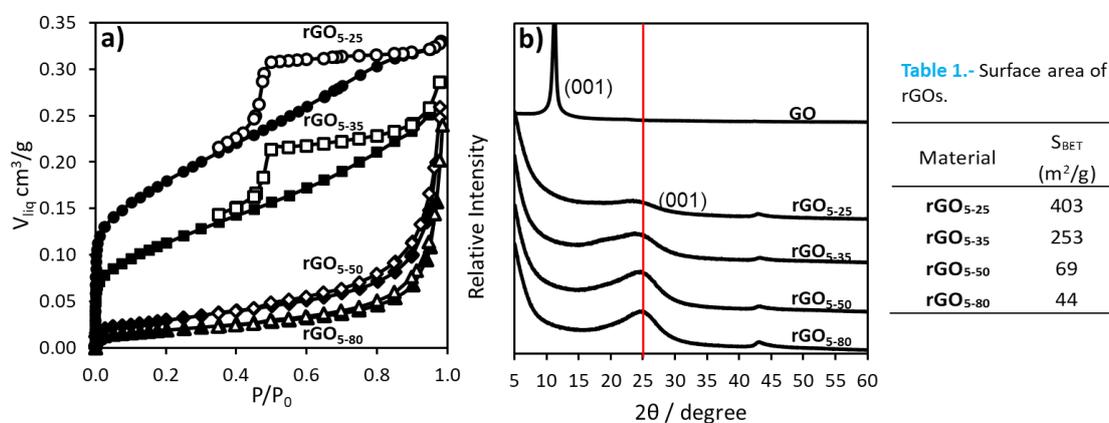
Figure 1: a) Nitrogen adsorption-desorption isotherms at 77 K and **b)** XRD patterns of rGOs synthesized at a fixed AA mass ratio of 5 at different temperatures.

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Arginine-modified graphene oxide for Carbon dioxide fixation

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The catalytic transformation of CO_2 into value-added organic compounds is matter of growing interest in organic chemistry.[1] A variety of catalytic systems have been explored, but the development of an environmentally benign, heterogeneous catalyst that is highly active at mild conditions remains challenging.[2] Due to its large surface area and chemical versatility,[3] Graphene oxide (GO), has received extensive attention as nanostructured carbon-based catalyst.[4]

In this work, we report on the synthesis and characterization of covalently modified GO with L-Arginine (GO-Arg) and on its use as CO_2 fixation substrate and carbocatayst.[5] GO-Arg was synthesized by epoxide ring opening reaction, purified by microfiltration and characterized by X-ray photoelectron spectroscopy and elemental analysis to measure the amino acid loading. GO-Arg nanosheets were then exploited as catalyst for chemo selective ring-opening of epoxides and conversion to cyclic carbonates under mild operating conditions on several different substrates (up to 15). High yields (up to 85 %), regeneration and reuse up to 5 cycles have been achieved and will be here reported.

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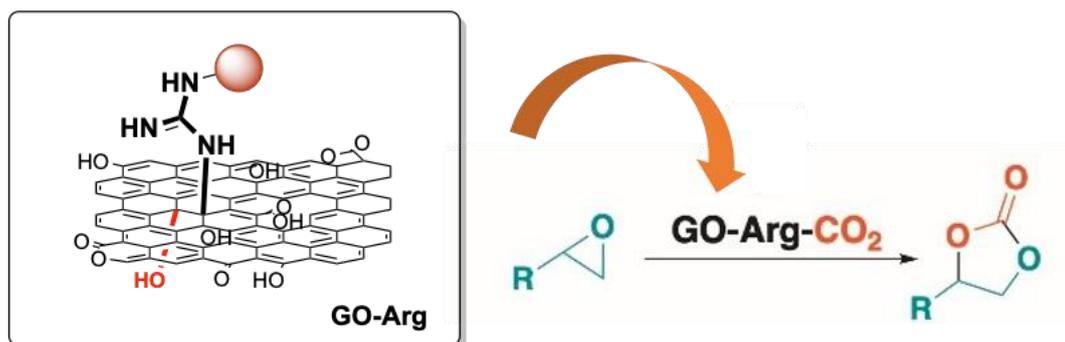
Figure 1: Nucleophilic activation of carbon dioxide by the guanidine group of GO-Arg.

Recrystallization of epitaxial MBE-grown MoS₂ monolayers induced by annealing in a CVD furnace

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A systematic study of MoS_2 grown by a combination of physical vapor deposition (PVD) and post-growth annealing treatment in a sulfur atmosphere has been conducted. Hereby, MoS_2 thin films with nominal thicknesses between 1-2 monolayers are first grown on sapphire by molecular beam epitaxy (MBE) at different growth temperatures and then transferred to S environment inside a chemical vapor deposition (CVD) furnace for a post-growth annealing. Depending on the growth temperature, the as-grown layers are either amorphous or form a crystalline structure composed of closely packed nm-size grains. The subsequent annealing leads to recrystallization of these layers significantly increasing the size of the MoS_2 crystalline domains to the range of 50 - 100 nm. While the originally amorphous layer displays randomly oriented domains after annealing, recrystallization of samples grown at high temperatures yields single crystalline layers. All samples show an increase of the crystallite dimension, which is accompanied by the disappearance of the defect-related peaks in the Raman spectra, sharpening of the excitonic signatures in absorption, and strong enhancement of the photoluminescence yield. The results represent a promising way to combine the tunability of PVD with post-growth CVD process towards fabrication of wafer-scale epitaxial transition metal dichalcogenide mono- and multilayer films on non-van der Waals substrates [1].

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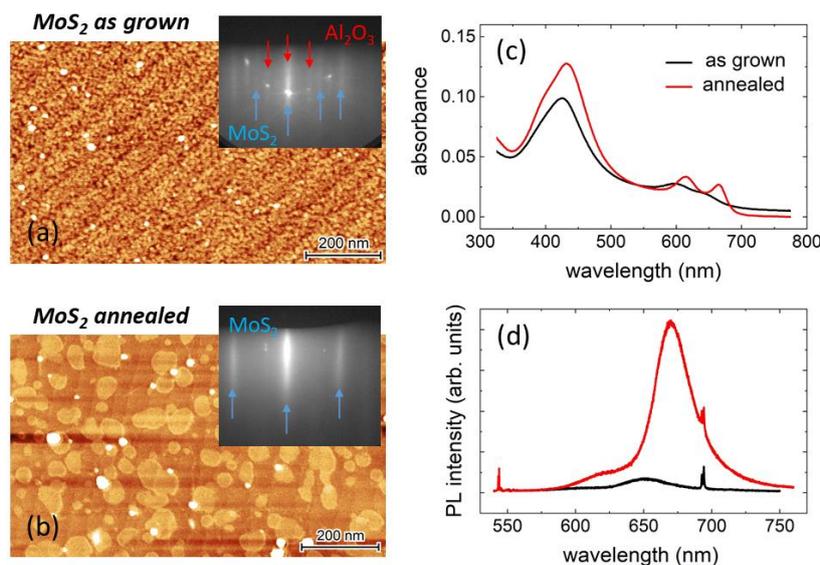
Figure 1: Exemplary properties of MBE-grown and annealed MoS_2 layers on sapphire. (a, b) AFM images. Inserts show reflection high energy diffraction (RHEED) patterns along <11-20> azimuth of the wafer. Reflections of sapphire and MoS_2 are marked by the red and blue arrows, correspondingly. (c, d) Absorption and PL spectra of the samples.

Effect of protocol optimization for MXenes synthesis on their photocatalytic activity toward hydrogen production

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Photocatalytic hydrogen generation using various 2D materials appears to have fascinating premises as a promising strategy for solar-driven water splitting. Titanium-based MXene ($Ti_3C_2T_X$) materials are anticipated to be applied as photocatalysts thanks to their remarkable properties, such as excellent conductivity, exceptional hydrophilicity, large electrochemically active surface, and tailored structure. These materials are expected to replace noble Pt in photocatalysis [1,2]. Nevertheless, there are many factors that can affect the photocatalytic activity of MXenes. Primarily, their synthesis and subsequent procedures applied for their purification are very important. In our investigation, we obtained various fractions of $Ti_3C_2T_X$ MXenes via differential centrifugation with decreasing RPMs. All the isolated fractions differed in terms of lateral sizes of MXene flakes, the number of intercalant layers, the amount and the kind of impurities. All the above-mentioned factors can strongly influence the photocatalytic activity of a given MXene fraction for hydrogen generation. We investigated and compared the achieved fractions of titanium-based MXenes using the most essential instrumental techniques, namely, X-ray diffraction, scanning electron microscopy, and Raman spectroscopy. Subsequently, we compared the photocatalytic activity of each of the fractions in dye-sensitized systems. It appeared that depending on the kind of impurities and their presence or absence the activity of MXenes can either dramatically decrease or remain almost without changes. For instance, the purification of the sample from a small amount of parental MAX-phase didn't influence their activity, whereas a significant reduction of lithium salts in the sample of MXenes led to its notable decrease. It is likely that the degree of oxidation of the sample influences the intrinsic and co-catalytic activity of MXenes in photocatalytic systems in opposite ways: either increasing or decreasing it, respectively. The most active MXene fraction exhibited the hydrogen evolution rate of 89,1 mmol h^{-1} g^{-1} for EY/$Ti_3C_2T_x$/$CoSO_4$ system. Our work shows huge potential of 2D MXenes used in dye-sensitized photocatalysis for hydrogen evolution.

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Epitaxial synthesis of boron-containing Lewis acid material

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Boron-containing materials have been developed, and generally show Lewis acidity Thus, those materials applied to a wide variety of applications such as anion sensors, electronic devices, and catalysts.[1-3] Although those materials have unique properties, the proprtion of boron is low and to control the structure is difficulut. In our study, we aimed to synthesize a novel 2D material with high boron content in order to increase Lewis acidity. We expected that a lot of Lewis acid sites and high surface area of the 2D material improved the performance in application such as catalysts. We adopted bottom-up synthesis to tune material structure precisely. Triethynylborane·pyridine (teb·py) complex was chosen as monomer because of its high boron content (B:C= 1:6). poly(phenyl)borane (**(BC$_6$)$_n$**) was synthesized by cyclotrimerization of alkynes (Figure 1). The release of pyridine was observed at 300 °C in TG-MS measurement (Figure 2). This result indicated that pyridine was strongly coordinated to Lewis acid sites on **(BC$_6$)$_n$,** and it was found that the Lewis acidity of **(BC$_6$)$_n$** emerged by this heat treatment.

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Figures

Figure 1: Synthesis route of **(BC$_6$)$_n$**

Figure 2: TG-MS measurement of **(BC$_6$)$_n$·**pyridine

Laser patterning of polymer composites with graphene, graphene oxide and aramid fibers, for the production of electric devices.

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The diffusion of distributed electronics and IOT (Internet-Of-Things) requires cheap and rapid integration of electronic circuits in everyday objects, typically made of insulating plastic. This however implicates an increased complexity of the objects; the inclusion of metallic wires, sensors and buttons increases the production steps needed and final cost of the IOT objects; furthermore, addition of electronic metallic components to polymeric objects renders their recycling or end-of-life disposal more challenging and, again, more expensive. An original solution to add electronic capabilities to plastic object is to avoid the use of metallic conductors, creating instead electrical circuits on the surface of the object by local treatment, as example by a laser scribing technology (LS). In this approach, a conductive additive is added to the polymer at a concentration which is however below the percolation threshold; in this way, the bulk of the material remains electrically insulating. Then, a powerful laser is scanned on the surface of the object. The laser partially ablates the polymer, increasing the local concentration of the conductive additives which, eventually, touch each other forming an electrically conductive percolated network.

In this work we studied the mechanism of laser scribing in polyurethane composites containing different kind of graphene derivatives or precursors. In all materials tested, the laser patterning allows to draw conductive patterns with a resistance up to nine orders of magnitude lower than the pristine polymer, reaching very low ultimate sheet resistances (<10 Ω/square).

Finally, we demonstrated the versatility of this approach by producing different devices on the PU-based composites like a heater and an amperometric electrochemical sensor for the detection of biological analytes.

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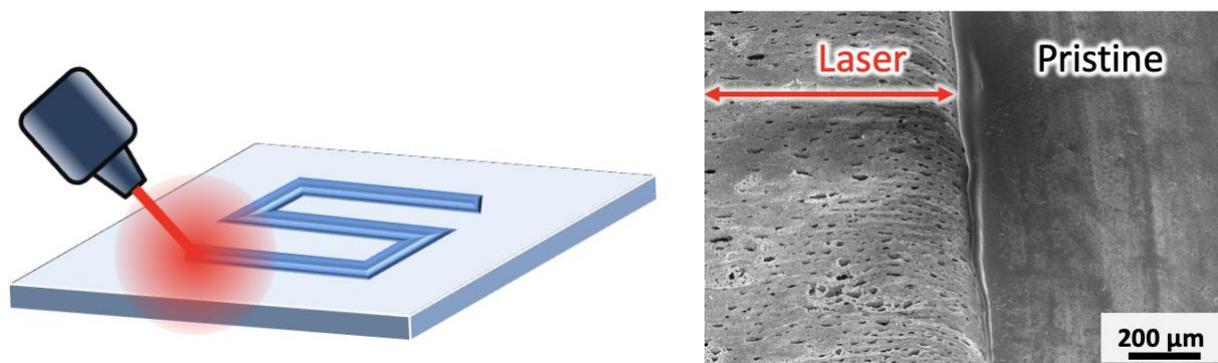
Figures

Figure 1: Schematic illustration of laser patterning. **Figure 2:** SEM image of a sample showing area irradiated with laser close to pristine, non-irradiated area.

Chemically tailored graphene for PFAS and other emerging contaminants removal from water

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The so called "emerging contaminants" (ECs) (which include pharmaceuticals, cosmetics, pesticides and polyfluoroalkyl substances (PFAS)) are increasingly found in tap water. [1] Graphene based nanomaterials have shown great potential for water purification due to their high surface area and their adsorption properties, promoted by multiple interaction pathways with organic molecules and metal ions. [2], [3] Here, we report on the synthesis of β-ciclodextrine (β-CD) modified graphene oxide (GO) as sorbent with high selectivity and capacity for PFBA, a particularly persistent short chain PFAS. Epoxide ring opening reaction was exploited to bind β-CD to GO, through different sized alkyl spacers. The relationships between alkyl chain length and adsorption capacity is studied by combined adsorption tests and molecular dynamic simulations. The performances have been compared to unmodified GO and other carbon nanomaterials and to those of granular activated carbons, the industrial sorbent benchmark.

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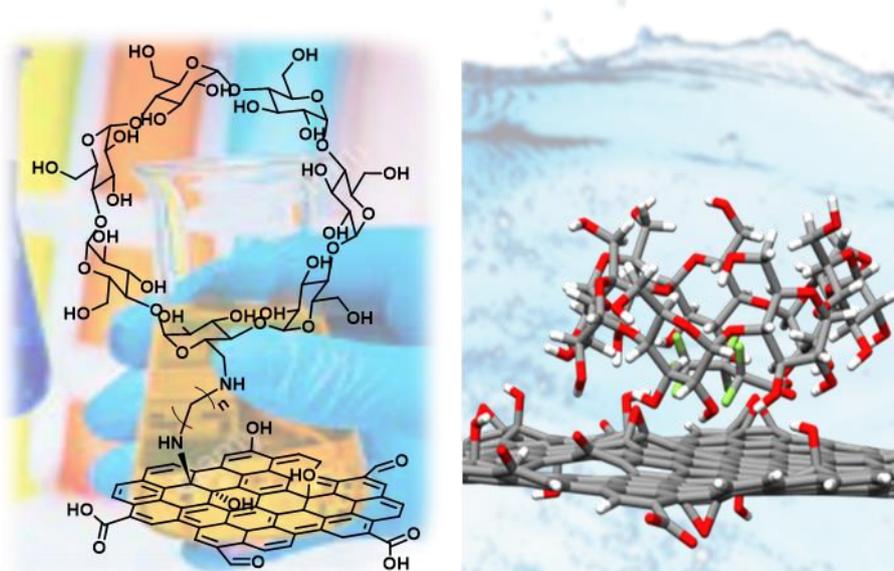
Figure

Figure 1: β-ciclodextrine modified graphene oxide (GO-βCD) for water remediation.

Electronic and Excitonic Properties of MSi2Z4 Monolayers

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Abstract

MA_2Z_4 monolayers form a new class of hexagonal non-centrosymmetric materials hosting extraordinary spin-valley physics [1]. While only two compounds ($MoSi_2N_4$ and WSi_2N_4) were recently synthesized, theory predicts interesting (opto)electronic properties of a whole new family of such two-dimensional materials [2]. Here, the chemical trends of band gaps and spin-orbit splittings of bands in selected MSi_2Z_4 (M = Mo, W; Z = N, P, As, Sb) compounds are studied from first-principles. Effective Bethe-Salpeter-equation-based calculations reveal high exciton binding energies. The evolution of excitonic energies under an external magnetic field is predicted by providing their effective g-factors and diamagnetic coefficients, which can be directly compared to experimental values. In particular, large positive g-factors are predicted for excitons involving higher conduction bands. In view of these predictions, MSi_2Z_4 monolayers yield a new platform to study excitons and are attractive for optoelectronic devices, also in the form of heterostructures. In addition, a spin-orbit-induced bands inversion is observed in the heaviest studied compound, WSi_2Sb_4, a hallmark of its topological nature.

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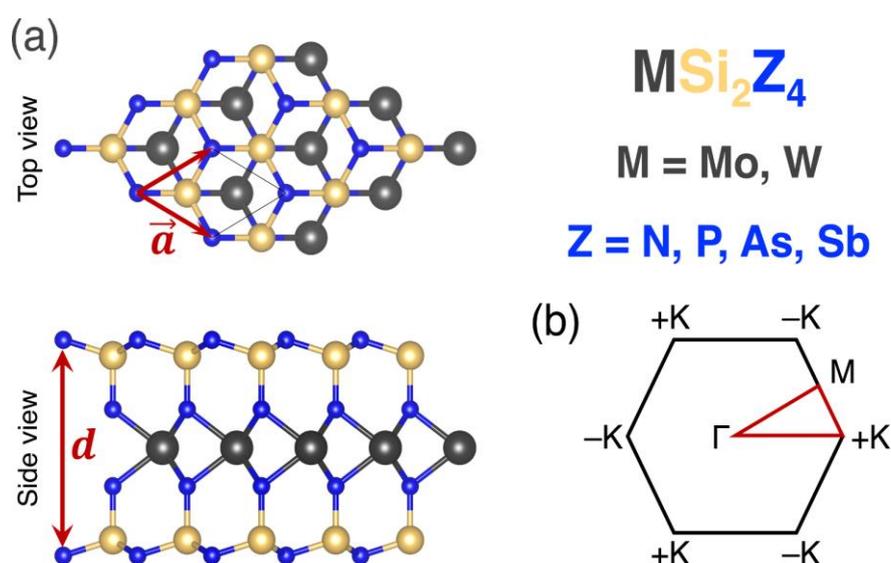[2] Wu, Qingyun, et al., *Applied Physics Letters*, 118.11 (2021): 113102.

Figures

Figure 1: (a) Top and side views of 1L MSi_2Z_4 monolayer generic structure. Hexagonal unit cell is marked together with lattice vector a and the layer thickness d, defined as a distance between the outermost Z atoms. (b) The corresponding hexagonal BZ with the high-symmetry points and a path for band structure calculations (red lines).

Graphene-based heaters for aeronautical applications

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Commercial aircrafts need protection systems against ice formation to avoid detrimental effects in the airfoils and any related safety problems. Current solutions are mainly based on purges that distribute hot air from the engine to the leading edge to prevent ice accretion on the wing surface. However, these systems have some disadvantages, including incompatibility with composite parts due to the high temperatures used. A promising alternative to the current de-icing system, solving the just mentioned issues, is given by GRM based heaters in which heat is generated by the Joule effect by applying electrical voltage [1-2]. In this work we developed heaters prototypes realized with GRM integrated in Carbon Fiber Reinforced Polymers (CFRP). The devices prepared showed good functionality and uniform heating without hotspots. Graphene heaters can achieve a wide range of operation temperatures in function of the system configuration, even capable of melting ice at -30°C in few seconds, showing promising results for anti-icing and de-icing applications.

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Figures

Fig. A: Typical de-icing process of an airplane through propylene glycole spray.
Fig. B and C: Graphene heater integrated in CFRP with ice accretion on the surface A) before and B) after de-icing process.
Fig. D: Curved panel (HTP leading edge shape) with integrated graphene heater by co-curing.

chem2Dmat
EUROPEAN CONFERENCE ON CHEMISTRY OF TWO-DIMENSIONAL MATERIALS

From lyophobic to lyophilic and back to lyophobic again: Towards Greener Dispersions of Carbon Materials

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Fundamental concepts of colloidal science will be presented as well as their application to overcome some issues common in carbon-based dispersions, like low colloidal stability of pristine materials in some solvents and low mass concentration of many systems [1]. First, the van der Waals (vdW) interactions between the nanostructures of carbon materials will be discussed, followed by strategies to decrease or opposing these interactions, which are the bases of many dispersion and exfoliation procedures, such as (i) increasing the electrostatic repulsion between dispersed particles, (ii) surface functionalization, or (iii) the use of passivating agents. These concepts were applied to model two carbon-based dispersions, one composed by fullerenol nanoaggregates [2] and other by graphite particles exfoliated in water [3]. In the case of the fullerenol dispersion, fine tuning of colloidal interactions was done by performing controlled surface modification of the fullerene, which decreases the strength of the vdW interactions and increases the lyophilic character in polar solvents. The modified material forms concentrated dispersions that are indefinitely stable, but preserving appreciable electrical conductivity due to the low number of functional groups on the surface [2]. For graphite dispersion, the pristine solid was treated with concentrated ammonium hydroxide, which provides electrons and raises the Fermi level of the carbon material. The treated solid was washed to remove ammonium hydroxide and exfoliated in water, resulting in an aqueous dispersion without surface modification or passivating agents. The raising of the Fermi level produces a negative zeta potential, which in turn generates an electrostatic repulsion between graphite particles. Since exfoliation contributes to break solid particles into smaller ones, the electrostatic interaction can balance the lower vdW attraction of smaller particles and it provides metastability for this lyophobic dispersion without the need of additives or passivating agents [3].

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Electrochemical delamination of a magnetic topological insulator

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Magnetic topological insulators are intensively investigated for their potential application in quantum computing and spintronics. The currently most important material is $MnBi_2Te_4$ [1-3], a layered van der Waals compound that consists of magnetic septuple layers [Te-Bi-Te-Mn-Te-Bi-Te]. The surface of the materials is of special interest, since the topological and also other physical effects manifest there or originate from it [1-4]. Moreover, the antiferromagnetic coupling of the layers makes a difference between few-layer 2D crystals of $MnBi_2Te_4$ with odd or even number of layers. Up to now, all investigations were performed on mechanically exfoliated material. We now developed an up-scalable electrochemical method for liquid-phase exfoliation. Unexpectedly, we obtained nanoscrolls of $MnBi_2Te_4$, which is an unprecedented morphology for (magnetic) topological insulators. Although rolling up is a continuous transformation that in principle should not affect the topology, the breaking of symmetry, the incommensurable layers at different radii, and the probable radial magnetism are some of the aspects that immediately come to mind as fundamentally new.

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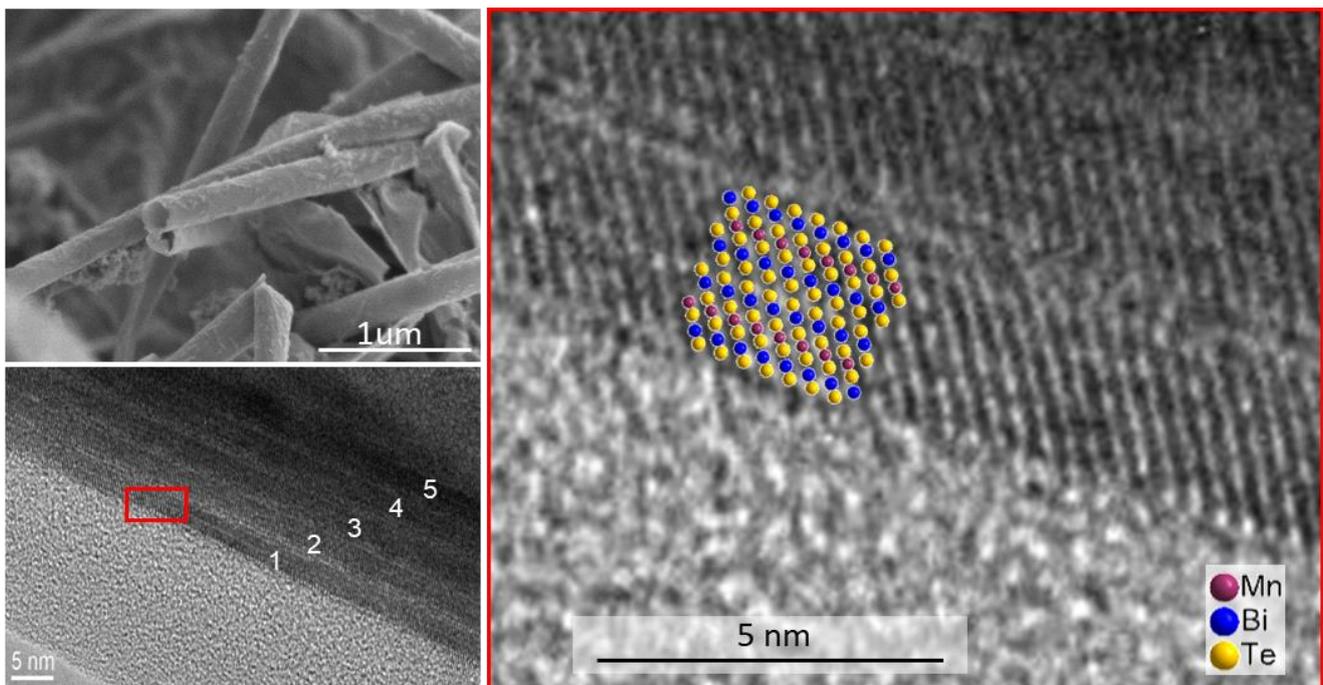
Figures

Figure 1: After applying voltage to $MnBi_2Te_4$ crystals, nanoscrolls with length up to 100 μm formed. HRTEM images reveal a rolled-up structure having a thickness of two septuple layers $MnBi_2Te_4$.

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Reaction Mechanism and Performances of Pioneer 2D $Si_xGe_{1-x}H$ Electrodes in Lithium-ion Batteries

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Abstract

2D monoelemental materials, such as silicene and germanene, have recently received a lot of attention due to their tunable structures and remarkable physicochemical properties [1,2]. The addition of covalently bonded hydrogen in the z-orientation of each silicene and germanene atom results in hybridized bonding site changes from sp^2 to sp^3 with new terms of silicane (*i.e.,* hydrogen-terminated silicene, SiH) and germanane (*i.e.,* hydrogen-terminated germanene, GeH) [3,4]. However, challenges in the synthesis of such materials impede their detailed study, exploitation, and applications. In this work, we present pioneer 2D silicane and germanane materials with different compositions, namely, $Si_{0.25}Ge_{0.75}H$, $Si_{0.5}Ge_{0.5}H$, and $Si_{0.75}Ge_{0.25}H$ that benefit from the simultaneous presence of both Si (high capacity) and Ge (high-rate performance and capacity retention). The three samples were synthesized through simple and efficient chemical exfoliation of bulk Zintl phases. The presence of both SiH and GeH in a single structure offers a synergistic beneficial effect on the electrochemical performances of $Si_xGe_{1-x}H$ (with *x* values from 0.25 to 0.75). Among them, the $Si_{0.5}Ge_{0.5}H$ electrode shows the highest capacity, up to 1526 mAh g^{-1} after 20 cycles. The $Si_{0.5}Ge_{0.5}H$ electrodes were respectively, subjected to 0, 10, 100, and 200 half-cell cycles followed by *ex-situ* SEM and SEM-EDX analysis to assess the effects of lithiation/delithiation and alloying/dealloying on the $Si_{0.5}Ge_{0.5}H$ flakes. Figure 1 shows the variations in morphology after different cycles.

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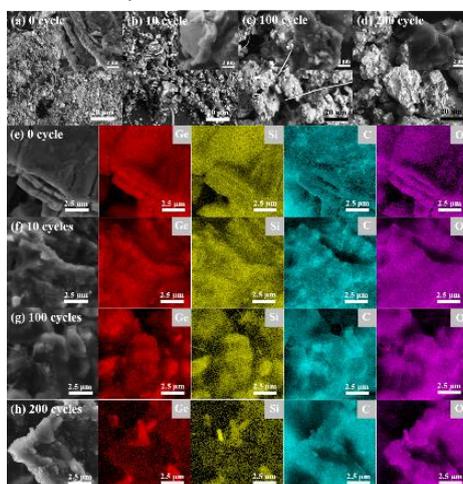**Figure 1:** SEM and SEM-EDX images depicting the progression of deformation caused by lithiation and delithiation on the $Si_{0.5}Ge_{0.5}H$ morphology upon cycling.

Topological Phase Transition Associated With Structural Phase Transition in Ternary Half Heusler Compound LiAuBi

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Discovering new materials is a key aspect of semiconductor physics for sustaining the continuous progress and improvements in current electronic devices. The discovery of the non-trivial topological phase was a deviation from the conventional classification of materials, i.e., metals, insulators, and semiconductors. The discovery of the topological phase has become a center of attention in the condensed matter community due to riveting underlying physics and opening vast opportunities for their applications in next-generation spintronic devices. The topological phase in the materials is realized by time-reversal protected surface states, a distinctive quantum state of matter for the transport of spins. In recent years, immense research ploughed into discovering many such new materials at the horizon of physics and material science [1]-[3]. More recently, the search has been extended to ternary compounds, particularly non-centrosymmetric half Heusler compounds. Over the decade, HH compounds have made considerable development in thermoelectric conversion technology. Half Heusler compounds with 18 valence electrons, such as RNiSn (R = Hf, Zr, Ti), were found to have significant values of the Seebeck coefficient and power factor, which are essential in determining the thermoelectric (TE) efficiency of a material [4]-[5]. The reason behind this was the small band gap of the compounds with high charge carrier density. Externally doping or applying strain resulted in enhancement of the efficiency of a TE material. In this work, we report detailed theoretical investigations of topological phases in non-centrosymmetric half Heusler compound LiAuBi upto a pressure of 30 GPa [6]. It is found that the compound forms into a dynamically stable face centered cubic (FCC) lattice structure of space group $F\bar{4}3m$ (216) at ambient pressure. The compound is topologically non-trivial at ambient pressure, but undergoes a quantum phase transition to trivial topological phase at 23.4 GPa. However, the detailed investigations show a structural phase transition from FCC lattice (space group 216) to a honeycomb lattice (space group 194) at 13 GPa, which is also associated with a non-trivial to trivial topological phase transition. Further investigations show that the compound also carries appreciable thermoelectric properties at ambient pressure. The figure of merit (ZT) increases from 0.21 at room temperature to a maximum value of 0.22 at 500K. The theoretical findings show its potential for practical applications in spintronics as well as thermoelectricity, therefore LiAuBi needs to be synthesized and investigated experimentally for its applications.

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One-Step Synthesis of Carbon Nanosheet-Polyacrylamide Composite Materials via Liquid Plasma Treatment

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In this study, we employ liquid plasma method to prepare carbon nanosheet-polyacrylamide composites in one step. Plasma is the fourth state of matter and possesses high electron energy comparable with tens of thousands Kelvin at room temperature, containing a large number of active particles, which can be used for the synthesis and modification of carbon materials and polymers. The conventional gas-phase plasma method can only modify the surface of materials, resulting in low efficiency. This research aims to synthesize a large amount of carbon nanosheet-polyacrylamide composite materials in one step using the liquid plasma. hanging the solvent system could control the degree of carbonization and polymerization. Finally, we investigate the reaction mechanism of the liquid plasma-derived reactions.

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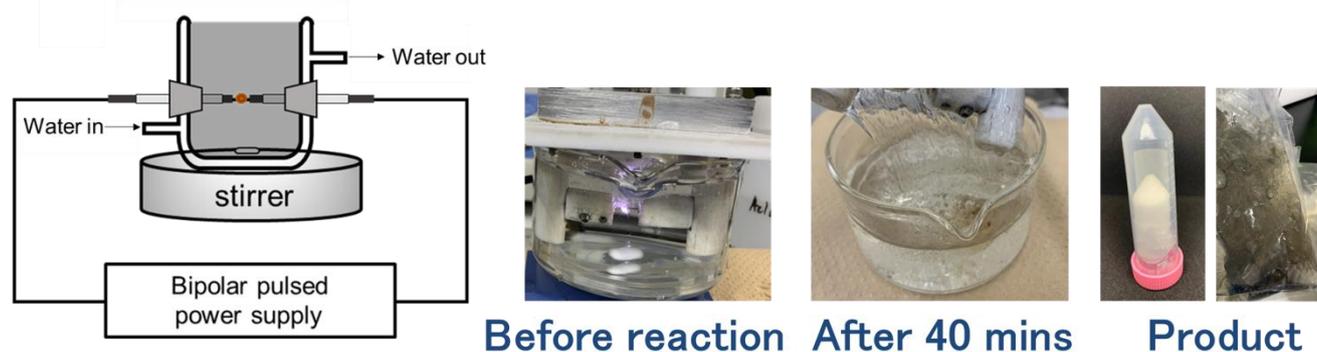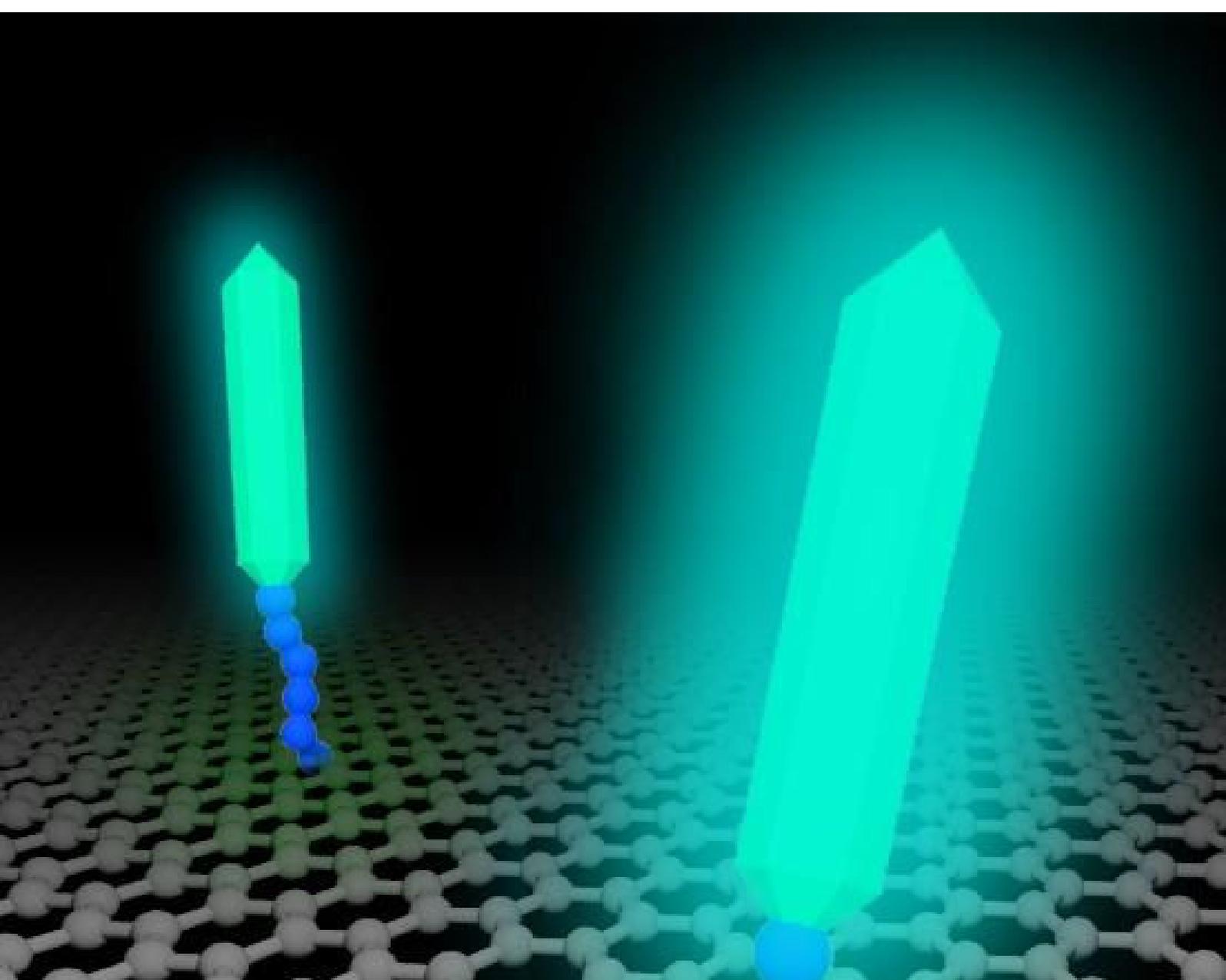
Figures

Figure 1: Effect of Liquid Plasma Polymerization Solvent on Products

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