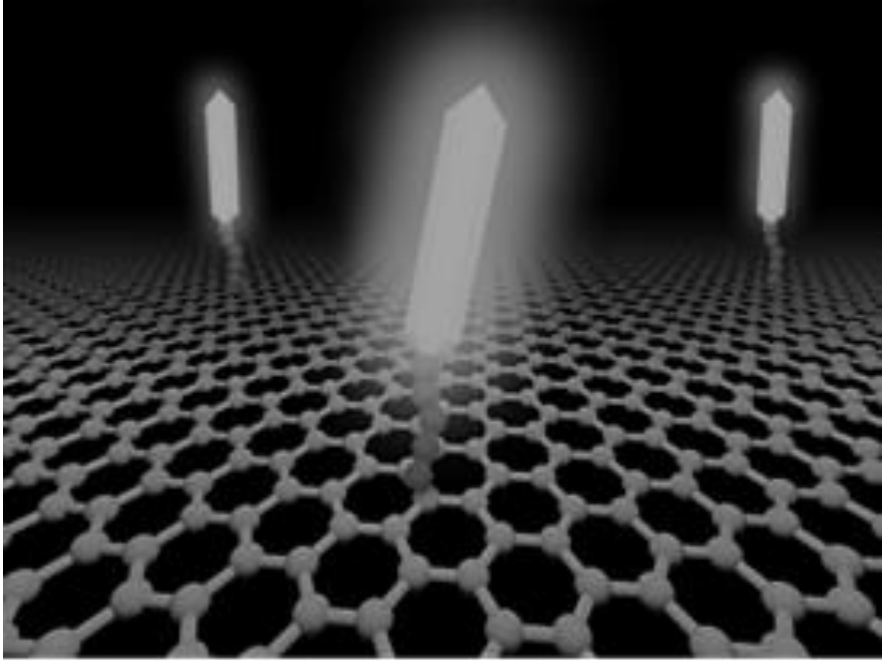
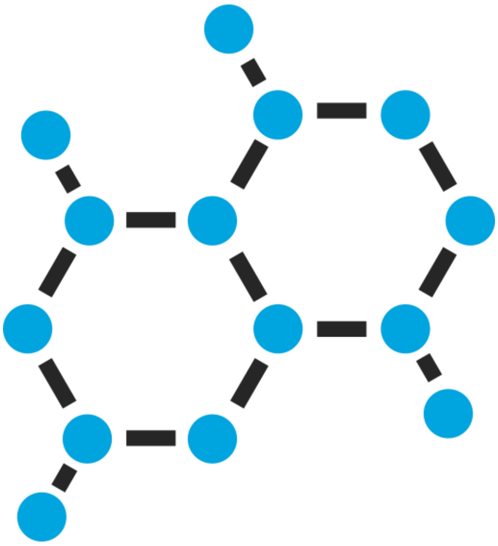
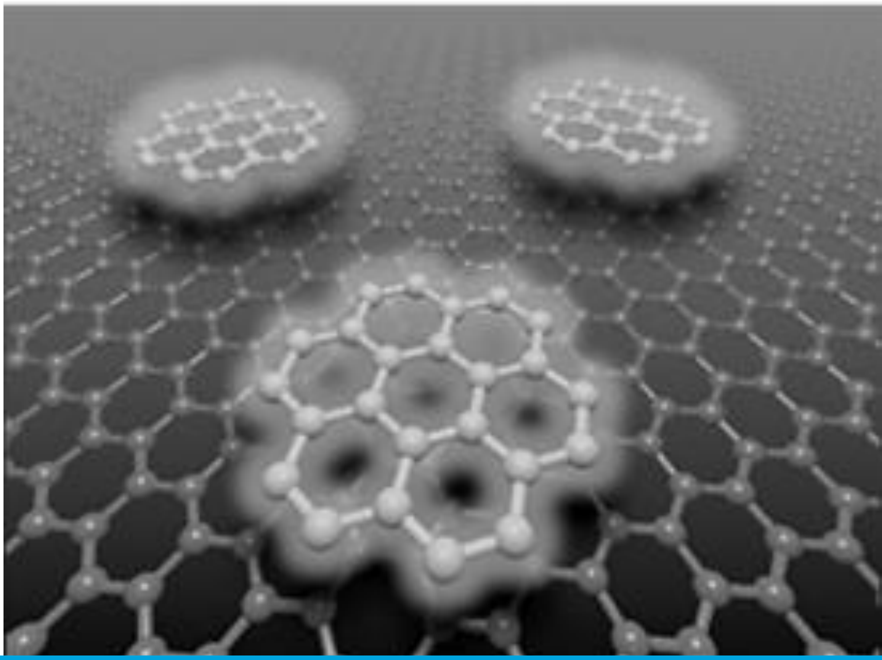
European Conference on Chemistry of Two-Dimensional Materials







chem2Dmat

AUGUST 31 - SEPTEMBER 03, 2021 ● ONLINE

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Foreword

On behalf of the Organising and the International Scientific Committees we take great pleasure in welcoming you to the 3rd edition of the European Conference on Chemistry of Two-Dimensional Materials. Due to the current COVID-19 worldwide situation, chem2Dmat2021 will be finally organised online.

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 with full control over the correlation between structure and function.

The 3rd 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. chem2Dmat2021 is now an established event, attracting global participant's intent on sharing, exchanging and exploring new avenues of graphene-related scientific and commercial developments in the chemistry sector.

chem2Dmat2021 Highlights:

- Expected online attendance: 200 participants
- 34 Keynotes & Invited Speakers
- 65 ePosters
- Nearly 60 oral contributions
- 1/2-day Industrial Forum in parallel to get an updated understanding of Graphene based technologies
- 2 awards to best ePoster contributions

We are also indebted to Graphene-XT (Italy) for their financial support (awards).

We also would like to thank all the 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 chem2Dmat2021 serves as an international platform for communication between science and business.

Hope to see you again in the next edition of chem2Dmat.

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1		Samsung Galaxy A52 5G	GRAPHENE-XT NEXT GENERATION MATERIAL	Best e-Poster contribution First prize
1		HUAWEI Watch GT 2 Smartwatch 46 mm	GRAPHENE-XT NEXT GENERATION MATERIAL	Best e-Poster contribution Second prize

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SPEAKERS LIST

Index alphabetical order

PLENARY SPEAKER

Small, Medium, Large - from Nanographenes to Graphene Nanoribbons and Graphene

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This is a chemistry-driven journey through the graphene landscape with size and dimensionality as guidelines. The key breakthrough comes from graphene nanoribbons (GNRs), quasi-1D-semiconductors which emerge as unique carbon nanostructures and versatile electronic materials. Their band structures can be widely tuned yielding semiconductors and even topological insulators. The most important features are i) the opening of a band gap due to the geometric confinement, ii) the detection of amplified spontaneous emission and iii) the occurrence of edge localized electronic states with spin polarization. All characteristics offer new technological opportunities, for example, adding the spin degree of freedom to graphene-based circuitry.

Conceptually, GNRs have two important functions: they close the gap between conjugated polymers and graphene and they utilize small nanographene molecules such as the “rhombenes” to create new electronic structures.

In the driver’s seat is precision polymer synthesis which becomes possible by i) repetitive cycloaddition in solution, ii) on-surface polymerization after immobilization of monomer building blocks and iii) chemical vapor deposition.

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KEYNOTE SPEAKERS

Advances in Organic 2D Crystals

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Abstract

Over the last decade, the discovery of graphene has triggered a new paradigm of two-dimensional (2D) crystal materials. They are characterized by a periodic network structure and topographical thickness at the atomic/molecular level, enabling the investigation of fundamental exotic physical and chemical properties down to a single-layer nanosheet. Thereby, robust technologies and industrial applications, ranging from electronics and optoelectronics to energy storage, energy conversion, membranes, sensors, and biomedicine, have been inspired by the discovery and exploration of such new materials.

In contrast to the tremendous efforts dedicated to the exploration of graphene and inorganic 2D crystals such as metal dichalcogenides, boron nitride, black phosphorus, metal oxides, and nitrides, there has been much less development in organic 2D crystalline materials, including the bottom-up organic/polymer synthesis of graphene nanoribbons, 2D metal-organic frameworks, 2D polymers/supramolecular polymers, as well as the supramolecular approach to 2D organic nanostructures. One of the central chemical challenges is to realize a controlled polymerization in two distinct dimensions under thermodynamic/kinetic control in solution and at the surface/interface. In this talk, we will present our recent efforts in bottom-up synthetic approaches towards novel organic 2D crystals with structural control at the atomic/molecular level and beyond. We will introduce a surfactant-monolayer assisted interfacial synthesis (SMAIS) method that is highly efficient to promote supramolecular assembly of precursor monomers on the water surface and subsequent 2D polymerization in a controlled manner. 2D conjugated polymers and coordination polymers belong to such materials classes. The unique structures with possible tailoring of conjugated building blocks and conjugation lengths, tunable pore sizes and thicknesses, as well as impressive electronic structures, make them highly promising for a range of applications in electronics and spintronics. Other application potential of organic 2D crystals, such as in membranes, will also be discussed.

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Covalent organic framework for energy applications

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Covalent organic frameworks are an emerging class of porous crystalline organic materials that can be designed and synthesized from the bottom up. Despite progress made in synthesizing COFs of diverse topologies, the synthesis methods are often tedious and unscalable, hampering practical applications. By considering the relationship between layer packing arrangement and the ability to restrict intramolecular rotation, we demonstrate a scalable, robust method of producing highly crystalline acylhydrazone two-dimensional (2D) COFs with diversified structures (six examples) under open and stirred conditions, with growth typically completed in only 30 min [1]. Our strategy involves selecting molecular building blocks that have bond dipole moments with spatial orientations that favor antiparallel stacking and whose structure allows the restriction of intramolecular bond rotation (RIR) via intra- and interlayer hydrogen bonding. We found that antiparallel stacking encourages interlayer hydrogen bonding interactions that lead to dual emission in photoluminescence, a phenomenon that can be exploited for tuning white light emission from COF for the first time [2]. At the same time, the presence of well-ordered one-dimensional (1D) channels and stability against phase transition in covalent organic frameworks (COFs) render them potential candidates for low-temperature SEs. Using hydrazine COF as a solid state electrolyte in lithium ion battery, we achieved an ion conductivity of 10^{-5} S cm^{-1} at −40 °C with a Li+ transference number of 0.92. Using 1,4-benzoquinone as the cathode, a lithium battery using hydrazine COF as a SE runs for 500 cycles at a steady current density of 500 mA g^{-1} at 20 °C [3]. Finally, we consider the question of how to render 2D COF, which is actually quasi-2D, truly 2D. Our strategy involves the integration of mechanically interlocked molecular architectures (MIMAs) into quasi-2D COF. Depending on the number of layers of COF that can be interlocked per molecular complex, this affords a strategy to partition the interlayer space into pseudo-unit cells [4], from which we can exfoliate high yield monolayer or bilayer COF.

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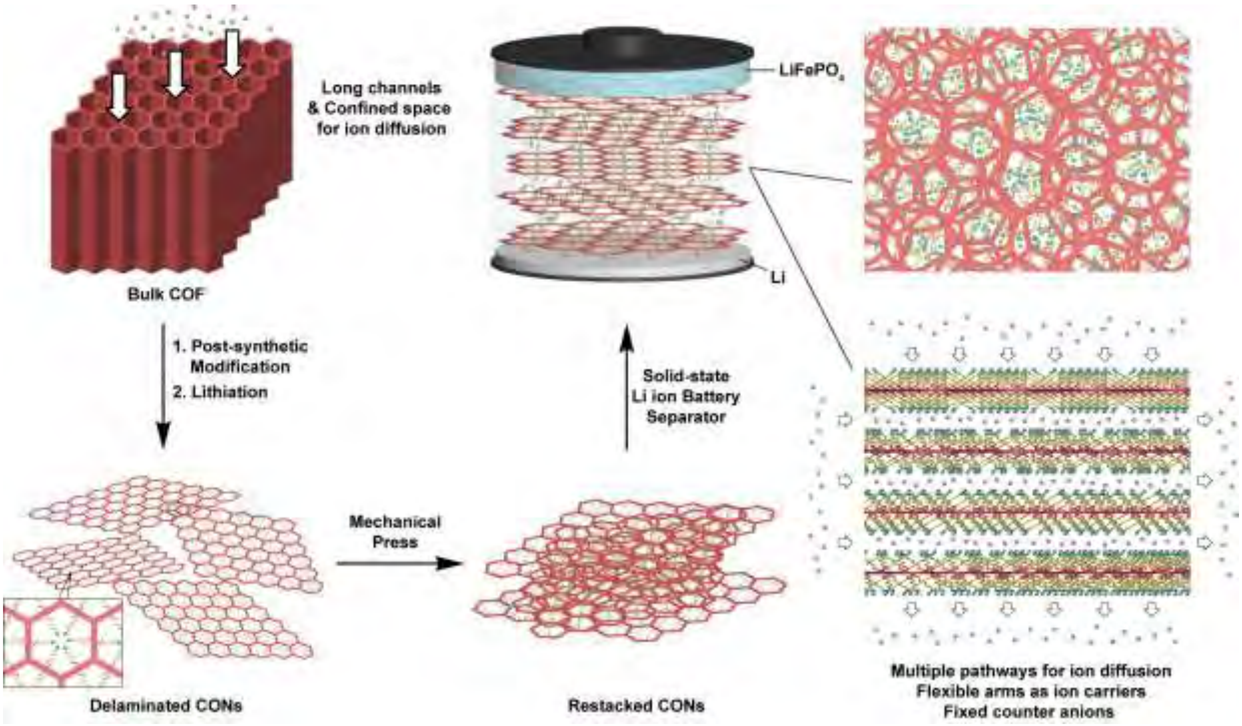
Figures


Long channels
& Confined space
for ion diffusion
Bulk COF
1. Post-synthetic
Modification
2. Lithiation
Delaminated CONs
Mechanical
Press
Restacked CONs
Solid-state
Li ion Battery
Separator
LiFePO$_4$
Li
Multiple pathways for ion diffusion
Flexible arms as ion carriers
Fixed counter anions

The excitons that you might not expect

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Excitons are a key to explore two-dimensional (2D) layers and nanosystems: Since the beginning of bottom-up nanoribbon fabrication, the predicted excitonic signatures are opening the way to understanding the structure [1], the growth process [2], the edge and distortion design [3], as well as many other phenomena of central importance for applications [4]. First-principles theory and computation beyond density functional theory is the main tool enabling such advances.

Excitons of 2D systems are now the leading actor also in a new movie, maybe less expected within the Chem2Dmat community: the Excitonic Insulator (EI). The name refers to the long-sought state of matter that may result when the electron-hole binding energy exceeds the band gap: in this case, a new excitonic ground state would from spontaneously, in analogy with the condensation of Cooper pairs in a superconductor. The search of the EI has long been hindered by the lack of materials with sufficient exciton binding, which in most systems scales with the gap size due to screening. This is why dimensionality and environment of 2D systems are central.

I will discuss how the EI phase is indeed realized in two-dimensional systems where screening of long-range Coulomb interaction is strongly reduced, and exciton binding is greatly enhanced. Using many-body perturbation theory, we single out the best candidate materials and discriminate between spurious insulating behaviour and genuine EI fingerprints, which are solely due to electron-electron interactions. We show that transition metal dichalcogenides are excellent candidates for the EI realization. In the case of MoS_2, we analyze the EI formation both in the monolayer [5] and in the bulk phase at high pressure [6]. The latter is found to be prone to the condensation of genuine excitons of finite momentum above 30 GPa, whereas the phonon dispersion remains regular; the EI sustains an out-of-plane permanent electric dipole moment with an antiferroelectric texture in the layer plane. We identify a unique Raman fingerprint for the EI formation and recognize that it was previously observed experimentally, thus providing direct spectroscopic confirmation of an ideal excitonic insulator phase in MoS_2.

Work in collaboration with D. Prezzi, M. Rontani, D. Varsano. Thanks to the whole CNR-Nano - UniMoRe team for many discussions and contributions. Work supported in part by EXC-INS (PRIN Project n. 2017BZPKSZ) and MaX-Materials design at exascale (European Centre of Excellence for HPC applications, EU grant n. 824143).

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Processing and applications of two-dimensional nanosheet inks

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Liquid phase exfoliation has been proved to be a cheap, scalable method for the mass production of 2D sheets. This talk will first discuss the galaxy of existent layered materials, with emphasis on synthesis, liquid-phase exfoliation, and characterization, focussing on some key applications recently developed in our laboratories, ranging from energy storage to printed electronics. We will for example discuss how two-dimensional Ti3C2 (MXene) can be formulated in aqueous and organic viscous inks for extrusion printing and inkjet printing, respectively, and demonstrate direct MXene printing on various substrates. The additive- and binary solvent-free MXene inks do not show coffee ring effect, enabling high-resolution printing without substrate pre-treatment. The resulting all-MXene printed micro-supercapacitors showcase excellent charge storage performance, including areal capacitance up to 43 mF/cm^2 and volumetric capacitance up to 562 F/cm^3 in protic gel electrolyte, coupled with long lifetime and good flexibility. We also show examples of all-inkjet-printed MXene arrays for ohmic resistors. The versatile direct-ink-printing technique highlights the promise of MXene functional inks for scalable fabrication of easy-to-integrate components of printable electronics. We will also discuss how MXenes can be used as a conductive binder for silicon electrodes produced by a simple and scalable slurry-casting technique without the need of any other additives. The nanosheets form a continuous metallic network, enable fast charge transport and provide good mechanical reinforcement for the thick electrode (up to 450 µm). Consequently, record high areal capacity anodes (up to 23.3 mAh cm^{-2}) can be demonstrated. EMI shielding applications will also be discussed.

Figures

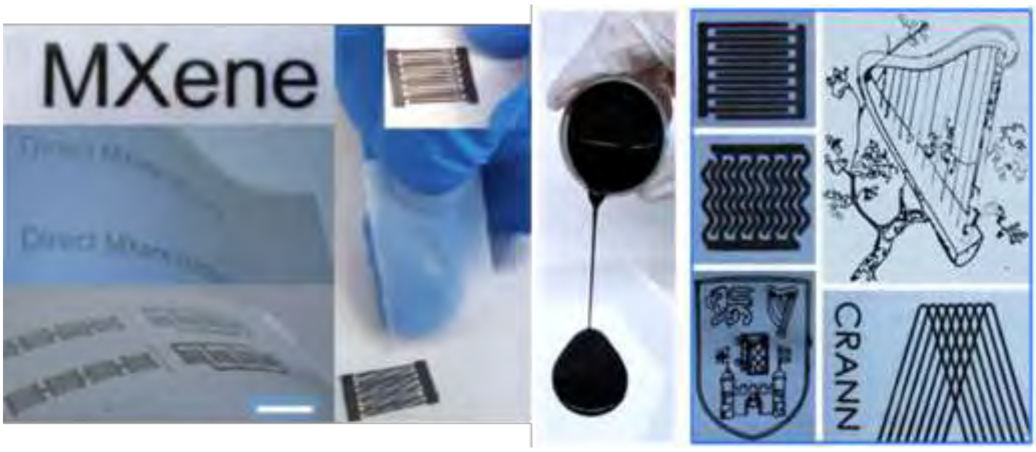

Figure 1: Printed devices based on MXenes inks

INVITED SPEAKERS

Exploring the Flatland of 2D materials by electrochemical STM: visualization of the active sites for the hydrogen evolution reaction with atomic scale precision

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2D materials such as chemically modified graphenes, transition metal dichalcogenides, layered double hydroxide to name only a few, are having a huge impact on electrocatalysis providing materials with outstanding activity for a variety of reactions.[1] However, despite the intense research efforts in this field, a clear identification of the real active sites in many reactions remains a great challenge, given the necessity to employ spatially and structurally sensitive techniques in *operando conditions* (i.e. during the application of an electrochemical potential in the presence of an electrolyte). Recently, we have developed an innovative approach to the study of 2D materials by using electrochemical Scanning tunneling microscopy. As demonstrated by a seminal paper,[2] this technique allows identifying catalytic processes at the nanoscale by observing a typical noise in the tunneling current, which is due to instantaneous variations of the tunneling junction. Starting from here, we have introduced a new quantity, the tunneling current roughness, which allowed us to acquire quantitative measurements of the electrocatalytic activity with subnanometric precision.

By using special model systems consisting of CVD grown transition metal dichalcogenides thin films ($MoSe_2$ and WSe_2), and iron ultrathin films covered by graphene, we achieved even atomic resolution in *operando* during the hydrogen evolution reaction. This allowed us to identify and quantitatively compare the chemical activity of several chemical and morphological features such as single atom vacancies, Fe-C4 defects, step edges, and even exotic line defects such as metallic twin boundaries.[3] In particular we could determine that iron single atoms trapped within the graphene basal plane are even more active than platinum, the benchmark catalyst for the hydrogen evolution reaction.

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The role of defects in liquid-exfoliated nanosheets: from degradation to functionalisation

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Liquid phase exfoliation has become an important top down production technique giving access to large quantities of nanosheets in colloidal dispersion. Importantly, this is a highly versatile technique that can be applied to numerous layered materials which can be exfoliated in a similar way using aqueous surfactant or suitable solvents as stabilisers. Nanosheets in dispersion are extremely polydisperse with broad lateral size and thickness distributions. To narrow size and thickness distributions, liquid cascade centrifugation has proven to be a powerful tool for efficient size selection yielding nanosheet dispersions with well-defined dimensions facilitating the characterisation. This has been the foundation to reach a better understanding of the exfoliation process which can be understood in terms of an equipartition of energy between exfoliation and tearing.[1] However, the role of defects present in the starting material or introduced during exfoliation has not been previously addressed. This is addressed here using graphite as model substance.

Furthermore, the size-selected nanosheet dispersions can be used to track degradation of the nanosheets by exposure to light or elevated temperature in different liquid environments.[2] The current status on degradation of various materials (different TMDCs, BP, MPS_3, $RuCl_3$, CrTe3, InSe) is summarised as function of nanosheet dimension and external stimulus.

In particular, degradation kinetics of WS_2 nanosheet ensembles in the liquid phase are investigated through photoluminescence measurements which selectively probe the monolayers.[3] Since it was observed that the reactivity towards oxidation of LPE WS_2 is strongly dependent on the surfactant,[4] data from sodium cholate (SC) and sodium dodecyl sulfate (SDS) is compared. Well-defined degradation kinetics are observed which enabled the determination of activation energies of the degradation and to decouple photo-induced and thermal degradation. The thermal degradation is slower than the photo-induced degradation, requires higher activation energies and is suggested to occur predominantly on the basal plane. Using SC as surfactant, it is sufficiently suppressed. The photo-induced degradation can be widely prevented through chemical passivation achieved through the addition of cysteine which, on the one hand, coordinates to defects on the nanosheets and, on the other hand, stabilises oxides on the surface which shield the nanosheets from further degradation.

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Graphene interfaces and devices for selective modulation of glial cells

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Abstract

Graphene based materials and devices has been in the spotlight for the next generation of neural interfaces. Most of the results achieved focused on optimizing the interface between grahene materials and neurons. However, the major cause of failure of neural engineering interfaces is the inflammatory reaction caused by glial cells, called astrocytes. These cells were frequently neglected or marginally considered as a barrier to be overcome between neural implants and neuronal targets. However, astrocytes are now recognized as responsible for the modulation of synaptic transmission, neurovascular coupling and control of central and peripheral nervous system homeostasis [1]. In addition, the alteration in their signalling and functional mechanism are implicated in all acute and chronic neuropathologies. Accordingly, knowledge on the interaction between astrocytes and graphene is essential to develop new implant-based therapies for the treatment of neurological disorders, such as epilepsy, brain tumours, and Alzheimer's and Parkinson's disease [1,2].

In this talk, we report on the results achieved on the interaction of graphene-based materials with astrocytes [3], and on the ability to successfully modulate selectively astrocytic function by means of GO-based electronic devices.

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Carbon dots for photodynamic therapy and imaging

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Carbon dots have been identified more than 15 years ago and with time they started to attract a lot of attention, as they are considered promising nanomaterials for future clinical translation. Carbon dots combine numerous characteristics including high photostability, low cytotoxicity, and superior biocompatibility. We have conceived and synthesised multifunctional carbon dots with deep-red emission properties through their controlled chemical modification using folic acid ligand. These conjugates, endowed of a high colloidal stability and an enhanced luminescence, are suitable for targeted intracellular production of reactive oxygen species by laser irradiation leading to efficient cancer cell death (Figure 1) [1]. In addition, we have modified the carbon dots with a chelating agent for gadolinium [2]. These dots showed a better magnetic resonance relaxivity than commercial MRI agents, resulting potential clinical tools as MRI/fluorescence dually functional imaging probes.

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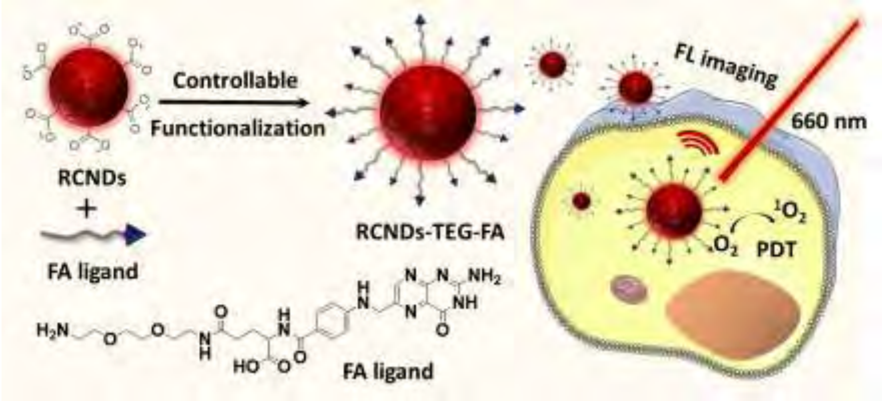

Figure 1: Design of multifunctional carbon dots for photodynamic therapy.

Water-based and Defect-free 2D Material Inks: from Printed Electronics to Biomedical Applications

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

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

Our formulation approach also allows to easily tune the charge of graphene, which is a key parameter in biomedical applications. [6-8]. Cytotoxicity tests confirm biocompatibility of the graphene inks, with cationic graphene dispersions having exceptional intracellular uptake profile as well as stability in the biological medium, even with protein serum, making this type of graphene very attractive to use in nanomedicine [8-9].

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Functionalized graphene oxide: A versatile platform for sensing

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During the last decade, two-dimensional materials (2DMs) have attracted great attention due to their unique chemical and physical properties, which make them appealing platforms for diverse applications in opto-electronic devices, energy generation, storage, and sensing. Among their various extraordinary properties, 2DMs possess high surface area-to-volume ratios and ultra-high surface sensitivity to the environment, which are key characteristics for applications in sensing. Furthermore, 2DMs' superior electrical and optical properties, combined with their excellent mechanical characteristics such as robustness and flexibility, make these materials ideal components for the fabrication of a new generation of high-performance physical and chemical sensors.

Graphene oxide (GO) combines the unique characteristics of graphene and related 2DMs such as the high mechanical strength and large surface area with an easy, low-cost, and scalable production. The oxygen functionalities, which consist mostly of hydroxyl and epoxy groups exposed on the basal plane and carboxy and carbonyl functionalities located at the sheet edges, are extremely reactive, thus allowing further modification of GO. Importantly, the electrical conductivity can be to a great extent restored and tuned during the reduction step of the functionalized graphene oxide (fGO), making it an extremely versatile material for sensing with electrical readouts.

Here, we will discuss piezoresistive pressure sensor based on a millefeuille-like architecture of reduced graphene oxide (rGO) intercalated by covalently tethered molecular pillars holding on-demand mechanical properties are fabricated. By applying a tiny pressure to the multilayer structure, the electron tunnelling ruling the charge transport between successive rGO sheets yields a colossal decrease in the material's electrical resistance.

We will also discuss novel generation of humidity sensors based on a simple chemical modification of rGO with hydrophilic moieties, i.e., triethylene glycol chains. Such a hybrid material exhibits an outstandingly improved sensing performance compared to pristine rGO such as high sensitivity (31% increase in electrical resistance when humidity is shifted from 2 to 97%), an ultrafast response (25 ms) and recovery in the subsecond timescale, low hysteresis (1.1%), excellent repeatability and stability, as well as high selectivity toward moisture.

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Synthesis and Stabilization of Large-Scale Monolayer 1T’-MoTe2

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Out of the different structural phases of molybdenum ditelluride (MoTe2), the distorted octahedral 1T’ hosts great interest for fundamental physics and could pave the way to the implementation of novel devices such as topological transistors. Indeed, 1T’-MoTe2 is a semimetal hosting superconductivity, which has been predicted to be a Weyl semimetal and a quantum spin Hall insulator in bulk and monolayer form, respectively. The large instability of monolayer 1T’-MoTe2 in environmental conditions, however, has made its investigation extremely challenging so far. In this work, we demonstrate the homogeneous growth of large single-crystal (up to 500 µm) monolayer 1T’-MoTe2 via chemical vapor deposition (CVD) and its stabilization in air with a scalable encapsulation approach [1]. The encapsulant is obtained by electrochemically delaminating CVD hexagonal boron nitride (hBN) from copper foil and it is applied on the freshly grown 1T’-MoTe2 via a top-down dry lamination step. The structural and electrical properties of encapsulated 1T’-MoTe2 have been monitored over several months to assess the degree of degradation of the material. We find that when encapsulated with hBN, the lifetime of monolayer 1T’-MoTe2 successfully increases from few minutes to several months. Furthermore, the encapsulated monolayer can be subjected to transfer, device processing, and heating and cooling cycles without degradation of its properties. The potential of this scalable heterostack is confirmed by the first observation of signatures of low-temperature phase transition in monolayer 1T’- MoTe2 both by Raman spectroscopy and electrical measurements.

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2D magnetic materials based on molecular/2D heterostructures

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The crossover between molecular magnetism and 2D materials affords the opportunity of creating novel molecule-based 2D materials and hybrid heterostructures formed by magnetic molecules and 2D materials [1]. In this talk I will present some relevant advances on this topic. In particular, I propose to create these hybrid heterostructures with the aim is that of tuning the properties of the 2D material *via* an active control of the hybrid interface [2]. To reach this goal the molecular system of choice will be based on spin-crossover complexes able to switch between two spin states upon the application of an external stimulus (temperature, light or pressure). As 2D materials we will focus on (semi)conducting graphene and transition metal dichalcogenides (MoS_2 and WSe_2). This concept will provide a new class of stimuli-responsive molecular/2D heterostructures, which may be at the origin of a novel generation of hybrid materials and devices of direct application in highly topical fields like electronics, spintronics or molecular sensing.

ONE page abstract format: including figures and references.
Do not change the font sizes or line spacing to squeeze more text into a limited number of pages.
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Please follow the model below.
Single-spaced and a single paragraph
Greek letters, sub- and superscripts should be formatted as such.

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Hofstadter's butterfly made labs accessible via 2D-COFs?

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The Hofstadter's Butterfly is one of the first and most fascinating examples of the fractal and self-similar quantum nature of free electrons in a lattice. Interestingly enough, its discovery was computationally obtained by Douglas Hofstadter already in 1976 by piercing with a magnetic field an ideal 2D square lattice [1]: The fractal plot of the allowed electronic states vs the intensity of the perpendicular magnetic field was soon after christened as the Hofstadter's Butterfly (HB). The HB encodes most exotic behaviors of quantum mechanics and topology, namely the quantum Hall effect and the conductance quantization which were then discovered in 1980s'. The fascination for the HB was then revived by the experimental isolation of 2D materials such as graphene: Although many exotic and very peculiar effects can be observed already at small magnetic fields [2,3], to observe an entire HB in a graphene layer, it is necessary to collect a single magnetic flux quantum within the area of a benzene ring, corresponding to a field of 79,000 T! For this reason, its experimental verification has only been realized in artificial periodic 2D systems, like Moiré lattices. This relegated the HB to a very peculiar physical *divertissement* for mainly theoretical interests. We propose here 2D covalent-organic frameworks (COFs) as the first pure materials for a direct experimental verification of the HB. Due to their large pore structures, the magnetic fields needed to measure most features of a HB are accessible in today's experiments. 2D COFs can thus turn this once-theoretical issue from the 70s into experimental reality and solve the quest for its proof in pure materials. Moreover, the intrinsic hierarchy of pores and the possibility to thread different fluxes at different pore scales adds to the COFs HB additional important structures which will be amply discussed in this invited talk.

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Figure

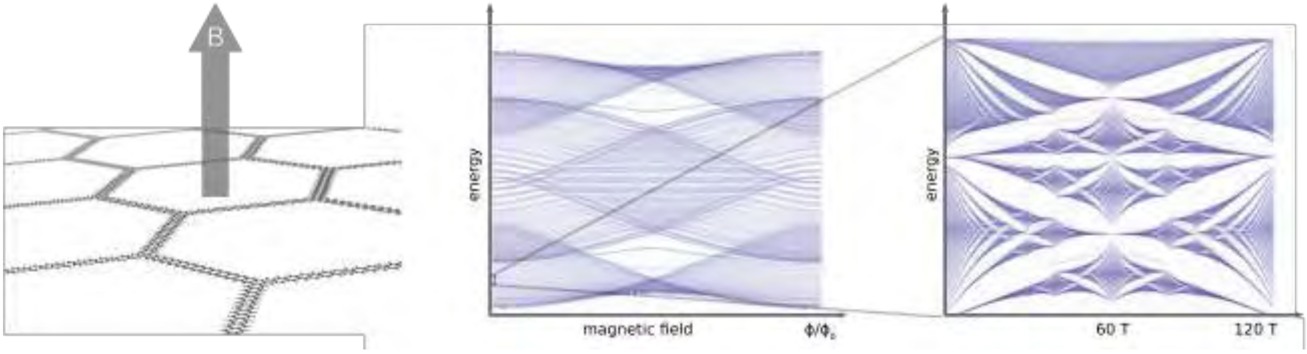

Figure 1: Butterfly spectrum arising from a 2D COF with a honeycomb lattice at low magnetic fields.

Formation and functionalization of 2D materials: a molecular approach

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In this presentation, I will mainly focus on the functionalization of graphite, graphene, and transition metal dichalcogenides using molecules, though the concepts can be applied to other 2D materials too [1]. Nanostructuring is at the heart of all functionalization protocols that we develop, because it opens new possibilities of control and functionality. A variety of scanning probe microscopy methods are used for visualization, characterization, and manipulation. A first approach is based on molecular self-assembly at the interface between a liquid or air, and graphite or graphene. I will discuss concepts of nanostructuring emphasizing the effect of solvent, solute concentration and temperature, stimulus-driven self-assembly and self-assembly under nanoconfinement conditions [2]. A second approach is based on grafting molecules on 2D materials via covalent chemistry. It will be demonstrated how in addition to bottom-up strategies [3] that provide control on the density and layer thickness, as well as submicron to nanoscale nanostructuring [4,5], also top-down scanning probe microscopy and optical lithography can be used to structure such covalently modified surfaces [2,6]. A third approach does not focus on the functionalization of the surface, but uses the surface as a support for the in-plane covalent stitching of molecules, leading to the formation of on-surface 2D polymers. The (de)polymerization can be controlled by scanning tunneling microscopy [7,8]. Some applications will be given [9].

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2Dmat Immune profiling by High-Dimensional Approaches

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We recently depicted the “Nano-immunity-by-design” where the characterization of 2D materials is not solely based on their physical-chemical parameters but also their immune-profiling. [1] The immune profiling can be revealed on its complexity in unique, informative ways: high dimensional approaches. [2,3] We exploited high-dimensional methods, such as single-cell mass cytometry and imaging mass cytometry on graphene and other novels two-dimensional materials, such as graphene and transition metal carbides/carbonitrides (MXenes). [4-6]

We revealed that the amino-functionalization of graphene oxide increased its immunocompatibility. [4] Moreover, we combined graphene with $AgInS_2$ nanocrystals, enabling its detection by single-cell mass cytometry on a large variety of primary immune cells. [5] Recently, we reported the immune modulation of specific Mxenes, Ti_3C_2Tx in particular, in combination with their antiviral properties against SARS-CoV-2 again by single-cell mass cytometry and other high dimensional approaches. [6]

Together with our published works, I will present unpublished results in a wider variety of novel 2D materials such as Mxenes, MoS_2, WS_2 on human immune cell subpopulations, as well as on mice and swine models.

Our results conceptualize that chemical and immunological designs of 2D materials offer new strategies for their safe exploitation in biomedicine.

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Real-Time monitoring and kinetic studies of graphene growth on solid and liquid copper

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Graphene is a perfect 2D crystal of covalently bonded carbon atoms and forms the basis of all graphitic structures with superior properties that can be exploited in many research areas. The synthesis of large, defect-free graphene is a major challenge towards industrial applications. Chemical Vapor Deposition (CVD) is the most well-known method of graphene growth. The growth process is rather complex, as it involves multiple reactions such as hydrocarbon decomposition, carbon adsorption and subsequently diffusion on the catalytic substrate the generation of the nucleation point and finally the growing. Chemical vapor deposition (CVD) on liquid metal catalysts (LMCats) is a recently developed method for the fast synthesis of high-quality single crystals of graphene. In contrast to a solid catalytic substrate, graphene growing on Liquid Metal Catalysts (LMCat) might be a solution for the production of defect-free single graphene domain at high synthesis speeds due to the enhanced atomic mobility, homogeneity, and fluidity of a LMCat. In-situ monitoring of such a complex procedure is of paramount importance for the control of graphene growth and the understanding of growing kinetics. However, up to now, the lack of *in situ* techniques enabling direct insight of the growth process has limited our understanding of the process dynamics and primarily led to empirical growth recipes. Therefore, *in-situ* monitoring of the graphene growth, coupled with a real-time control of the growth parameters, is necessary for efficient synthesis. Herein, we report on the development of a real time monitoring of graphene growth via in situ reflectometer for the case of graphene grown on solid and via in situ optical microscopy, Raman spectroscopy and X-Ray diffraction for graphene grown on liquid metal substrates.

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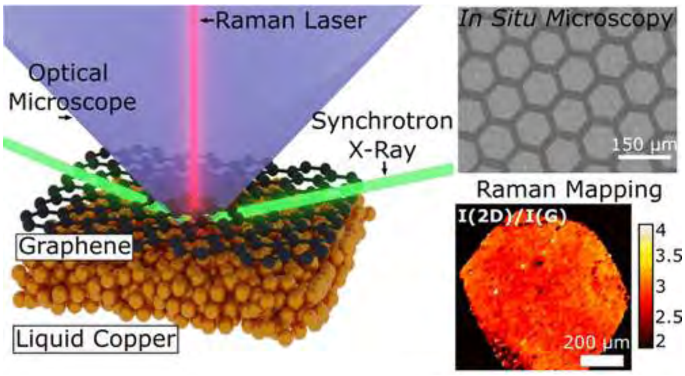

Topological Two-Dimensional Polymers: a chemistry way towards quasiparticle physics

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Quasiparticles and collective excitations have been in the focus of condensed matter physics of the past decades. Their in-depth exploration has led to a significantly better understanding of the nature of matter in a quite general sense, beyond the boundaries of the materials-oriented disciplines. Following Carlo Beenakker, by taking “what nature offers” and to deeply explore the intriguing physics inherent to known and newly developed materials has led to the discovery and ultimately the deliberate control of many exotic phenomena, including topological insulators, Majorana fermions, skyrmions and polaritons, to name just a few. The impact of this research is not restricted to condensed matter physics or the related emerging field of quantum materials, it indeed drives our very fundamental understanding of matter.

In my talk I will demonstrate a path beyond “what nature offers”, extending the realm of quantum materials to “what is mathematically possible and chemically feasible”. I will show that the proper and precise arrangement of molecular building blocks in regular lattices, linked together by strong bonds with controlled electronic interactions [1], opens the door to advance electronics and optoelectronics, to manifest exotic physics with Dirac points and flat bands [2] (Figure 1), and to establish new chemical concepts that allow us to face current global challenges. I will bridge our work on two-dimensional semiconductors to the rather novel class of crystalline two-dimensional polymers, a materials class that relies solely on the compounds of organic chemistry, and thus is abundant, non-toxic and potentially bio-compatible.

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Figures

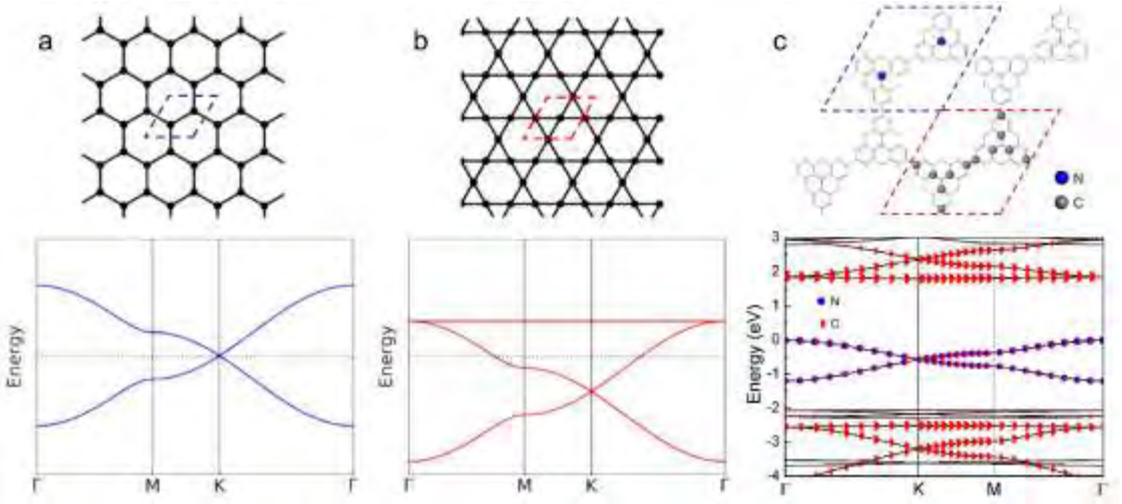

Figure 1: Tight-Binding band structure of the (a) honeycomb and (b) the kagome lattice. (c) Atomistic band structure (DFT) calculated for a honeycomb-kagome polymer based on heterotriangulenes.

Patterned Functionalization of Graphene and Inorganic 2D-Materials

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A fundamental challenge of graphene functionalization is the spatially resolved covalent patterning of this 2D-system. We will also emphasize our recent success in this direction. We have demonstrated that both mask assisted patterning of graphene and laser writing can be used and even be combined to generate hierarchically ordered multifunctional 2D-architectures. The potential of practical applications is enormous. This includes chemical information storage exemplified by complete write/read/erase cycles. Moreover, we will present our recent on the chemical functionalization of other 2D-materials such as particular black phosphorus (BP) and MoS2.

Chemistry of low-dimensional materials on the atomic level

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In this study we demonstrate that the accelerated electrons in the transmission electron microscope (TEM) can act as stimulus and initiator for reactions while imaging; detailed understanding of the beam electron– specimen interactions is required. We present recent results on atomically-resolved, time-dependent in-situ TEM imaging using the chromatic- and spherical-aberration-corrected low-voltage SALVE instrument operating in the voltage range between 80kV and 20kV [1-5]. First, we elucidate the accelerating-voltage-dependent formation of defects in the case of single-layer MoS_2. The results suggest that elastic and inelastic interactions are strongly connected resulting in a twostep interaction process and density functional theory molecular dynamics shows that excitations in the electronic system can form vacancies through ballistic energy transfer at electron energies, which are much lower than the knock-on threshold for the ground state [6].

We further identify the structure of electron-beam-induced defects and their electronic properties and follow the migration paths and associated property changes in a variety of 2D TMD and TMPT crystals [6,7] and analyse in-situ structural and chemical modifications of different freestanding transition metal phosphorus tri-chalcogenides (TMPTs) from atomically resolved imaging, low-loss and high-loss EELS and 3D electron diffraction. We calculate the displacement thresholds, electronic properties, and the displacement cross-section of single vacancy S and P by ab-initio calculations which help understanding the observed structural transformations. Moreover, our results provide insight into layer-number-dependent changes in the electronic and crystallographic properties as result of lowering the dimensionality. As the TMPTs are often very oxygen-sensitive, they were prepared with the help of our newly-developed polymer-assisted sample preparation method [8,9].

We show moreover that also 2D polymers and their defects can be resolved at near-atomic level [10] which can be further increased, when imaging at 120kV.

On the fundamental base of chemistry, we show that differentiating between the bond nature by measuring the distance between two metal atoms is possible, when confined in the narrow space of a SWNT [11]. We show here the interaction between the moving matter and the carbon nanotube and its application for carrying metal atoms to a nucleation seed, realizing in situ observation of metal nucleation. we find that crystal nucleus formation occurs through a two-step nucleation mechanism [12]. Finally, we intercalate bilayer graphene in-situ by lithium, study not only the in-situ the lithiation and delithiation processes [13], as well as the formation process of the new high-density crystalline Li- phase.

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Precise synthesis of 2D crystals for energy applications

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Layered transition metal dichalcogenides (TMDs) display a variety of structural polymorphs defined by the symmetry of transition metal coordination polyhedra. Tailoring the lattice symmetry within individual TMD layers enables to achieve very different electronic properties ranging from semiconducting (2H phase) to metallic and semimetallic (1T/1T' phases) with the same material composition. Exhibiting metallic behaviour, the metastable 1T' phases are particularly appealing for electrocatalytic hydrogen production from acid water as they approach Pt performance. The direct synthesis of the metastable phases of high purity and in measurable quantities remains challenging. Here, we present our work on the bottom-up synthesis of the metastable 1T' phase of WSe_2 based on the reaction between molecular precursors in liquid phase [1]. We design a kinetically-controlled bottom-up synthesis from molecular precursors to enable the formation of the metastable phase. We further demonstrate that the 1T' phase is stable up to 400 °C and it is convertible into the semiconducting 2H phase at higher temperatures, making it suitable for a wide range of applications. The 1T' WSe_2 nanosheets exhibit a metallic nature evidenced by an enhanced electrocatalytic activity for hydrogen evolution reaction as compared to the 2H WSe_2 and different sulphides. Further, we demonstrate how this synthesis approach can be applied to design of new catalytic systems.

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Chemistry and Catalysis Mediated by 2D Black Phosphorus Decorated with Transition Metals Species

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Among 2D-materials exfoliated black phosphorus (*i.e.* phosphorene) [1] is still attracting a great interest mostly as a consequence of its peculiar electronic and optical properties, which encompass a strong anisotropic behavior, a tunable band-gap, dependent on the thickness of the exfoliated phosphorene flake, and a high electron mobility. These intriguing properties follow from the unique corrugated two-dimensional structure of this p-type semiconducting material and have stimulated a huge amount of research mostly addressed to explore and exploit its potential applications in different areas of physics and materials sciences and technologies. [2] In contrast, much less attention has been paid to study the chemical and biologic properties of this innovative material and only recently intriguing results have appeared also in these areas. [3,4]

Here, we present our recent results showing that phosphorene could behave as an extended, flat, molecular platform to be used for catalytic applications. In particular, we have demonstrated that nanoparticles of different transition metals (nickel, copper, palladium, etc.) can decorate the surface of the exfoliated material imparting to phosphorene a higher chemical stability towards air oxidation and forming a sort of inert support to host catalytically active nanoclusters.[5,6] Remarkably, attempts to functionalize the surface of the few-layer exfoliated material with organopalladium precursors do not result in the formation of any organometallic derivative atop the polyphosphorus surface, but affords a very unusual nanocomposite featuring dipallada units covalently bonded amidst two contiguous layers of the exfoliated black phosphorus.[7] The seclusion of the palladium centers in this latter material, makes its catalytic activity in standard hydrogenation reactions dropping to zero, thus indirectly confirming the inaccessibility of the metal centers.

Acknowledgements

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The authors also acknowledge the MAECI Italy−China bilateral project "Graphene related Innovative 2D Materials for Sustainable ENerGetIcs and catalysis (Ginseng PGR00953)

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Recent Developments in the Chemistry of Graphene and Other 2D Materials

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The chemistry of 2D materials (2DMs) offers several advantages:
1) Improved solubility and easier handling of otherwise “difficult” materials;
2) Additional functions can be implanted on the 2DMs, such as chromophores, electroactive units, drugs, etc.;
3) Potential toxicity of the 2DMs can be at least partially lifted by organic functionalization, thanks to improved solubility and de-aggregation in physiological media.
However, usually, 2DMs are unreactive chemical species. In order to force the reactivity of 2DMs, either we need to employ particularly harsch conditions or we need to activate the substrate towards additions.
During this talk, we will present the various approaches to graphene functionalization and will also analyze other important challenges in graphene chemistry, such as the lack of standardization in the production of the graphene family members. Control of lateral size, aggregation state (single *vs.* few layers) and oxidation state (unmodified graphene *vs.* oxidized graphenes) is essential for the translation of this material into standardized applications. We will also address the toxicological impact and the limitations in translating graphene into advanced materials.
We will also discuss how exfoliated MoS_2 shows significant surface enhanced Raman scattering (SERS) activity towards specific dyes with low detection limits. The versatility of this approach allows the covalent functionalization of MoS_2 without relying on edge or basal-plane defects of the structure. This effective process is very useful for the preparation and functionalization of metallic TMD materials for further SERS applications.
This work was supported by the European Commission, Graphene Flagship project, Core 2 and 3 (no. 785219 and 881603).

From polycyclic aromatic hydrocarbons to nanopore-nanogap 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 – 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.

Chemistry of 2D graphene analogues – silicene and germanene

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Monoelemental two-dimensional (2D) materials are at the forefront of current material research. Beyond graphene, the large family of unexplored materials remain unexplored. The development of these materials starts rapidly in last few years. In the carbon or so called tetrel group are beyond carbon silicon, germanium and tin. These elements are capable to form a layered allotrope, however the synthesis methods are not so straightforward as for the graphite. All these materials are non-zero band-gap semiconductors with huge application potential in electronic and optoelectronic devices. This property opens new application possibilities in electronic and optoelectronic devices. Also, the research in the field of energy storage and conversion, as well as sensors and other fields, is rapidly growing. The properties strongly correlate with chemical modifications and functionalization. Compare to graphene, the chemistry of its heavier counterparts remains significantly less explored.[1] The main rote for top-down methods of synthesis is based on exfoliation and functionalization of Zintl phases with general formula AB_2 consisting from hexagonally arranged Si/Ge layers separated by alkaline earth atoms, typically calcium. The exfoliation procedure is typically based on reaction with acid at ow temperature forming hydrogen terminated surface. In this contribution will be demonstrated novel methods and strategies in synthesis and functionalization of silicene and germanene monolayers. The methods providing controlled functionalization surfaces are based on formation of negatively charged silicene/germanene and subsequent reactions with halogenderivatives, formation of reactive halogenated intermediates or direct reactions of Zintl phases with bromine or iodine derivatives. The developed methods were used for introduction of various alkyl and aryl derivatives in order to control transport and optical properties of functionalized materials. The functionalized germanium derivatives exhibit strong photoluminescence, which maxima can be tuned by substitution with various alkyl and aryl derivatives. For newly developed materials were utilized various applications including gas sensors, hybrid organic-inorganic OLED devices and photocatalytic water splitting.

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van der Waals and Lateral Heterostructures of Organic and Inorganic 2D Materials: Synthesis and Device Applications

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van der Waals and lateral heterostructures of 2D materials open broad avenues for the engineering of novel nanomaterials for both basic research and applications. In particular hybrid heterostructures of organic and inorganic materials enable to combine their most attractive and complementary intrinsic properties (e.g., chemical functionalization, charge carrier transport, photo-response, etc.) into one material system with novel functionalities. In this presentation I will give an overview of our recent progress on the synthesis, characterization and device applications of such heterostructures composed of various 2D materials such as graphene, transition metal dichalcogenides, molecular nanosheets. It will be demonstrated how these innovative hybrid materials are employed in a variety of devices with advanced properties including phototransistors, chemical sensors, optical fibers for non-linear photonics, rectifiers, solar cells, photodetectors, ambipolar and anti-ambipolar transistors, and electroluminescent light emitters.

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Figures

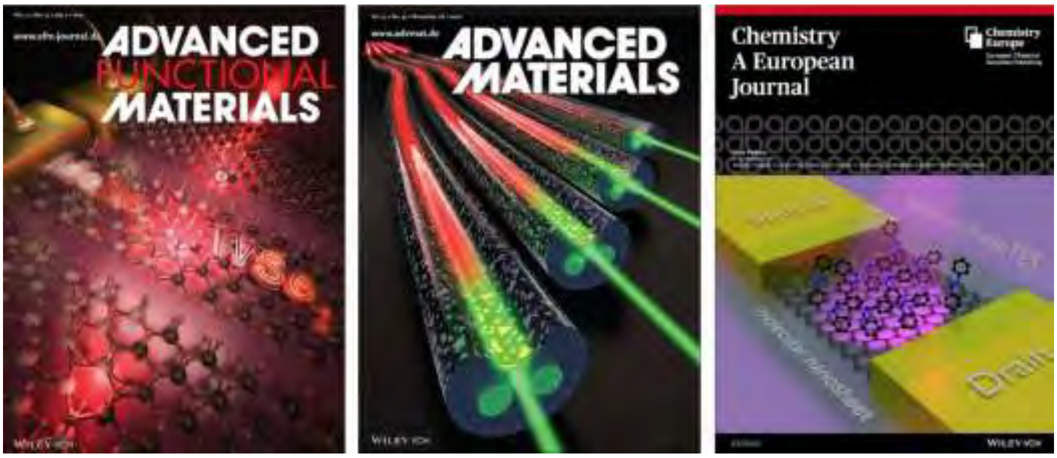

Figure 1: Cover artworks for Refs. [1] (left), [6] (middle) and [7] (right).

INVITED SPEAKERS

(Industrial Forum)

Solution processed 2D crystals for energy applications

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Abstract

Solution processing represents an appealing industrially scalable, reliable, inexpensive production processes of graphene and related two-dimensional materials (GRMs).[1,2] These are key requirements for the widespread use of GRMs in several application areas,[1-6] providing a balance between ease of fabrication and final product quality.

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

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Graphene oxide in the multi-barrier system provided by the Water Safety Plans

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Water Safety Plans are recognized in the new directive on drinking water as the first tool to guarantee the quality of water to the consumer through a preventive approach.

The deployment of a Water Safety Plan consists in an olistic risk assessment activity, in which are identified the dangerous events that can occur in the different parts of the supply chain.

If the measures implemented reduce the risk to an adequate level, no improvement actions are necessary.

If the risk analysis leads to a medium-high residual risk, improvement actions will be activated.

Among the Water Safety Plans that the Hera Group has already completed there is the one related to the Pontelagoscuro plant near Ferrara, that serves 9 municipalities and distributes over 14 million cubic meters per year.

The plant treats water from both groundwater and surface sources, as it draws water from the Po river.

The Hera - CNR collaboration was born for the study of innovative methods for the removal of some molecules such as those of PFAS.

The current agreement Hera-CNR will use for these purposes the reduced graphene oxide (RGO) applied to the unused material of the filters used in the biomedical field (scaffold), pursuing objectives of circular economy in the materials used in the experimentation

Figure 1: Pontelagoscuro Plant: near Ferrara, it treats Po river water on which there will be applied the innovative technology on emerging pollutants using graphene oxide

Opportunities for 2D materials to facilitate research in extreme environments

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In Antarctica, temperatures reach almost -90 °C, winds rise to over 300 km/h, and the average elevation is 2500 m. It holds the key to understanding the environmental history of our planet and our impact on it, and is an ideal location to study everything from biology and glaciology to geomagnetism and astronomy. However, such an inhospitable environment poses countless problems for the researchers who work there and the logistical teams that support them. In this presentation, I will recount my experience of a year spent at the Franco-Italian research station, Concordia, isolated on the Eastern Antarctic Plateau at an elevation of 3300 m and a distance of 1200 km from the coast, from the unique perspective of a materials scientist. I ask the question, how can 2D materials facilitate research in a location such as this, considering such themes as energy generation and storage, smart clothing, and de-icing. In pushing technologies to their limits, we can not only support current research at the Poles and high altitudes but also prepare ourselves for other hostile environments that we will find as we continue our exploration of Space. These potential new applications of 2D materials emphasise the benefits of looking outside our own bubble for new research and industrial opportunities.

Figures

Figure 1: Photos of Concordia station and the surrounding scientific and logistic laboratories and warehouses (left); and the caravan of tractors that resupplies the base in a 1200 km journey from the coast 2-3 times per year (right).

Carbon dots as radiosensitizers in tumor treatment.

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In the last decade nanotechnology became decisively in the biomedical research and carbon-based nanomaterials are among those most promising in a plethora of bio-applications [1]. In particular, Carbon Dots (CDs) that are the youngest member of this family are carbonaceous nanoparticles less than 20 to 60 nm with an irregular surface rich of polar functional groups that confers intriguing chemical properties [2]. Aqueous disperdibility, brilliant photoluminescence and good biocompatibility together with easy synthetic procedures make these nanomaterials appealing systems for multiple biological applications.

In particular, they are very promising material for new approaches in cancer application [3]. In this context, radiotherapy is largely used for tumor treatment. However, its effectiveness is highly dependent on the patient specific answer [4] and also side effects can be relevant since the dose levels of ionizing radiations can largely damage adjacent normal tissue [5].

Therefore, currently great efforts are made to develop effective and biocompatible radiosensitizers. A Nano-radiosensitizer is an ideal material to improve radiotherapy due to its high degree of tumor tissue uptake and secondary electrons or radical production.

In this work, surface oxygenated CDs prepared from olive solid waste (CDs-B) [6] have been fully characterized and investigated as radiosensitizers in tumor treatment. The enhanced radio-sensitization effect of CDs-B at different dose irradiation was studied on two cellular cancer lines, Human Osteosarcoma (U-2 OS) and Lung Carcinoma Steam Cells (LCSC) and the possible involved mechanism was preliminarily investigated. Data show for the first time that CDs-B in synergy with ionizing radiation could noticeably inhibits cells proliferation and improve apoptosis at irradiation dose level lower than standard treatment. This is mainly due to the production of reactive oxygen species (ROS) by CDs-B in combination with irradiation. This study indicates that the CDs-B are new promising nano-radiosensitizers for tumor radiotherapy paving the way for innovative treatments of tumors.

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The fundamental role of two-dimensional materials for perovskite solar modules and panels

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Abstract

Two-dimensional (2D) material are playing an important role in perovskite photovoltaics. Halide perovskite and 2D materials, including 2D perovskites, can be combined to enhance efficiency and stability of solar cells. Beside graphene and related materials, such as graphene oxide and MoS_2, a new perspective class of 2D materials the MXenes, such as Ti_3C_2, demonstrated a beneficial role for interface engineering in perovskite solar cells (PSCs) [1,2]. The use of 2D materials for perovskite photovoltaics does not limit to lab scale cells but it is a milestone in the scaling up of this technology to large are solar modules and panels.

In this talk, I will present the progresses made with 2D materials to improve the performance and the stability of large area perovskite photovoltaics. With a thorough multiscale experimental investigation, we point out that 2D materials can tune interfaces properties, reduce ion migration and modify the work-function of the perovskite absorber and charge transporting layers, all aspects that directly impact on the final efficiency and the stability under accelerated stress tests.

An optimized 2D material strategy has been successful extended from lab-scale cell dimensions to large area module on 25 cm^2, 121 cm^2 till to 210 cm^2 substrate area with efficiency on active area of 20%, 17.2% and 14.7%, respectively. Moreover, the use of 2D materials allows us to reach more than 26% efficiency in a tandem graphene-perovskite/silicon cell [3]. By using 2D materials we realize a solar farm with 0.5 sqm panels obtained with single junction graphene-perovskite sub-modules with efficiency up to 16% (on a substrate area of more than 100cm^2) and panel efficiency exceeding 10%

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Graphene: opportunities for multifunctional lightweight structures in automotive sector

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In the automotive sector, several motivations push the industry to achieve better performances at low weight. Environmental constrains, fashionable appearances and electronical comfort can be reached by new materials that are capable of multifunctional and lightweight behavior. Graphene-based composites are one of the most promising categories of such materials, due to the multiple properties that graphene related materials can give to a plastic automotive component. Since many years, CRF is working to face the challenges of this integration, keeping in mind the safety and the durability of the automotive product. The presentation will give an overview of the activities performed and a glance to the future possible applications.

References

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Figures

Figure 1: Dashboard plastic component filled with graphene nano platelets for invisible button integration

2D material for lubrication, a commercial application.

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Additive formulation is crucial step in lubricating oil industry for improving some intrinsic properties of the base oil, removing some of its undesirable characteristics and eventually displaying some new features. In this contest, 2D material can play an important role not limited to the pure technical performance of a new technology, but also by contributing to the transition to a more ecofriendly products.

Graphene-XT (GXT), an innovative start-up with a proprietary graphene production patent, which core business is the application in various industrial fields through customer-designed solutions, is about to lunch its first product line of graphene-based engine oils for traditional cars, mileage cars and classic cars.

Thanks to its "sliding" chemical nature, graphene emerged as a perfect lubricating agent to enhance the anti-friction and anti-wearing characteristics of engine oils, but we found it is much more than that.

Tests unveiled the enhanced properties of our graphene-based additive for engine oils. Additionally, the graphene's effect was also demonstrated by bench test and on high-performance oils for motocross directly on track.

GXT-LUBE®, our new product line, is worth being known.

Figures

Figure 1: GXT Lube range.

Abalonyx' Expansion Plan for GO Production and Applications

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Abstract

Abalonyx has recently been taken over by a major Norwegian industrial company, with ambition to invest both in production facilities and certain applications. The takeover will be officially announced with a press-release by mid-August.

Over the last 8 months we have seen dramatically increased interest for graphene oxide and reduced graphene oxide from industry worldwide. Abalonyx is one of few producers in position to meet the increased demand. With the resources of the new owner we will be able to scale up to any quantities in response to market demand.

We will also continue our work with standardization of different derivative products, but with increased focus on customer specific needs.

Further details of our plans will be presented and discussed.

ORAL CONTRIBUTIONS

Continuous-flow synthesis of high-quality few-layer antimonene hexagons

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Abstract

2D-Pnictogens (P, As, Sb and Bi) have gained increasing attention due to their semiconducting behavior, with thickness-dependent band gaps that can be modulated by strain, doping or chemical functionalization, which can be useful for fabricating optoelectronic devices. Additionally, these 2D-materials offer unique photonic, catalytic, magnetic, and electronic properties. [1] Within this group, antimonene shows exceptional physico-chemical properties. Although some of its theoretically-predicted remarkable properties have already been experimentally demonstrated, others remain a challenge to corroborate because of the absence of a suitable synthetic method to produce the required high-quality material. [2] Antimonene can be isolated using top-down and bottom-up approaches. [3,4] A new bottom-up approach has been recently reported, involving a solution phase synthesis of well-defined hexagonal few-layer antimonene via anisotropic growth, [5] which has facilitated large-scale production of this material. In this context, we optimized the synthetic parameters for the production of high quality few-layer antimonene hexagons, and their implementation in a large-scale manufacturing process under continuous-flow conditions to pave the way for optoelectronic device fabrication. [6]

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Zeolite-Templated Carbon: a Promising Material for Supercapacitors

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Chemical vapor infiltration (CVI) of a hydrocarbon in a molecular sieve is a synthesis technique used to generate a crystalline structure of carbon that remains up to now purely theoretical: Schwarzite [1-2]. This structure has indeed been foreseen as a promising material to manufacture electrodes for supercapacitors. Nonetheless, many technological challenges still have to be overcome in order to make this synthesis technique more accessible [1].

The molecular sieve that was selected for this study is zeolite, for its extraordinary adsoption properties. Zeolite is used as a template: the aim is to replicate its structure by infiltrating carbon atoms inside the nanopores [3]. The idea is to obtain, after zeolite dissolution by means of hydrofluoric acid treatment, a material that is exclusively composed of carbon, with a 3D porosity network consisting of nano-sized pores and thus displaying a high specific surface (see figure1).

SEM observation shows that the obtained material has a very similar structure to that of the initial zeolite (see figure 2) which augurs well for the successful replication of the zeolite structure.

Therefore, the presentation will focus on the synthesis and characterization of these materials, using thermogravimetric analysis, X-Ray diffraction, Raman, etc.

Figures

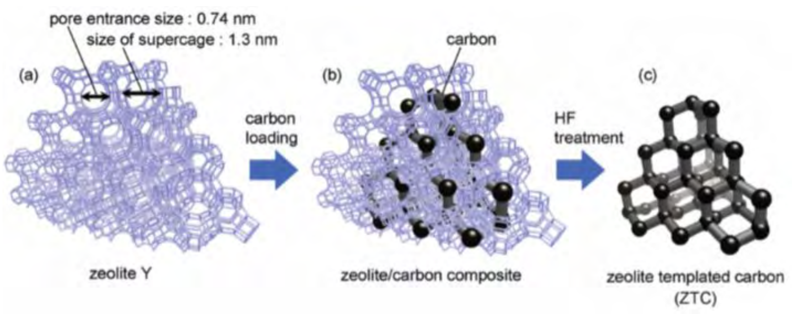

Figure 1 : *: Schematic Zeolite-Templated Carbon (ZTC) Synthesis [3]*

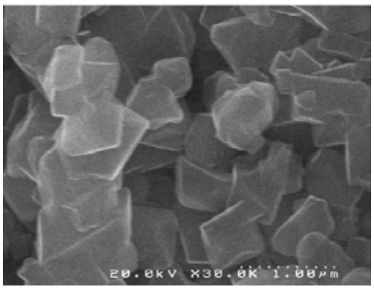

Figure 2 : *SEM image of carbon material obtained after zeolite dissolution with hydrofluoric acid*

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Water Surface Unlocks Chemo-Mechanical Properties of Graphene

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Abstract

The mechanics of graphene is commonly probed in tensile tests which inevitably perturb the thermally fluctuating membrane [1]. Compressive tests are expected to preserve the natural out-of-plane fluctuations in graphene, however only in experimental designs where the mechanics of the graphene and of underlying substrate are not intermixed [2]. Water offers numerous advantages to conduct graphene compression experiments: i) The surface of water is strictly planar and serves as an appropriate mattress for the two-dimensional graphene. ii) The adhesion energy between hydrophobic graphene and water is lower than graphene on typical substrates which guarantees a negligible graphene/substrate interaction. In addition, iii) graphene can smoothly slide on the surface of water (no dry friction) which allows free deformation upon compressive buckling. Here, we compress graphene floating on water in a Langmuir-Blodgett trough. Remarkably, the Young's modulus respects a scaling law [3] and falls two orders of magnitude below the previous reports. The chemical functionalization/modification of the graphene lattice affect the mechanics of graphene; particularly we explored the effect of the sp^3 hybridization and crystalline voids. Compression of graphene beyond the elastic limit yields wrinkles, the evolution of which, in a progressive compression, gives rise to internal friction, i.e. viscoelasticity, observed for the first time in graphene.

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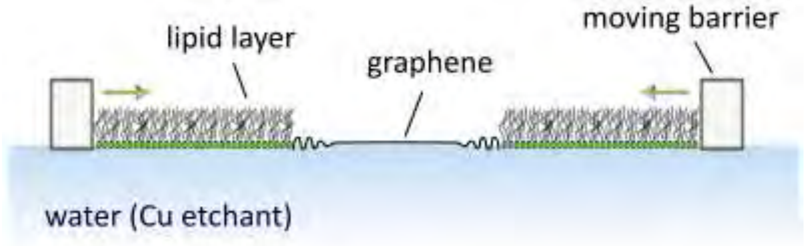

Graphene (pristine or chemically functionalized) floating on the surface of water is subject to the external compression from a lipid layer in a Langmuir-Blodgett trough

The Importance of Relaxation Effects on the Properties of Twisted van der Waals Materials

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The stacking of single layer 2D crystals, such as transition-metal dichalcogenides, creates a new class of materials: van der Waals [hetero]structures. [1] In these materials, a variety of structures can be realized by controlling the stacking order and the twist angle between adjacent layers. In our work, the influence of the twist angle on the structural and electronical properties of MoS_2 bilayers was studied using reactive force field (ReaxFF) and density functional theory (DFT) calculations.

Interlayer twisting leads to the formation of moiré patterns of rapidly increasing size with decreasing twist angles towards 0° and 60°, resulting in huge simulation cells that are only accessible computationally using force fields. [2] This concept of constructing twisted bilayers, by a rigid rotation between the individual layers, is used in many studies. However, it neglects the importance of relaxation effects – these result in a significant deformation of the individual layers, especially for small twist angles, and strong changes of the interlayer distance in different areas of the structure. Our work gives a detailed overview of the influence of relaxation on the structural properties in such systems and how different structural regimes – soliton, transition, and moiré regime – form depending on the interlayer twist angle. We further demonstrate how these changes can strongly influence the analysis of electronic properties, as shown in the Figure 1, thus emphasizing the need for thorough relaxation in computational studies of van der Waals [hetero]structures.

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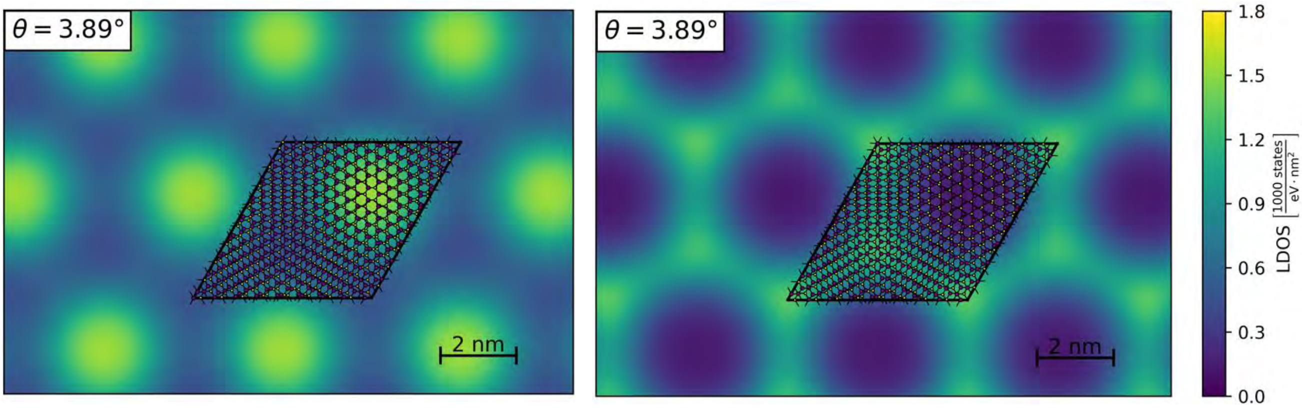

Figure 1: Atom-projected density of states map in the valence band region (E = -0.268 eV) of a bilayer MoS_2 with a twist angle of 3.89°. The atomic structure is included for the primitive moiré cell. In the case of (left) rigidly twisted layers the valence band is localized in strongly confined regions. Extensive changes can be observed in the case of (right) a fully relaxed structure where a delocalized hexagonal network, associated with the appearance of strain solitons, is formed.

Electrochemistry at the edge of a single graphene sheet

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Abstract

The investigation of electron transfer at an isolated edge of a single graphene sheet is important to evaluate the (electro) chemical reactivity of the edge at a single object level and assess the prospects for applications. Here, we first outline a simple photolithography-based method to realize a high aspect ratio (millimeter-to-nanometer) nanoelectrode at the edge of an isolated graphene monolayer on an insulating substrate. Subsequently, we present the electrochemistry of two redox probes at such electrodes. The voltammetric response at these graphene edge (GrEdge) electrodes show quasi steady state behavior exhibiting high mass transfer rates, attributed to their nanoscale geometry and a unique diffusion profile. Consequently, the heterogeneous electron transfer is found to be kinetically limited at the GrEdge – a behavior similar to that observed at single nanowire electrodes. These characteristics allow the observation of fast electron transfer kinetics at such electrodes and enable the detection of molecules such as the reduced form of nicotinamide adenine dinucleotide (NADH) or flavine adenine dinucleotide (FAD) down to low micromolar concentrations. Furthermore, we demonstrate the use of electrochemical modification to attach nanoparticles or organic moieties selectively to the graphene edge. In contrast to an unmodified GrEdge, gold nanoparticle modified GrEdge electrodes show steady state voltammetric response for the classical redox probes, indicating that the electron transfer is reversible and mass-transport-limited. After the modification, the sensitivity to the detection of FAD could be improved, while the performance for sensing NADH was only slightly affected. These results indicate that single edge nanoelectrodes with or without chemical modification are promising candidates for electrocatalytic and sensing applications.

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Selective Covalent Organic Functionalization Of Patterned Graphene Via 1,3-Dipolar Cycloaddition

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The outstanding mechanical, optical, and transport properties of graphene are of great interest for a plethora of applications. However, these often require graphene manipulation, while preserving its exceptional properties has proved to be extremely complex. A promising strategy to finely tune graphene's physical and chemical properties consists in the covalent functionalization of graphene with organic molecules, resulting in a synergistic combination of the individual features of each component. We report here the selective graphene surface functionalization via electrons irradiation, which allows both a controlled enhancement of the chemical reactivity of high quality graphene flakes and the precise design and engineering of the functionalized area. Pristine exfoliated monolayer graphene flakes are characterized by AFM and Raman spectroscopy, and then exposed to electron beam irradiation with energy of 30 kV and dose of 40.000 μC/cm^2 (as previously reported[1]). Subsequent AFM images clearly resolve the pattern designed by the electron beam, with 0.1 μm step size (Fig. 1a). Raman maps show a homogeneous defects coverage in the exposed area, with the emergence of the characteristic D peak only in the patterned region. Graphene is functionalized via 1,3-dipolar cycloaddition of azomethine ylides. This reaction in-situ involves the localization of a C=C bond, which is favorable in presence of the defects[2], hence introducing a selective control of the chemical modification of graphene. The Raman analysis on the functionalized flakes exhibits new features in the region 1050 – 1750 cm^{-1}, only in the patterned area. Ab initio DFT simulation of the power spectrum of functionalized graphene (model in Fig. 1b) allows to identify the vibrational contribution both of the functional groups of the azomethine ylides grafted on the graphene surface and of the modified vibrational modes of the graphene sheet (Fig. 1c). Finally, under laser irradiation (up to 1.6 mW) the recovering towards the Raman spectrum of non-functionalized defected graphene indicates the desorption of the ylide and the reversibility of the functionalization. Functionalization of patterned graphene using 1,3-dipolar cycloaddition is shown to be a significant step towards the controlled synthesis of graphene-based complex structures and devices at the nanoscale.

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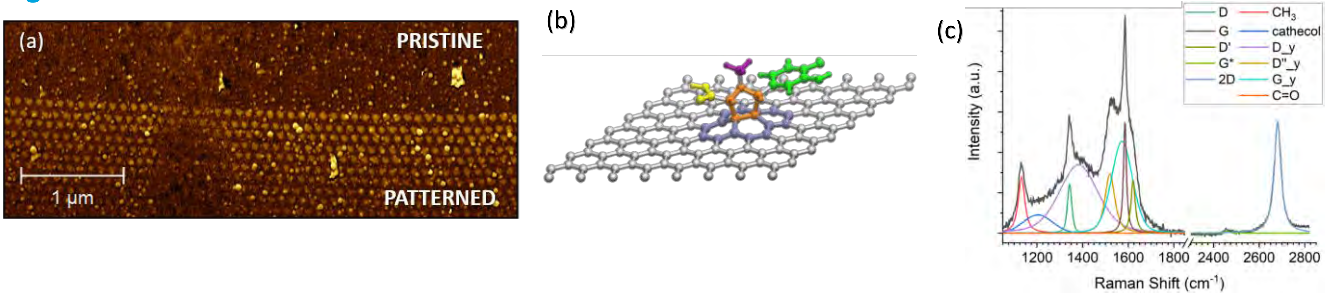

Figure 1: (a) AFM image showing the defects pattern after electrons irradiation; (b) DFT model of the azomethine ylide attached to graphene (the functional groups of interest are highlighted with different colors); (c) Raman spectrum of functionalized patterned graphene, showing the fit of the new features.

Tuning the electrode work function by deposition of chemically functionalized MXenes-an SPM study

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Graphene has triggered a great interest in the promising world of two-dimensional (2D) materials: thanks to their chemical and physical properties, this new class of compounds is expected to be employed in several applications in future and emerging technologies addressing numerous societal needs, such as faster and better performing electronics, as well as energy storage and conversion. Following the success of graphene, MXene, a new family of 2D transition metal carbides/nitrides/carbonitrides, has recently attracted considerable attention due to its combination of excellent metallic conductivity and rich surface chemistry features. Independent from its high conductivity, the variable surface chemistry make MXene unique for photo-/electronic applications [1].

In this study, MXenes, in their pristine form as well as chemically-functionalized with different organic molecules, are studied with atomic force microscopy to understand their morphology and with Kelvin probe force microscopy (KPFM) [2] to monitor the changes in the work function of different substrates after their deposition on them (Fig. 1 and 2). The possibility to tune the work function of MXenes and/or of different surfaces by chemical functionalization is expected to be of key importance for many applications, including energy harvesting and conversion [3]. Combining KPFM with macroscopic Kelvin Probe we are able to understand the origin of these changes.

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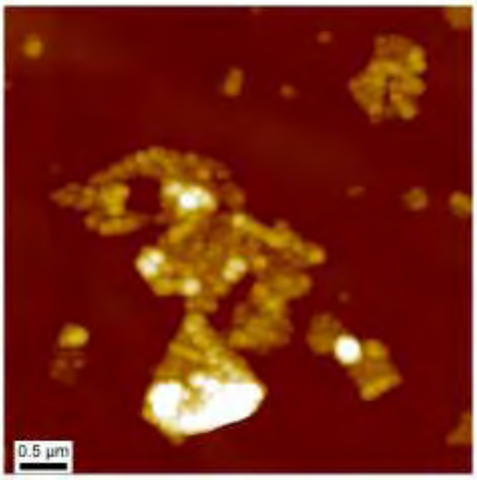

Figure 1: Topography of functionalized MXenes on HOPG substrate.

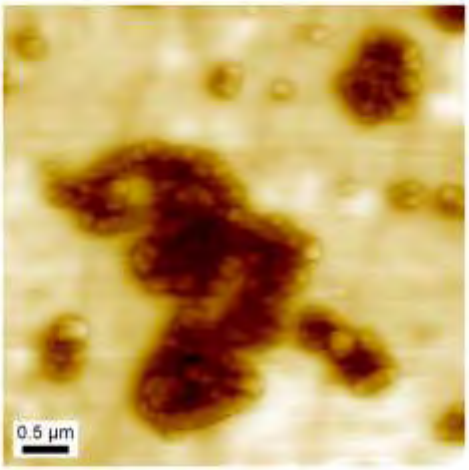

Figure 2: Corresponding surface potential difference of functionalized MXenes on HOPG substrate.

Advanced water and air quality sensing through 2D nanomaterials for smart appliances and smart homes

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Abstract

Home appliances are evolving towards integrated, smart equipment able to exchange information with the surrounding environment. To fully enable this vision, distributed, intelligent and accessible sensing technologies are necessary. Nanotechnology represents a promising tool to reach the cost-performance trade-off, as it allows to realize inexpensive and effective sensing elements. Moreover, nano-sized sensors require minute amounts of power, making them compatible with portable applications. As they can be used to explore and characterize the environment around home appliances, they allow to optimize performances in terms of water usage, energy consumption, food spoilage monitoring, and other consumer-relevant environmental parameters, with a sizeable impact on user perception and on sustainability. Here we will report about progresses in the field of nanostructured sensors for water and air quality in the view of possible applications in the home appliance industry. Opportunities offered by the use of nanostructured materials to make sensing devices have been explored for the sensing of volatile organic compounds in air and of organic and inorganic contaminants in water. Dedicated measurements setups have been created so to emulate real working conditions. The developed nanostructured sensors showed good repeatability over the time, as well as sensitivity towards the targets of interest. Nanostructured sensors for water and air quality characterization are a promising technology for achieving the objective of smart, integrated home appliances at acceptable costs for the user.

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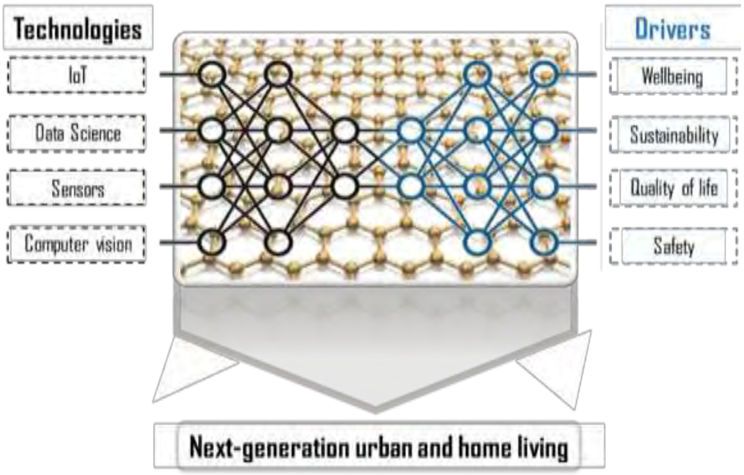

Figure 1: Development drivers vs. technologies for next-generation urban and home living.

Graphene oxide coating of hollow fibers for simultaneous adsorption&microfiltration in water purification

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The 6th Sustainable Development Goal of the United Nations aims to giving clean and safe drinking water to everyone on Earth[1]. In order to achieve it, it is necessary to develop innovative and highly efficient water purification technologies. In particular, the removal of a class of new contaminants, known as Emerging Contaminants (ECs) is strongly incentivized and investigated[2], due to the lack of effectiveness of standard purification systems in their removal from water. Graphene oxide (GO) is one of the most promising materials for this kind of application, thanks to its elevated superficial area and the abundance and versatility of interactions it can express. Its main drawback is the non-trivial recovery from water after treatment, which can lead to secondary contaminations. For this reason, GO-based 3D structures, such as foams, aerogels and membranes, are under intense study. We report[3] the synthesis of composite polyethersulfone-GO core-shell hollow fibers (HF-GO) from commercial microfiltration modules. Through simultaneous adsorption (thanks to intercalation between GO nanosheets) and microfiltration (thanks to PES cut off, 200 nm), these modules can remove up to 15 mg of ciprofloxacin, an EC, per gram of GO after few seconds of contact time (90% efficiency after 2500 L) and fully retain nanoparticles with 300 nm of diameter. Working mechanism is studied by XRD analysis and molecular modelling and the performance compared to granular activated carbon, the industrial standard.

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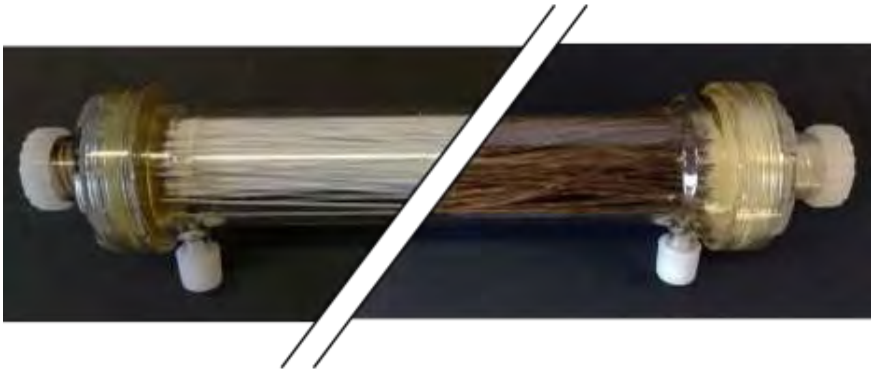

Figure 1. A hollow fiber microfiltration module before (left) and after (right) functionalisation with GO.

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

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

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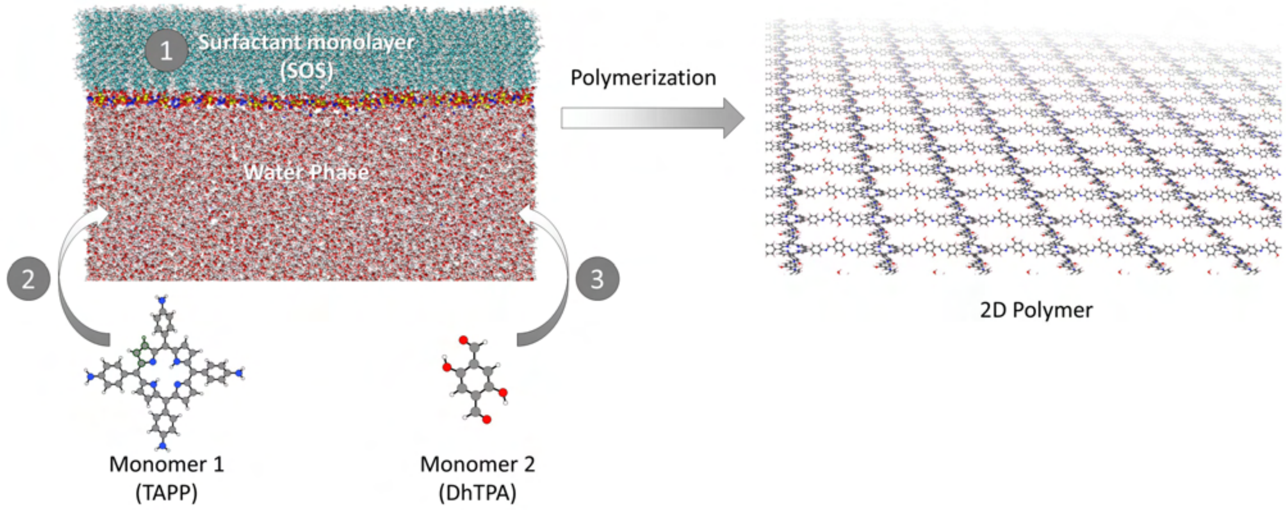

Figure 1: Steps for the polymerization at the water-surfactant monolayer interface, with sodium oleyl-sulfate (SOS) as surfactant, 5,10,15,20-tetrakis(4-aminophenyl)-21*H*,23*H*-porphyrin (TAPP) as monomer 1 and 2,5-dihydroxyterephthalaldehyde (DhTPA) as monomer 2.

Excitonic effects in graphene-like C_3N

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Monolayer C_3N [1] is an emerging two-dimensional indirect band gap semiconductor with interesting mechanical, thermal and electronic properties. In this work we present a full description of C_3N electronic and dielectric properties, focusing on the so-called momentum-resolved exciton bandstructure (Fig.1). The study is performed using GW+BSE approach for zero and finite momentum transfer, as implemented in the Yambo code [2].

Excitation energies and oscillator strengths are computed in order to characterize bright and dark states. Activation of excitonic states is observed for finite transferred momentum. We find an indirect excitonic band gap of 0.8 eV, significantly lower than the direct optical gap of 1.96 eV. Excitonic binding energies ranging from 0.6 to 0.8 eV for the lowest excitonic states, are indicative of strongly bound excitons. Excitonic wavefunctions are discussed with respect to crystal symmetries.

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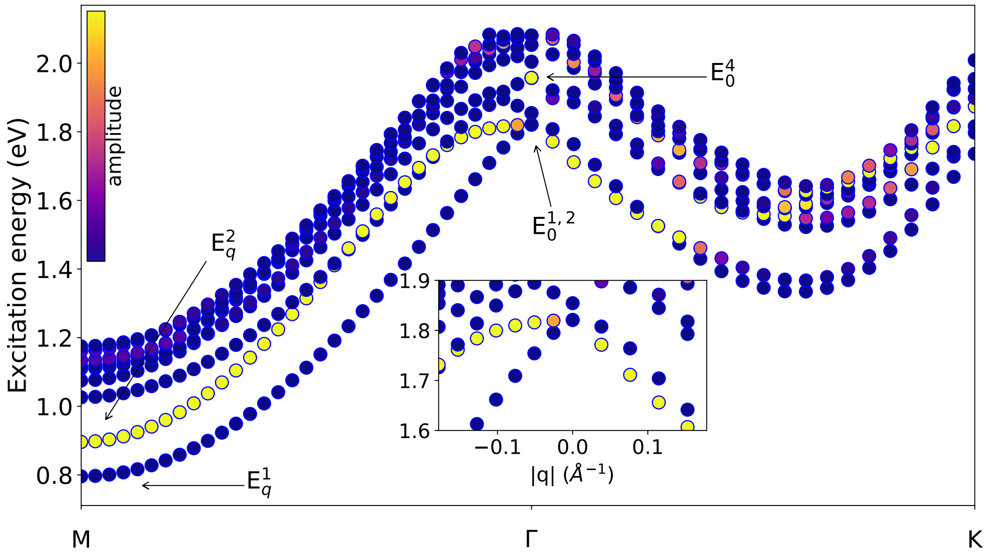

Figure 1: Momentum-resolved exciton bandstructure of C_3N for high-symmetry directions.

Charge transport mechanisms in GRM thin films: interplay between different length scales

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The processability and tunability of graphene 2-dimensional nanosheets make them an ideal test bed to study charge transport (CT) in systems with low dimensionality [1]. Here, we study CT in graphene-based materials with varying morphology at the atomic and mesoscopic scale, at temperatures from 2 to 300 K. We compare continuous layers of reduced graphene oxide (RGO, featuring higher sp^2 carbon content, high conductivity of the nanosheets but loose packing) with layers of exfoliated graphene oxide (EGO, featuring lower sp^2 carbon content but a better nanosheets packing).

We observe standard Variable Range Hopping (VRH) transport in RGO; conversely, EGO shows a power-law CT where the resistivity neither follows metallic nor insulating behavior. Such PL behavior is observed for EGO down to 10 K, and mimics CT in highly doped semiconductors near the metal-insulator transition. While the VRH mechanism was known for RGO networks [2], the PL behavior observed in EGO at low temperature is unique, and is attributed to the presence of an effective interaction between stacked nanosheets which, despite the low intrinsic conductivity of the single nanosheet, allow the resistivity to increase less than an order of magnitude in EGO as T approaches 0 K. Further insights in CT are given by magnetoresistance and electrical noise measurements. The striking differences in CT observed between RGO and EGO show how fascinating and complex such materials, that combines features of 1D, 2D and 3D systems, can be.

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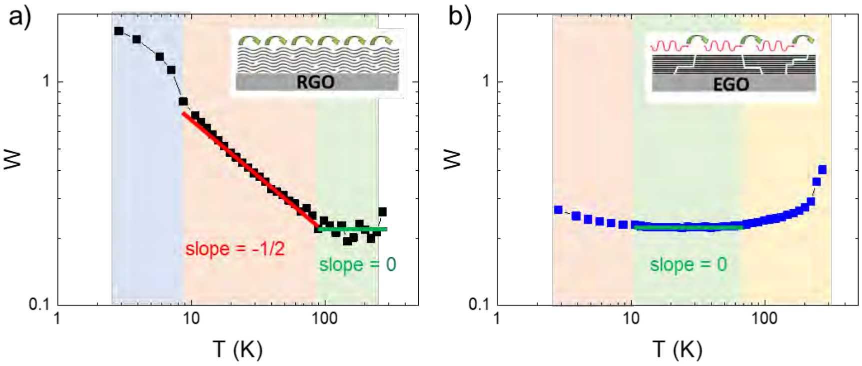

Figure 1: Reduced activation energy W as a function of temperature for the two systems compared in the study: a) RGO and b) EGO. The insets show a sketch of the charge carrier transport in the GRM network structure.

$MnPS_3$: Exfoliation and stabilization with different Capping Agents

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Among layered materials, $MnPS_3$ has attracted the attention of many researchers due to a wide variety of interesting properties (tunable bandgap, magnetic behaviour, and electrocatalytic performance amongst others), making it suitable for applications in several fields (catalysis, optoelectronics, magnetism...).[1] These properties can be tuned by separating its layers, therefore, a huge effort has been made to exfoliate bulk $MnPS_3$ material, trying to obtain thin and good quality two-dimensional (2D) layers in a scalable way.[2]

Despite the fact that $MnPS_3$ has been successfully exfoliated by the well-known scotch-tape method, the obtaining of stable suspensions of high-quality flakes that can be processed as inks remains elusive. So far, it has been possible to obtain stable dispersions of $MnPS_3$ 2D layers by using polyvinylpyrrolidone (PVP) as a capping agent. [3] However, there are no reports of liquid exfoliation methods that provide good-quality naked flakes in solution, preventing the use of this material in several applications which require a free accessibility to $MnPS_3$ surface. Moreover, the effectiveness of different capping agents that can modulate the stability in different solvents or the chemical tunning of the flakes, has not been explored.

For this reason, in this work, we present our last results about the liquid exfoliation of $MnPS_3$ as bare high accessible flakes and with different polymers and isolated molecules as capping agents. In this way, depending on the desired final application, it is possible to modulate the surface of the layers at will.

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Figures

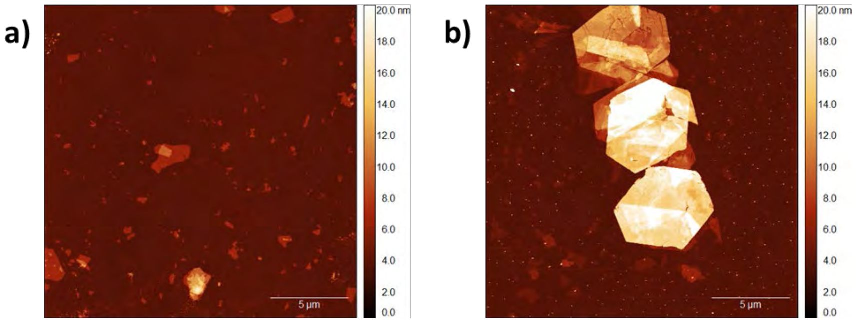

Figure 1: a) $MnPS_3$ flakes with polyvinylpyrrolidone as capping agent b) $MnPS_3$ flakes without any capping agent

The use of graphene electrodes for nanodevices with low-dimensional materials: the case of 1D graphene nanoribbons

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Molecular scale materials are a promising resource for the development of functional devices for the next generation of nanoelectronic components. The key challenge is how to address and exploit them in scalable architectures. Our idea is to use graphene as a suitable material for the realization of the contact electrodes in devices with low-dimensional systems. Indeed, the (2D) planar geometry of graphene reduces the "dimensionality mismatch", optimize the electrical coupling with the gate through reduced screening and allows for the anchoring of a wide variety of molecular compound through specific functionalization. In recent years, we have demonstrated the use of graphene electrodes for several class of low dimensional materials, form 0D magnetic molecules [1] to organic semiconductors thin films[2].

Here we focus on the use of graphene electrodes to contact atomically precise 1D graphene nanoribbons (GNRs), which represent the ultimate miniaturization of graphene devices with controllable edge properties and functionalities[3]. We report a systematic study on the structure-property relationship in GNR-based devices, enabled by the use of graphene electrodes, showing that the final electrical behavior is determined by the specific type of nanoribbon employed, in accordance in theoretical predictions[4]. Our results highlights the use of graphene in devices with low dimensional materials and the promising potential of "all-graphene" devices for electronic and optoelectronic applications[5].

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Figures

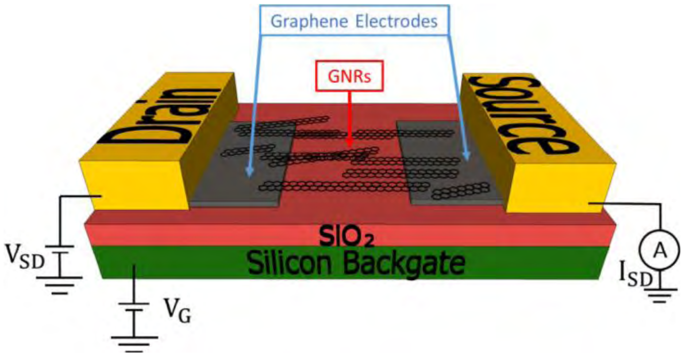

Figure 1: Schematic view of a GNR device with graphene electrodes

Graphene oxide as nanotool to target dysfunctional neuronal plasticity: a synaptic approach to anxiety disorders.

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Small graphene oxide nanosheets (s-GO) were previously reported to reversibly down-regulate the excitatory synaptic activity of rat hippocampus *in vivo* [1], suggesting a translational potential of these nanomaterials in the field of precision nanomedicine as specific modulators of glutamatergic synapses. Synaptic communication between neurons is dynamically regulated, phenomenon known as synaptic plasticity and fundamental for brain functions such as memory and learning. However, dysfunctional synaptic plasticity has been observed recently also as a pathological mechanism characterizing several brain diseases, including anxiety disorders. In details, overactivity of glutamatergic synapses in the lateral nucleus of the amygdala (LA) is a hallmark of an aversive memory acquisition induced by stressful events involved in post-traumatic stress disorder (PTSD). By using an animal model of PTSD, we showed the ability of s-GO, when stereotaxically administered into the LA, to rescue the pathologically potentiated glutamatergic transmission and to prevent the anxiety related behavior due to long-term aversive memory. In addition, we dissected *in vitro* the mechanisms through which s-GO revert amygdala glutamatergic plasticity, that could be involved in the nanomaterial induced rescue of PTSD pathological aspects [2]. The interference of s-GO with the pathological excitatory plasticity might find applications for the treatment of a broad spectrum of neuro-pathologies.

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Figure

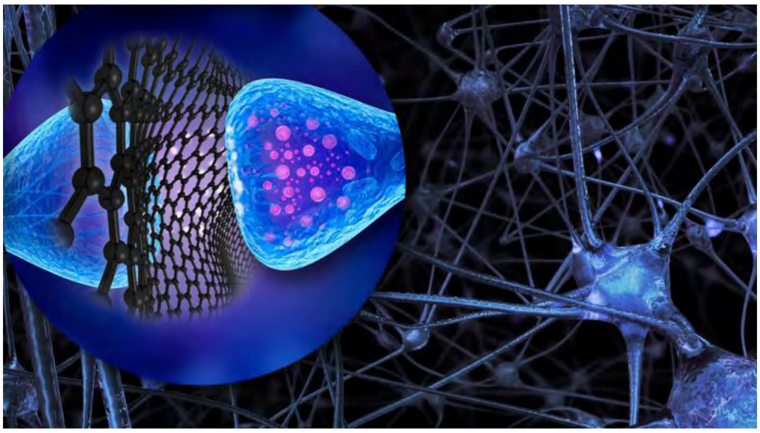

Figure 1: s-GO interfere with glutamatergic neuronal transmission at synaptic level.

Single-molecule study of the intermediate steps in a coupling reaction

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Breaking and formation of intermolecular bonds are the processes underlying the bottom-up growth of 2D materials and their covalent functionalization. A deeper knowledge of how a bond breaks or forms is of fundamental importance to control the synthesis of 2D architectures at the atomic or molecular level. Ullmann coupling on metal surfaces is a chemical reaction often employed for the synthesis of covalently bonded 2D networks [1]. Therefore, the study of this chemical reaction between single building block molecules adsorbed on crystalline metal surfaces is important to understand polymerization processes.

Bond breaking and formation, in single molecules on a surface, can be triggered by tunneling electrons in a scanning tunneling microscope (STM) [2, 3]. STM manipulation allows the geometrical arrangement and characterization of the precursor molecules [4]. Thus, the consecutive steps involved in the Ullmann coupling can be studied, from the activation of the precursors to their covalent linking, including the organometallic intermediates that can be involved [5, 6]. However, the function of catalytic active sites, like single metal atoms, needs to be further investigated. Moreover, in many cases, chemical reactions between small molecules have been studied with STM. Thus, there is very limited, or no, access to the geometrical arrangement of the building blocks during the coupling reaction.

Here, we use the STM tip at low temperature (7 K) to induce step-by-step the coupling reaction between two molecules adsorbed on a Ag(111) surface. The elongated shape of this molecule allows to arrange them in specific relative orientations prior to the reaction. Thus, an organometallic complex is synthesized, and the geometrical conformations of the complex are explored to study the coupling reaction. The results show the important role of the metal substrate in on-surface polymerization reactions. Moreover, this precise and controlled synthesis demonstrates new methods for studying the function of single metal atoms in coupling reactions. A deeper understanding of these reactions would allow better control over the structure of 2D materials and targeted engineering of their functions.

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Switchable Optoelectronic Devices based on Spin Crossover/Graphene Heterostructure

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Spin crossover (SCO) molecular materials exhibit a change of magnetic state that can be triggered by several external stimuli, in particular temperature, pressure, electric field and light irradiation. Despite their important potential, their use in multi-functional devices is hampered by several technological locks: (i) optoelectronic devices remain scarce because of complex intricate phenomena into the SCO channel, (ii) the low intrinsic conductivity of SCO material prevent their use for several sensing applications, (iii) optoelectronic switch based on SCO phenomena and operating at room temperature is not yet demonstrated. Here, I will present some of our recent achievements and on-going works illustrating the possibilities offered by ***SCO-2D materials heterostructures*** **for switchable optoelectronic applications**, and how they can unlock these challenges.

First, magneto-opto-electronic properties are shown for a hybrid device constructed from a spin crossover (SCO) thin film of molecular material evaporated over a graphene sensing layer. The principle of electrical detection of the ***light-induced spin transition*** (LIESST) and reverse-LIESST effects in SCO/graphene heterostructures is demonstrated at low temperature. **[1]** The switchable spin state of the molecular film is translated into a remanent change of the conductance of the graphene channel, using two distinct excitation wavelengths to write/erase the two states.

Then, I will present a hybrid device that can be **optically switched at *room temperature*** with **non-volatile electrical memory effect.** For this molecular system, device operation at room temperature is realized, with multi-state stabilization obtained by varying the irradiation intensity or time. **[2]**

These results reveals the full potential of mixed-dimensional heterostructures for molecular (opto)electronics and spintronics, and opens the door to the use of spin crossover materials for room temperature optoelectronic operations.

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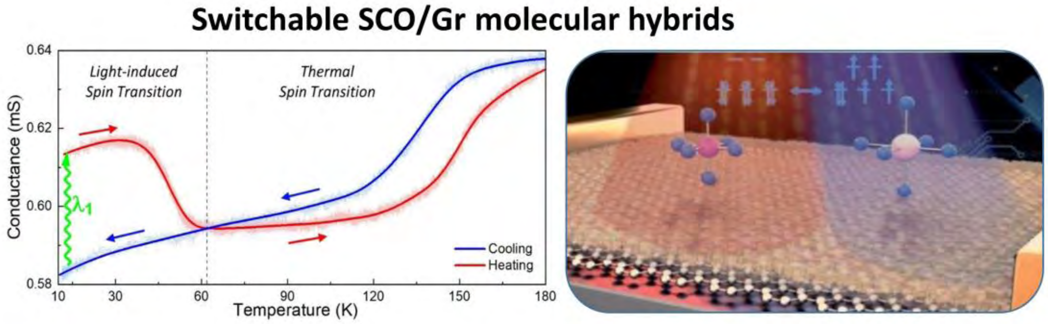

Figure 1: *Left:* Light and Thermal Spin transition of SCO molecular thin film detected by a graphene sensor. *Right:* Artistic view of the experiment.

Hierarchical Electrocatalysts for the oxygen reduction reaction with a Graphene *“Core”* and a Carbon Nitride *“Shell”* exhibiting a Low Pt loading

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The worldwide energy system is currently undergoing a major transition towards a future where electrochemical energy conversion and storage (EECS) systems are becoming crucial. In this framework, proton exchange membrane fuel cells (PEMFCs) are particularly relevant due to their outstanding efficiency and compatibility with the environment [1]. The operation of PEMFCs is based on the conversion of the chemical energy associated with the oxidation of hydrogen into electrical energy. The oxygen reduction reaction (ORR), taking place at the PEMFC cathode, is one of the most critical bottlenecks in this process. The ORR is sluggish and it must be promoted by suitable electrocatalysts (ECs) to ensure that the PEMFC achieves a performance level compatible with the intended application [2]. The most effective ORR ECs for PEMFCs comprise active sites based on platinum, whose scarcity in Earth’s crust might give rise to supply bottlenecks. Thus, the development of ECs that are high-performing, durable and comprise a low loading of platinum (giving so rise to *“Low-Pt ECs”*) is a major goal of PEMFC research. This contribution overviews the development of an innovative family of ORR ECs including a low loading of Pt and characterized by active sites located on the surface of sub-nanometric clusters (SNCs) where Pt is alloyed with a first-row transition metal (*e.g.*, Ni, Cu). The latter operates as a *“co-catalyst”*, significantly improving the intrinsic performance of the active sites in comparison with the Pt baseline [3]. The EC supports comprise a hierarchical graphene-based (H-GR) *“core”* covered by a carbon nitride (CN) *“shell”*. H-GR consists of highly defective graphene nanoplatelets and carbon black NPs [4] to promote mass and charge transport. The CN *“shell”* is decorated with C- and N-based *“coordination nests”*, stabilizing the SNCs and boosting the EC durability. Here is elucidated the interplay between the EC preparation parameters, the physicochemical properties, the electrochemical behavior and the performance in a single PEMFC tested under operating conditions.

Acknowledgements

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Rb-functionalized epitaxial graphene on SiC(0001)

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Since its discovery, graphene has received much attention due to its outstanding properties. However, the technological application of the pristine material has faced some challenges. Incorporation of metal atoms in the pristine graphene can overcome some of these limitations by varying its electronic, electrical, thermal, and magnetic properties, making the metal-functionalized graphene system more suitable for applications. The attention around Rubidium functionalization of carbon nanostructures already started in the 1930s. The potential applications of Rb-graphene in hydrogen-storage and superconductivity has driven the research towards a further understanding of the system. Among the many questions that arise on this system, the most compelling is whether Rb can and does intercalate monolayer graphene, as Li, or bilayer graphene, as in graphite intercalation compounds. Besides, we need to understand what is the energy required for the process, i.e. whether intercalation can be obtained at room temperature or only at low-temperatures, and how the adsorption changes the surface and the electronic properties of the graphene substrate. We will present an answer to some of these open questions. In our work we studied the interaction of epitaxial monolayer graphene on SiC(0001) with Rb deposited at room temperature. We performed diffraction analysis by means of low-energy-electron-diffraction (LEED) and obtained atomically resolved images by scanning-tunneling-microscopy (STM). We will report successful intercalation at room temperature of Rb on epitaxial monolayer graphene and different Rb ordered structures that can form. The combined results from LEED and STM lead to a better understanding of the adsorption dynamics, interaction between graphene and Rb atoms, the surface structure, as well as the Rb intercalation mechanism.

Figures

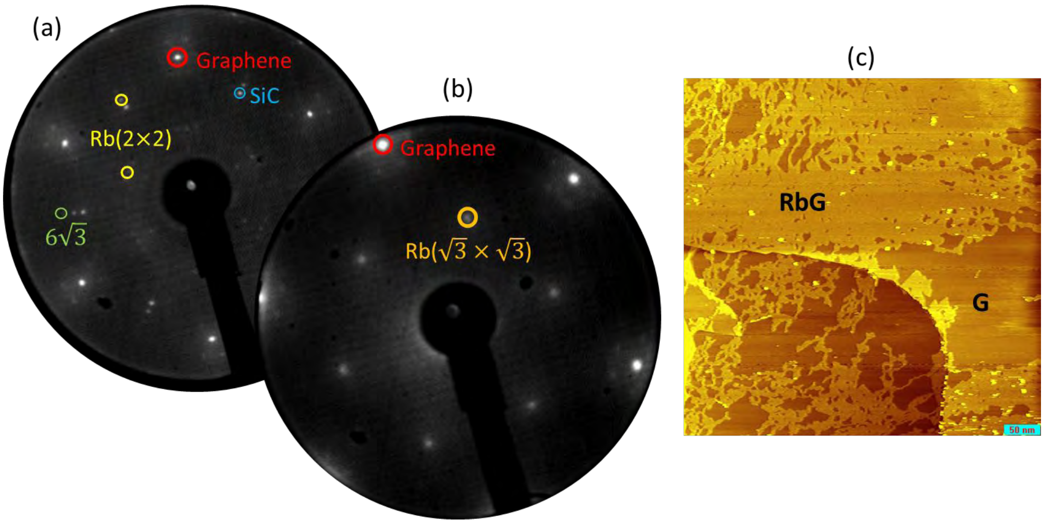

Figure 1: LEED patterns of different Rb-graphene structures [(a) 2×2 and (b) √3×√3] and (c) large area [500 nm × 500 nm] STM scan of the Rb-graphene surface. G: clean monolayer graphene, RbG: Rb-intercalated graphene.

Enhancing triboelectric performances of electrospun poly(vinylidene fluoride) with graphene oxide sheets

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Poly(vinylidene fluoride) (PVDF) is an easy processable and electroactive polymer, widely investigated for the preparation of electrospun membranes for triboelectric nanogenerators (TENG) [1]. The presence of graphene-oxide (GO) fillers into the PVDF nanofibers has been established to improve the TENG performances of the material since GO acts as charge storage site [2] [3]. In this work, we investigated the effect of graphene-oxide (GO) on the electrospinning process of PVDF-GO composite solutions. In particular, we found that the addition of GO in PVDF solutions, modifies their rheological properties by increasing their viscosity and reducing their elastic behaviour. Consequently, compared to the PVDF solution, the electrospinning process of PVDF-GO composite solution results in more homogenous and thinner nanofibers. Both PVDF and PVDF-GO naofibers showed a fraction of electroactive β-phase of PVDF higher than 80%. Nevertheless, there was no significant effect of GO on the β-phase increase of the polymer chains within the nanofibers.

Therefore, besides acting as the charge storage site, the only other effect of GO that synergistically contributes to the improvement of the TENG performances of PVDF-GO nanofibers compared to PVDF ones is the thinning of the fibers which results in a electrospun membrane with increased specific surface area. This improved the electrical performances of the developed TENG prototype, but further tests are still being performed.

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Tuning superconductivity in large-area $NbSe_2$ monolayers via molecular functionalization

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The ultrahigh surface sensitivity of 2D Materials makes it possible to tune their intrinsic electronic properties through molecular functionalization [1]. While several studies have reported how molecules can be used as dopants to improve the performance of optoelectronic devices based on 2D Materials [2], their impact on other intrinsic physical properties of TMDs, such as superconductivity, remains largely unexplored. Here, we manipulate the critical temperature (T_C) of large-area monolayer $NbSe_2$ in a deterministic way employing ultra-thin self-assembled adlayers [3]. Functionalization with a fluorinated or an amine-containing molecule results in a 55% increase and a 70% decrease in the T_C of $NbSe_2$ monolayers, respectively (Figure 1). Spectroscopic evidence indicates that the recorded changes in T_C are related to electric fields generated by the molecular adlayers, which act as an effective fixed gate terminal. Importantly, the polarity of the field-effect is programmable, as it is determined by an accurate choice of appropriate functional groups. The reported functionalization is efficient, practical, up-scalable and perfectly suited to functionalize TMDs extending over large areas.

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Figures

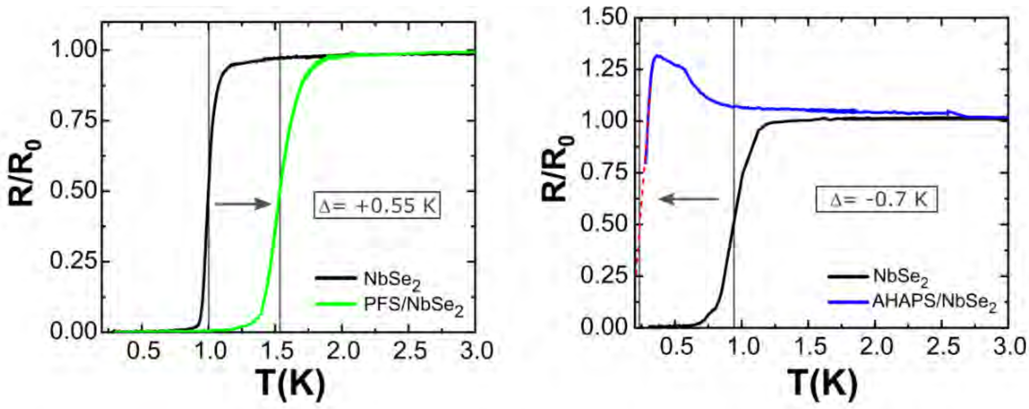

Figure 1: The critical temperature of $NbSe_2$ single layers increases after functionalization with a self-assembled adlayer of Trichloro(1H,1H,2H,2H-perfluorooctyl)silane (PFS), while it decreases after functionalization with a self-assembled adlayer of N-[3-(trimethoxysilyl)propyl]ethylenediamine (AHAPS).

Site selective oxidation of monolayered liquid-exfoliated WS_2 by shielding the basal plane through adsorption of a facial amphiphile

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In recent years, various functionalization strategies for transition metal dichalcogenides have been explored to tailor the materials' properties and to provide anchor points for the fabrication of hybrid structures. However, often functionalization approaches are carried out in the presence of additional components (e.g. stabilizers) other than the reagents which are often neglected. In this report,[1] new insights into the role of the surfactant in functionalization reactions are described. Using the spontaneous reaction of WS_2 with chloroauric acid as a model reaction, the regioselective formation of gold nanoparticles on WS_2 is shown to be heavily dependent on the surfactant employed. A simple model is developed to explain the role of the chosen surfactant in this heterogeneous functionalization reaction. Variations in the surfactant coverage for classical and facial amphiphiles are identified as the crucial element that governs the dominant reaction pathway and therefore can severely alter the reaction outcome. This study shows the general importance of the surfactant choice and how detrimental or beneficial a certain surfactant can be to the desired functionalization.

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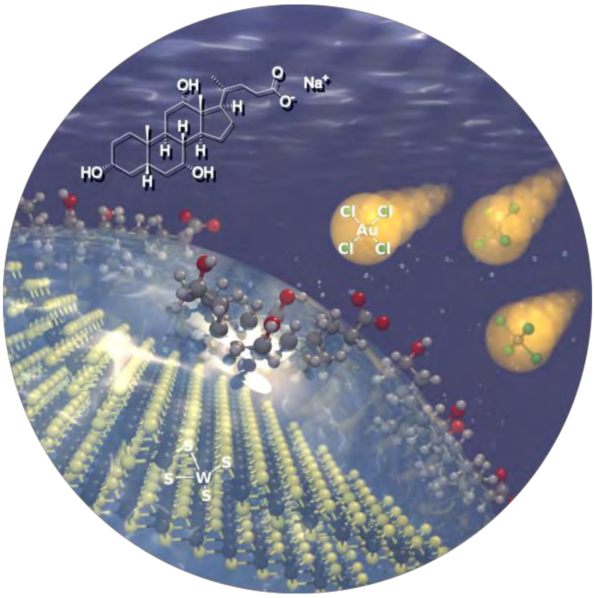

Figure 1: The heterogenous reaction of chloroauric acid at the nanosheet-solution interface reveals that the employed surfactant plays a significant role in governing the reactivity of the nanomaterial and consequently on the functionalization outcome.

Nanographene Catalysts for the Oxygen Reduction Reaction

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The Oxygen Reduction Reaction (ORR) is an electrochemical process important in fuel cells and metal-air batteries. The bare reduction shows a rather sluggish reaction kinetics requiring catalysts to achieve larger electrical currents. Precious metal Pt-alloys show good performance and serve as a reference; however, their rareness, high prices and poor long-term durability inhibit large scale applications. Recently, a set of well-defined heteroatom-doped polyaromatic hydrocarbons have been reported as ORR catalysts [1], displaying a range of activities despite their structural similarity. To explain this observation and deduce the design criteria for nanographene ORR catalysts, we investigate the reaction pathway from the physisorbed oxygen towards the chemisorbed minimum by density functional theory [Figure 1]. We find that the initial chemisorption occurs *via* negatively charged catalysts, which is confirmed by exergonic reaction energetics. Electron affinity arises as a simple indicator of how likely an electron is to be transferred from the charged electrode to the catalyst. Beyond the experimentally reported systems, the electron affinities of several other polyaromatic hydrocarbons are partially correlated with their catalytic activities, therefore putting forward the electron affinity as an insightful descriptor for subsequent rapid catalyst pre-screening [2].

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Figures

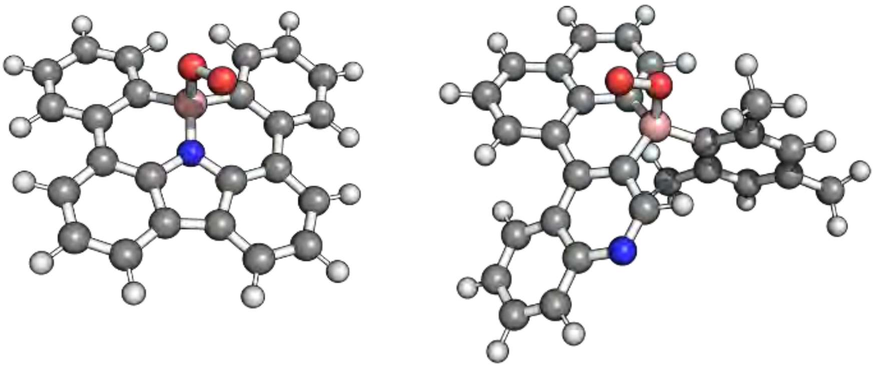

Figure 1: Oxygen physisorbed on nanographene catalysts.

On-surface synthesis of an imine based 2D-COF using the 2-in-1 strategy: Characterisation at multiple length scales

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In the wake of the “graphene rush”, many two-dimensional materials (2DMs) caught attention because of their promising properties for various applications such as optics, catalysis, energy storage and (bio)imaging. Within those 2DMs, 2D covalent organic frameworks (2D-COFs) are interesting because of their straightforward synthesis by classical organic reactions and their easy tunability. Imine-based COFs, synthesised by the solvothermal method, are long-known but both the synthesis of high-quality monolayer 2D-COFs and the mechanism of their formation are not completely understood yet. For the on-surface synthesis of 2D-COFs, the concentration and the ratio of the precursors must be tuned carefully and the composition on the surface is often unknown.[1] To overcome these hurdles, we applied a monomolecular approach, using a pyrene-based two-in-one imine COF precursor.[2,3] After drop casting of a solution of the precursor onto highly oriented pyrolytic graphite (HOPG), scanning tunnelling microscopy (STM) at the liquid/solid interface revealed a densely packed self-assembled molecular network at higher concentrations, while small COF patches formed at lower concentrations (see figure). The kinetics of the imine COF formation were probed using UV-vis spectroscopy which allowed the extraction of the reaction rates and the activation energy. Comparison of the on-surface synthesised COF nanopatches with the solvothermally synthesised bulk 2D-COF using UV-vis spectroscopy and grazing-incidence wide angle X-ray scattering (GiWAXS) provided further insights into the formation mechanism. Lower precursor concentrations lead to better crystallinity on surface, as shown by STM for monolayer nanopatches and by GiWAXS for bulk 2D COFs. Together these results imply that imine formation occurs rapidly in acidic medium and low concentrations favour the formation of ordered structures, both in solution and on surface.

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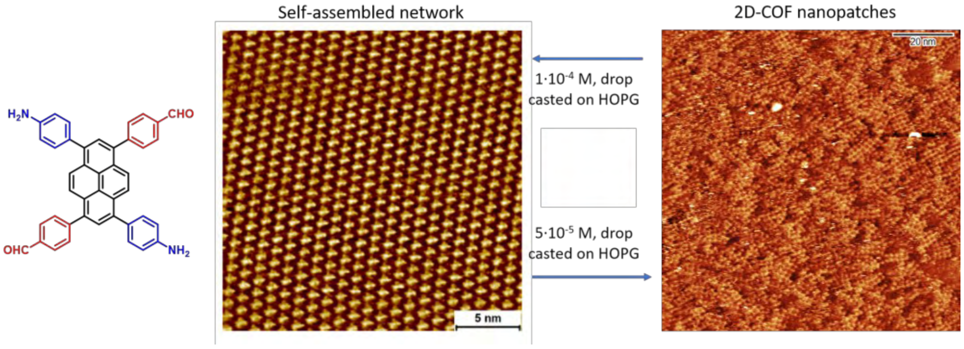

Figure 1: STM at the liquid/solid interface reveals the effect of the monomer concentration on the outcome of the on-surface synthesis of 2D-COFs: Higher concentrations lead to a densely packed SAMN, while lower concentrations favour the formation of 2D-COF nanopatches.

Investigation of radical formation on chemically modified graphene oxide under near infrared irradiation

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Within the different classes of carbon materials, graphene family materials have gained a lot of consensuses as tools in cancer therapy. These two-dimensional materials are good photothermal absorbers in the near-infrared (NIR) region.[1] Graphene oxide (GO) is the oxidized form of graphene. The Hummers oxidation process of graphite enriches the graphene surface with a wide variety of organic groups such as epoxides, hydroxyls and carboxylates, leading to a good colloidal stability in water and allowing to introduce anchoring points for covalent functionalization.[2] GO is also endowed of defects and unpaired electrons that make its surface highly reactive by generation of radicals.[3] Moreover, it has been shown that GO radical formation can be induced by heat and it can be activated by NIR irradiation.[4] In this work, we investigated the mechanisms of radical generation on different functionalized GO conjugates in the context of a treatment against cancer cells. The covalent functionalization relies on Diels-Alder modified molecules covalently grafted by epoxide ring opening onto the surface of GO through an amino moiety. Both pristine and functionalized GO were irradiated by a NIR laser and radical production was investigated with different probes, analyzed by fluorimetry and electron paramagnetic resonance. The radical species were then exploited in cancer treatment by *in vitro* experiments on a breast cancer cell line (Figure 1).

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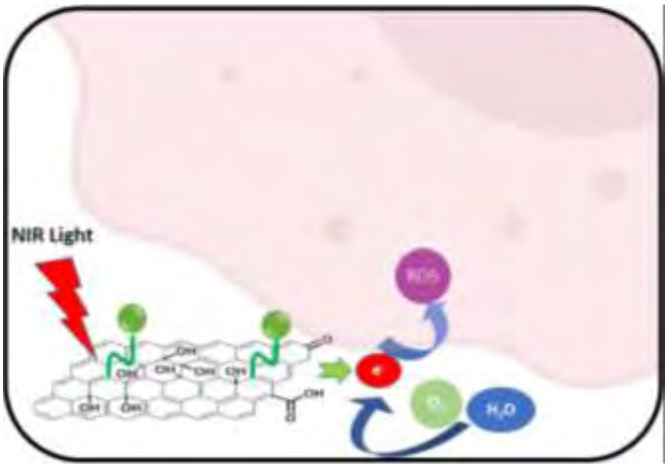

Figure 1: Covalently modified graphene oxide to modulate ROS generation under near infrared irradiation for anticancer treatment.

Pre-doped oxygenated defects activate nitrogen-doped graphene for the oxygen reduction reaction

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Abstract

The presence of defects and chemical dopants in metal-free carbon materials plays important roles in the electrocatalysis of the oxygen reduction reaction (ORR). The precise control and design of defects and dopants in carbon electrodes will allow the fundamental understanding of activity-structure correlations for tailoring catalytic performance of carbon-based, most particularly graphene-based electrode materials. Herein, we adopted monolayer graphene – a model carbon-based electrode – for systematical introduction of nitrogen and oxygen dopants, together with vacancy defects, and studied their roles in catalyzing ORR. Compared to pristine graphene, nitrogen doping exhibited a limited effect on ORR activity. In contrast, nitrogen doping in graphene pre-doped with vacancy defects or oxygen enhanced the activities by 3.7 and 6.8 times, respectively. The optimal activity was achieved for nitrogen doping in graphene functionalized with oxygenated defects – 4.6 times more than nitrogen-doped and 7.3 times more than pristine graphene. More importantly, oxygenated defects is highly related to the 4e− pathway instead of nitrogen dopants. This work indicates a non-negligible contribution of oxygen and especially oxygenated vacancy defects for the catalytic activity of nitrogen doped graphene.[1-4]

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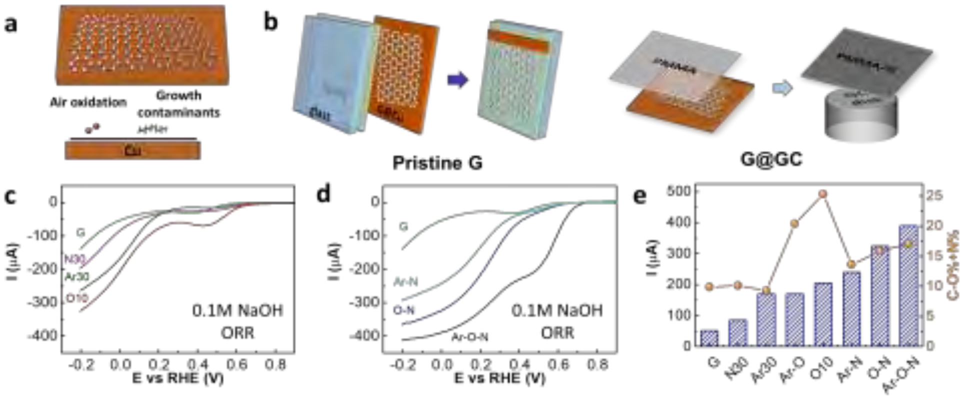

Figure 1: a) Illustration of air-face and copper-face of graphene. b) Preparation of pristine G supported by an epoxy substrate using the copper-face and G@GC using the air-face. c) LSV curves of G, N30, Ar30 and O10 samples at a rotation speed of 800 rpm. N30 represents 30 s nitrogenation, Ar30 for 30 s of argon plasma treatment, O10 for 10 s of oxygen plasma treatment. d) LSV curves of G, Ar-N, O-N and Ar-O-N samples. Ar-N represents graphene co-doped with Ar30 and N30, O-N for O10-N30, Ar-O-N for Ar30, O10 and N30 treated graphene. e) ORR activities correlate with atom % of carbon-oxygen and carbon-nitrogen (C-O%+N%) for non-, single- and dual-doped graphene samples.

The role of graphene oxide 'defects' on the adsorption of emerging water contaminants from water

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Academic and industrial interest is increasingly focusing on water treatments, especially on the removal of the "emerging contaminants" (ECs), identified as potential environmental threats.[1] The current water treatment technologies are not efficient in the removal of most of these contaminants from drinking waters and new materials and technologies are required. Due to their high surface area and multiple interactions pathways with organic molecules, graphene-based materials have shown great potential for water purification purposes. In particular, graphene oxide (GO) has shown high performance in the removal of some of these emerging contaminants [2], and the adsorption seems to be mainly related to surface interaction with the GO oxygenated groups. However, a clear understanding on the role of oxygenated groups on the adsorption mechanism is still missing. Here, we consider different types of GO having a different amount of C=O groups ('defects'): i) defective GO (dGO), Hummers GO (hGO), Brodie GO (bGO) [3]. Dedicated isotherms studies performed on a selection of ECs, allows us to estimate the adsorption performances of each specific pair substrate–molecule and to compare the maximum adsorption capacity of GO samples (i.e. Ofloxacin, dGO: 650 mg/g, hGO: 204 mg/g, bGO: 125 mg/g) to that of the Granular Activated Carbon (GAC; 95 mg/g), the industrial adsorption standard technology. The mechanism and role of defect on the adsorption performances will be discussed.

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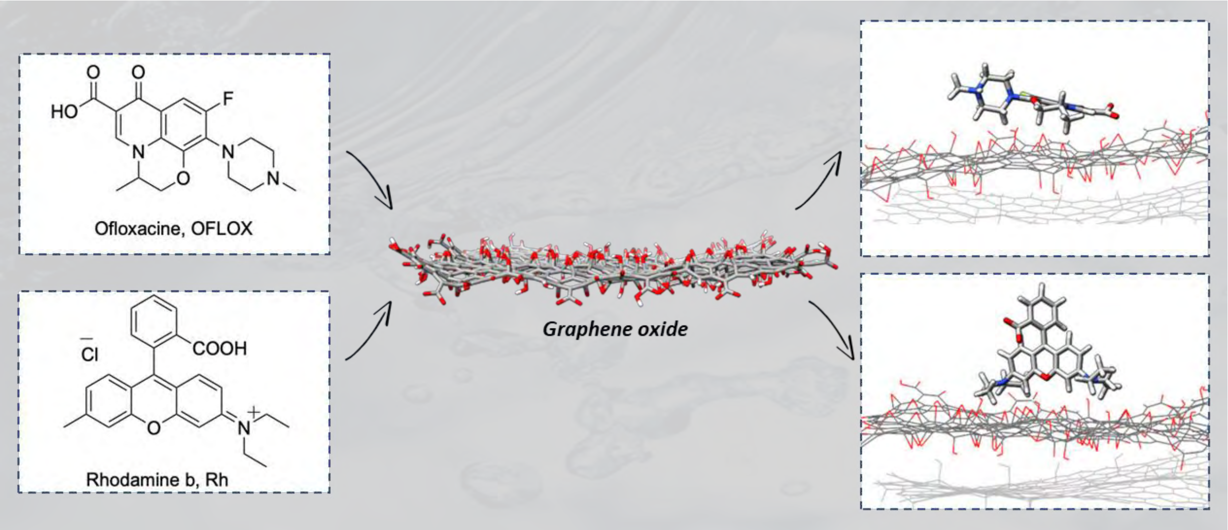

Figure 1: Adsorption of ECs (i.e. Ofloxacin and Rhodamine) on Graphene Oxide.

Imaging the atomic-scale effects of controlled disorder on an ordered electronic state in 2D quantum materials

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Use of controlled disorder in 2D quantum materials to design electronic states at the atomic scale is a major goal in quantum materials research [1]. 2D quantum materials often show remarkable properties arising as a result of a complex interplay of charge, lattice, spin, and orbital degrees of freedom. This interplay gives rise numerous electronic phases including superconductivity, anti-ferromagnetism, charge-density waves (CDW), spin-density waves, Mott-insulating among others [2-4]. Systematic introduction of external perturbations such as controlled disorder through doping or irradiation is one approach that has been used to probe this interplay [5-7]. However, the influence of induced disorder coupled with the intricate interaction between electronic and lattice degrees of freedom can trigger complex structural evolution and distribution of various electronic phases at the atomic scale [1, 4]. It's therefore necessary to understand how disorder-induced changes in the atomic lattice and the electronic ordered states are correlated at the atomic scale. We have investigated the correlation between the atomic-scale responses of the charge density wave electronic state and the underlying atomic lattice in 1T-$TiSe_2$ and O-TaS_3 exposed to controlled electron irradiation. Atomic-scale transmission electron microscopy imaging supported by electron energy loss spectroscopy shows that the CDW electronic phase responds with an elastic-like strain response to irradiation induced defects and deformations in the atomic lattice. This is characterized by a proliferation of phase defects including CDW dislocations, discommensurations, and domain walls. Our results show the importance of disorder-induced defects in modulating, stabilizing or destroying electronic phases at the atomic scale in 2D quantum materials.

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Graphene Oxide as promoter for chemical reactions monitored by X-Ray Photoelectron spectroscopy

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Graphene Oxide (GO) presents an extremely rich and complex chemical structure, this one-atom thick material is composed by large sp^2 aromatic region (few nm) surrounded by a plethora of defective Carbon atoms arranged in different chemical moieties: C-C sp^3 defects, hydroxyl, epoxy, carbonyl and carboxyl groups[1]. Such chemical variety offers a unique opportunity for chemical functionalization and carbocatalysis, but the mechanisms behind this phenomena are non-trivial issues. The ability to quantify the different chemical groups is the key for a complete understanding of reaction path and mechanisms. Unfortunately, only few spectroscopic techniques allow a quantitative study of GO structure: Solid State Nuclear Magnetic Resonance Spectroscopy and X-Ray[1] Photoelectron Spectroscopy[2] (XPS).

In this framework we present two distinct case studies reactions that involve the role of GO: i) the allylic alkylation of thiophenes with alcohols by using Friedel–Crafts-type protocol[3] and ii) the site-selective allylative and allenylative dearomatization of indoles with alcohols under carbocatalytic regime[4,5]. In both cases, by using XPS data, we found that the covalent activation was the main reaction mechanism, moreover, the mechanistic view was further supported by using density functional theory calculations based on XPS data.

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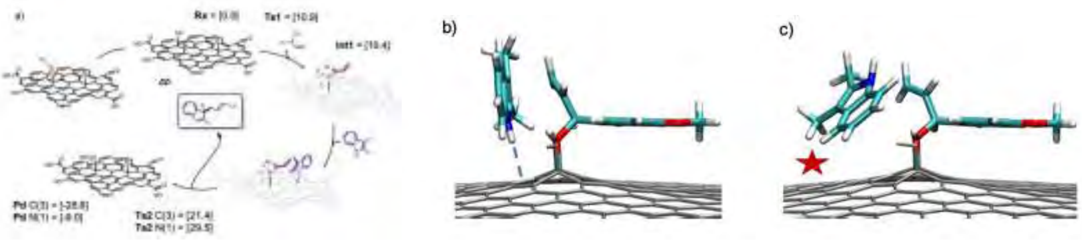

Figure 1: (a) Schematic representation of the reaction mechanism. The energies of the identified critical points in square bracket (kcalmol@1); 3D representation of the identified transition states for the C(3) (b) and (N1) (c) attack of the indoles. Figure adapted from reference[4].

Neural-network-based investigation of defect-rich carbon monolayers

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Defect-rich and amorphous 2D carbon monolayers are highly interesting in the grand family of 2D materials with potential applications in, e.g., DNA sequencing, catalysis. Since aberration-corrected high-resolution transmission electron microscopy (AC-HRTEM) allows for unambiguous elucidation of atomic structures down to sub-Angstrom scale, revealing the atomic structure of defect-rich and amorphous 2D can be achieved [1,2,3]. However, due to the lack of long-range order, quantitative description (e.g., degree of disorder, defect density and distribution) of such materials over large areas and sampleset sizes is still lacking. Conventional image analysis methods, e.g., handcrafted filter kernels, often require heavy user supervision and tremendous time cost, posing strong limitations on the data volume which can be realistically evaluated. The incompetence in handling big data volume also incurs the risk of user-induced selection bias, leading to overestimation of low-probability phenomena. Image analysis technique that could offer automation, precision, and extensive statistics, is thus highly desired. To reach this goal, convolutional neural networks [4] are employed. By determining the positions of every single atom in the AC-HRTEM images, the distribution and local variation of bond lengths and angles can be evaluated statistically and tracked through an image series. In addition, the neural network is capable of polygon mapping, providing not only the occurrence frequency of *n*-membered carbon rings but also their real-space distribution. A combination of networks can be applied to automatically evaluate image series, including automatic exclusion of image regions unusable for evaluation. This method results in large statistics thus reducing the impact of individual errors, such as, image artefacts or misinterpreted spots in an image. The networks are trained with simulated data, which reduces user bias and gives a time efficient way of generating the required training data.

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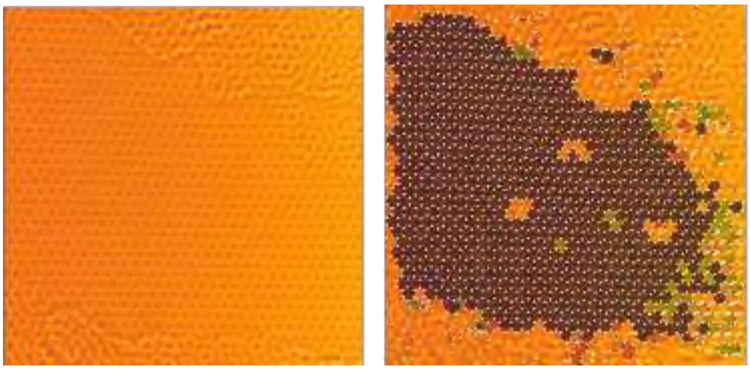

Figure 1: Left: AC-HRTEM image (false-colored) of CVD graphene acquired using SALVE microscope under 80 kV. Right: result after automatic evaluation. Atom positions marked in white, bonds between them in black, hexagons in brown, pentagons in orange and heptagons in green.

Electron Transfer Mediated Antibacterial Property of 2D Materials: From Graphene to MXene

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Abstract

The novel antimicrobial concept “bacteria starvation therapy” is developed to empower extraction of extracellular electrons from bacterial membrane respiration chain and interruption of energy metabolism of bacteria. The antimicrobial behaviours of large-area graphene film on Cu conductor, Ge semiconductor and SiO_2 insulator show a strong dependence on the band structure of substrate, in the order of graphene-Cu > graphene-Ge > graphene-SiO_2.[1] Moreover, increase of electrical conductivity of graphene-Ge heterojunction by improving graphene crystallinity can enhance the antimicrobial ability.[2] To further verify the antimicrobial correlation with band structure, cobalt doped TiO_2 coatings are designed with tunable bandgap (3.10 eV to 1.55 eV) and the results reveal that narrowing TiO_2 bandgap can remarkably boost the antimicrobial capacity.[3] Recently, through in-situ oxidation of $Ti_3C_2T_x$ MXene, TiO_2-$Ti_3C_2T_x$ heterojunction is fabricated to tailor the band structure (Figure 1). Under light irradiation, the heterojunction can exhibit favourable antibacterial activity. In summary, semiconductor-based materials with tailored band structure are able to act as extracellular electron acceptors, which can disturb the electron transfer and energy metabolism of bacteria, thereby leading to bacteria starvation and death. The “bacteria starvation therapy” can provide new insight into the interactions between bacteria and 2D materials and contribute to the design of novel antimicrobial agents based on 2D nanomaterials.

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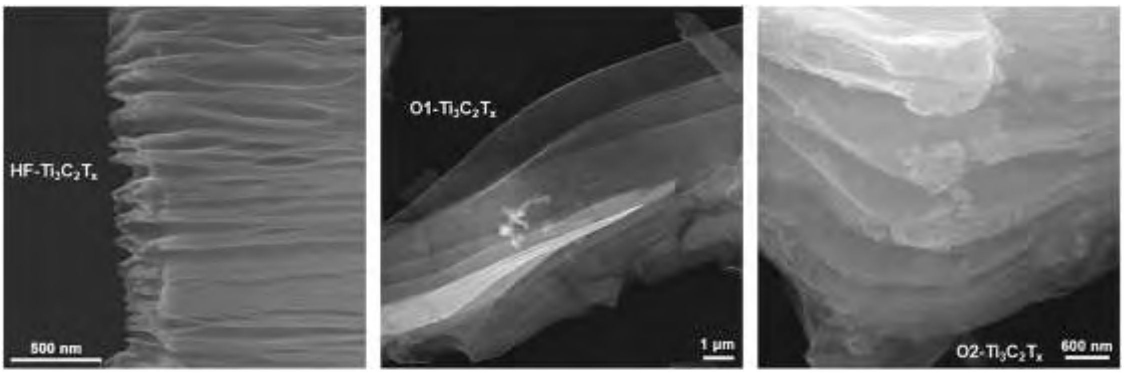

Figure 1: SEM images of pristine $Ti_3C_2T_x$ MXene sample (left) and different oxidation degrees of TiO_2-$Ti_3C_2T_x$ heterojunction samples including lightly oxidized O1-$Ti_3C_2T_x$ (middle) and heavily oxidized O2-$Ti_3C_2T_x$ (right).

Electromagnetic interference shielding materials based on assembly of $Ti_3C_2T_x$ MXene

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Transition metal carbides and nitrides (MXenes), especially $Ti_3C_2T_x$ MXene, have revolutionized the field of electromagnetic interference (EMI) shielding due to the unique combination of outstanding metallic electrical conductivity and rich surface chemistry [1]. In 2017, we reported the fabrication of flexible and hydrophobic MXene foams and demonstrated that the EMI shielding performance of shielding materials can be enhanced by designing porous structures without increasing material consumption [2]. However, easy oxidation and swelling of MXene materials in water severely deteriorates their properties with time. To improve the stability of MXene materials, we then proposed a universal ion diffusion induced gelation method to synthesize lightweight, foldable, and highly stable MXene foams, in which the MXene sheets are cross-linked and stabilized by metal ions and a small amount of graphene oxide [3]. The unique cross-linking structure ensures outstanding durability and stability in wet environments. More recently, in order to enable high application adaptability and multifunctionality of shielding materials, we prepared a hydrogel-type shielding material incorporating MXene and poly(acrylic acid) through a biomineralization-inspired assembly route. The composite hydrogel demonstrates excellent stretchability and recyclability, fast self-healing capability, unique absorption-dominated shielding property, and sensing ability [4]. These works not only provide inspiration for developing high-performance EMI shielding materials but could also bring opportunities for extending the applications of MXenes in the 3D macroscopic form.

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Stitch up the Grain Boundaries in WS2 Monolayers with Conjugated Molecules

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Abstract

Transition metal dichalcogenides (TMDCs) are pioneering an era of low-dimensional electronics. Recent progress in large-area synthesis of monolayer tungsten disulfide (WS_2) is paving the way for various potential optoelectronic applications, because of its inherent high photoluminescence (PL) yield and high electron mobility.[1] However, the arbitrary distribution of point defects and grain boundaries (GBs) diminishes its spatial homogeneity, obstructing the further development of system-on-chip (SoC). Large efforts have been made to suppress the inhomogeneity from synthesis to post-treatment[2], yet little is made about cross-GB electron transport.[3] Herein, we utilize a conjugated small molecule (benzene-1,4-dithiol, BDT) to heal the point defects and stitch up the line defects in chemical vapor deposition (CVD) method grown WS_2. Remarkably, the treated CVD-grown WS_2 exhibits drastically improved uniformity in terms of PL brightness and electron mobility (200 times enhancement for devices across GBs), comparable or superior to scotch-tap exfoliated single crystals. Furthermore, using temperature dependent PL spectroscopy and transmission electron microscopy (TEM), we identify the defective nature of GBs and manifest the interaction between the GBs and the conjugated molecule BDT.

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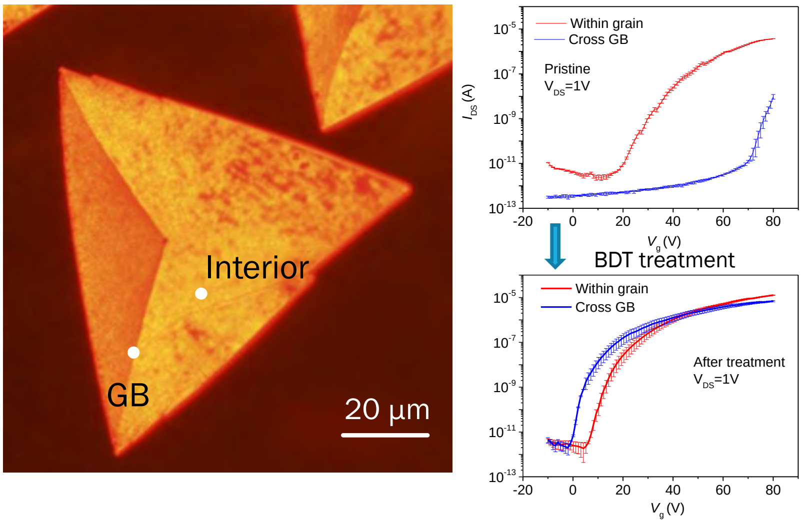

Figure: Photoluminescence spectrum mapping of a CVD grown WS2 monolayer. And the transfer curves of the transistor devices before and after BDT treatment.

Curved Nanographenes and Graphene Nanoribbons: Bottom-up Synthesis and Characterizations

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Curved π-conjugated polycyclic hydrocarbons (or nanographenes) has become an important research targets owing to their fascinating intermolecular packing and extraordinary chiraloptical properties resulting from their contorted conformation. In general, two distinct approaches have been established for the synthesis of curved nanographenes: one is the incorporation of steric strain in their periphery, the other is to introduce the non-hexagonal rings (i.e. pentagon, heptagon, octagon) in their skeleton which induce the nonplanar nature. The resultant curvature in a π-conjugated system often yields an unusual electronic structure and unprecedented physical properties. Here, I will talk the reasonable synthesis of several curved nanographenes and graphene nanoribbons with different topologies, such as saddle-shaped and wavy-shaped open-shell radicaloids,[1] azulene-embedded helical nanographenes,[2] and curved graphene nanoribbons with multiple edge structures.[3] Apart from the synthetic strategies, the structure-property relations of these π-systems as well as their optical, electronic and magnetic properties will be also presented. Our work provides a new insight into the synthesis of functional curved aromatics as well as their potential applications in nanoelectronics and spintronic devices.

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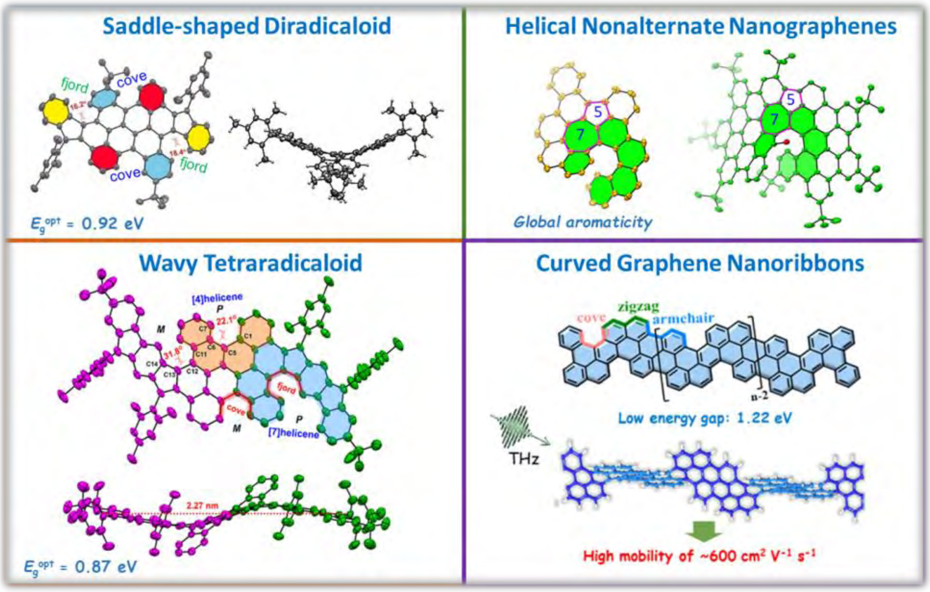
Figures



High-performance synthesis of functionalized graphene oxide nanosheets for water remediation

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Covalent modification of graphene oxide (GO) is a widely exploited strategy to tailor the surface and structure of graphene and enable new applications.[1] In recent years, a plethora of modified GO have been engineered and proposed as specific sorbent materials for water purification from organic and metallic contaminants[2]. However, scale-up methods optimization to produce modified GO is required to guarantee large amount of the targeted materials and reproducible batch purity levels. Here we report a microwave (MW) accelerated synthesis combined with microfiltration (MF) on commercial hollow fiber modules. This procedure enables fast and scalable preparation of highly pure polyethyleneimine (PEI) modified GO nanosheets. Moreover, we demonstrate the suitability of GOPEI as adsorbent of arsenic and lead and organic contaminants from tap water[3]. PEI functionalization turns the surface charge of GO nanosheets form negative (Z_{Pot}= -23.2 mV) to positive values (Z_{Pot}= 14.9 mV) this allowing the removal of anions generally not removed by GO nanosheets. Alongside with the removal kinetic a mechanism insights will be provided.

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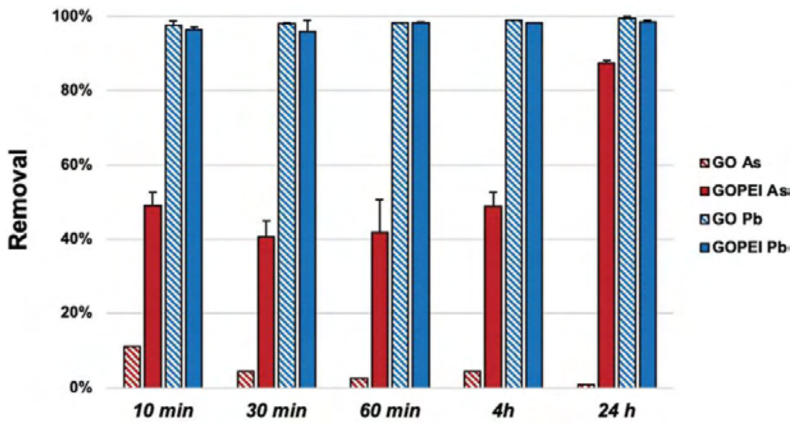

Figure 1: As and Pb adsorption kinetics C_i = 100 µg/L (each), (pH = 7.0). And solid/liquid ratio of 13 mg/30 mL.

Scalable high-mobility graphene/hBN heterostructure

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The high-mobility of graphene can be exploited in several applications, from high-frequency electronics to photonics and opto-electronics[1]. Chemical vapour deposition (CVD)-grown graphene has proved to perform in pair with the highest quality exfoliated flakes, when integrated into heterostructures with hexagonal Boron Nitride(h-BN)[2]. In this framework, the research of a growth method of h-BN that is scalable and suitable for integration with graphene and TMDs heterostructures is very active[3].

Here we present the realization of graphene/h-BN heterostructures with scalable techniques. h-BN continuous films were grown by Ion Bean Assisted Deposition (IBAD)[4] directly on Si/SiO_2 substrate. Atomic force microscopy (AFM) analysis reveals the atomic flatness of the material (Fig. 1a and 1b). High-quality graphene single-crystal arrays were grown by CVD[5] on copper and transferred on the target h-BN using a semi-dry approach. Raman spectroscopy reveals a reduction in the graphene strain on h-BN. The residual carrier density is in the range between $8X10^{10}$ cm^{-2} and $20x10^{10}$ cm^{-2}, and carrier mobilities around 10000 cm^2/Vs (Fig. 1c) , in ambient condition.

This work represents a first step toward the realization of high-mobility graphene/based scalable devices. The quality of the presented scalable heterostack paves the way to the implementation of high-performing devices in electronics and opto-electronics applications.

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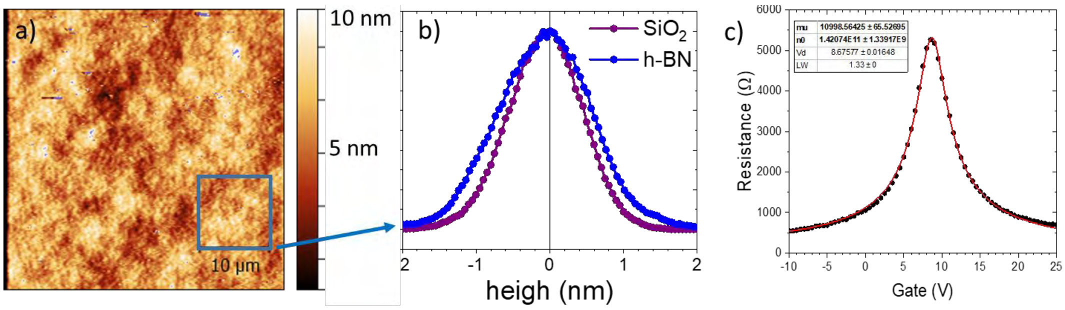

Figure 1: a) AFM characterization of the pristine h-BN film. b) Height distribution on an area of 100 μm^2 on h-BN and on SiO_2. c) Electrical characterization of the graphene on h-BN performed in ambient condition, with mobility of 10 000 cm^2/Vs and $n_0 = 1.5X10^{11} cm^{-2}$.

Acknowledgments

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Graphene composites for enhanced drinking water purification

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The occurrence of the so called 'emerging contaminants' in worldwide surface, ground and even drinking water is current one of the most urgent challenge to be faced.[1] The European Commission has recently published the new Drinking Water Directive EU2020/21844 which regulated the quality of EU waters, aims at enhancing the public access to safe water and introduce the water safety plan approach, this asking to the water suppliers and operators to be ready to exploit new and efficient depuration technologies when required. [2]

Among nanomaterials, graphene derivatives hold great promise in this sector, mainly due to the large commercial availability, high surface area and promising results in both adsorption and filtration scenario.

Here, we report on several new technologies developed in our laboratory and based on graphene oxide (GO) and modified GO composites, for the removal of ECs from water. We describe the synthesis, characterization working mechanisms of different graphene-based materials and the removal performance towards selected ECs (including drugs and perfluorinated alkylate substances, PFAS), in comparison to that of standard materials such as granular activated carbon (GAC).

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Figures

Figure 1. Tap water purification by graphene enhanced materials and filters.

Frictional Response of Texture Induced Strained Graphene

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Friction-induced energy dissipation impedes the efficiency of nanomechanial devices during their relative motion. Nevertheless, modification of nanoscale interfaces, such as by application of graphene, enables modulation of frictional dissipation in such devices. This work reports on the tribology of graphene deposited on artificially corrugated silicon surfaces consisting of long parallel grooves separated by a short variable distance [1]. The morphology and the periodicity of the substrate defines the strain induced in graphene as revealed by scanning probe techniques, Raman spectroscopy [2] and molecular dynamics simulation. The presence of graphene not only lubricates the textured surface by reducing friction force a factor of ≈10 but also induced modulated friction force dissipation [3,4]. The asymmetric straining of graphene coating layer over the corrugated architecture is revealed through frictional force microscopy in two different directions, namely orthogonal and parallel to corrugation axis. Here, we show the transformation of the lubrication into an ultra-low friction force scanning parallel to the groove axis. Such frictional disparity is found to be insignificant at the bare textured system, clearly demonstrating the strain-dependent regulation of friction force. Our results are applicable for graphene, and other 2D materials covered corrugated structures with movable components such as nanoelectromechanical systems, nanoscale gears and robotics.

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Advanced water and air quality sensing through 2D nanomaterials for smart appliances and smart homes

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Abstract

Home appliances are evolving towards integrated, smart equipment able to exchange information with the surrounding environment. To fully enable this vision, distributed, intelligent and accessible sensing technologies are necessary. Nanotechnology represents a promising tool to reach the cost-performance trade-off, as it allows to realize inexpensive and effective sensing elements. Moreover, nano-sized sensors require minute amounts of power, making them compatible with portable applications. As they can be used to explore and characterize the environment around home appliances, they allow to optimize performances in terms of water usage, energy consumption, food spoilage monitoring, and other consumer-relevant environmental parameters, with a sizeable impact on user perception and on sustainability. Here we will report about progresses in the field of nanostructured sensors for water and air quality in the view of possible applications in the home appliance industry. Opportunities offered by the use of nanostructured materials to make sensing devices have been explored for the sensing of volatile organic compounds in air and of organic and inorganic contaminants in water. Dedicated measurements setups have been created so to emulate real working conditions. The developed nanostructured sensors showed good repeatability over the time, as well as sensitivity towards the targets of interest. Nanostructured sensors for water and air quality characterization are a promising technology for achieving the objective of smart, integrated home appliances at acceptable costs for the user.

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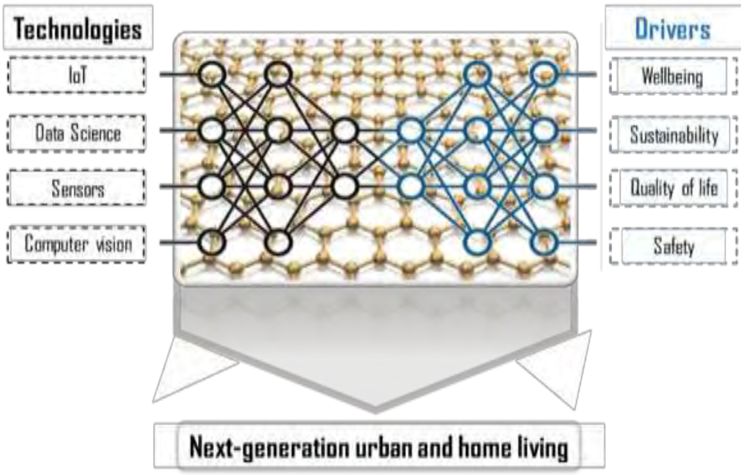

Figure 1: Development drivers vs. technologies for next-generation urban and home living.

Two-dimensional water confined in layered heterostructure of gypsum

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Water molecules exhibit peculiar behaviour when confined in nanoscale. Gypsum, $CaSO_4 \cdot 2H_2O$, a widespread layered mineral consisting of bilayers of $CaSO_4$ sandwiched between water monolayers, offers a natural platform to study behaviour of water under strong confinement. Using van der Waals technology we explore the dynamics and structuring of water layers in gypsum at the nanoscale via Raman and infrared spectroscopy, combined with theoretical calculations. The confined water exhibits two vibrational modes with vibrational frequency lowered by hydrogen bonding compared to that of free water molecules. The activity of both modes shows high anisotropy on (010) plane due to stretching vibration direction, and different confining environment. Further study on the confining effect of hydrogen bonds is given by Raman spectroscopy in a hBN/graphene/gypsum heterostructure. Our work provides a novel method and a good understanding for further study on water confinement and dynamics in different nano-systems.

Covalent functionalization of photoluminescent liquid-exfoliated WS_2 nanosheets

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Abstract

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, which might allow for localized emission. In this project the covalent aryl functionalization of WS_2 nanosheets and effects upon optical properties were investigated.

Liquid-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 of WS_2 nanosheets were obtained, which were used for further film fabrication. Extinction, Raman and photoluminescence 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. A potential correlation between the observed Raman modes and surface coverage with aryl moieties is discussed. Characterization of films, assembled at liquid-liquid interfaces, suggests that functionalization leads to improved high film homogeneities and increased hydrophobicity of surfaces.

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Graphene derivatives for energy storage

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Graphene, its composites, and derivatives are promising materials for energy storage applications. Graphene derivatives are particularly interesting because they offer new horizons for supercapacitor and battery electrode materials. Preparation of graphene derivatives directly from graphene/graphite is, however, hampered by a high graphene inertness. A low reactivity of graphene can be bypassed by utilization of chemistry of fluorographene, which can be carried out at mild and controllable conditions.[1] The fluorographene chemistry benefits also from an easily available pristine material, graphite fluoride, on the market. We have shown that the fluorographene can be converted into various graphene derivatives, which show promising properties as electrode materials of supercapacitors and batteries. A two-step synthesis leads to graphene acid, i.e., graphene bearing ~15% of covalently grafted carboxyl groups on both sides [2]. Graphene acid is perfectly water dispersible, and conductive (∼25 S/m) material. These features predispose it as an electrode material for supercapacitors with a capacitance of ~100 F/g and very high specific capacitance retention above 95% after 60,000 C/D cycles at a current density of 3 A/g in a two-electrode cell system [3,4]. The performance of GA can be significantly enhanced by its hybridization with a metal-organic network (UiO-66-NH_2). The hybrid acts as an effective charge storing material with a capacitance of up to 650 F/g.[5] Reduction of fluorographene by nitrogen-containing compounds leads to nitrogen doped graphenes.[6] The nitrogen-doped graphenes with high-level of nitrogen doping represent another class of interesting supercapacitor electrode materials with high energy and power density. The chemistry of fluorographene can be used to conjugation of graphene with polysulfide chains. The as obtained highly (80 mass%) sulfur doped graphene delivers very high full-cathode-mass capacity and rate capability, combined with superior cycling stability. These features predispose it as an efficient cathode material of LiS batteries with a low shuttling effect [7].

The work is supported by ERC grant (2Dchem.org) ID 683024 from H2020 programme.

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Towards atomic resolution imaging of beam-sensitive 2D polymers and metal-organic frameworks

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Two-dimensional (2D) polymers and metal-organic frameworks (MOFs) hold great promise in the rational materials design tailored for next-generation applications. However, unlike inorganic 2D materials whose atomic structures can be readily revealed via aberration-corrected high-resolution transmission electron microscopy (AC-HRTEM), direct imaging of organic 2D materials has been substantially hindered by their low resilience against electron irradiation. This work will present the key strategies to achieve higher image resolution on 2D polymers and MOFs, even down to atomic scale.

Our recent study demonstrated that, among a wide range of available electron energies (i.e., 80 keV – 300 keV), 120 keV offered the highest amount of structural information per unit damage. When combined with the low-dose imaging technique, 1.9 Å image resolution has been successfully achieved on multiple 2D polymer thin films. The enhanced resolution revealed structural details such as additional molecules and layer shifts, which were not accessible in previous AC-HRTEM studies [1].

Meanwhile, AC-HRTEM investigation on a hydrogen-free 2D BHT-Cu (BHT = benzenehexathiol) MOF (Fig. 1) unraveled that the absence of hydrogen in the framework could significantly increase the sample stability against electron irradiation. Strikingly, we were able to achieve a resolution of 0.95 Å on Cs+Cc-corrected SALVE microscope under 80 kV [2]. It is worth mentioning that the BHT-Cu MOF could withstand an accumulated dose of 1.5×10^5 e$^-$/Å^2 before total structural disintegration, which is comparable to that of inorganic materials, rendering it a superb candidate for subsequent in-situ heating experiments.

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Figure

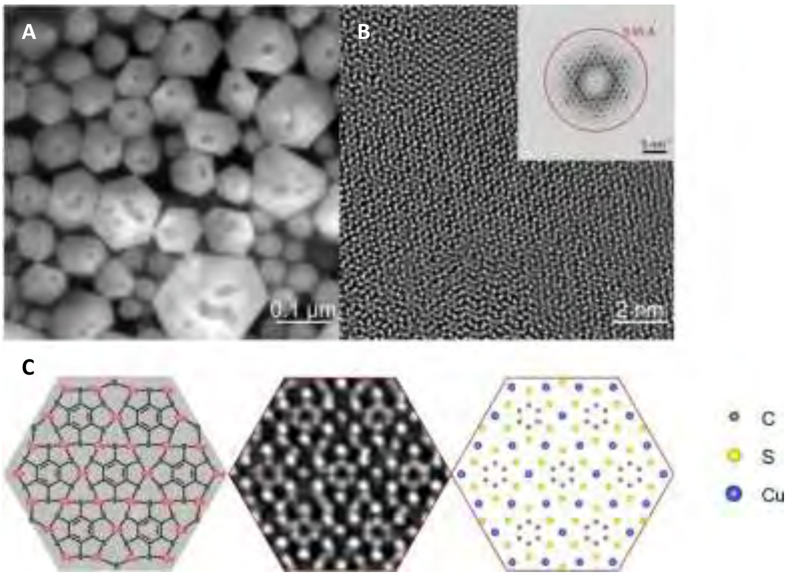

Figure 1: (A) High-angle annular dark-field image showing the morphology of 2D BHT-Cu MOF particles. (B) AC-HRTEM image of 2D BHT-Cu MOF obtained on the SALVE microscope under 80 kV. Inset: fast Fourier transform pattern of the image showing an image resolution of 0.95 Å. (C) Comparison between the atomic structure and experimental AC-HRTEM image.

Defect-modulated photocatalytic response in 2D carbon nitride: a joint computational and experimental study.

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Graphitic carbon nitride (g–CN) is an interesting photoactive 2D material capable of catalyzing reactions such as water-splitting, CO_2 conversion and selective organic transformations and disinfections[1], with the advantage of being completely metal-free and presenting a narrower band-gap with respect to common metallic catalysts[2].

Recently some of us have demonstrated that the photo-catalytic response of g–CN can be modulated by convenient post-synthetic treatments[3]. More specifically, three correspondent post-synthetic forms, i.e. reduced (red. g–CN), amorphous (am. g–CN) and oxidized (ox. g–CN), were obtained, the amorphous (**am. g–CN**) showing the highest catalytic activity[3]. Through an experimental characterization, the enhanced photocatalytic efficiency of am. g–CN was hypothetically linked to the formation of a halogen-bond between an iodine atom of the perfluorobutyliodide (C_4F_9–I) and the am. g–CN's surface.

However, recent experimental investigations indicate that all the g–CN forms mentioned contain structural defects (nitrogen vacancies) with a radical carbon species, as confirmed by recent EPR measurements.

Herein, in order to provide a rational to the photocatalytic response of different defective g–CN forms, we employed (Time-Dependent) Density Functional Theory calculations to study the ground-state and excited-state interactions between the C_4F_9–I substrate and the different g–CN forms. We find that the nitrogen vacancies in am. g–CN contain radical carbon/nitrogen units that not only interact strongly with C_4F_9–I but also generate mid-gap defect states within the electronic band-gap. These latter are directly responsible for the enhanced photo-induced charge transfer from defective g–CN's surface to C_4F_9–I, boosting the photo-catalytic response of am. g–CN's surface.

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Figures

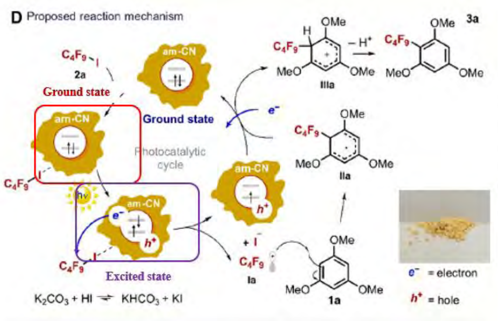

Figure 1:
The reaction mechanism proposed in [3]

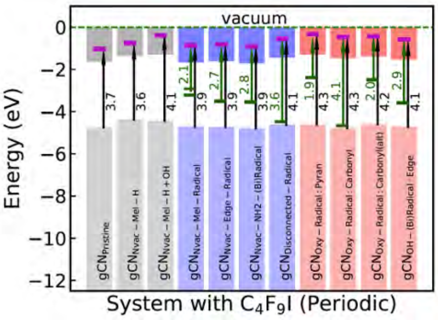

Figure 2:
Electronic structure of the pristine (1st entry left) and the defective forms

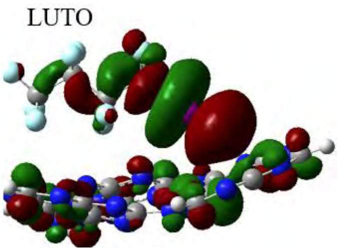

Figure 3:
Electron density showing hybridization between the surface and the substrate

Predicting the bulk modulus of single-layer 2D COFs from their molecular building-blocks properties

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Two-dimensional Covalent Organic Frameworks (2D COFs) have attracted a lot of interest due to their large range of potential applications. Bottom-up engineering of their molecular building-blocks can lead to novel structures with fine-tuned physical and chemical properties. We have carried out a computational investigation of the elastic properties of different 2D COFs with square and hexagonal lattices. Specifically, the 2D bulk modulus and equivalent spring constants of the respective molecular building-blocks were calculated. Considering the material as a spring network, an analytical model for each topology was derived, which can be used to predict the 2D bulk modulus based on the properties of the monomeric units.

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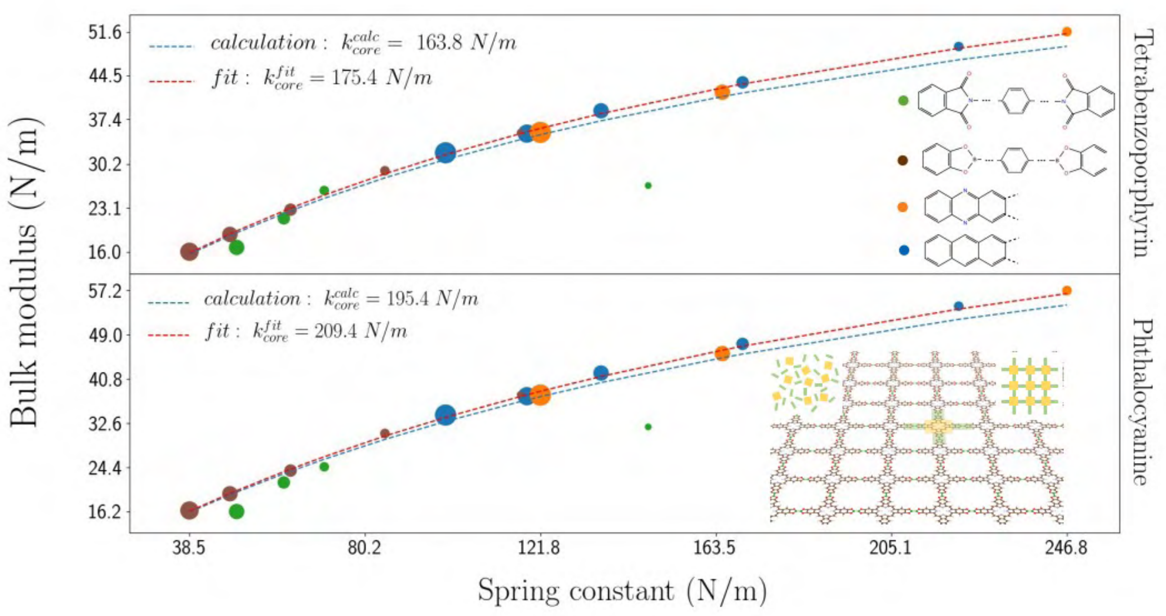

Figures

Figure 1: Correlation between spring constant and bulk modulus for the different cores with square lattice topology. The size of the circles for the structures is related to the number of the added benzene rings, while the color corresponds to the selected linker molecule as shown in the legend.

Multicomponent Covalent Chemical Patterning of Graphene

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The chemical patterning of graphene is being pursued due to exciting possibilities in electronics, catalysis, sensing, and photonics applications. Despite the intense efforts, spatially controlled, multifunctional covalent patterning of graphene is not straightforward. [1] The intrinsically poor reactivity of the basal plane of graphene implies the use of harsh chemistries to obtain the desired surface modification. However, chemical protocols to promote the reduction of aryl diazonium ions and the consequent functionalization of carbon-based surfaces have been recently reported. [2] These chemical protocols and conventional lithographic methods could provide the perfect combination to achieve well-defined covalent chemical patterning of graphene.

Here, we demonstrate spatially resolved multicomponent covalent chemical patterning of single layer graphene using a facile and efficient method. [3] Three different functional groups were covalently attached in dense, well-defined patterns. The fidelity of the pattern transfer was found to be exceptional, and the layer thickness of the covalent films was controlled down to 1 nm. The chemically patterned surfaces were characterized using Raman mapping, atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS). The chemical composition of the covalent films was mapped at the nanoscale using AFM-IR measurements, showing the precise compartmentalization of the functional groups along the basal plane. Finally, Kelvin probe force microscopy (KPFM) indicated that such precise multicomponent patterning leads to changes on the graphene surface potential.

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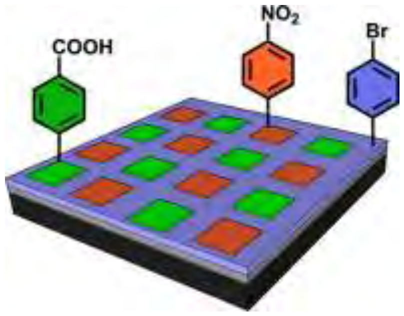

Figure 1: Scheme of the multicomponent covalent chemical patterning of graphene achieved in this work.

Molecular Engineering of Hybrid Layered Double Hydroxides for Energy Applications

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Layered double hydroxides (LDHs) are a class of anionic clays with a layered structure, that can be exfoliated giving place in 2D materials. They have a great tunability regarding the metallic composition and the interlayer anion. Recently, these materials are attracting increasing attention from the point of view of their electrochemical performance towards energy storage and conversion applications, highlighting mainly their excellent performance as electrode materials in supercapacitors and electrocatalysts for the oxygen evolution reaction. [1]

On the one hand, we focused on deciphering the influence that the interlayer space has in the behaviour of NiFe(3:1)–LDHs as oxygen evolution reaction (OER) electrocatalyst. Increasing the basal space of the LDH results in a higher electrochemical surface area and a reduction of the resistance related to the chemisorption of oxygen leading to better kinetic behaviour. Indeed, the Tafel slope for the NiFe–LDHs with the highest basal space studied is similar to that obtained for benchmark exfoliated NiFe nanosheets and shows better stability as a consequence of the tridimensional robustness of the hybrid material. However, an excessive increment of the interlayer space compromises the onset potential. [2]

On the other hand, it was investigated the influence of the interlayer space and the metallic ratio in the specific capacitance of a CoAl–LDH family when used as electrode materials for supercapacitors. Best specific capacitances were achieved for the lowest Co(II)/Al(III) ratio revealing the role of the electrochemically inert Al in the structure. In addition, the specific capacitance increases with the basal space, achieving an improvement of 46 % in the specific capacity for the CoAl(2:1)–LDH. This enhancement is ascribed to the increment of the electrochemical surface area. [3]

Figures

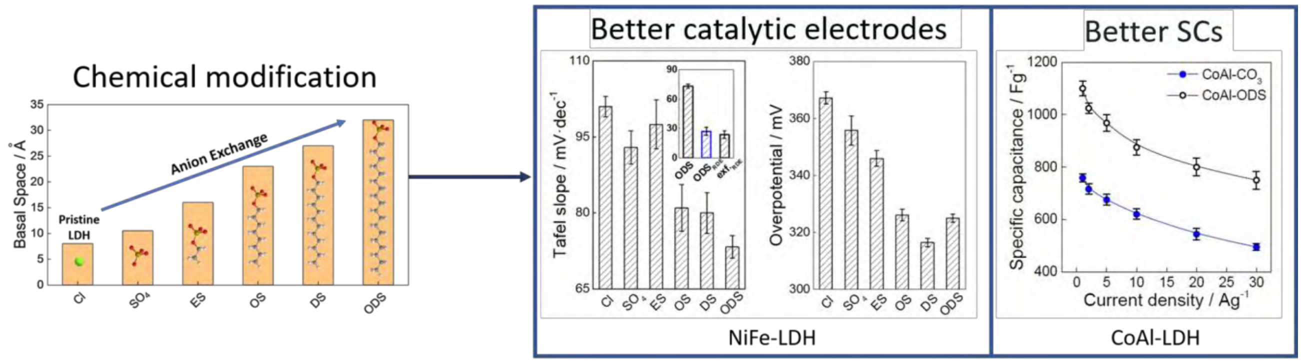

Figure 1: Influence of the Layered Double Hydroxides Interlayer Space on energy applications.

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Two-dimensional covalent crystals by chemical conversion of thin van der Waals materials

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Exfoliation of van der Waals materials has been the go-to approach to obtain 2D nanosheets. But recent efforts in expanding the 2D library has resulted in fabricating synthetic 2D crystals which have no layered bulk analogues [1,2]. These efforts have been focused mainly on the surface growth of molecules in high vacuum or using template assisted growth techniques. Here, we report an alternate approach to making 2D crystals of covalent solids by chemical conversion of van der Waals layers [1]. As an example, we used 2D indium selenide (InSe) obtained by exfoliation and converted it by direct fluorination into indium fluoride (InF_3), which cannot be obtained by direct exfoliation (Fig. 1). The conversion of InSe into InF_3 is found to be feasible for thicknesses down to three layers of InSe, and the obtained stable InF_3 layers are doped with selenium. We study this new 2D material by optical, electron transport, and Raman measurements and show that it is a semiconductor with a direct bandgap of 2.2 eV, exhibiting high optical transparency across the visible and infrared spectral ranges. We also demonstrate the scalability of our approach by chemical conversion of large-area, thin InSe laminates obtained by liquid exfoliation, into InF_3 films. The concept of chemical conversion of cleavable thin van der Waals crystals into covalently bonded non-cleavable ones opens exciting prospects for synthesizing a wide variety of novel atomically thin covalent crystals. The method can be extended to other materials. I will discuss our most recent results in this area of research.

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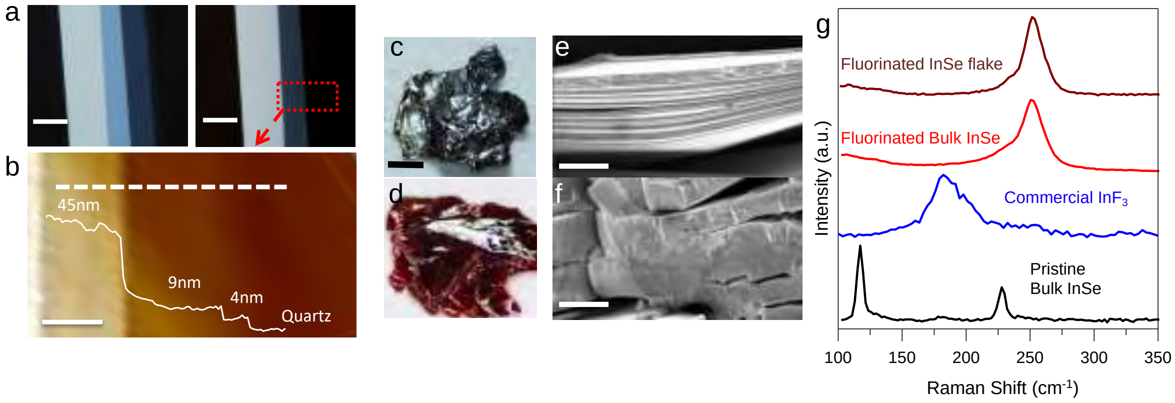

Figure 1: Characterization of fluorinated InSe. (a) Optical microscope images of InSe flakes on quartz substrate before (top left) and after (top right) fluorination. Scale bars, 7 µm. (b) An AFM image of the area marked with the red rectangle in Figure 1a. Scale bar, 5 µm. White curve: height profile along the dashed line. (c,d) Photographs of bulk InSe before and after the fluorination, respectively. Scale bars, 1 mm. (e,f) Cross-sectional SEM images of bulk pristine InSe and fluorinated InSe, respectively. Scale bars, 5 µm. (g) Raman spectra of a fluorinated InSe flake (~10 nm thick), fluorinated bulk InSe, commercial InF_3, and pristine bulk InSe

Carbide Formation at Graphene/Nickel Interface: The Decisive Role of Graphene Orientation

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When graphene (G) is grown on nickel substrate, the restructuring of the metallic surface upon carbon segregation resulted in the formation of nickel carbide (Ni_2C) phase at the interface but solely in rotated graphene (RG) domains and not under the epitaxial graphene (EG) [1]. Motivated by this experimental puzzle, we perform density functional theory calculations to illuminate the microscopic mechanisms governing the structural changes of a C-rich nickel surface under G cover [2]. We show that high concentration of subsurface carbon destabilizes the Ni(111) surface and gives rise to the formation of thermodynamically advantageous Ni_2C monolayer. We point out the crucial role of G rotation in enabling high density of favorable C binding sites in nickel subsurface. As opposed to RG, EG cover locks the majority of favorable C binding sites preventing the build-up of subsurface carbon density to a phase transition threshold. In line with strong experimental evidence, we explain why the Ni_2C phase formation can take place only if G is misaligned with the Ni(111) surface.

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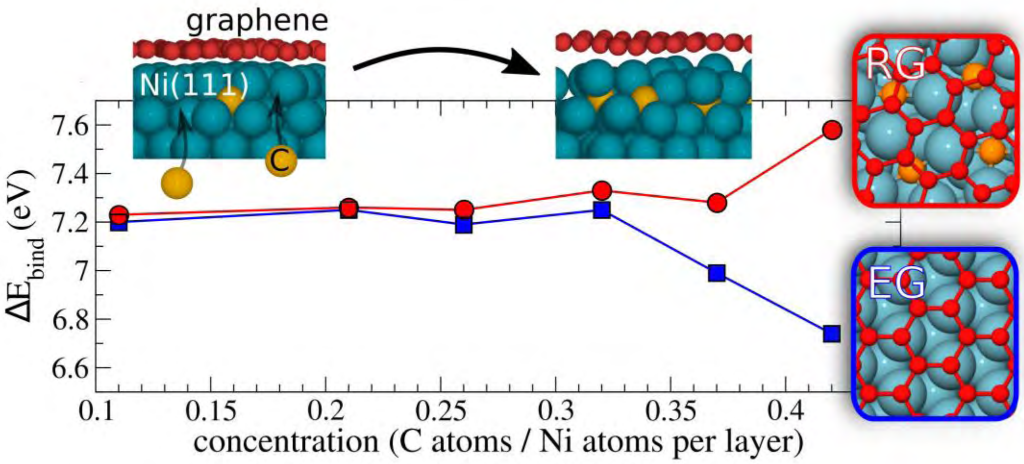

Figure 1: dependence of binding energy of subsurface carbon on the concentration of C atoms at RG/Ni(111) (red) and EG/Ni(111) (blue) interfaces.

Critical role of functional groups containing N and S on graphene surface for stable and fast charging Li-S batteries

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Lithium-sulfur (Li-S) batteries are considered one of the most promising energy storage technologies with the possibility to replace the state of-the-art lithium-ion batteries. However, the migration of high-order lithium polysulfides (LiPs) to the lithium surface and the sluggish electrochemical kinetics pose challenges to their commercialization. Instead of doping carbon hosts with heteroatoms to enhance their interactions with LiPs, which is limited with relatively low doping content (<10%), we propose in this study the grafting of versatile functional groups with designable properties (e.g., catalytic effects) directly on the surface of the carbon host.[1] As model systems, nitrobenzene and benzene sulfonate with N/O and S/O atoms were grafted vertically on the surface of highly conductive expanded reduced graphene oxide (eRGO). The immobilized functional groups with high density are uniformly distributed, which provide anchor points for the soluble LiPs. The Density Functional Theory (DFT) calculations demonstrated that the presence of these functional groups improved the binding energy of eRGO with both elemental sulfur and Li_2S_n polysulfide species. As a result, a stable interface was formed by absorbing/depositing the LiPs on the vertical nitrobenzene or benzene sulfonate functional groups. The combination of experiments and DFT calculation showed an improved retention of Li_2S_n at the cathode side with enhancement in electrochemical kinetics. The practical power and energy densities Li-S batteries significantly improved after introducing vertical functional groups on carbon hosts.

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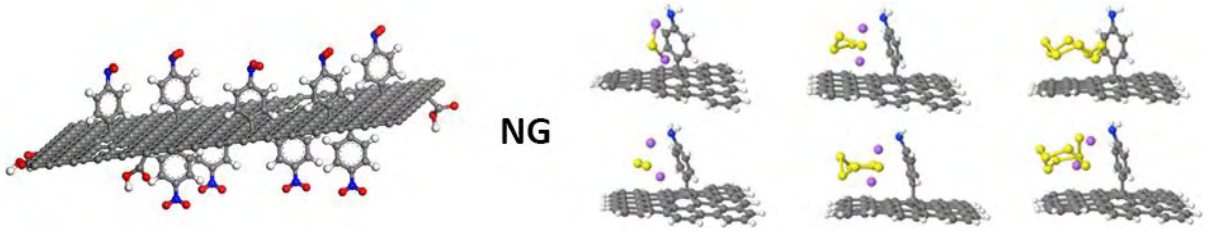

Figure 1. Molecular structure of functionalized graphene and its interaction with lithium polysulfides.

Covalently Interlinked Graphene Sheets with Sulfur-Chains Enable Superior Lithium Sulfur Battery Cathodes at Full-Mass Level

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Sulfur represents a low-cost, sustainable and high theoretical capacity cathode material for lithium-sulfur batteries, which could meet the growing demand in portable power sources. However, the shuttling-effect of the formed lithium polysulfides, as well as their low electric conductivity, compromise the electrochemical performance of lithium-sulfur cells.[1] To tackle this challenge, a so far unexplored cathode was developed, composed from sulfur covalently bonded directly on graphene. This was achieved by leveraging the nucleophilicity of polysulfide chains, which reacted readily with the electrophilic centers in fluorographene (Fig 1a). The reaction lead to the formation of carbon-sulfur covalent bonds and a particularly high sulfur content of 80 wt. %. Owing to these features, the developed cathode exhibited excellent performance with only 5 wt. % of conductive carbon additive, delivering very high full-cathode-mass capacities and rate capability, combined with superior cycling stability (Figure 1b,c). In combination with a fluorinated ether as electrolyte additive, the capacity persisted at ~700 mAh g^{-1} after 100 cycles at 0.1 C, and at ~644 mAh g^{-1} after 250 cycles at 0.2 C, keeping ~470 mAh g^{-1} even after 500 cycles.[2]

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Figures

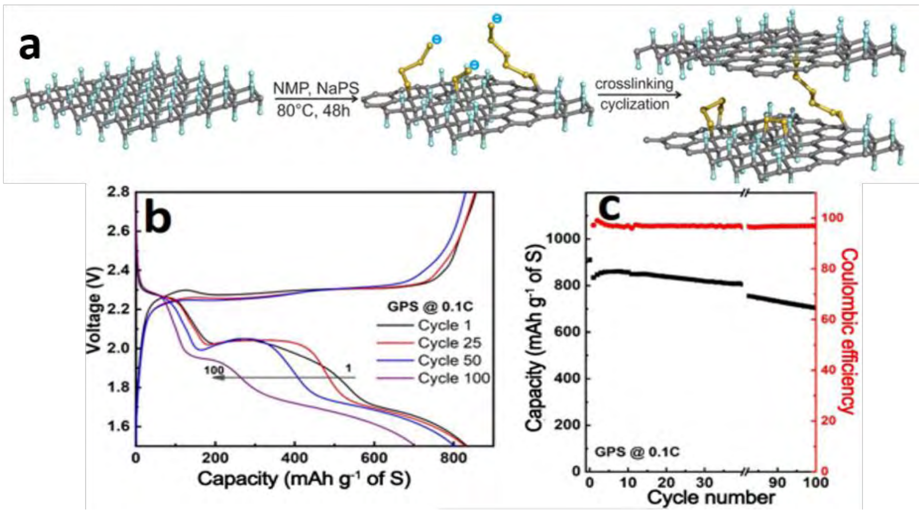

Figure 1: (a) Reaction scheme for covalent binding of sodium polysulfide (NaPS) to fluorographene (FG) leading to graphene-polysulfide (GPS), (b,c) Electrochemical performance of the prepared cathode against lithium in 1 м LiTFSI in 1:1 DOL:TTE electrolyte

Inducing carbon magnetism in nanographenes

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Magnetism is historically associated to d- and f-block elements of the periodic table, which form the basis for modern information storage technologies. However, recent advances on the bottom-up synthesis of low-dimensional materials revealed the emergence of non-trivial magnetic states in all-carbon compounds. The low spin-orbit and hyperfine couplings in carbon, along with the possibility of electric-field control of magnetism, provides unique opportunities in emerging technologies such as quantum computation. The electronic structure of nanographenes can be selectively controlled through variation in size, shape and edge structure, allowing to experimentally realize new quantum properties, including magnetism. In this contribution, we investigate the on-surface synthesis of z-shaped nanographenes belonging to the zethrene family. Single molecule scanning probe measurements reveal the transition from a closed-shell to an open-shell singlet ground state with increasing zethrene length. In the longest analogue, singlet to triplet spin excitation are detected via inelastic electron tunneling spectroscopy, unveiling a magnetic exchange coupling of 50 meV. These results open new perspectives for the realization of organic magnetic devices operating at practical temperatures.

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Figure 1

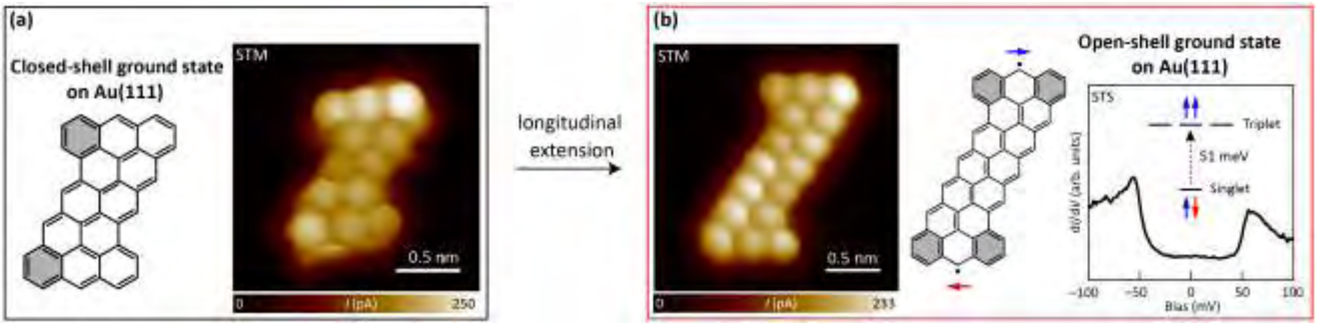

Figure 1: (a)(b) Bond-resolved STM imaging shows the on-surface synthesis of two z-shaped nanographenes with increasing length. (b) In the longest analogue, high resolution tunneling spectroscopy reveals inelastic singlet-triplet spin excitations.

Ultraclean High-Mobility Graphene on Technologically Relevant Substrate

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Graphene grown via chemical vapor deposition (CVD) on copper foil is nowadays recognized as a high-quality, scalable material, that can be easily integrated on technologically relevant platforms to develop a number of promising applications in the fields of optoelectronics and photonics. Most of these applications require high-mobility graphene (~ 10 000 cm^2 V^{-1} s^{-1} at room temperature) to have reduce device losses and compact design. To date, these mobility values are only obtained when suspending or encapsulating graphene with other 2D materials. In this work we demonstrate a two-step cleaning approach that yields high mobilities for scalable graphene directly on the most common technologically relevant substrate: silicon dioxide on silicon (SiO_2/Si). Which is done by using acetone and remover (1,3-Dioxolane, 1-Methoxy 2-Propanol) and analyzed by atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy confirming rapid elimination of the polymeric residues which remain on graphene after transfer and fabrication and adversely affects the electrical transport properties. We apply this approach on matrixes of graphene single crystals that can be used to populate 6” wafers [1]. Transport measurements demonstrate that ultra-clean single-crystal graphene consistently present mobilities up to 9000 cm^2 V^{-1} s^{-1} over wafer scale without any kind of encapsulation, thus paving the way to the adoption of this material in optoelectronics and photonics [2].

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Figures

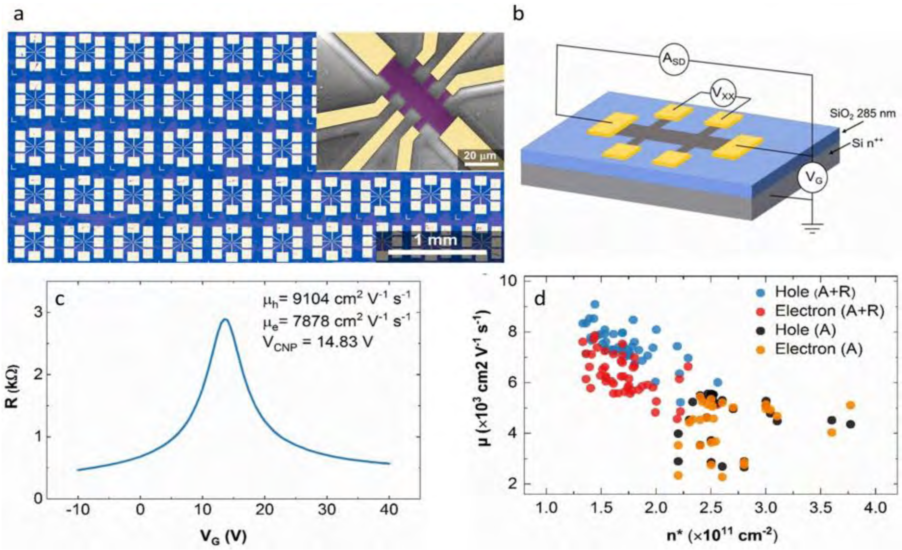

Figure 1: (a) Optical image of 50 graphene Hall bars on SiO_2/Si. Inset: false-colour SEM image of a single Hall bar. (b) Schematic diagram of the 4-terminal electrical characterization setup. c) Typical resistance curve of a graphene device. (d) Mobility statistics of graphene Hall bars prepared with conventional acetone cleaning method (black, orange) and two-step cleaning (red, blue) approach.

Field emission from WSe_2: A vertical field effect transistor

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Electric control of carrier concentration by gate biasing, in field-effect transistor structures, is an effective way to tune the doping level of semiconducting materials. Such strategy is viable, for instance, in field emission (FE) applications, where electrons are extracted from the material by quantum tunnelling through the surface potential barrier upon the application of a strong electric field. FE is of great relevance to a variety of applications, ranging from electron microscopy and lithography to display technology or vacuum electronics. Indeed, lateral field emission transistors have recently gained popularity due to their potential for many high-frequency and high-power applications [1-2].

The gate control of doping and therefore of the FE current is particularly effective when the cathode is made of a low-dimensional material [3]. We report the first observation of gate-controlled field emission current from a tungsten diselenide (WSe_2) monolayer, synthesized by chemical-vapour deposition on SiO_2/Si substrate. Ni contacted WSe_2 monolayer back-gated transistors, under high vacuum, exhibit n-type conduction, suitable for field emission.

The electron emission, at 400 nm distance between anode and cathode, occurs under an electric field ~100 V/µm and exhibit good time stability. Remarkably, the field emission current can be modulated by the back-gate voltage. The first field-emission vertical transistor based on WSe_2 monolayer is thus demonstrated and can pave the way to further optimize new WSe_2 based devices for use in vacuum electronics [4].

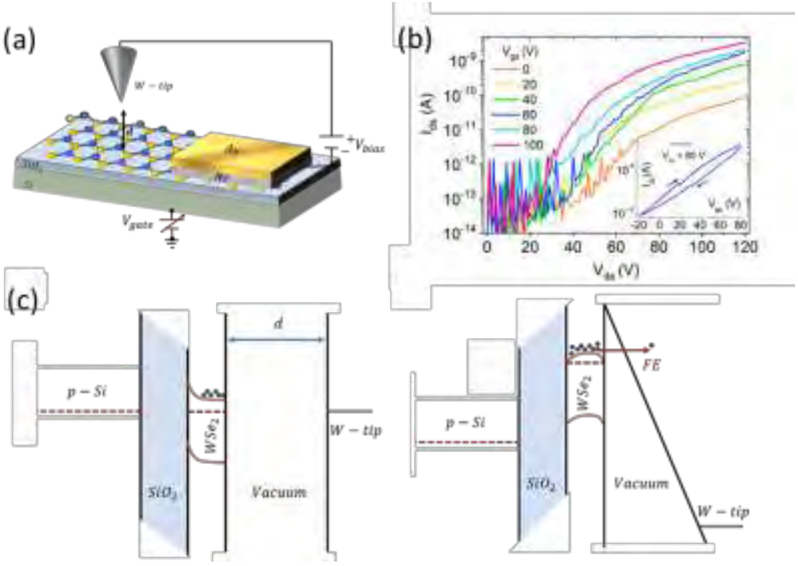

Figure 1: (a) Layout of a back-gate FE transistor with a WSe_2 monolayer channel over a SiO_2/Si substrate. (b) FE current measured at given back-gate voltages (V_{ds} steps of 1 V). (c) Band diagram for the unbiased device (left panel) and for the device under $V_{ds} > V_{gs} > 0$ V bias condition (right panel).

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Solution-processed Janus 2D-layers

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Asymmetrically decorated Janus nanoparticles (NPs) have attracted tremendous attention during the last decade. Asymmetric particles of this newly emerging family possess at least two surfaces resulting in the combination of a vast variety of properties, often contrary in nature [1, 2]. Due to their morphology Janus NPs exhibit curious coexistence of amphiphilic and anisotropic features that expand boundaries in potential applications [3, 4].

Although the most common Janus NPs are usually spherical, general synthetic approaches could be extended towards two-dimensional (2D) monolayers as well. The conventional way to obtain asymmetric 2D-materials generally involves masking of one side of the 2D layer with an inert template, allowing interaction only to take place on the exposed side. Thus, for example, H. Wu et al. achieved fabrication of Janus graphene oxide by isolating one surface through the formation of wax-in-water Pickering emulsion template [5]. However, Janus 2D materials are not necessarily limited to asymmetric graphene. During past few years considerable attention has also been drawn towards recent developments in asymmetric decoration of molybdenum disulfide (MoS_2) known for its appealing properties widely employed in optoelectronics, gas sensing, hydrogen evolution reactions, fabrication of solar cells or lithium-ion batteries [6]. For example, A. Lu et al. [7] reported processing of Janus-MoSSe structures by chemical vapour deposition. Contrariwise, so far, the solution approach for the synthesis of Janus-MoS_2 layers remains almost unexplored [8].

Here we are presenting a new strategy for asymmetric functionalization of MoS_2 in liquid-phase. First of all, negatively charged flakes of chemically exfoliated MoS_2 were electrostatically displaced onto silica beads template. In this manner the exposed plane became readily accessible for upcoming chemical grafting. Once functionalized, Janus flakes may be recovered by chemical etching of SiO_2 surface.

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Graphene Meets Ionic Liquids: Fermi Level Engineering via Electrostatic Forces

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Graphene, a single layer of carbon atoms in a two-dimensional (2D) hexagonal lattice, showcases key properties suitable for electrode materials such as high specific surface area, good electrical and thermal conductivities.[1] Ionic liquids (ILs) are a class of molten salts that are entirely composed of ions. These liquids possess exceptional properties appropriate for electrolytes, such as high electrochemical window, electrochemical stabilities and extremely low vapor pressure.[2] Graphene-based 2D materials are promising candidates for a number of different energy applications. A particularly interesting one is in next generation supercapacitors, where graphene is being explored as an electrode material in combination with ionic liquids as electrolytes. Because the amount of energy that can be stored in such supercapacitors critically depends on the electrode – electrolyte interface, there is considerable interest in understanding the structure and properties of the graphene/IL interface. Here, we present the changes in the properties of graphene upon adsorption of ILs and ILs – organic solvent mixtures using a combination of experimental and theoretical tools. For example, Raman spectroscopy reveals that imidazolium tetrafluoroborate ILs ($C_nMIM\ BF_4$) cause n-type doping of graphene, and the magnitude of doping increases with increasing cation chain length despite the expected decrease in the density of surface-adsorbed ions (Fig 1). Molecular modeling simulations show that doping originates from the changes in the electrostatic potential at the graphene/IL interface. The findings described here represent an important step in developing a comprehensive understanding of the graphene/IL interface.[3]

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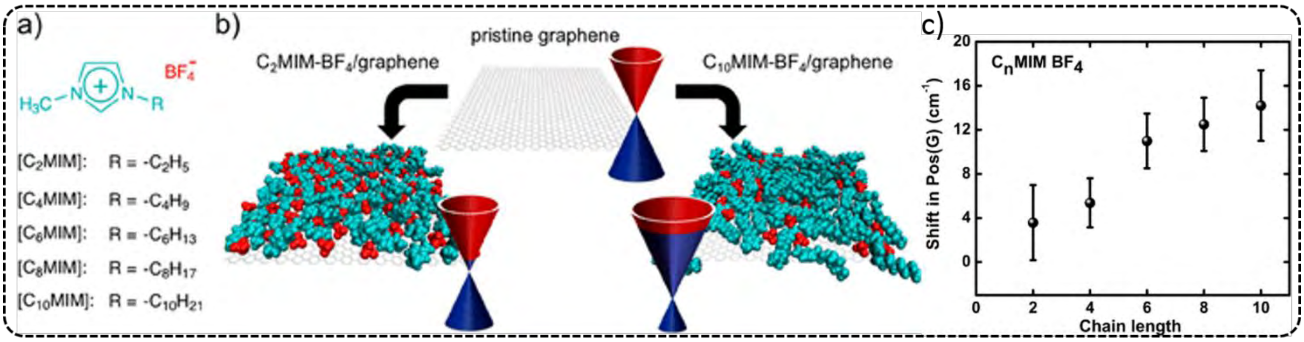

Figure 1: (a) Molecular structures of the ILs employed in this study. (b) Scheme showing the influence of the adsorption of ILs with increasing chain length on the Fermi level of graphene. (c) Shift in Pos(G) versus the number of carbon atoms present in the alkyl chain on the imidazolium cation.

CVD graphene coating of Cu cables for low voltage domestic and industrial wiring

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Copper is commonly employed in industrial wiring applications, owing to its excellent thermal, electrical and mechanical properties. However, Cu wires are easily oxidized when exposed to air [1] and conventional anticorrosion coatings have several issues, such as affecting the dimension, and the properties of the underlying material. Thereby, research efforts are devoted to develop effective and lightweight coatings to successfully prevent oxidation of Cu wires and possibly increase the electrical conductivity of the material with the aim of saving production costs. Graphene grown via chemical vapor deposition (CVD) is an interesting candidate material for ultrathin coating of Cu wires thanks to its extraordinarily high thermal and electrical conductivity, strength and adhesion to the original morphology of the surface [2-4]. We report the successful CVD growth of graphene on commercial Cu wires by controlling and optimizing sensitive growth parameters, and the morphological, spectroscopic, and electrical characterization of the samples as prepared and after natural aging. Our results demonstrate that graphene can effectively enhance the electrical properties of Cu cables, leading to 0.7-2.0% improvement in conductivity, with respect to pristine Cu wires, after 1 year. This process, carried out in safe conditions and using short times, paves the way for the development of an innovative reactor to enable in-line coating at industrial scale.

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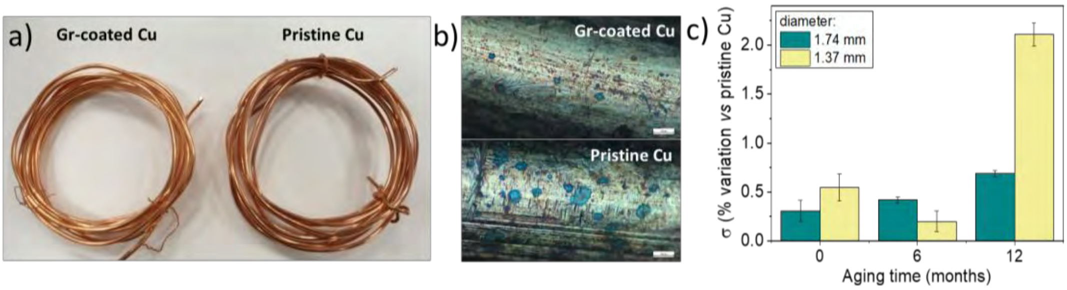

Figure 1: Appearance (a) and optical images (b) of pristine and Gr-coated Cu wires. Conductivity improvement of Gr-coated Cu wires through aging (c).

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Collective Dipole-Dominated Doping of Transition Metal Dichalcogenides:Orientation and Magnitude Control via the Supramolecular Approach

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Molecular doping is a powerful, tuneable, and versatile method to modify the electronic properties of 2D transition metal dichalcogenides (TMDs). While electron transfer is an isotropic process, dipole-induced doping is a collective phenomenon in which the orientation of the molecular dipoles interfaced to the 2D material is key to modulate and boost this electronic effect, despite it is not yet demonstrated. A novel method toward the molecular functionalization of mono-to-few layer TMDs relying on the molecular self-assembly of metal phthalocyanine and the orientation-controlled coordination chemistry of axial ligands is reported here. It is demonstrated that the subtle variation of position and type of functional groups exposed on the pyridinic ligand, yields a molecular dipole with programed magnitude and orientation which is capable to strongly influence the opto-electronic properties of TMDs. In particular, experimental results revealed that both p- and n-type doping can be achieved by modulating the charge carrier density up to 4.8x10^{12} cm^{-2}. Density functional theory calculations showed that the doping mechanism is primarily resulting from the effect of dipole-induced doping rather than charge transfer. The strategy to dope TMDCs is a highly modulable and robust, and it enables to enrich the functionality of 2D materials-based devices for high-performance applications in optoelectronics. [1]

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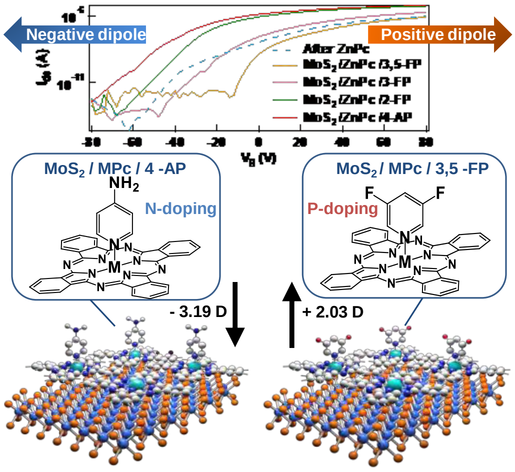

Figure 1: Collective dipole-induced doping of monolayer MoS_2 by axial ligands.

Electrophoretic deposition of graphene-related materials for positive electrodes in structural batteries

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Structural battery composites, typically based on Carbon Fibers (CF), are a class of structural power composites which can be included in the framework of vehicles to reduce weight and provide energy for distributed electronics simultaneously (Figure 1a).[1] CF can be easily used as anode in Li ion batteries, but need chemical functionalization to be used as cathode. Here, we describe a binder-free method to deposit a composite of lithium iron phosphate ($LiFePO_4$) and electrochemically exfoliated graphene oxide (EGO) on CF. To this aim, we use Electrophoretic Deposition (EPD) which is a versatile, scalable and cost-effective technique to deposit uniform coatings on electrodes for Lithium Ion Batteries (Figure 1b).[2] Various parameters such as deposition time and potential were evaluated to achieve uniform $LiFePO_4$/EGO coatings. The electrode composite yields specific energy density of 222.14 $Wh.kg^{-1}$ and power density of 0.29 $kW.kg^{-1}$ with 88.1% capacity retention at 1 C over 300 cycles in a full battery cell. Besides the promising performance of the $LiFePO_4$/EGO we describe here, the EPD method shall be used for deposition on CF of composite materials made of carbon and metal oxides,[3] paving the way towards facile electrophoresis synthesis of positive electrode materials.

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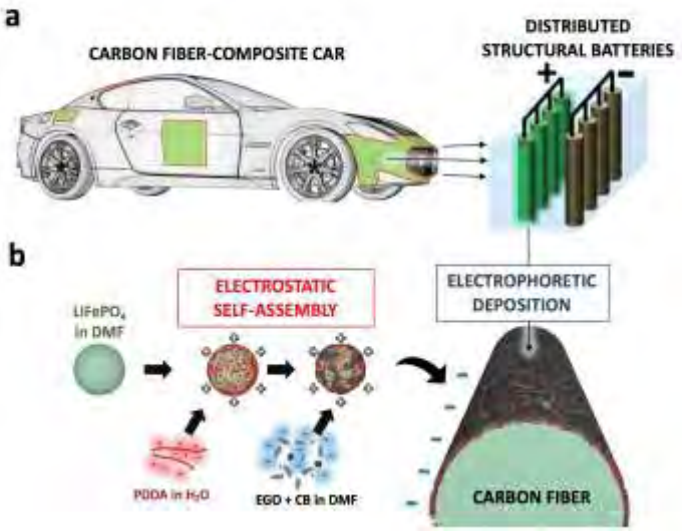

Figure 1: a) Structural Battery Concept b) Schematic illustration of EPD synthesis of the $LiFePO_4$/EGO electrode composite.

High-power energy storage enabled by 2D layered materials

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Electrochemical energy storage technologies have been brought into the spotlight as they provide elegant and efficient approaches to store, transport, and deliver energy harvested from sustainable energy resources.[1, 2] Typically, supercapacitors and batteries differ in electrochemical mechanisms, hence featuring almost opposite energy and power characteristics. However, the demand for power and energy supply is equally imperative in actual use and is keen to expand in the future. Thus it is highly desirable to design new electrode materials or rationally re-construct the recognized electrode materials for energy storage devices to mitigate the power-energy tradeoff.

2D layered materials are a class of materials with strong atom bonding in the basal plane and weak van der Waals (vdW) interaction between layers. These materials are equipped with versatile physical, chemical, electronic properties, as well as broad structural diversity. Importantly, the weak vdW interaction between the stacked layers enables layered materials with diverse possibilities for rational structure engineering, such as exfoliation into 2D nanoflakes, interlayer expansion with guest molecules, and hybrid structure construction. These structure engineering strategies are highly desired for layered materials to tailor their intrinsic properties (*e.g.,* electronic structure, conductivity, and redox capability) and electrochemical behaviours (*e.g.,* ion desolvation energy, solid-state ion diffusion kinetics, charge-storage mechanism) for diverse energy storage devices.[3]

Here, we will present our recent efforts in exploring 2D layered organic/inorganic materials for high-power energy storage applications.[3, 4] We will show 2D redox-active carbon-rich frameworks as promising electrode alternatives for high-power energy storage devices by demonstrating 2D polyarylimide covalent organic framework (COF) as the first COF anode for Zn-ion aqueous batteries[5] and dual-redox-site 2D conjugated metal-organic framework as a high-capacitance and wide-potential-window pseudocapacitive electrode. Moreover, we have demonstrated several interlayer engineering strategies for inorganic 2D layered materials to regulate the ion transport behaviors and boost the power-energy performance of the assembled energy storage devices.[6, 7]

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All-graphene flexible electrodes: novel platforms for wearable biosensing

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In recent years, the increasing request for a personalized approach to health and fitness goals is drawing research efforts on the development of wearable, non-invasive devices for continuous detection of biomarkers such as glucose, cholesterol, or lactate in sweat and in other biological fluids. Graphene and its related materials have attracted a growing interest in various field and are increasingly exploited in electrochemical (bio)sensing thanks to their unique properties [1,2]. In particular, graphene paper (G-paper) is a flexible, electrically conductive, paper-like material which has a large surface area and can be shaped in different ways; it features a high electrical conductivity ($1x10^5$ Sm^{-1}), mechanical and chemical stability even after one billion bending times [3]. We report the advantages in the use of G-paper for the realization of electrodes on flexible plastic and textile supports, as well as their application as wearable (bio)sensing platforms (Figure 1). A comparison with commercial graphite electrodes demonstrates that our novel devices outperform them in sensing of nicotinamide adenine dinucleotide (NADH), a key molecule for enzymatic biosensing. The possibility to functionalize the surface of our electrodes by stably anchoring suitable enzymes and redox mediators, or even to modify pristine G-paper with proper amount of graphene oxide to tune its properties, allows the realization of a wide plethora of flexible electrochemical biosensors. As an example of application of this new sensor platform, we report the stable deposition of lactate dehydrogenase for enzymatic detection of lactate.

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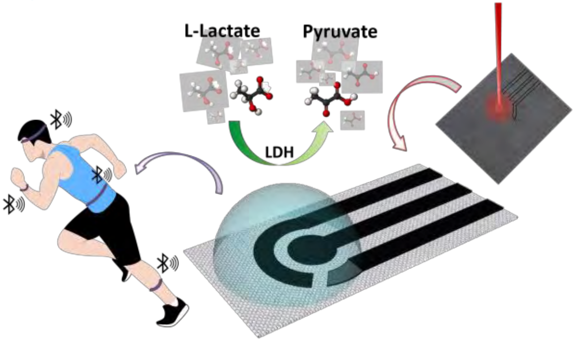

Figure 1: Exemplificative preparation of G-paper platform on cotton textile and its application for lactate detection during training.

A statistical model for representing stacking disorder of 2D covalent organic frameworks

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Since rise of the two-dimensional covalent organic framework (2D COF) field, there is a systematic discrepancy between predicted theoretical and experimental structures. [1] It is attributed to that the experimental materials do not have ideal structure, but contain diverse stackings, or even some extent of disorder. [2] The structure models commonly used in theoretical calculations are too idealistic, and cannot represent this configurational entropy in the materials, which is also existed in experimental interpretation. We have therefore built statistical models correctly describing both local structure and the long-range disorder in 2D COFs and 2D polymers in general. We studied honeycomb lattice as found in COF-1, COF-5 and square lattice in ZnPc-pz COF as examples, and were able to create realistic models with PXRD patterns consistent with the experimental results for those materials, for the first time. Our statistical model takes different slip directions into account, which contain broader peaks at correct positions and lacking the typical small peaks known from theoretical predictions. We have also demonstrated that the experimental samples exhibit stacking disorder combining different configurations, such as a mixture AA and ABC stacking. This has large implication on the properties of the material, especially on electronics, as it means that most lot of currently used models inherently lack important features present in the real materials.

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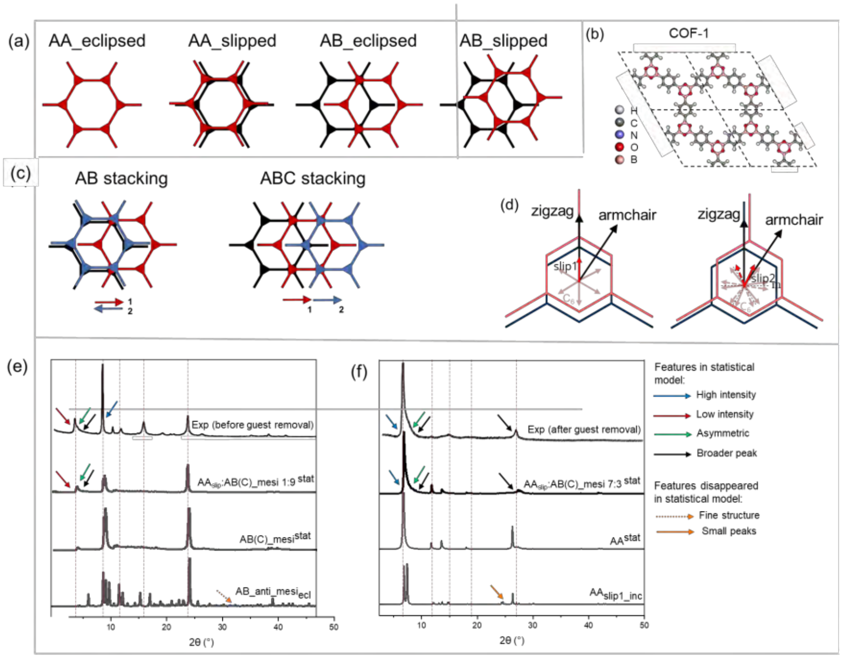

Figure 1: (a) AA and AB stacking configurations of honeycomb lattice with (*_slipped) or without (*_eclipsed) lateral interlayer slip. (b) Top view of COF-1. (c) Representation of main possible AB and ABC configurations. Successive layers depicted in black, red and blue. (d) Depictions of the slip vectors in COF-1 as models of planar COFs with honeycomb lattice. The calculated XRD of the best fitting statistically built structures, and the most stable small-UC bulk models configurations of (a) AB(C)^{stat}, (f) AA^{stat} stacking for COF-1.

POSTERS

Microfabricated Graphene Liquid Cells for the imaging of microtubules and protein structures using liquid phase EM

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Cryo-Electron Microscopy has produced high resolution 2D and 3D reconstructions of proteins and entire cells, yet this technique always provides a static snapshot of the system. Exciting challenges for EM now lie in expanding into the temporal dimension, where the dynamics of processes can be captured at nanoscale resolution. Liquid phase EM, where material is imaged in their native state in liquid water is therefore an exciting new avenue for research. The separation of the liquid sample from the TEM vacuum by ultrathin membranes is essential to realise high resolution and minimise electron dose. 2D materials represent the ultimate membrane material, in terms of thinness, mechanical and chemical properties. We use cleanroom microfabricated liquid sample chips for EM with graphene membranes (i.e. graphene liquid cells) to image biomolecules. Microfabrication of liquid cells yields well defined liquid volumes with large windows, enabling higher throughput than existing methods. With this setup and the unique properties of graphene we seek to answer questions about microtubules (protein filaments) and their dynamics that could up to now not be directly investigated.

Electronic properties of MA_2Z_4 family of layered 2D materials

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Layered MA_2Z_4 family of materials has recently drawn a great interest as a promising class of 2D semiconductors, due to their exceptional electronic and mechanical properties [1]. For instance, $MoSi_2N_4$ and WSi_2N_4 monolayers have been successfully synthesized using chemical vapor deposition, however, many more members of this material's family were predicted theoretically [2]. Motivated by this research, we have explored the electronic properties of this new family of layered 2D materials. In this work, we systematically investigated the MA_2Z_4 (M = Mo, W; A = Si; Z = N, P, As, Sb) monolayers in pure form as well as mixed forms, with two different Z elements in the same layer, using density functional theory (DFT) calculations. Phonon dispersion relation showed that most of the models are stable. The band decomposed charge densities were plotted for these monolayers, showing localization of electron and hole states (see Figure 1) The exciton g-factors from first principles, which can be measure experimentally, were also calculated for all possible spin-valley configurations of excitons in a monolayer. The theoretical aspect of our work provides insights into the future nano(opto)electronic applications of MA_2Z_4 monolayers.

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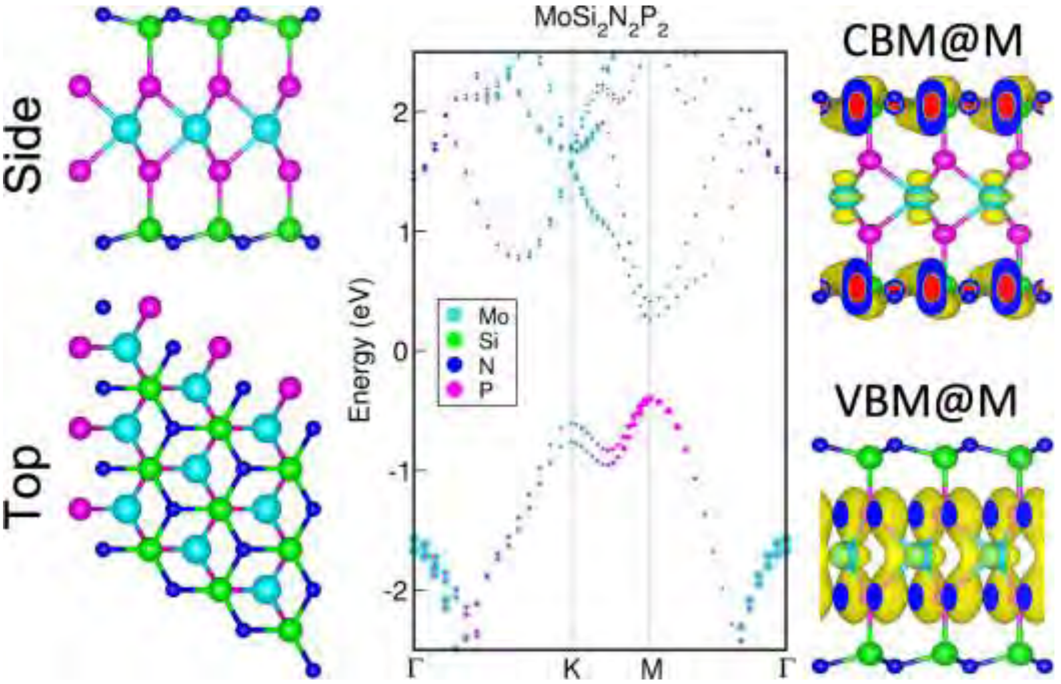

Figure 1: Structure, electronics and band decomposed charge densities of $MoSi_2N_2P_2$ monolayer.

The application of functionalized 2D materials in solid-state electrolyte for flexible supercapacitors

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Solid-state flexible supercapacitors (SSFSs) have drawn an increasingly attention due to their special mechanical properties (*e.g.*, foldability) and high power density (*i.e.*, fast charge-discharge rate) [1]. Owing these properties, SSFSs represent appropriate candidates for powering portable electronic devices, including wearable power-supply units [2]. The SSFSs intrinsically overcome the electrolyte leakage of traditional supercapacitors, eliminating safety and environmental concerns without requiring rigid and robust packaging strategies[3]. However, solid-state electrolytes still suffer from poor ion mobility and reactivity that undermine the distinctive high power density of supercapacitors[4]. To address these issues, incorporation of transition metal dichalcogenides (TMDCs), *i.e.*, sulfonated 2D niobium disulphide (S-NbS_2), in proton-conducting sulfonated poly(ether ether ketone) (SPEEK) was investigated as solid-state electrolyte for high-power SSFSs. Single-/few-layer NbS_2 flakes were produced through ultrasonication-assisted liquid-phase exfoliation of their bulk counterpart[5]. The as-produced material was subsequently functionalized with sodium 3-mercapto-1-propane sulfonate to promote its interaction with the polymeric matrix through the formation of hydrogen bonding between functionalized groups of S-NbS_2 and sulfonated groups of SPPEK [6]. The incorporation of S-NbS_2 into the SPEEK matrix increases the proton conductivity and dimensional stability of the pristine polymer. By optimizing the weight of S-NbS_2 into the nanocomposite electrolytes, a maximum proton conductivity of 94.35 mS cm^{-2} was achieved at room temperature, coupled with an improvement of 18% of the mechanical strength compared to pristine SPEEK (up to 38.3 MPa). To design advanced SSFSs, either SPEEK or polyvinylidene fluoride was used as different binding agents for the electrodes. The aim is to elucidate the importance of the interaction between the solid electrolyte and the binder to maximize the electrostatic charging of electrode active materials. The use of optimized solid-state electrolyte in SSFSs, based on proton-conducting SPEEK binder, allowed us to achieve a specific capacitance of 115.724 F g^{-1} at 0.02 A g^{-1}, showing optimal rate capability (75.94 F g^{-1} at 10 A g^{-1}) and electrochemical stability over galvanostatic charge/discharge cycling tests. Overall, our results rationalize the use of S-NbS_2 as additive for solid-state electrolytes, promoting the development of high power SSFSs.

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SUPRAMOLECULAR AGGREGATION OF POLYCYCLIC AROMATIC HYDROCARBONS ON THE WATER SURFACE: DFT AND MOLECULAR DYNAMICS

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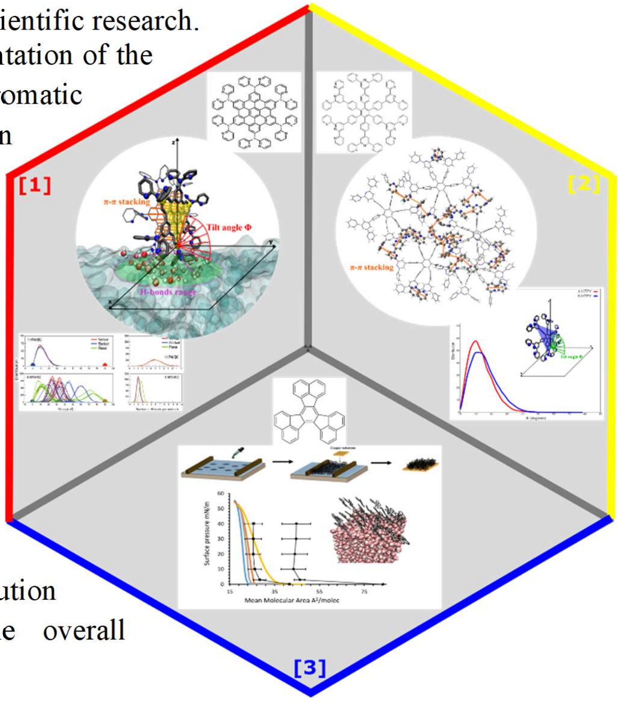
Simulations are always the other face of the Moon in the scientific research. In this context, the structure, the aggregation, and the orientation of the core-rim amphiphilic and propellerenes polycyclic aromatic hydrocarbons (PAHs) on the water surface have been explored by DFT calculations and molecular dynamics (MD) simulations. We find that the supramolecular arrangements of PAHs on the water slab depend on the balance between competitive π-π stacking of PAHs and possibly hydrogen bond interactions between water and functional groups of PAHs.

An investigated core-rim structured PAHs with a conjugated planar core (hexabenzocoronene core) presents an evident change in the aggregation properties by increasing the number of interacting monomers on the water slab: the π-π stacking becomes the dominant contribution compared to the hydrogen-bond in determining the overall arrangement. [1]



On the other hand, a core-rim PAHs with a less-conjugated non-planar core (hexaphenyl benzene) shows a significant role of hydrogen-bonds guiding the arrangement on the water surface. In this case, the π-π stacking interaction between edges moieties is also observed, which is consistent with results from the single-crystal structure. [2]

Finally, the decacyclene propeller shows to form thin films without requiring any covalent crosslinking. Thin films were found mechanically stable enough to be free-standing over micrometer distances, held together solely by non-covalent interactions. We got a molecular picture of the packing of decacyclene at the air-water interface and we simulate the Lagmuir-Blodgett compression extracting a computational isotherm in agreement with the experimental one. [3]

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Chemistry at the graphene edge

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Graphene edges have obtained interest due to their higher reactivity compared to the basal plane allowing functionalization, resulting in a covalent carbon-carbon bond, to alter the electronic and chemical properties without affecting the electron mobility. However, current development is hampered by the inability to characterize covalently functionalized edges. Herein, we provide a bottom-up approach for the characterization by introducing a protected thiol moiety that upon electro-grafting to the edge can be released. This will then allow nucleation of AuNPs on the edge. By performing Atomic force microscopy we expect to observe AuNPs exclusively on the edge and by Surface-Enhanced Raman Spectroscopy we expect to be able to identify our grafted molecule. By doing we hope to have set a first step in the ability to characterize covalently functionalized graphene edges.

Liquid exfoliation of hydrothermally synthesized MoO_3 mesostructures in low toxicity solvents for the production of “green” 2D materials inks

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α-MoO_3 is a promising material for use in charge extracting layers within optoelectronic devices, due to its wide gap and deep work-function, characteristics that makes it an established constituent of “hole transporting layers” in last generation solar cells and light emitting diodes. This material possesses a layered structure that makes it also suitable for mechanical exfoliation to produce 2D nano-sheets, allowing to further tune its electronic properties.[1]
Here, we will report on the synthesis of pristine bulk MoO_3 meso-structures and on their liquid phase exfoliation, that produces functional inks of few-layers 2D MoO_3. The first process is carried out employing a hydrothermal synthesis,[2] as a green and easily scalable method, while the second, makes use of both shear-mixing and tip sonication in different liquid media, so as to ascertain whether differences emerge in the resulting inks and 2D materials there contained. First characterizations, made through optical/Raman spectroscopy, dynamic light scattering and high-resolution transmission electron microscopy allows to frame the exfoliation process and identify the best conditions. In particular, we found good yields in exfoliated products employing water-based media. We then proceeded in further characterizing these materials through X-Rays Absorption (XAS) and other advanced optical and microscopy techniques to improve our understanding of their structural and functional properties for the future use in next generation optoelectronic devices.

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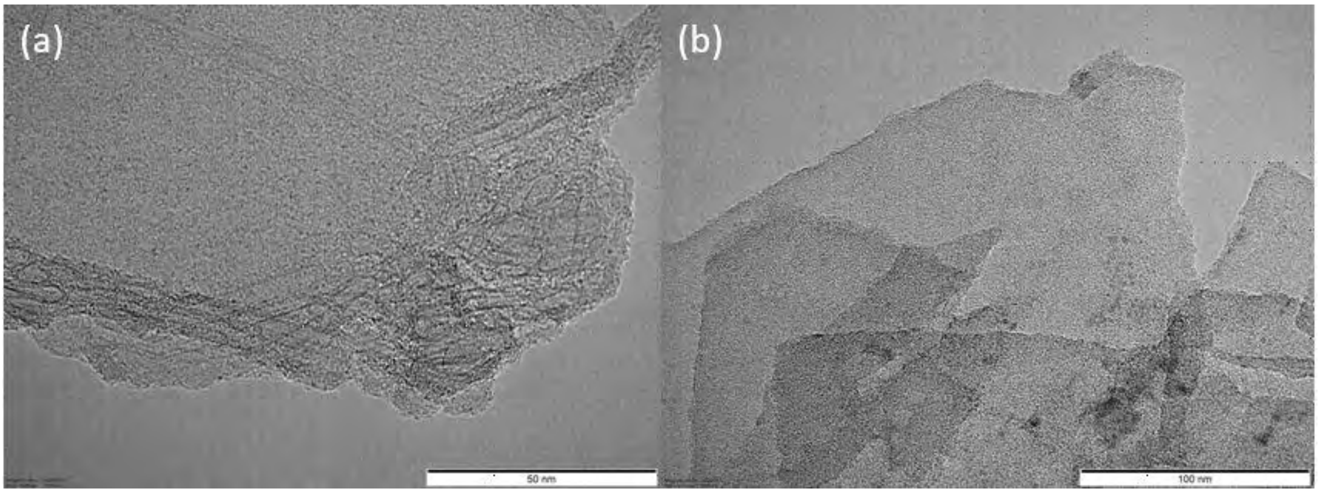

Figure 1: TEM images of (a) IPA/H_2O and (b) water exfoliated MoO_3

Optoelectronic processes in triphenylamine-based 2D covalent organic frameworks

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Bidimensional, porous, crystalline, covalent organic frameworks (2D COFs) are currently an appealing candidate for advanced applications in optoelectronic devices. The combination between the vast choice of building-blocks and linkages available enable the fabrication of polymeric materials with specific functionalities and adjustable plane-extended pi-conjugation.[1]

Recently, triphenylamine (TPA)-based moieties have emerged as possible building-blocks in 2D COFs. TPA is a thermally stable, propeller-shaped molecule which exhibits interesting photoactive and electroactive behaviors. These features are related to the stability of corresponding radical cation, easily generated by mono-electron oxidation. TPA-based advanced materials such as molecular derivatives, linear and branched polymers have been developed for various optoelectronic applications such as photoconductive, light-emitting, electrochromic devices and especially as hole transporting materials.[2]

Herein, we report the integration of two types of triphenylamine (TPA) moieties in 2D COF thin films. Polymerization of the C_3-symmetric tris(4-aminophenyl)amine with linear dialdehydes leads to the formation of a hexagonal topology while the reaction of the C_2-symmetric N,N,N',N'-tetrakis(4-aminophenyl)-1,4-phenylenediamine with the same dialdehydes leads to the formation of a Kagome topology.[3] Our results show appealing photoconductive and hole-transporting properties of the resulting materials and suggest that the topology of the framework might have a deep impact in the final behavior.[4]

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Unravelling Optical Properties Of Extended Core Conjugated Chromophores With Computational Strategies: From Single Molecule To Aggregates

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Carbon-based conjugated molecules with extended π cores can be considered as *building blocks* for carbon nanotubes and *models* for graphene nanoribbons and defected graphene. Among polycyclic aromatic hydrocarbons (PAHs), those possessing diradical character have undergone a strong resurgence of interest due to their potential applications in optoelectronic devices [1]. Beside small singlet-triplet gaps, one distinctive character of their optical properties is the presence of a low-lying double-exciton (DE) state dominated by the H,H→L,L configuration[2] which may influence photophysical properties such as two-photon absorption efficiency and quenching of the fluorescence. Thanks to their efficient π-π interactions, aggregation in PAH derivatives affects remarkably the optical properties of their condensed phases [3] a fact that has a strong impact in real optoelectronic devices.

In recent years, we have been interested in modelling the optical properties of large conjugated systems, focusing not only on isolated molecules but also considering aggregation effects. The goal of this contribution is therefore twofold. On one side, we report our recent results on the investigation on the DE state of conjugated diradicals with cost-effective computational methods such as *TDUDFT*, *SF-TDDFT* [4] and *DFTMRCI* [5]. On the other hand, we present an investigation on the modulation of exciton states in aggregates of perylene di-imide, a well-known example of n-type organic semiconductor. To disentangle the crucial role played by charge transfer contributions to exciton states [6,7], we discuss a diabatization procedure and a simple, dimer-based, model Hamiltonian able to reproduce the results of quantum-chemical calculations on full aggregates [8].

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Spin-orbit induced splitting in presence of non-uniform strain in 2D materials

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Abstract

Strain is omnipresent in 2D materials whether due to preparation methods or as a part of the post processing steps to obtain some special tailored properties. While the uniform strain is thoroughly studied and even data is present in public databases [1, 2], the knowledge of the effect of non-uniform strain in 2D materials is scarce. Many challenges are ahead to grasp the physics and chemistry in non-uniformly strained structures. Here, we want to investigate if 2D wrinkled structures, where non-uniform strain with different direction and magnitude is present, can be modeled as nanotubes. Moreover, Density Fuctional theory (DFT) was utilized in order to gain information about the changes in the electronic structure. Investigating WSe_2 and MoS_2 as prototypical 2D materials we found that spin-orbit coupling plays a crucial role in determining the properties especially of the valence band. Interestingly, we observed Rashba type splitting [3] which is a consequence of the symmetry breaking and is associated to the charge redistribution due to strain in these structures.

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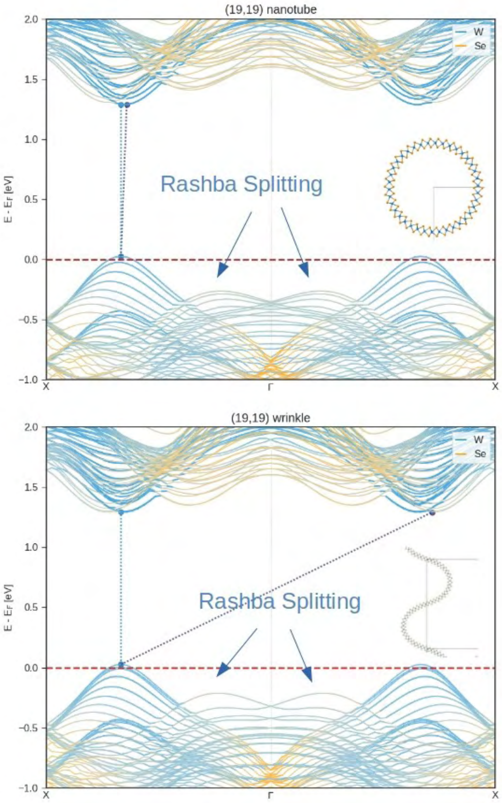
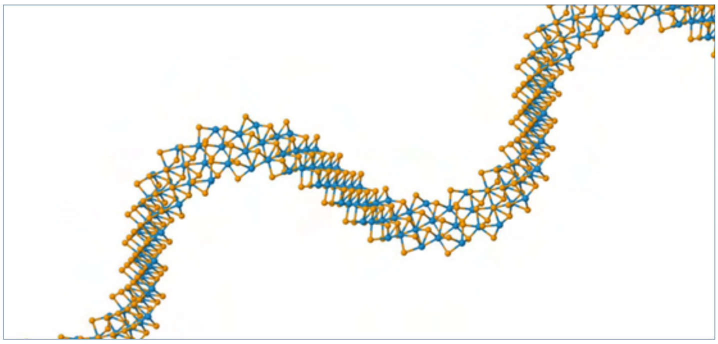


Figure 1: (right) electronic structure of the nanotube and wrinkles of (19,19) WSe_2 , appearance of momentum direction spin-orbit coupling splitting is also shown on the figures.

Figure 2: (below) relaxed structure of wrinkled monolayer of the WSe_2



Tuning Graphene Oxide Nano-Flakes Reduction Differently Affects Neuronal Networks in the Zebrafish

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Graphene related materials (GRMs) are characterized by diverse chemical and physical properties which may impact the nervous system. This ability has become a relevant issue following the increasing use of GRM's based technology in the design of neuro-biomedical devices [1-2]. In addition, the increased production of GRMs-based technologies might favor the dispersion in the environment of nanoparticles whose neurotoxicity needs investigation [3]. We exploited the thermal reduction of graphene oxide nanoflakes (GO) to generate materials with different oxygen/carbon ratio (Fig. A-B), we used a high throughput analysis of early stage-zebrafish locomotor behavior to investigate whether modifications of a specific GRMs chemical property influenced how these nanomaterials affect sensory motor neurophysiology. While zebrafish exposed to GO exhibited a quick reduction of locomotor activity, the reduced GO (rGO) induced an enhanced swimming performance (Fig. 1C). Histological analysis revealed that GRMs did not alter larval spinal cord morphology (Fig. 1D). Such modifications in locomotor behavior could emerge from GRMs direct interfacing of sensory/motor functions in the nervous system. We concluded that reducing the GO thermally is sufficient to produce differential effects on nervous system physiology, probably interfering with synaptic communication between neurons.

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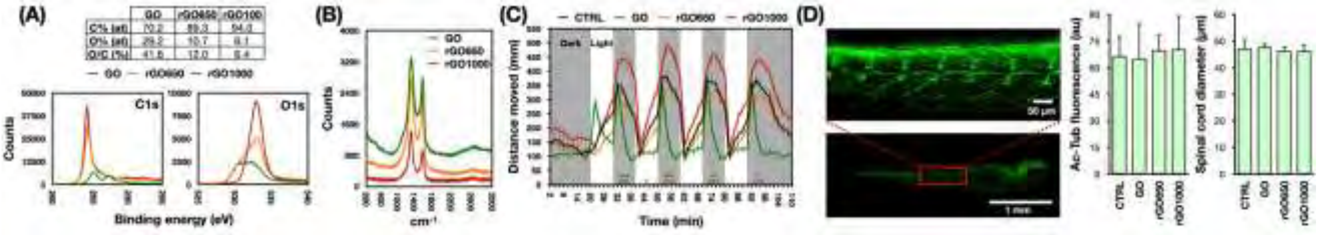

Figure: Characterization of GO and rGO 650-1000 °C using **(A)** XPS analysis and its oxygen/carbon quantification. **(B)** Raman spectroscopy. **(C)** Zebrafish locomotor activity measured as distance moved during light (white bars) and dark (grey bars) alternating periods. **(D)** Representative image of a whole mounted zebrafish larvae labelled with the neuronal marker acetylated-tubulin (Ac-Tub) and plots of spinal neurons fluorescence intensity and spinal cord diameter.

Strain engineering of MoS_2/graphene heterostructrures by thermal treatment

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Two-dimensional (2D) transition metal dichalcogenides (TMDCs) and graphene constitute a new class of atomically thin materials that possess exotic mechanical, electrical and optical properties [1]. Thanks to their characteristic exceptional mechanical strength and flexibility, 2D materials provide an ideal platform for strain engineering, enabling tunable modulation and significant improvement of their optical properties [2]. With the application of external fields such as uniaxial or biaxial strain, one can demonstrate flexible control over their electronic states. Meanwhile, many nondestructive spectroscopic and microscopic characterization tools can be readily harnessed to quantitatively determine strain-engineered alterations in these properties. Furthermore, transferring 2D materials onto pre-patterned substrates provides a means of introducing inhomogeneous and guided local strains into any type of 2D material, which is of great technological interest [3].

In the work presented here, molybdenum disulfide (MoS_2) was directly exfoliated on top of transferred CVD graphene, which enabled directed strain distributions hailing from the wrinkled graphene topography. Additionally, another degree of strain was introduced and controlled by a simple thermal treatment owing to the thermal expansion of the substrate, which also affected the interlayer bonding of the heterostructures. The variations in the resulting optical and electrical properties were assessed with Raman spectroscopy, Photoluminescence and Kelvin Probe Force Microscopy, and displayed effective control in temperatures as low as 125 ^oC for the aforementioned properties. The prospect of these findings can pave the way for low-cost and controllable engineering of devices directly on insulating substrates.

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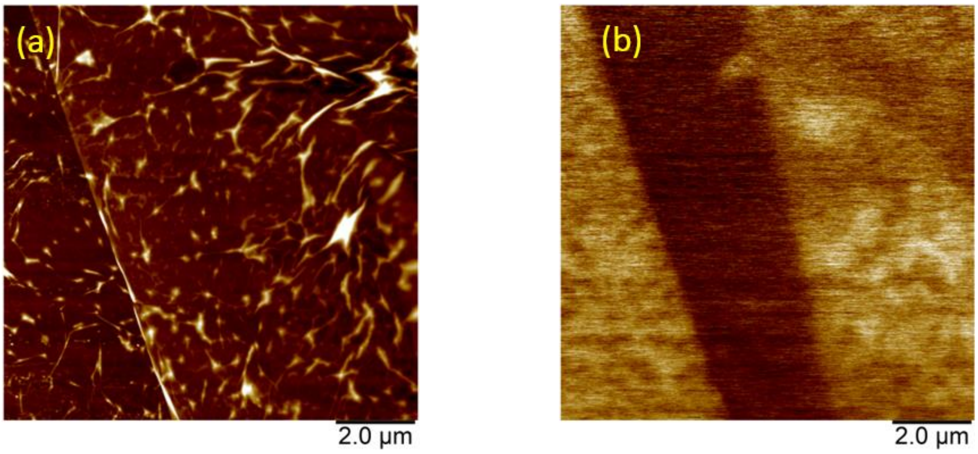

Figure 1: (a) Topography and (b) surface potential of MoS_2/graphene heterostructure

Mechanistic Insights into the redox properties of conjugated 2D-MOFs via electrochemical Raman Spectroscopy

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Abstract

Conjugated 2-dimensional Metal Organic Frameworks (MOFs) consisting of Phthalocyanine (Pc) monomers have shown to be great catalysts for the oxygen reduction reaction (ORR). [1]In the present work CuPc MOFs linked by Cu-O were synthesized on a water air interface, which resulted in a perpendicular orientation of the MOF in respect to the water surface. The CuPc-CuO_4 MOFs were subsequently attached to roughened silver electrodes through Langmuir Blodgett technique. Electrochemical Surface enhanced Raman spectroscopy (EC-Raman) [2], assisted by DFT simulations gave important information on the redox potentials of the CuPc in the monomer, MOF and the copper in the O-nodes. Additionally, for a more organized attachment of the MOFs onto graphite electrodes, the electrodes were modified with self -assembled monolayers of Copper and Nickel Nitrilotriacetic acid [3] before the attachment of the MOFs. This is shown to give better Raman signals and improved ORR activity.

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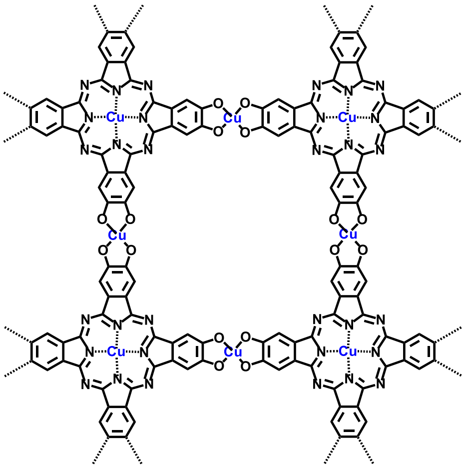

Figure 1: Chemical structure of $CuPcCuO_4$ MOF

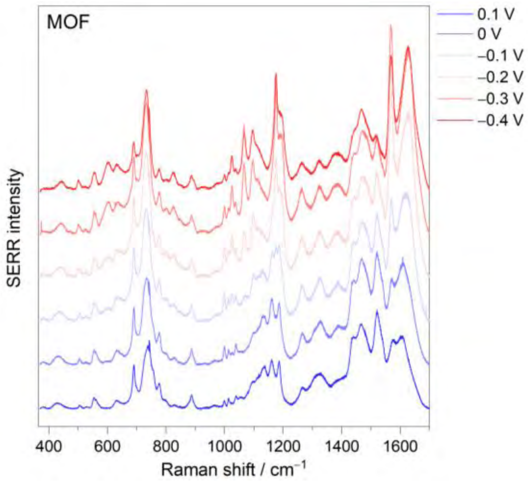

Figure 2: Surface enhanced Resonance Raman Spectrum of $CuPcCuO_4$ with varied potential

London Dispersion Corrected DFT and its Impacts on Electronic Band Structure Calculations

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It must be a twist of fate that Sir Isaac Newton developed the foundations of classical mechanics by unwittingly using the quantum mechanical London dispersion interactions thanks to his pencil. However, graphene layers of the pencil are not the only layers that hold together by London dispersion interactions. A wide spectrum of layered materials exist, and novel properties of their single or few layers got the attention of scientists due to their novel properties. To reveal these novel properties, London dispersion interactions also needed to be taken into account properly in addition to the other electromagnetic interactions. In the Density Functional Theory (DFT) formalism, these interactions are not included in the standard DFT functionals due to their local and semi-local natures [1,2]. In this study, we showed the computationally affordable PBE-rVV10L non-local DFT functional is predicting London dispersion interaction governed interlayer distances and interlayer interaction energies of eighteen bulk layered systems with mean absolute errors (MAE) of 0.092 Å and 3.25 meV/atom, respectively. In addition to this, we revealed the importance of the interlayer distances on electronic band structure calculations.

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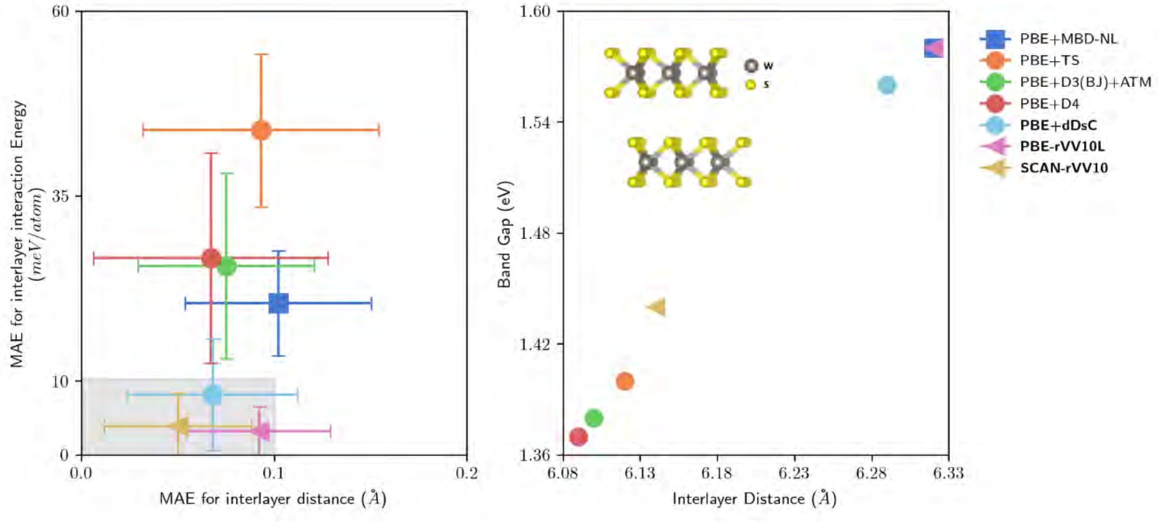

(a) (b)

Figure 1: (a) Interlayer distance and interlayer interaction energy mean absolute errors (MAE) of 18 layered bulk systems with their standard deviations for the tested methods. We took experimental interlayer distances and our Random Phase Approximation (RPA) interlayer interaction energy calculations as reference data. (b) The impact of the initial interlayer distance on the HSE06+SOC band gaps for the WS_2 bulk system. The same pattern also exists for other systems. While the x-axis shows the interlayer distances of the WS_2 bulk system determined with corresponding methods, the y-axis shows HSE06+SOC band gaps determined on top of those geometries.

Graphene-based devices for selectively triggering calcium signals in brain astrocytes

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Abstract

Due to its advantageous electrical and mechanical properties, Graphene represents a potentially suitable material as neuronal interface for electrical stimulation and modulation of brain signals.
Astroglial cells in the brain processes and exchange different neuronal information through intracellular calcium signaling communication to critically regulate the cerebral homeostasis and control the synaptic transmission.
Increasing experimental evidence indicates the positive impact of graphene nanoflakes and functionalized graphene membranes on viability and physiological properties of astrocytes [1]. However, the biophysical mechanisms of interaction of Graphene nanomaterials with astrocytes need to be further investigated.
We exploit different properties of Graphene-based devices to achieve selective electrical stimulation of astrocyte brain cells [2]. We performed Fluo-4 calcium imaging experiments on primary rat cortical astrocytes plated on indium tin oxide (ITO) coated with Graphene Oxide (GO) or reduced GO (rGO) films. We demonstrate that electrical stimulation of primary astrocytes plated on conductive substrates of rGO induces rapid calcium dynamics. Conversely, astrocytes on insulating GO thin layers trigger slower, stronger calcium response.
Our results support the hypothesis that cell stimulating by GO and rGO activates distinct calcium pathways on astrocytes depending on the electrical conductivity of the device. This finding suggests the great potentialities of graphene devices for engineering advanced glial interfaces devoted to the selective modulation of astrocytes dynamics in the study and therapy of brain functions and dysfunctions [3].
Supported by AFOSR-3D Neuroglia, ASTROMAT; EU-GRAPHENE FLAGHIP

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An explorative study on the potential of 2D materials-based membranes for enhanced water desalination processes

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The use of 2D materials has been demonstrated to have a great impact on the research dedicated to water desalination [1,2]. In this work, we discuss how the inclusion of 2D materials in hydrophobic porous PVDF membranes improves the fluxes while a better quality of water can be achieved. Also, we demonstrate how salts can be recovered from hypersaline solutions; crystals with somewhat uniform size and well-shaped geometry can be obtained. Specifically, we discuss the fabrication of new-concept exfoliated few layers materials-enabled membranes aimed at enhancing the performance of two eco-sustainable technologies such as Membrane Distillation (MD) and Membrane Crystallization (MCr)[2-4]. We assess how water is diffused through the membrane when applying a difference of temperature across the membrane. This diffusion can be amplified in presence of a suitable loading of few layers 2D materials. Larger water fluxes are thus produced. Assisted water uptake causes also quicker water sequestration from water-salt clusters reaching supersaturation conditions in a shorter time. As a subsequent effect, rapid formation of nuclei and controlled growth of crystals are obtained [3]. Herein, a summary of the most interesting achievements is given and the behaviour of 2D materials functional membranes is described as a function of chemical composition and salt concentration as well as running conditions selected for membrane operations. This study provides new insights about the promising role of 2D materials in water desalination through the implementation of enhanced eco-sustainable membrane distillation and membrane crystallization processes.

Acknowledgements

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Figure

Figure 1: Inclusion of 2D flakes in PVDF-based membrane for desalting highly saline waters and recovery salt crystals [3]

Nanocrystal deposition of 2D-transition metal trihalide solid solutions by chemical vapor transport

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The search for new 2D materials with exceptional properties has not slowed down even almost 20 year after the discovery of graphene. The development of solid solutions of established 2D materials has gained more and more interest in recent years [1], as it opens up great possibilities to optimize certain material properties or to discover completely new ones. In this regard the class of transition metal trihalides offers a wide playground of possible solid solution combinations since a lot of these compounds already offer a 2D crystal structure, as seen in figure 1a. [2] In this presentation we demonstrate the synthesis of $CrCl_3$-$RuCl_3$ solid solutions as an example of this material class with the focus on a bottom-up approach for the deposition of nanocrystals directly on a substrate. By optimizing our chemical vapor transport method, we are able to obtain nanosheets with high crystallinity of about 30 nm in height and several µm in lateral size. By applying a consecutive delamination step with a short ultrasonication step we are able to uncover fewlayer and even monolayer structures directly on the substrate. These structures were investigated by Raman-spectroscopy and transmission electron spectroscopy and can also be used for further research on possible downscaling effects. We show detailed results for $CrCl_3$-$RuCl_3$ solid solutions with an outlook for further solid solutions of $CrCl_3$-$CrBr_3$-CrI_3, $CrCl_3$-$MoCl_3$ or $RhCl_3$-$RhBr_3$, which are also accessible by the presented method.

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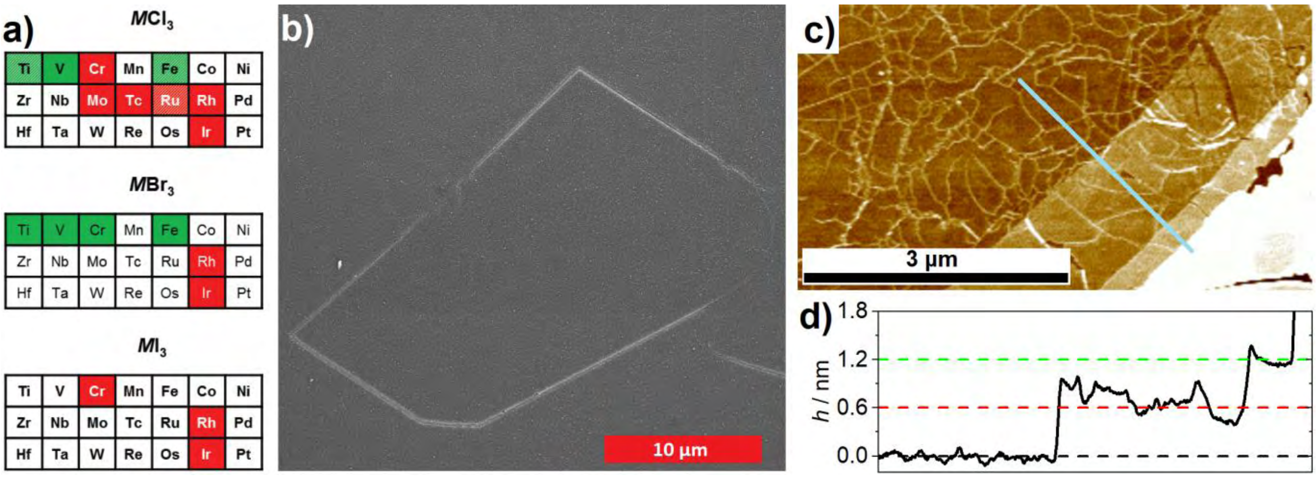

Figure 1: a) overview of transition metal trihalides with 2D structure (red: $AlCl_3$-type, green: BiI_3-type) [1], b) SEM image of an as grown $Cr_xRu_{1-x}Cl_3$ nanocrystal with a height of ca. 30 nm (surface particles and cracks can be attributed to carbon sputtering), c) AFM image of a $Cr_xRu_{1-x}Cl_3$ fewlayer structure obtained by delamination, d) height profile of the in c) shown step of a mono- and bilayer.

MXenes against SARS-CoV-2

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Abstract

Two-dimensional transition metal carbides/carbonitrides (MXenes)[1,2] are rapidly growing as multimodal nanoplatforms in biomedicine, including against infectious diseases [3]. Here, taking SARS-CoV-2 as a model, we explored the antiviral and immunomodulatory properties of four MXenes - $Ti_3C_2T_x$, $Ta_4C_3T_x$, $Mo_2Ti_2C_3T_x$ and $Nb_4C_3T_x$. We first selected and deeply analyzed four different SARS-CoV-2 genotypes, common in most countries and carrying the wild type or mutated spike protein. When inhibition of the viral infection was tested *in vitro* with four viral clades, $Ti_3C_2T_x$ in particular, was able to significantly reduce infection only in SARS-CoV-2/clade GR infected Vero E6 cells. Among the other MXenes tested, $Mo_2Ti_2C_3T_x$ also showed antiviral properties. Moreover, proteomic, functional annotation analysis, and comparison to the already published SARS-CoV-2 protein interaction map revealed that MXene-treatment exerts specific inhibitory mechanisms. Envisaging future antiviral MXene-based drug nanoformulations and considering the central importance of the

immune response to viral infections, the immune impact of MXenes was evaluated on human primary immune cells by flow cytometry and single-cell mass cytometry on 17 distinct immune cell subpopulations. Moreover, 40 secreted cytokines were analyzed by Luminex technology. MXene immune profiling revealed i) the excellent bio and immune compatibility of the material, as well as the ability of MXene ii) to inhibit monocytes and iii) to reduce the release of pro-inflammatory cytokines, suggesting an anti-inflammatory effect elicited by MXene. Taken together, our results provide a compendium of knowledge for new developments of MXene-based multi-functioning nanosystems as antivirals and immune modulators.

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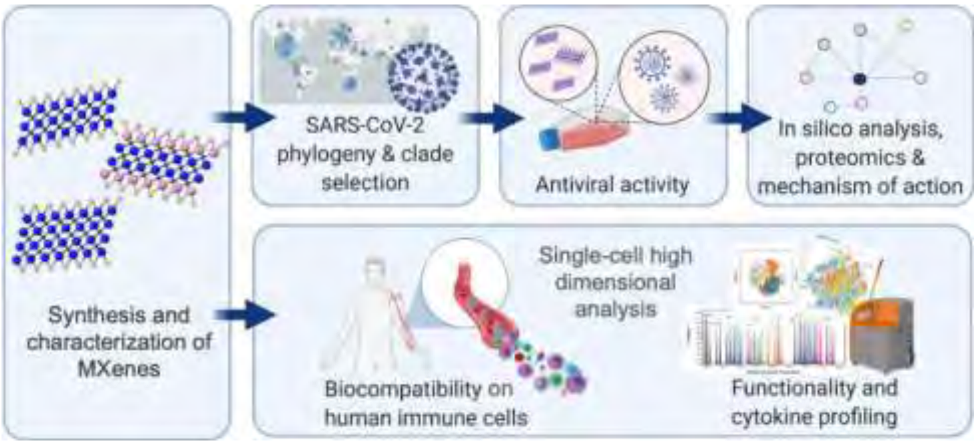

Figure 1: Overview of the study.

Self-assembled monolayers of bis-tridentate SCO complexes

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Switchable materials are growing in interest for different applications such as sensors, memories, or spintronic devices. Among them, spin crossover (SCO) complexes are perfect candidates thanks to their response in front of a large variety of external stimuli *i.e.* temperature, pressure, light… Prior to integration of SCO complexes in such devices, they must be deposited on solid surfaces maintaining their switchability. Regarding this step, most of the previous research has been focused on ultrahigh vacuum deposition of thermally evaporable neutral SCO complexes onto metal surfaces. Herein we propose an alternative and simpler approach based on self-assembly onto surfaces of the complexes from solution.

To reach this goal, a family of tridentate ligands with bis(pyrazol-1-yl)pyridine core functionalized with a carboxylic acid group was obtained. These family has led to homoleptic and heteroleptic SCO Fe(II) compounds with interesting SCO properties in the bulk [1]. However, due to the lability of Fe(II), deposition of such molecules onto metal oxide surfaces by wet-chemistry protocols has been unsuccessful. To improve these results, we have prepared and characterized a family of SCO Co(II) complexes based on the prototypical terpyridine ligand containing carboxylic acid groups for grafting on noble metal and metal-oxide surfaces (see Figure for an example). Magnetic characterization of the bulk compounds has revealed interesting SCO properties such as reverse and abrupt SCO with thermal hysteresis of some of these compounds. On the other hand, preliminary X-ray Photoelectron Spectroscopy (XPS) and X-ray absorption spectroscopy (XAS) results of the deposited complexes suggest that they are stable on these surfaces and that the SCO properties are preserved.

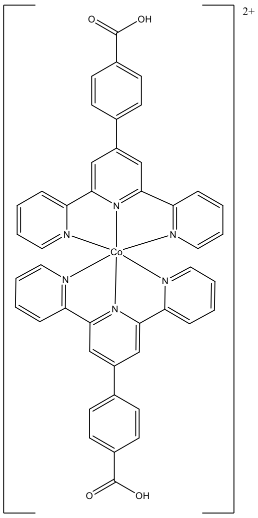

Figure: $[CoL_2]^{2+}$ (L = 4′-(4-carboxyphenyl)-2,2′:6′,2″-terpyridine)

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Organic Molecules on the Cu(110)-(2×1)O Striped Phase

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The deposition of molecules onto single-crystal surfaces allows their investigation at the single-molecule level by scanning tunneling microscopy (STM) and gives access to the controllable on-surface synthesis of 2D materials.

Here, we have studied dibromo-p-terphenyl molecules on the Cu(110)-(2×1)O striped phase under ultra-high vacuum conditions with low-temperature STM. The Cu(110)-(2×1)O striped phase is of particular interest since it offers alternating stripes of (metallic) copper areas and of oxygen-covered areas where the adsorbed organic molecules are slightly decoupled from the metal substrate and hence have higher mobility.

Previously, the Cu(110)-(2×1)O striped phase was used as a template for the synthesis of organometallic structures having different sizes and shapes depending on the width of copper stripes [1]. The focus of our study is how thermal annealing affects the molecular adsorption on the surface. It turns out that the molecules form organometallic chains on the copper areas, oriented in three surface directions. Increasing the sample temperature from 300 K to 450 K changes the orientation of the organometallic chains. Additionally, the shape of the Cu-O areas is distorted after annealing so that the stripes loose their long straight borders.

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Impact of Twist Angle on Electronic Transport Properties of Bilayer MoS_2

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Tuning the twist angle between adjacent layers of two-dimensional semiconductors (2DS), to control the topology and interlayer interactions, offers an additional degree of freedom, which facilitate optical, mechanical, and electronic properties different than in the untwisted case. Twisted 2D crystals result in a moiré pattern, where lattices of the 2D material form a superlattice, which would bring well-defined positioning and changes in the behavior of electrons in the material. To understand the application of twistronics, it is crucial to control the interlayer twist angle on a large scale.

In this study, we performed density-functional-based tight-binding calculations combined with Landauer- Büttiker formalism and non-equilibrium Green's function approach to study electronics of twisted bilayer MoS_2 and to analyze the impact of twist angles on transport properties.

Twisted MoS_2/MoS_2 model shows slightly changes in transmission as function of energy when compared with the untwisted systems. Furthermore, we show a comprehensive overview of the impact of twist angle, ranging from 0˚ to 40˚, on the ballistic transport for both flat and corrugated twisted bilayer MoS_2. An example is shown in Figure 1.

Figures

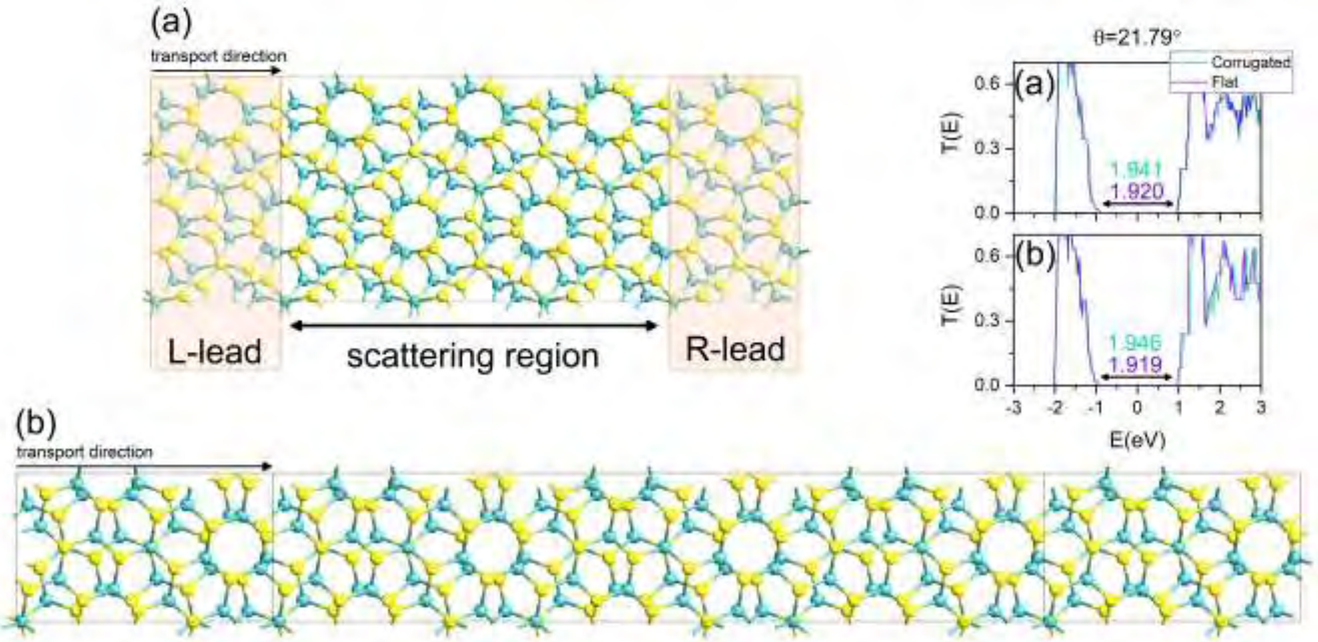

Figure 1: Schematic representation of MoS_2/MoS_2 device configuration and corresponding transmission as function of energy along *a* and *b* directions.

Fast polymeric functionalization approach for the covalent coating of MoS_2 layers[1]

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Moybdenum disulfide (MoS_2) is undoubtedly the flagship of the transition metal dichalcogenides family, due to its scalable preparation through simple exfoliation methods and a developed surface functionalization through chemical design.[2] Recent development of MoS_2 chemical functionalization has permitted a fine tuning of the physical and chemical properties with large impact on the processing and use of this material.[3] However, this surface covalent functionalization is often characterized by the limited density of attached molecules.

In this work, we present the covalent coating of chemically exfoliated MoS_2 based on the polymerization of functional acryl molecules. The method relies on the *in situ* radical polymerization and covalent adhesion of large amounts of molecules to form functional coatings.[4] In particular, we successfully implement hydrophobicity on the exfoliated MoS_2 in a direct, fast, and quantitative synthetic approach. The covalent functionalization is proved by multiple techniques including X-ray photoelectron spectroscopy and TGA-MS. This approach represents a simple and general protocol to reach dense and homogeneous functional coatings on 2D materials.

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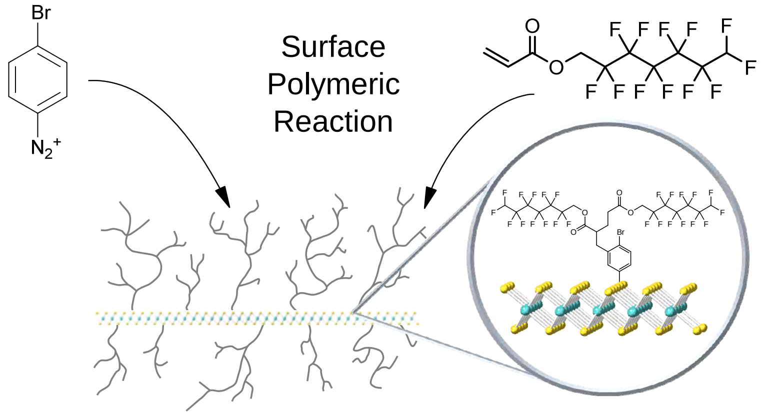

Figure 1: Schematic representation of the proposed polymeric reaction on MoS_2.

Post-synthesis functionalized Covalent Organic Frameworks as proton conduction materials

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Covalent Organic Frameworks (COFs) are a class of novel porous materials with tailored functionalities and highly ordered crystalline structures deriving from the reversibility of the crystallization process. Indeed, *de novo* synthesis of COFs with strong covalent connections usually results in amorphous phase rather than crystalline structures.[1] However, the reversibility of the covalent linkages is generally accompanied by poor chemical and thermal stability of these materials, limiting their applications in catalysis, gas storage or separation, etc.[2] Recently, COFs gained growing attention as proton conducting materials, for applications as solid electrolytes in proton exchange membrane fuel cells (PEMFCs).[3] Herein, we report the post-synthesis functionalization of an imine-linked COF (COF-LZU1) towards the enhancement of its proton conductivity. To this end, evolution of the linkage from imine to secondary amine and, finally, to tertiary amine carrying a propylsulfonic moiety was investigated and confirmed by infrared and Raman spectroscopy, thermogravimetric analysis coupled to mass spectrometry, X-ray photoelectron spectroscopy, and energy dispersive X-ray analysis. Scanning electron microscopy images demonstrate the retained morphology (Figure 1). Electrochemical impedance spectroscopy is employed to unravel the proton transport behavior of the synthesized material.

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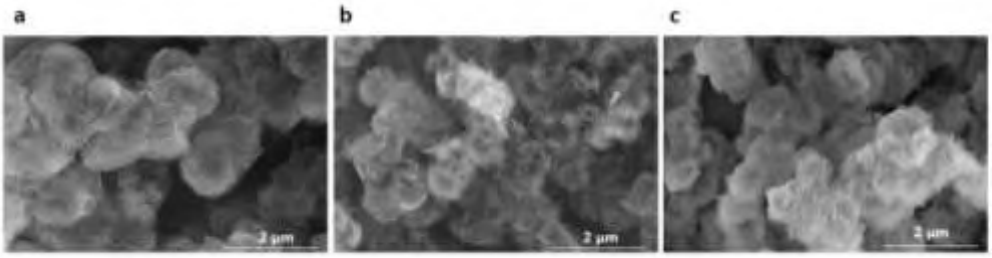

Figure 1: Scanning electron microscopy images of a) imine linked COF LZU1, b) amine-linked and c) propylsulfonic COF.

Graphene Field Effect Transistor on Liquid Substrate

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Abstract

Traditional graphene field effect transistors (GFETs) are fabricated on solid substrates, with which uneven strain and stress are often introduced in Graphene. The defects destroy the inherent quality of graphene and also reduce the charge carrier mobility of Graphene. Here, we used the polycaprolactone (PCL) material with a melting point of 60 degrees Celsius as the substrate of the GFET to explore the potential in improving the sensing performance of the GFET. By comparing the GFETs supported by solid PCL and GFETs supported by liquid PCL, we found that the liquid substrate better retains the intrinsic properties of graphene and restores a part of the charge carrier mobility. At the same time, GFETs with liquid substrates exhibited better-sensing performance. This is due to the stress release of the liquid substrate to the graphene of the solid substrate.[1] In the future, stress-relieving graphene will bring more sensitivity and higher performance in graphene field effect transistors.

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Rational design and synthesis of PAH-based porous 2D thin films for membrane applications

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Accurate *in silico* prediction on how polycyclic aromatic hydrocarbons (PAHs) assemble into 2D thin films could assist in chemically designing new PAHs to integrate functionality into membranes. However, *in silico* design of molecules in the context of membrane formation is still in its infancy. Instead, most *in silico* calculations have been aimed at confirming the experimental results. Similarly, decacyclenes are found to form supramolecular 2D thin films through a combination of Van der Waals forces and π-π stacking both experimentally and *in silico* with corresponding results.[1] The next objective is switching the workflow around by experimentally confirming a computationally generated 2D thin film. The confirmation of *in silico* predictions with experimental data is a step further to a membrane-forming molecule generation algorithm.

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MoS_2 FETs for Ultrasensitive Heavy Metal Ion Sensing

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Pollution of water with heavy metal ions represents one of the most severe environmental problems associated with societal development[1]. Among the assorted hazardous compounds, mercury ions (Hg^{2+}) are in the class of the most poisoning ones. Their accumulation in human bodies results in health deterioration, affecting all vital organs and eventually leading to chronic illnesses, overall lifespan shortening, and, in the worst-case scenario, premature death[2]. Because of this reason, 10 nM represents the maximum permitted level of Hg^{2+} in drinkable water[3].

The most common ways of detection of Hg^{2+} in water are based on chromatographic or electrochemical methods[4]. On the other hand, chemical sensors comprising highly sensitive and selective materials represent powerful approaches to detect tiny amounts of specific analytes. As sensory materials, low-dimensional materials, displaying a highest surface-to-volume ratio, combine high sensitivity with low limit-of-detection[5]. Among 2D materials, 2D transition metal dichalcogenides (TMDCs) have attracted great attention because of their unique physical and chemical properties. In this work, we have used MoS_2-based field-effect transistors (FETs) as a platform for Hg^{2+} sensing, relying on the affinity between heavy metal ions and point defects in TMDCs (i.e. sulfur vacancies). We found that Hg^{2+} acts as a dopant of MoS_2, evidenced by monitoring the transfer characteristics of FETs. Interestingly, we discovered a strict dependence of the doping with the concentration of Hg^{2+}, following a semi-log tendency. Preliminary results showed MoS_2 FETs can be used as ultrasensitive sensors, with an ultra-low limit of detection, below 100 pM.

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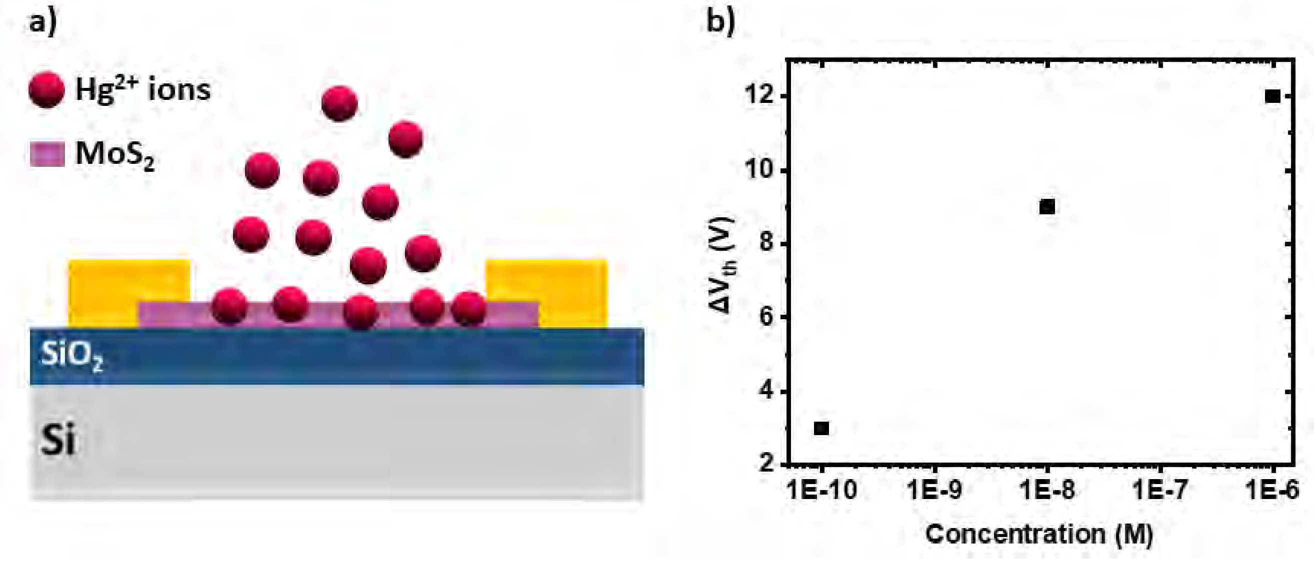

Figure 1: a) Schematic representation of Hg^{2+} ions interacting with MoS_2. b) Threshold voltage (ΔV_{th}) variation as a function of the Hg^{2+} concentration. Semi-log relationship shows the limit of detection is lower than 100 pM.

Self-powered graphene triboelectric biochemical sensor for specific detection

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Abstract

By converting mechanical energy to electrical energy, flexible triboelectric nanogenerators (TENG)[1] have inspired great research interests on self-powered active sensors for wearable and implantable electronics,[2] where a sustainable power source is of key importance. Nevertheless, most of the current developed TENG sensors are based on 1 TENG/1 sensor structure with limited biochemical sensitives, representing a key challenge for its point-of-care (POC) applications.[3] Here, by combining the superior electrical properties of two-dimensional graphene[4] in TENG configuration, we reported self-powered sensors with desired compact device geometry. Such TENG sensors exhibit excellent sensitivity towards different DNA nucleobases, which can be unambiguously ascribed to the change of graphene Fermi level upon biomolecule adsorption. Along with the demonstrated dual-channel self-powered sensing scheme, these achievements open the avenue for compact, multifunctional TENG biochemical sensor platform.

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Figures

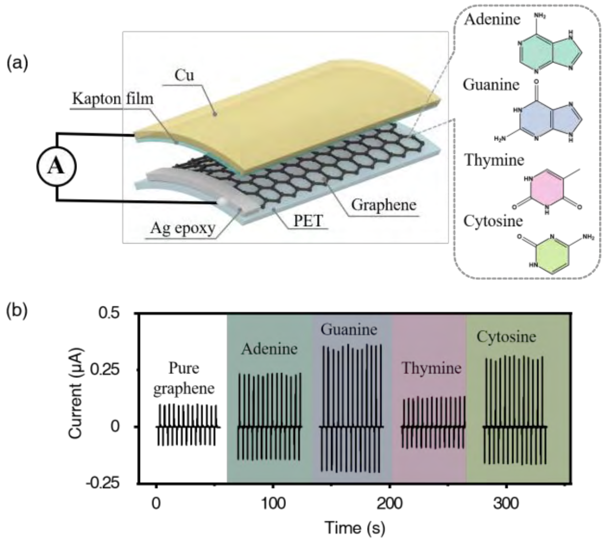

Figure 1: (a) Structure diagram of the graphene-based TENG. (b) The output current of graphene based-TENG adsorbed by different DNA nucleobase solutions.

Single crystal graphene growth for Graphene Liquid Cell fabrication

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Graphene Liquid Cells (GLCs) offer a promising platform for LP-EM, due to the minimal loss of resolution caused by the atomically thin membrane and its radical scavenging properties. Currently multiple fabrication methods exist for GLC fabrication, most of which require support-free transfer of the top graphene layer. In our group loop-assisted transfer (LAT) of graphene is used, which is a process that produces intense mechanical stress on the support-free graphene. Therefore, the quality of the graphene is of the utmost importance for the GLC yield. Here we present our efforts to grow graphene with larger single crystalline domains, based on work by others, to obtain high-quality graphene for more efficient GLC fabrication. The basis of this procedure is to anneal a pre-oxidized copper substrate, to cause surface rearrangements and to have oxygen present during growth. The oxygen will reduce the amount of nucleation sites, leading to larger single crystalline domains. This approach has yielded larger domains, but is still being optimized to obtain the desired mm-cm sized single crystal graphene.

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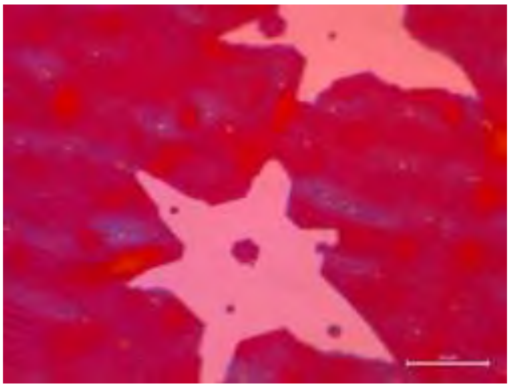

Figure 1. *Graphene flake obtained using reduced methane flow and increased growth temperature*

3D-Graphene based Pressure and Strain Sensor

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Abstract

We demonstrate a broad range and fast response pressure and strain sensor using a flexible and conductive 3D graphene structure. The sensor can detect small pressures/strains and various biological signals from the movement of human skin. The active element of sensor consists of a 3D graphene nanoporous framework made of graphene sheets separated with air-filled pores. A simple hydrothermal technique followed by freeze-drying and high-temperature thermal annealing is used for the synthesis of 3D graphene aerogel. The resulting graphene aerogel is highly elastic and the contact resistance between aerogel and rigid metal electrode is highly sensitive to applied stimuli. The extraordinary sensitivity of the contact resistance permits the detection down to a few micrometers by a small change of the sample size. In addition, the elastic nature of graphene aerogel provides high responsivity to the sensor, allowing detecting fast actions down to a few milliseconds and temperature independent. We show that the 3D graphene-based sensors can be used as wearable electronic sensors for diverse kinds of biological motion detection, human-machine interface and soft robotics applications.

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Selective ion transport in graphene oxidemembranes and cartridges

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The growing of the world population and the consequent decrease in drinking water due to pollution requires the development of new technologies capable of desalinating sea water. In the latest years two dimensional materials, like graphene and graphene oxide (GO) are used to produce membrane and new coatings useful to ion storage and filtering applications[1]. We investigated the difference in the transport of monovalent ions (Na^+) and bivalent ions (Ca^{2+}) thought graphene oxide membranes (GOM) forced by an electric potential. In view of a future industrial application of this phenomenon, we realized GO coatings on hollow fibers[2] (HF) to realize innovative filtration modules: GO layers were immobilized inside polyethersulfone-polyvinpyrrolidone (Versatile PES®) hollow fibers to achieve selective transport of Na^+ inside the cartridge.[3] The transport inside the HF system was activated by applying an electric potential of -0.5V for 120 minutes, continuously measuring the ion transport consequently induced through in-situ impedance measurements. Spectroscopic analysis of the resulting filtered solutions confirmed the amount of ions transported by cartridges possessing a different amount of GO and also containing a cationic polymer, namely polyethylenimine (PEI), covalently linked to the GO coating. These measurements led us to unravel the mechanism of ion transport induced by the GO coating.

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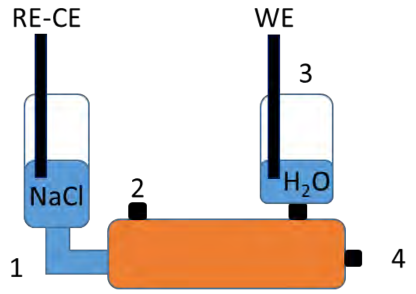

Figure 1: experimental for the ion transport. WE: working electrode, CE: counter electrode, RE: reference electrode

Atomic reconstruction in twisted transition metal dichalcogenide heterostructures

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The interlayer van der Waals (vdW) interactions enable two single layers of a two-dimensional material to vertically stack together and form van der Waals heterostructures (vdWHs). If the two layers have different distinct symmetries or lattice sizes or if they are twisted with respect to each other, a moiré pattern with much larger length scale than the periodicity of each layer is formed. The moiré superlattice can be further modified by twist angle, which means moiré superlattice is also formed in twisted homostructures. As moiré patterns deeply alter the physical properties of bilayer systems, the controllable design of twisted heterostructures clearly allows for new physics and engineering directions. In this case, lattice reconstruction will be vital for further understanding electronic and optical properties of these complicated moiré interfaces. Here, we performed structure relaxation for MoS2/MoSe2 vdWHs with different twist angles using the force-field method[1] employing the Stillinger-Weber (SW) and Kolmogorov-Crespi (KC) potential to capture the intralayer and interlayer interaction. Standard energy minimization and classical molecular dynamics simulations using the canonical ensemble were adopted. Significant in-plane and out-of-plane deformation can be observed for certain twist angles. Furthermore, domain-wall patterns are formed, where areas with matching lattice constants are separated by domain walls that accumulate the generated strain. This can be also observed in twisted bilayer graphene[2] and graphene/h-B heterostructures[3].

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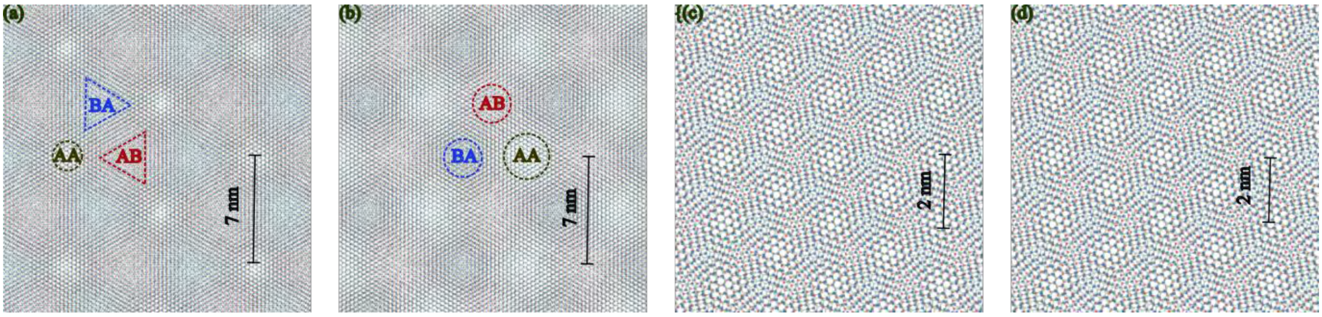

Figure 1: Lattice reconstruction of $MoS_2/MoSe_2$ bilayer, (a) parallel alignment and (b) antiparallel alignment without twist, commensurate domains with different stacking orders are highlighted by dashed lines, (c) parallel alignment and (d) antiparallel alignment with twist angle 7.3 degree.

How to image the structural details in molecular framework of the imine-based 2D polymers

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Due to the high electron beam sensitivity of 2D polymers (2DPs), TEM imaging of their single molecular building blocks remains a challenging task. One crucial factor influencing the specimen stability is the acceleration voltage. Here we quantitatively analyzed the dependence between the acceleration voltage and the available structural information, similar to [1]. A systematic analysis of the 2DPs at the acceleration voltages of 80, 120, 200, and 300 kV was applied. Our results demonstrated that 120 kV is superior to the traditionally applied high acceleration voltages of 300 kV by approximately 5-7 % higher information gain.

By utilizing 120 kV and combined with low-dose technique, we have successfully imaged imine-based 2DPs with sub-2 Å resolution (see Fig. 1), which enables the direct observation of the structural details in the moleculer framework. The enhanced image contrast compared to imaging at 300 kV allowed for image acquisition with low defocus values, this greatly facilitates direct image interpretation and avoids confusion due to delocalization under high defocus, which is important for elucidating non-periodic features such as defects, grain boundaries, and pore interfaces. Thanks to this high image contrast, we have also obtained HRTEM images of glassy 2DP, for an efficient quantitative image analysis, a neuro-network was applied.

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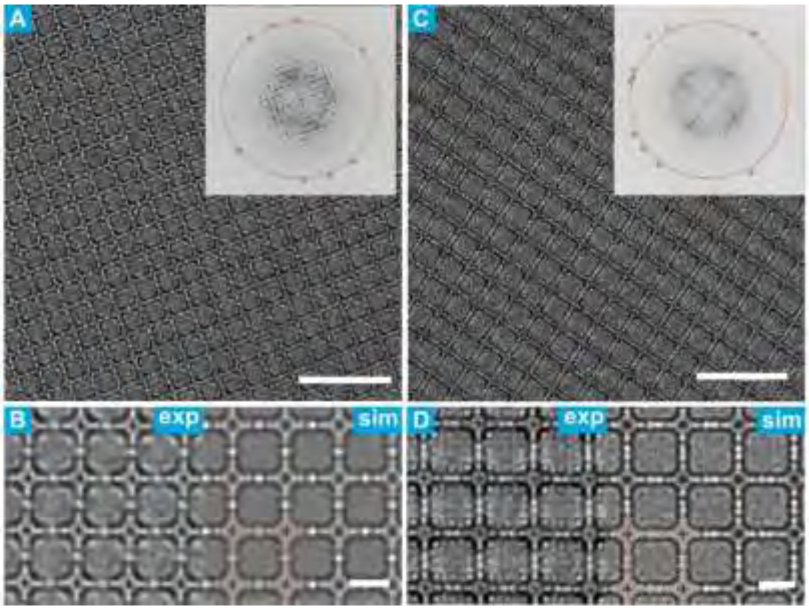

Figure 1: Experimental HRTEM images and simulations of 2D polyimine (PI) and biphenyldiyldimethanol (BPH). (A) shows the HRTEM image of 2D PI, scale bar: 10 nm. Inset: fast Fourier transform (FFT) patterns. The orange circle marks the spatial resolution of 2 Å. (B) includes enlarged experimental image and simulation result, scale bar: 2 nm. The atomic model is overlaid. (C) the HRTEM image of 2D BPH, scale bar: 10 nm. Inset: FFT patterns. The orange circle marks the spatial resolution of 2 Å. (D) enlarged experimental image and simulation, scale bar: 2 nm. The atomic model is overlaid. The DFT caculations were conducted for the atomic models.

2D polymers synthesis and 2D-polymer-based vdW heterostructure fabrication at air-water interface

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A 2D polymer is a sheet-like monomolecular macromolecule consisting of laterally connected repeat units with end groups along all edges. Ever since Hermann Staudinger discovered linear polymers in 1920, synthetic scientists have dreamed of extending the polymerization into 2D. From the application perspective, given the enormous chemical and structural diversity of the building blocks (i.e., monomers), 2D polymers hold great promise in the rational material design tailored for next-generation applications, such as membrane separation, electronics, optical devices, energy storage, and conversion, etc. However, despite the tremendous developments in synthetic chemistry over the last century, the bottom-up synthesis of 2D polymers with defined structures remains a formidable task.

Since 2014, we have started to pursue this intriguing yet challenging goal. We innovatively developed two novel synthetic routes: One is to use surfactant monolayer as a soft template to guide the supramolecular organization of monomers and the subsequent 2D polymerization at an air-water interface. This synthetic methodology is now termed surfactant-monolayer-assistant interfacial synthesis (SMAIS). Using the SMAIS method, we achieved the controlled synthesis of highly-crystalline few-layer 2D polyimide and polyamide for the first time. The other method is Langmuir–Blodgett technique to synthesize monolayer 2D polymers. Furthermore, the 2D polymer film can be fabricated with graphene via cation-π interaction to prepare 2DPI-Graphene hybrid materials. This material shows ultra-fast (~60 fs) charge transfer from protonated 2DPI to graphene under UV radiation, comparable with the best records of inorganic vdWH materials.

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Two-Dimensional Polymers: Playing with Structural Topology

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In two-dimensional (2D) world, graphene is one of the most popular material for its intriguing electronic and topological properties. Beside graphene's honeycomb structure, there are a large amount of mathematically possible 2D lattices, e.g., square (**sql**), kagome (**kgm**) and hexagonal (**hxl**) lattice. These lattices might be difficult to synthesize as Haeckelites like graphene, but there are possibilities to realize them as conjugated 2D polymers. The electronic properties of these conjugated polymers are determined by structural topology and chemical composition. It has been shown that if 2D polymers can be designed within certain structural topology, similar characteristic bands could be obtained [1]. With the efficiency provided by tight-binding (TB) model with its low computation cost, we ran through Reticular Chemistry Structure Resource (RCSR) database [2], and got electronic band structures for 101 different lattices [3]. We further show that band gaps could be tuned by choosing different 1st- and 2nd-neighbor interactions (Fig. 1) or different on-site energies. And then we also give an example, in which we propose hypothetical 2D polymers with **fes** structure, and implement band tuning by inserting different linkers in these polymers.

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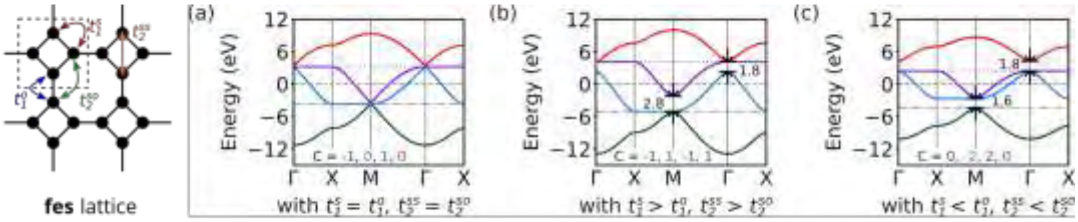

Figure 1: Band structures and the corresponding Chern numbers for each band of **fes** (also known as square-octagon) lattice as representative example. With different 1st- and 2nd-neighbor interactions *t*, gaps can be opened at certain high symmetry points.

Calcium Alginate-Nanographene Oxide hybrid hydrogel for improved biomedical applications

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Due to its high surface-volume ratio and the presence of both hydrophilic and hydrophobic portions in its structure, in recent years, graphene oxide sparkled interest for its biomedical applications [1]. In this work, graphene oxide nanosheets (NGO) without any previous modification has been blended into alginate polymer with a straightforward approach, resulting in a homogeneous dispersion. Alginate has been widely used in biomedicine, mostly because of its biocompatibility [2]. Here, the capacity of alginate to form physical hydrogels in the presence of divalent ions (e.g. calcium ions), through ionotropic gelation [3], has been exploited to achieve a flexible and mechanically stable hydrogel film. Such system has been loaded (before and after gelation) with curcumin, as natural bioactive compound, in order to evaluate its ability to synergize the biological activity of the loaded therapeutic. Preliminary *in vitro* analyses showed promising results: compared to blank hydrogel synthesized in the absence of NGO, hybrid hydrogel was found to show selective toxicity towards Squamous Cell Carcinoma (*SCC*), with reduced toxicity towards healthy Primary Human Bronchial Epithelial Cells (*HBEpC*). This effect was ascribed to the ability of synthesized hybrid material to control the curcumin release over time: after 6 h, release amounts (%) of 60 and 100 were reached for hybrid and blank hydrogel, respectively.

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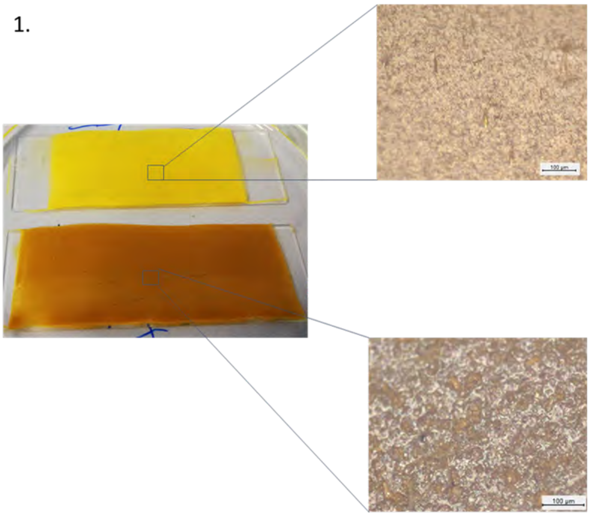

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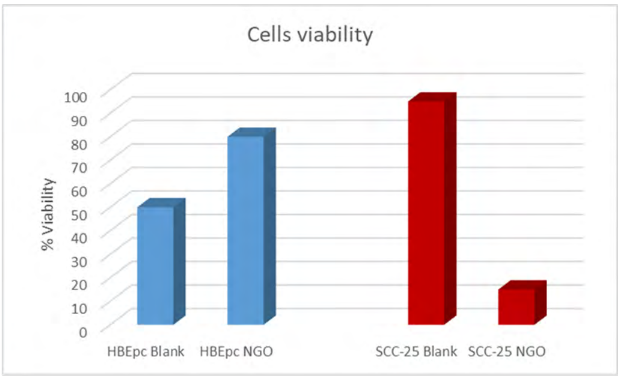

Figure 1. Blank and hybrid hydrogel films loaded with curcumin. Aside, their optical microscope images.
Figure 2. Biological activity of blank and hybrid hydrogels towards healthy and cancer cells.

Nanostructured covalent functionalization of 2D materials

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The research on graphene and related 2D materials has matured into an independent field of scientific inquiry. An important aspect is the chemistry of graphene. The interest in the covalent chemistry of graphene started pretty much with its first successful isolation. The lack of band gap and poor solution processability of graphene meant that there was pressing need to explore its covalent chemistry. However, given the poor reactivity of the basal plane, highly reactive chemistries are often needed for achieving meaningful functionalization.[1]

When carried out with bulk exfoliated material, covalent attachment of organic units onto the basal plane of graphene allows dispersion of these materials in (organic) solvents thereby improving their processability. Such dispersions can be used in composite materials and as functional inks. When studied on pristine graphene supported by solid substrates, covalent functionalization of graphene serves as a testbed for evaluating the efficiency of the chemistry used for functionalization, and moreover, it also allows modification of the intrinsic electrical, electronic and optical properties. The covalent chemical patterning of graphene, where one targets the precise positioning of organic functional groups on its basal plane, is relevant to several applications such as those in electronics, catalysis, sensing and photonics.[2]

In this contribution, I will discuss covalent modification of graphene, graphite and MoS_2 using diazonium chemistry. Our approach is to invest into simple, straightforward protocols that allow nanostructured functionalization of 2D materials with a special focus on chemical patterning ranging from micrometer to the nanometer scale. I will also highlight a judiciously chosen toolbox of surface analytical techniques employed for the characterization of such functionalized materials which involves scanning probe microscopy (STM, AFM, AFM-IR), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS).[3]

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Study of the steric hindrance in grafting reactions

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Graphitic materials can be modified for tailoring their properties and for the introduction of different functionalities in which, subsequently, other molecules can be anchored. In particular, the electrochemical reduction of different aryldiazonium salts has been shown to be a valuable tool for this purpose.[1] As a result, the diazonium chemistry on carbon surfaces has been studied intensively. The impact of the nature of substituent groups on the grafting density and also the ability of sterically hindering functional groups for circumventing dendritic multilayer growth,[2] has been reported. Herein we report on the influence of the substituent position on the grafting density for three diazonium salts. Among several factors that are at play, we hypothesize that steric hindrance of the radical structure is key to the reaction efficiency. To address this, we have studied the reduction of different aryldiazonium salts in aqueous solution using ascorbic acid as reducing agent.[3] This protocol leads to a self-limiting growth of monolayers with high grafting densities. We have discussed the differences observed in the grafting density, morphology and surface coverage as a function of the position and the nature of the substituent. Differences between grafting efficiencies were assessed by Raman spectroscopy whereas scanning tunneling microscopy (STM) provided nanometer scale insight into the structure of the covalent films.

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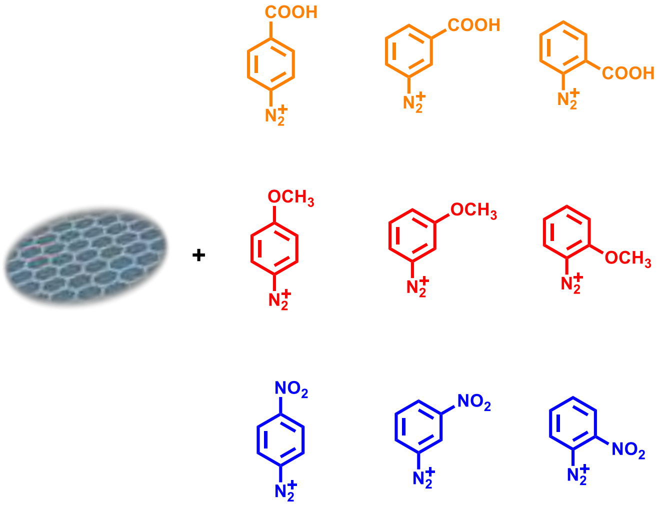

Figure 1: Molecular structures of the diazonium salts used in the study.

Carbon nanostructures decorated with Cerium Oxide as multi-functional electrocatalysts for CO2 conversion

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The electrocatalytic reduction of CO_2 is a captivating strategy for the conversion of CO_2 into fuels, to realize a close loop for carbon footprinting. The research has focused on the development of new materials and technology capable of capturing and converting CO_2 into useful products.[1] Among all reduction products, formic acid is particularly attractive for its high volumetric hydrogen density, low toxicity, and liquid state, that make it a valuable hydrogen storage vector.

The design of new electrocatalysts that reduce CO_2 in a selective and efficient fashion is a key step for future exploitation of this technology.

Here we present how the combination of different building blocks in a single nanostructure might be a good strategy to achieve a good selectivity in the CO_2 reduction process.

Combining the unique physico-chemical properties of functionalized nanomaterials (such as carbon nanotubes and carbon nanohorns) and nanocrystalline cerium dioxide (CeO_2) we revealed faradaic efficiency for formic acid production as high as 55% at an overpotential as low as 0.02V in acid solutions. These performances have been possible by the formation of partially reduced ceria ($Ce^{4+/3+}O_{2-x}$) responsible of an increased CO_2 adsorption and a more efficient electron transfer at the surface.[2] In the nanocomposite, the carbon nanostructures are used as support and they have a fundamental role in to counteracting the insulating effect of oxide nanoparticles and promoting the generation of Ce^{3+} sites. Their elevated surface area and high electrical conductivity guarantee a greater process efficiency.[3] In particular, the nanohorns have a unique conical geometric, where the nano-tips terminals act as “electron collector”, increasing the charge mobility.[4]

We demonstrated that the interconnections between various components are fundamental for the efficient CO_2 reduction to formic acid and opens new possibilities in the design of optimized electrocatalytic materials.

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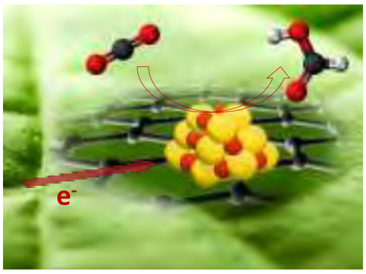

Figure 1: Schematic CO_2 reduction into formic acid on MWCNT@CeO_2

Novel configurations for Photo-Induced Microscopy

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We present an instrument for examining samples of Gr/Cu with the possibility of using mechanical and infrared measurement methods in parallel. We have upgraded the existing A.P.E. Research instrument (AFM-A100) to include the ability to apply a heterogeneous configuration to reveal the chemical properties of the surface of interest. We perform a generalized Photo-Induced Microscopy (PiFM) heterodyne configuration by introducing a novel schemes: harmonic heterodyne detection and sequential heterodyne detection. For this reason, we have designed an experimental apparatus to obtain generalized heterodyne configurations for PiFM and semicondact mode AFM. In past we compared study of the apparent barrier height distribution and surface potential of the sample and nanoparticles of semiconductors. We have implemented the experimental setup which was build based on ambient Scanning Tunneling Microscope (STM) and Kelvin Probe Force Microscope (KPFM) by A.P.E. Research. Photo-Induced Force Microscopy uses the detection of a mechanical heterodyne signal generated by the mechanical resonance oscillations of the cantilever and the photoinduced force induced by the interaction of light with matter. The aim of the job is to explore the possibility of using light sources with a moderate pulse repetition rate to perform PiFM measurements. More in detail, to overcome the diffraction limit of infrared microscopy, we use mechanical modulation mixed with light by atomic force microscopy (AFM) (heterodyne configurations) in which a signal frequency is created by combining or mixing two different frequencies. The heterodyne configurations for PiFM open up new possibilities for chemical mapping and broadband spectroscopy with a spatial resolution of less than $\lambda/2$. They are suitable for a wide range of heterogeneous materials in various fields, from structured polymer films to polaritonic boron nitride materials and isolated bacterial cell walls. This project is supported by MSCA under Horizon 2020 ULTIMATE (Grant Agreement No. 813036 - ETN).

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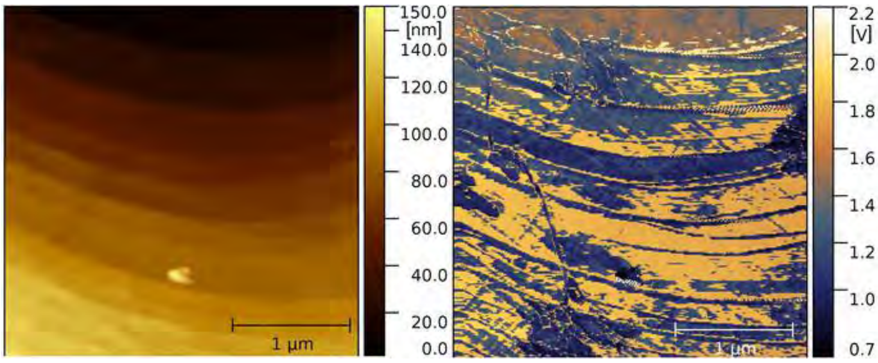

Figure 1: AFM (non contact) Topography and Phase of Gr/Cu. Topography (left) showes steps of about 20 [nm] in height. Phase (right) show a contrast due to different properties of the Graphene top layer.

Biocompatibility and antibacterial activity of Carbon dots in vitro

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Carbon dots (CDs) are quasi-spherical carbonaceous nanoparticles less than 20 to 60 nm constituted by sp^2-sp^3 core and an irregular surface rich of polar functional groups that confers intriguing and tunable physico-chemical properties [1]. They display brilliant and excitation wavelength dependent photoluminescence, aqueous dispersibility, easy synthetic and functionalization conditions [2]. Recently great attention has been paid to the CDs, due their variegated physical-chemical properties that makes them appealing for multiple biomedical application. In this work we assessed the biocompatibility of sustainable CDs prepared, according to Sawalha et al method [3], recycling the discard of olive oil production. Firstly, the physico-chemicals properties of new synthetized CDs were evaluated. HRTEM analysis performed on the produced CDs confirm their presence with a range from 5 to 25 nm, UV-Vis spectroscopy showed broadband UV absorption and fluorescence spectroscopy an excitation wavelength dependent photoluminescence. Cell imaging displayed that CDs are mainly located in proximity of the cell membrane. Lastly, we assessed the biological properties of CDs. Biocompatibility studies were performed on two osteoblastic cell lines (U2-OS and hFOB) after 24 and 48 h of CDs incubation. Antibacterial activity was evaluated on a Gram+ bacterial strain *S. aureus,* after 24 h of culture in presence of CDs. Our results showed that Carbon dots exhibit a good biocompatibility up to 240 µg/mL, while at 360 µg/mL become cytotoxic. Differently, antibacterial assays showed that the bactericidal activity is slight at 240 µg/mL, but become more important at the concentration of 360 µg/mL. These results on CDs biosafety get the base for their promising application for biomaterial engineering. Further experiments may be performed for surface nano-functionalization obtaining new materials with CDs physico-chemical properties exploitable for many bio-applications.

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Synthesis of MOFs@COFs porous hybrid materials via aza-Diels-Alder reaction towards high performance supercapacitors

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Metal-organic frameworks (MOFs) and covalent organic frameworks (COFs) attracted enormous attention in recent years. The growing interest in MOF@COF hybrid materials, which contain the structural traits and combine the merits of individual components and allow the generation of materials with unprecedented physicochemical properties and hold great potential in various applications. Herein, for the first time, by employing an aza-Diels-Alder cycloaddition reaction as postsynthetic modification (PSM) of MOF@COF-LZU1, we facile approach towards aza-MOFs@COFs hybrid porous materials with extended π-delocalization. Moreover, as a proof-of-concept the obtained aza-MOFs@COFs is used as a supercapacitor electrode and exhibits specific capacitance of 20.35 µF cm^{-2} and high volumetric energy density of 1.16 F cm^{-3}. Our approach of PSM of MOFs@COFs hybrids implement rational design for the synthesis of functional porous materials and expands the plethora of promising application of MOFs@COFs hybrid porous materials in energy storage applications.

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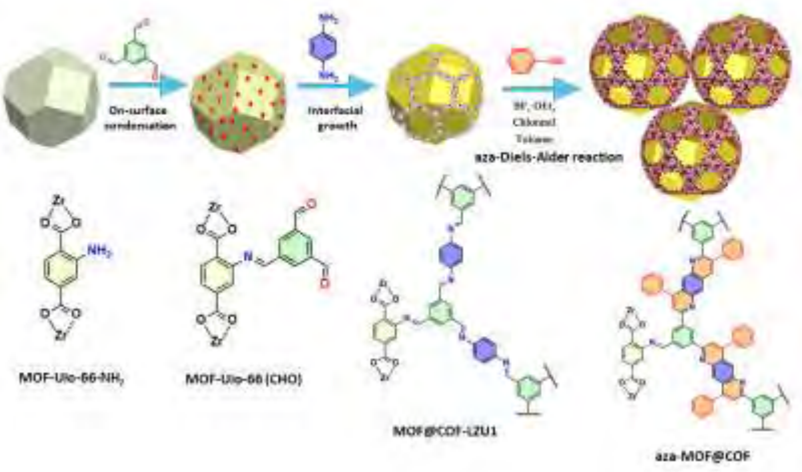

Figure 1: Schematic illustration of the synthetic route of aza-MOF@COF hybrid structure.

How can we simulate the detection of nitroaromatic contaminants by graphene-based sensors?

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The number of applications of graphene-based materials is quickly increasing. Their high surface-to-volume ratio, electrical and mechanical properties, and number of possible chemical modifications allow producing efficient electrochemical sensors. Computational chemistry is indispensable in clarifying the sensing mechanism and the key factors influencing it [1]. We focus on the detection of two representative dangerous and pervasive nitroaromatic contaminants (NACs), tri-nitro-toluene (TNT) and di-nitro-toluene (DNT). Different graphene-based electrochemical sensors have been developed to detect NACs in water samples [2]. We first studied the role of the analyte’s physisorption on the surface with respect to the sensor performance, establishing a qualitative correlation between the strength of adsorption and the experimental limit of detection (LOD), as well demonstrating the definitive effect of physisorption on the sensor’s selectivity [3]. These findings were then applied to the design of new potentially high-performance sensor materials based on B,N co-doped graphene derivatives, which displayed good analytical performance at a low level of co-doping. We then proceeded to investigate the electrochemical reduction of the NACs on the sensor surface. Our findings provide key guidelines for designing new and better detection systems.

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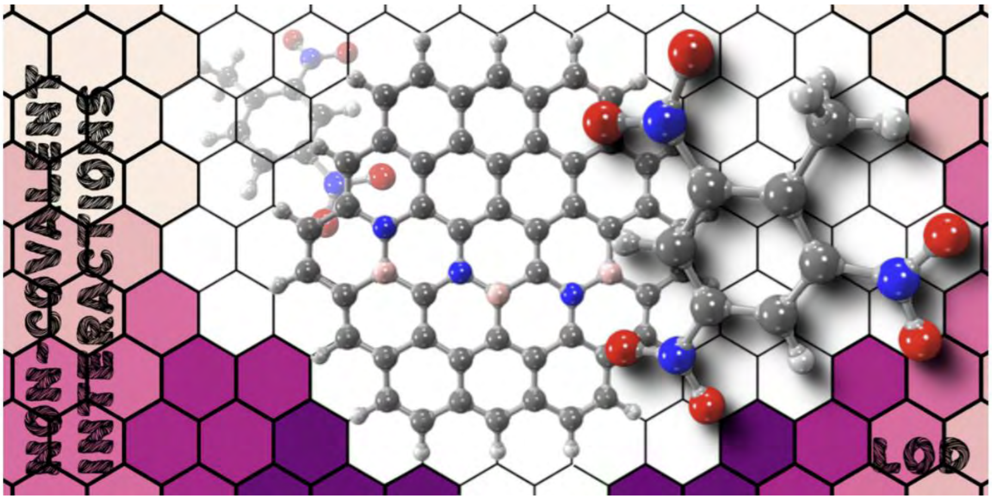

Figure 1: The relationship between in silico estimated non-covalent interactions and the experimental performance is explored for the detection of nitro-aromatic contaminants with graphene-based sensors.

Structure of grain boundaries in a layer-stacked 2D polymer

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Two-dimensional (2D) polymers hold great promise in the rational materials design tailored for next-generation applications. However, little is known about the grain boundaries in 2D polymers, not to mention their formation mechanisms and potential influences on the material's functionalities. Using aberration-corrected high-resolution transmission electron microscopy, supported by quantum chemical calculations, we presented a direct observation of the grain boundaries in a layer-stacked 2D polyimine with a resolution of 2.3 Å [1]. We found that the polyimine growth followed a "birth-and-spread" mechanism. Antiphase boundaries implemented a self-correction to the missing-linker and missing-node defects, and tilt boundaries were formed. Notably, we identified grain boundary reconstructions featuring closed rings at tilt boundaries. This contribution focuses mainly on the character of the reconstructed grain boundaries, which we have characterized using quantum chemical calculations. These revealed that boundary reconstruction is energetically allowed and can be generalized into different 2D polymer systems. We envisage that these results may open up the opportunity for future investigations on defect-property correlations in 2D polymers.

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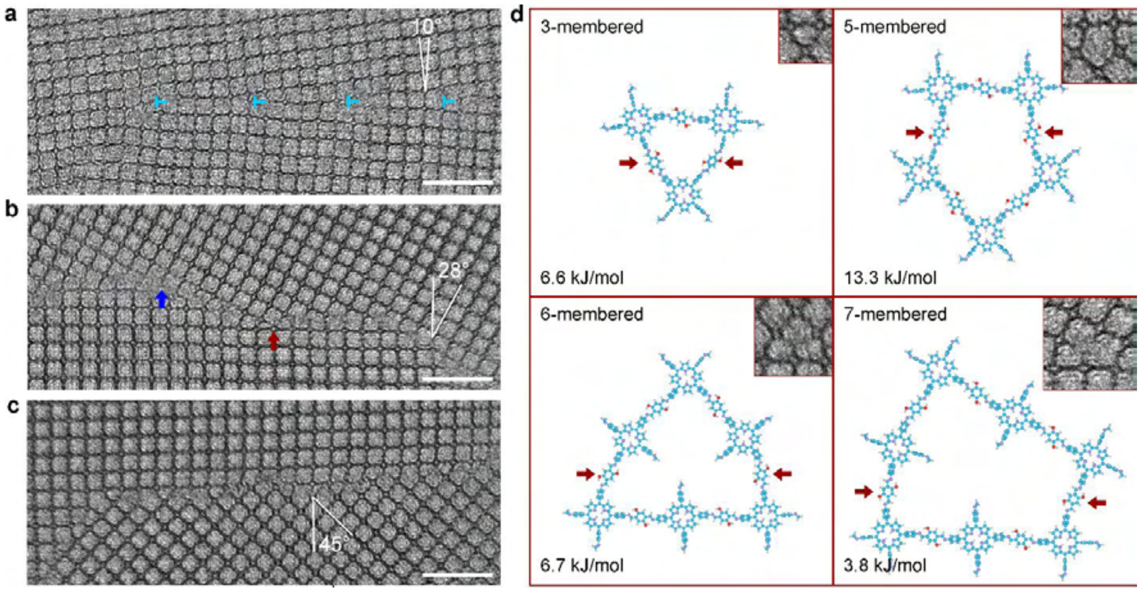

Figure 1: Low-angle and high-angle grain boundaries visualized by AC-HRTEM imaging and atomic models of the novel grain boundary structures

Graphene based heating mats as anti-icing system on aircrafts

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A key target for modern technology is to replace metals with lighter, cheaper, less energy-consuming materials. This “metal replacement” goal is already well established for structural applications in aeronautics and automotive, where the search for higher efficiency and reduced CO_2 emission is pushing toward the use of carbon-based materials (e.g. carbon fiber composites and high-performance polymers), replacing up to 50% of the metal parts of the vehicle [1]. The advantages in the use of carbon-based composite materials does not stop to structural reinforcement and weight loss: carbon based materials such as graphene may help to overcome some limitations in electronic applications as well. Due to its unique properties such as low weight, mechanical strength, thermal and electrical conductivity, graphene could be a promising material for the development of electrothermal heaters for efficient anti/de- icing system in aircrafts.
In this presentation we will show the development of heaters prototypes realized with GRM integrated in Carbon Fiber Reinforced Polymers (CFRP) or flexible substrates with different design and configurations. The devices prepared showed good functionality, uniform heating without hotspots also in bended configuration. Graphene heaters can achieve a wide range of operation temperatures with respect 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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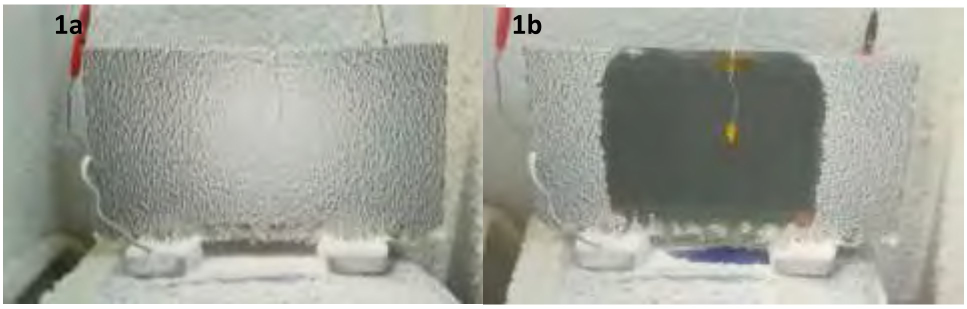

Figure 1: Graphene heater integrated in CFRP with ice accretion on the surface **a)** before and **b**) after the de-icing process
Figure 2: SEM image of the graphene based material used to fabricate the heating module

Lighting up the Electrochemiluminescence of Carbon Dots through Pre- and Post-Synthetic Design

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Biomarkers are biological indicators with a key role in identifying human body function changes. Their quantitative detection is fundamental in clinical monitoring implementation and early screening of diseases. Recently, a huge number of sensors are developed with these goals.[1] In this context, electrochemiluminescence (ECL) is a leading technique in the field of immunoassays-based biomarker detection and biosensors fabrication thanks to the great sensitivity of the technique.[2] Electrochemiluminescence is a luminescent phenomenon induced by an electrochemical stimulus with a high signal-to-noise ratio. In the quest for ever-increasing sensitivities, ECL can ideally be coupled to nanotechnology to develop new systems and strategies for analyte determination even in very complex matrices.[3] Nanotechnologies can improve the sensitivity and sensibility of ECL technique thanks to their advantageous and tuneable properties.[4] For example, Carbon Dots are a class of photoluminescent and electrochemiluminescent nanomaterials, specifically carbon-based nanoparticles, with ECL elusive properties. Here we focus our attention on ECL proprieties of BCDs, Carbon Nanodots functionalized with boron-dipyrromethene (Bodipy), and how pre- and post-synthetic design strategies improve the ECL emission properties, opening new opportunities for exploring CDs in biosensing applications. BCDs are excellent candidates as an alternative to $Ru(bpy)_3^{2+}$ luminophores thanks to their features, such as nontoxicity, chemical inertness, high resistance to photobleaching and unique ECL properties. The final goal is the development of an efficient ECL nanomaterial with high ECL intensity and simple bioconjugation. [5]

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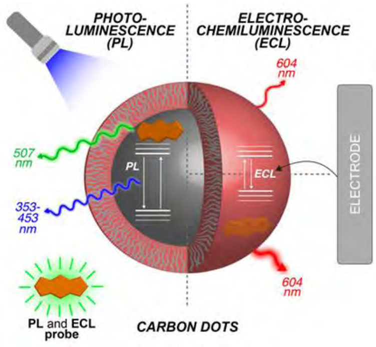

Figure 1: Schematic representation of the ECL and PL mechanism of Bodipy Carbon Nanodots.

Benzo[rst]pentaphene derivatives as building blocks for 2D material with intense ECL emission

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Planar and curved polycyclic aromatic hydrocarbons (PAHs) constitute a large class of organic molecules with an extended and delocalized π-system that provides interesting properties for optoelectronic [1] and energy storage applications [2]. In the framework of our recent work on corannulene oligomerization [3], we investigated a series of rationally designed benzo[rst]pentaphene (BPP) derivatives which, in principle, could lead to an extension of the aromatic π-system through an anodic oligomerization on the electrode followed by an electrochemically induced cyclodehydrogenation reaction.

In this study, we report the electrochemical characterization by cyclic voltammetry of a family of pristine and mesitylen-substituted mono- and dimeric BPP. The presence of bulky and non-linear side groups, as mesitylene (Mes), provides a more stable electrochemical behavior, as well as prevents the π-π stacking in solid state films, which is generally deleterious for light emitting devices (OLED) [4]. Furthermore, the interesting optical properties of BPP and derivatives have been investigated by electrochemiluminescence (ECL) in solution.

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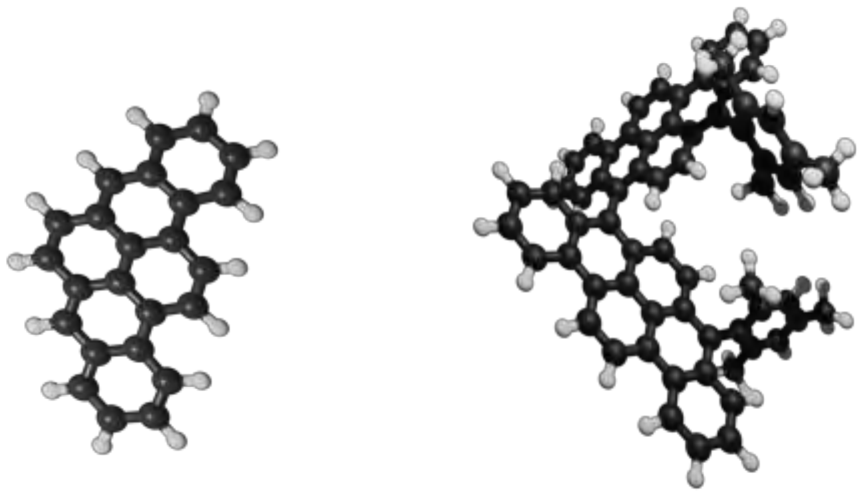

Figure 1: Molecular structure of BPP (left) and mesitylen-substituted dimer (right)

Electronic and Thermal Transport in Black Phosphorene tunned by Grain Boundaries and Strain.

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Grain Boundaries are a type of lattice defect that is common to find after the synthesis of 2D materials due to the growing and merging of two grains with different nuclear sites and lattice orientations. This type of defects influences the mechanical and electronic properties of the materials, therefore, with the understanding and control of this issue it is possible to engineer grain boundaries to tune transport properties of low dimensional systems.

In this work we used density functional based tight-binding (DFTB) method combined with atomistic Green Functions technique to calculate the transport properties. We show the electronic and phonon transport properties of two grain boundaries types in Black Phosphorene. Additionally, we included strain as additional parameter to tune their transport properties.

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Towards quantification of covalent modification on semiconducting MoS_2

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2-dimentional (2D) materials are a recent class of nanomaterials that are characterized by their lack of a bulk state. They are a class of extremely thin nanomaterials that are confined to thicknesses of few atoms in one of the three dimensions. Albeit being a handful in number, this class of materials manage to manifest a wide range of optical and electronic properties among them. These materials have spread their impact to a range of fields from energy and catalysis, nanoelectronics, to drug delivery and biomaterials. One of the most representative examples of such a material is molybdenum disulfide (MoS_2). What makes this material interesting to us is its peculiar phase-dependent optoelectronic properties. MoS_2 has two notable phases: a semiconducting 2H phase, which is fluorescent with a direct bandgap, and a non-fluorescent but metallic 1T/T' phase. There is a growing interest in the research community on modulating and diversifying the properties of such materials. Covalent chemistry offers a solution to this problem as it is a simple and scalable approach for functionalizing these materials and tuning their properties. Different covalent chemical functionalization approaches have been reported on various 2D materials including MoS_2.[1] But such approaches on MoS_2 have more focused on the 1T phase and defect sites in 2H phase rather than on the 2H basal plane.[1,2] This can be accounted to the relatively inert nature of the 2H phase towards chemical reactions. Diazonium chemistry tackles these issues with its high reactivity and has recently been proven to be efficient for the covalent modification of 2H-MoS_2 with covalent bond formation between aryl groups and the basal plane of MoS_2.[3]

We will be discussing the molecular functionalization and modification of semiconducting MoS_2 using diazonium salts towards interfacing these methods to technological applications by controlling and quantifying the modulation in properties. We combine scanning probe microscopy techniques along with Raman spectroscopy and photoluminescence studies to provide a broader understanding of these surface processes and their effect on material properties.

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Graphene paper for applications in flexible electronics

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Abstract

Thanks to its excellent mechanical, electrical and chemical properties, graphene is a promising material as a conductive flexible platform for new sustainable, flexible devices in many application fields, like wearable electronics, automotive and aeronautics, sensors, domotics, IoT and more [1-2].
Graphene Related Materials can be also reassembled in free-standing foils by mechanical compression, obtaining a flexible, electrically conductive, paper-like material called "graphene paper", which features a high electrical conductivity ($1x10^5$ S/m) and a mechanical stability even after a hundred of thousands bending times [1]. In this work, we report the advantage of using graphene paper for the realization of flexible heaters, NFC antennas, sensors and conductive tracks. The devices developed were prepared with easy, scalable and sustainable processes avoiding high temperatures annealing, chemical etching, pollutants and other high-energy consuming processes typical of metals. Further, graphene paper has a high compatibility with many substrates like textile, paper, plastic or composites, on which can be laminated with good adhesion widening the possible applications.

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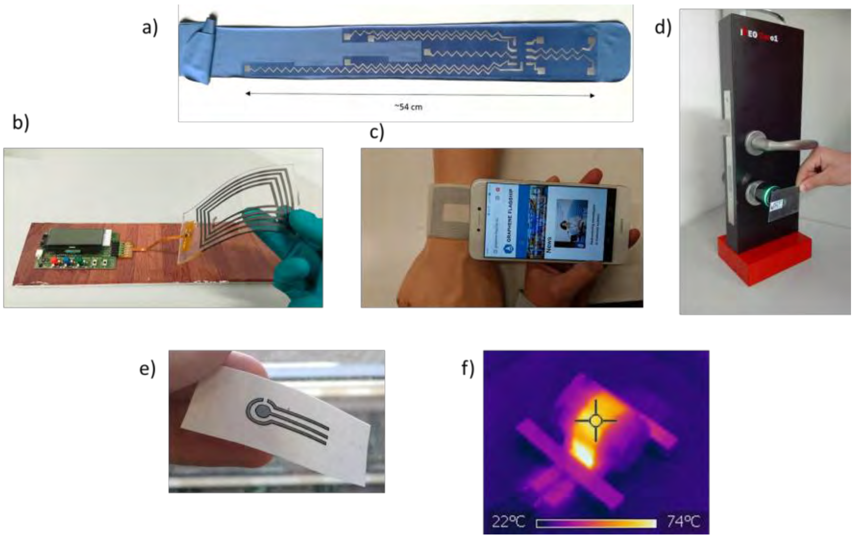

Figure 1: Prototypes developed with graphene paper for flexible electronics (conductive tracks, NFC antenna, electronic key, sensors, heaters).

Nitrogen doped graphene with diamond like bonds achieves unprecedented energy density

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Supercapacitors have attracted great interest because of their fast, reversible operation and sustainability. However, their energy densities remain below those of batteries. In the last decade, supercapacitors with an energy content of ~110 Wh L^{-1} at a power of ~1 kW L^{-1} were developed by leveraging the open framework structure of graphene-related architectures. We report reaction of fluorographene with nitrogen source which enables the preparation of a material combining graphene-type sp^2 layers with tetrahedral C-C bonds and nitrogen superdoping (16%). This material, with diamond-like bonds and and an ultra-high mass density of 2.8 g cm^{-3}, is delivering unprecedented energy densities of 200 Wh L^{-1} (at power of 2.6 kW L^{-1}) and 143 Wh L^{-1} (at power of 52 kW L^{-1}). These findings open a route to materials whose properties may enable a transformative improvement in the performance of supercapacitor components.

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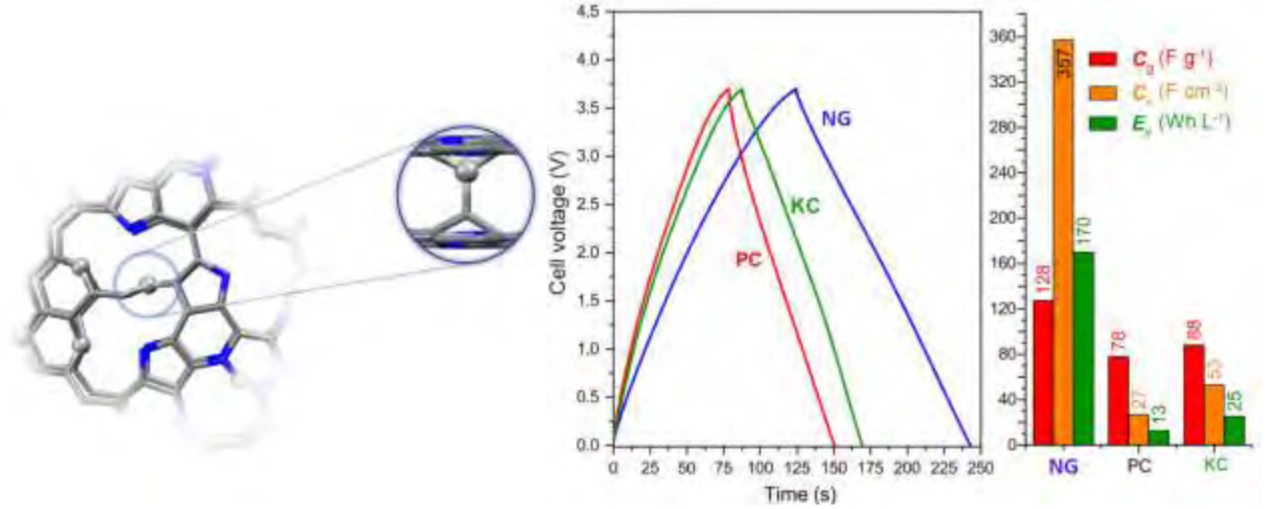

Figure 1: **Left panel:** Theoretical model of GN3 structural fragment (C:N atomic ratio of *ca.* 84:16) optimized by first-principles spin-polarized DFT calculations. **Right panel:** Comparison of the GN3 cell with symmetric cells made using commercial carbons with their performance at 2 A g^{-1}.

Electronic Structures of Two-Dimensional PC_6-type Materials

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Electronic properties of π-conjugated 2D materials are dictated by the underlying network topology.[1] Such materials are under investigation for their electron transport properties and potential topological non-triviality. The structure of the recently discovered material family of PC_6[2] corresponds to a $\sqrt{7} \times \sqrt{7}R19.1°$ superstructure of graphene with atoms substituted such that a second honeycomb lattice of phosphorous atoms evolves (distance in xy plane is 3.89 Å, cf. orange network in Fig. 1(a)). The monolayer band structure shows two Dirac points above and below the Fermi level (cf. Fig. 1(b)). PC_6-based structures with the Fermi level at the upper Dirac cone were proposed[3] and potential applications as battery storage material have been described.[4] However, there was no systematic investigation into the fundamental structure-property relationships in the family of PC_6-type materials. Herein, we demonstrate strategies to shift the Fermi level and to tune electronic properties.

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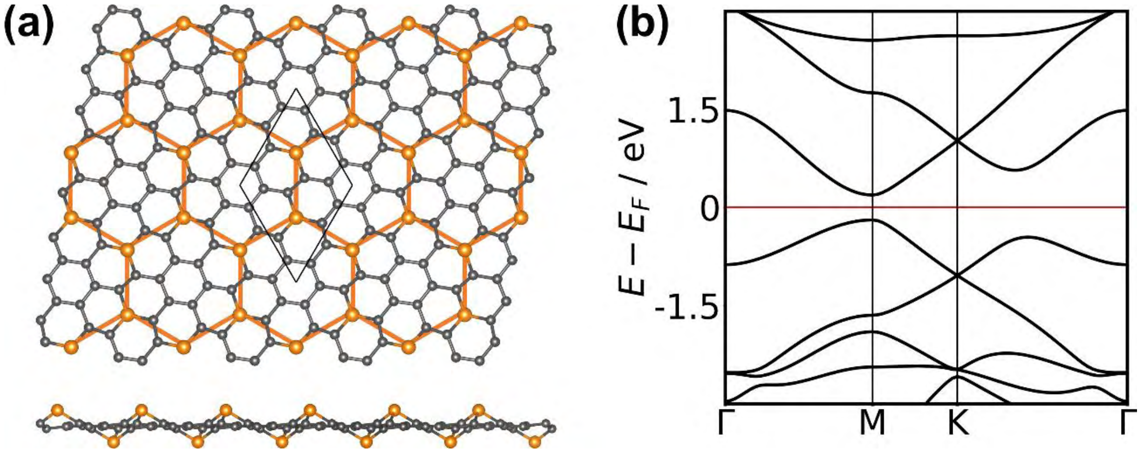

Figure 1: (a) Top and side view of the PC_6 monolayer structure (C: grey, P: orange). It corresponds to a supercell of graphene with atoms substituted to form a second honeycomb lattice (orange lines), (b) band structure of PC_6 monolayer with Dirac cones above and below the Fermi level.

Manipulating the magnetism of $NiPS_3$ via organic ion intercalation

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Intercalation of layered materials is as a powerful fabrication and processing tool to modify the optical, electronic and magnetic properties of the host lattice [1-3]. In this study, we performed an electrochemical intercalation of different alkylammonium cations into $NiPS_3$ bulk crystals (Fig. 1a). Moreover, we explored an interlamellar alkylammonium-$Co(Cp)_2^+$ exchange, which is thermodynamically favored for $NiPS_3$. X-ray diffraction spectra show the appearance of new (00l) peaks' families at lower 2θ angles, attributed to an increase of host lattice's interlayer distance (Fig. 1b). Raman spectra reveals clear fingerprints of the intercalation. Finally, magnetization measurements demonstrate a dramatic change in the $NiPS_3$ magnetic properties, with the suppression of the pristine antiferromagnetism and the emergence of ferrimagnetism or paramagnetism (Fig. 1c), depending on the guest specie. Our results indicate that molecular intercalation is a promising route to tailor the magnetic properties of layered materials.

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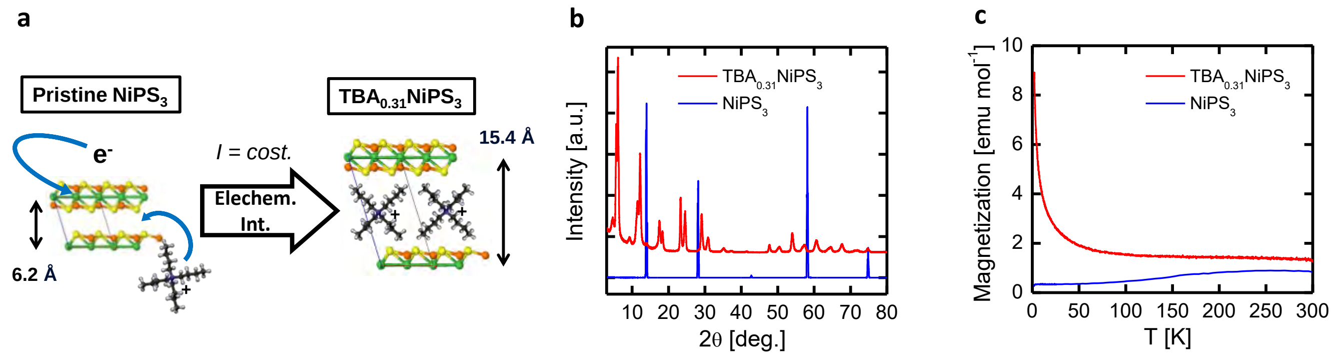

Figure 1: (a) Schematic of the electrochemical intercalation. Upon reduction of $NiPS_3$ host lattice, TBA^+ cations are readily intercalated in between the Van der Waals gaps. (b) XRD patterns of pristine $NiPS_3$ and TBA^+ int. $NiPS_3$. (c) Magnetization vs. temperature of pristine $NiPS_3$ and TBA^+ int. $NiPS_3$ at 500 Oe. Pristine-antiferromagnetism is replaced by paramagnetism.

In situ kinetic studies of CVD graphene growth by reflection spectroscopy

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Monitoring of large-scale synthesis of two-dimensional materials (2DMs) such as graphene is a prerequisite for industrial applications. Chemical vapor deposition (CVD) is currently the most widespread synthesis method as it is efficient and easy to automatize. The process itself is quite complex and poorly understood, but it is generally believed to involve a number of distinct steps such as hydrocarbon decomposition into surface-bound intermediates, diffusion on the catalytic substrate, generation of nucleation points and, finally, graphene growth. In situ monitoring and tailoring of such a complex procedure is beneficial for understanding the growth kinetics and, eventually, for controlling the graphene growth. Herein, we report on a novel metrology system based on in situ reflectance spectroscopy that has been developed for real-time monitoring of surface changes during graphene growth on Cu foils at high operating temperatures. The implementation of this technique for extracting kinetic parameters of the growth process is presented. Furthermore, a microkinetic model of graphene growth based on density-functional theory (DFT) and the hindered translator/rotator model for enthalpy and entropy corrections is constructed and used to obtain a microscopic understanding of the apparent activation energy and related rate-determining steps in graphene.

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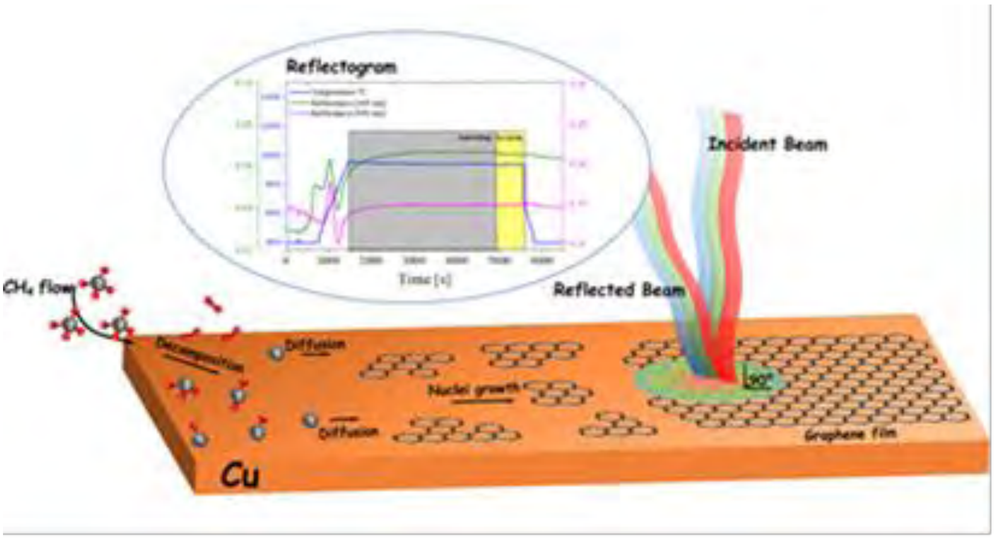

Charge Transport Characterization in 2D COFs

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Two-dimensional (2D) materials have attracted great attention owing to their unique physical and chemical properties and as well as their wide range of applications in electronics, sensing, energy storage and conversion. Among these materials, 2D covalent organic frameworks (COFs) are an emerging class of crystalline porous polymers with structural tunability and diversity [1]. Despite the intensive studies on 2D COFs, charge transport properties of most of these materials are still unknown. In particular, their relation to molecular building block properties is a great challenge due to the combinatorial nature of reticular chemistry. Herein, we investigate the structural and electronic properties of porphyrin-based 2D COFs using density functional theory (DFT)-based first-principles approaches [2,3]. We are modelling charge transport properties by combining the semi-classical Boltzmann transport theory [4] and deformation potential theory (DPT) for acoustic and optical phonons [5,6]. The results are bechmarked against state-of-the-art electron-phonon averaged (EPA) calculations [7].

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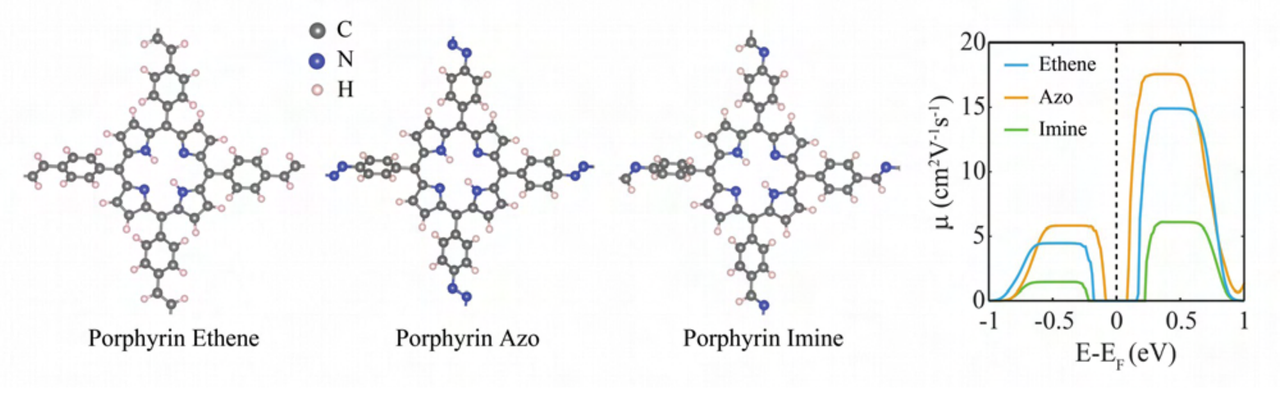

Figure 1: Top views of porphyrin-based structures and their calculated charge carrier mobilities within the acoustic DPT.

Tuning Graphene Oxide electronic properties through low-temperature thermal annealing

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Abstract

Graphene Oxide (GO) is a single-atom layer of carbon with both the sides and area of the flake functionalized with groups containing oxygen such as, epoxide hydroxyls, ketones and carboxyl acids.[1–4] The presence of these functional groups makes the flakes well dispersible in water making them easy to be processed. However, GO is not suitable for application electronics due to insulator behaviour for the presence of oxygenated functional groups. To restore the conjugation into the carbon framework, removal of oxygen atoms from the flake surfaces is needed and several methods have been investigated in these years.[5,6] Among the vastness of protocols studied, GO thermal reduction is one of the most promising route due to the absence of chemical reagents involved in the process that does not require any further purification steps.[5,7,8] We investigated the thermal reduction of GO in a range of temperature < 300 °C in air and inert atmosphere, characterizing the chemical modification on the flakes surface via XPS and solid-state NMR spectroscopy. The change of oxidation degree in GO by varying the reduction temperature and the atmosphere leads to chemically different materials with different electronic behaviours. Those differences have been highlighted by measuring the electrical resistivity on thin films and using the different thermally reduced GOs as electrodes in supercapacitors.

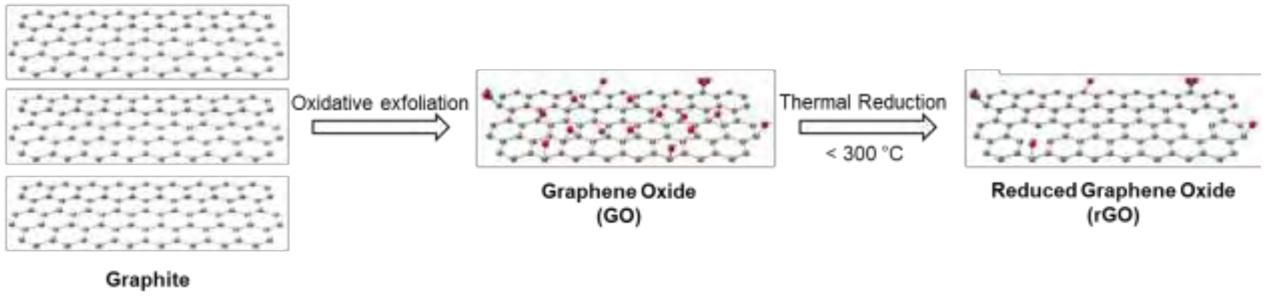

Figure 1: Low-temperature thermally reduced Graphene Oxide production process.

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Piezo resistive behavior of GRMs coated glass fiber composite applied to structural health monitoring

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Thanks to its exceptional properties, glass fiber reinforced polymer composites are widely employed as advanced engineering material, notably in the automotive industry. Damage and failure of composites, unlike metals, are difficult to forecast under real-time stress due to their anisotropic structure. With that focus, we studied the use of Graphene Related Materials (GRMs) as electrical conductive fillers in insulating glass fiber reinforced composites (GFRC). The objective is to add new functionality to the resulting material such as piezo resistivity, a key property that might represent the breakthrough point for FRC components, allowing their structural health monitoring (SHM) which will increase their reliability. In particular, the piezo resistive effect is a change in the electrical resistivity of a material when mechanical strain is applied and in our case is due to the rearrangement of the electrical conductive GRMs network inside the polymer matrix [1]. First, we demonstrated the piezo resistive behavior in the developed composite and second, we proved that it is possible to correlate its resistance variation with the structural health of the SHM prototype.

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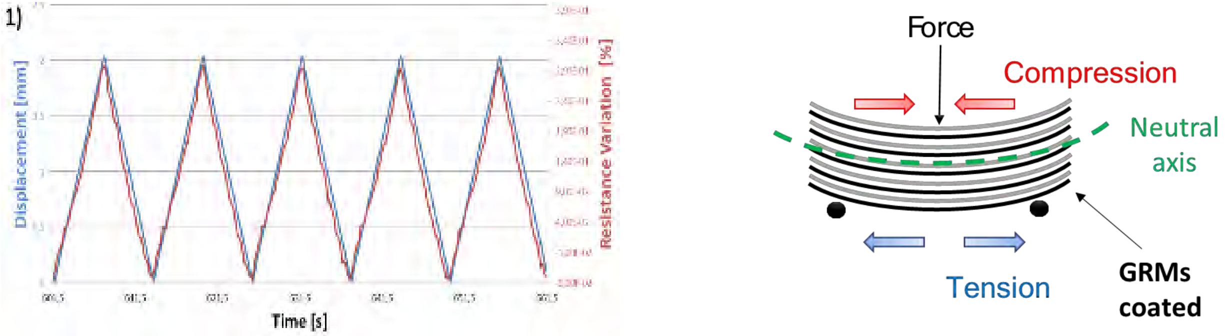

Figure 1: piezo resistive behavior of GRMs coated glass fiber (GF) composite

Docking DNA at the edge of graphene

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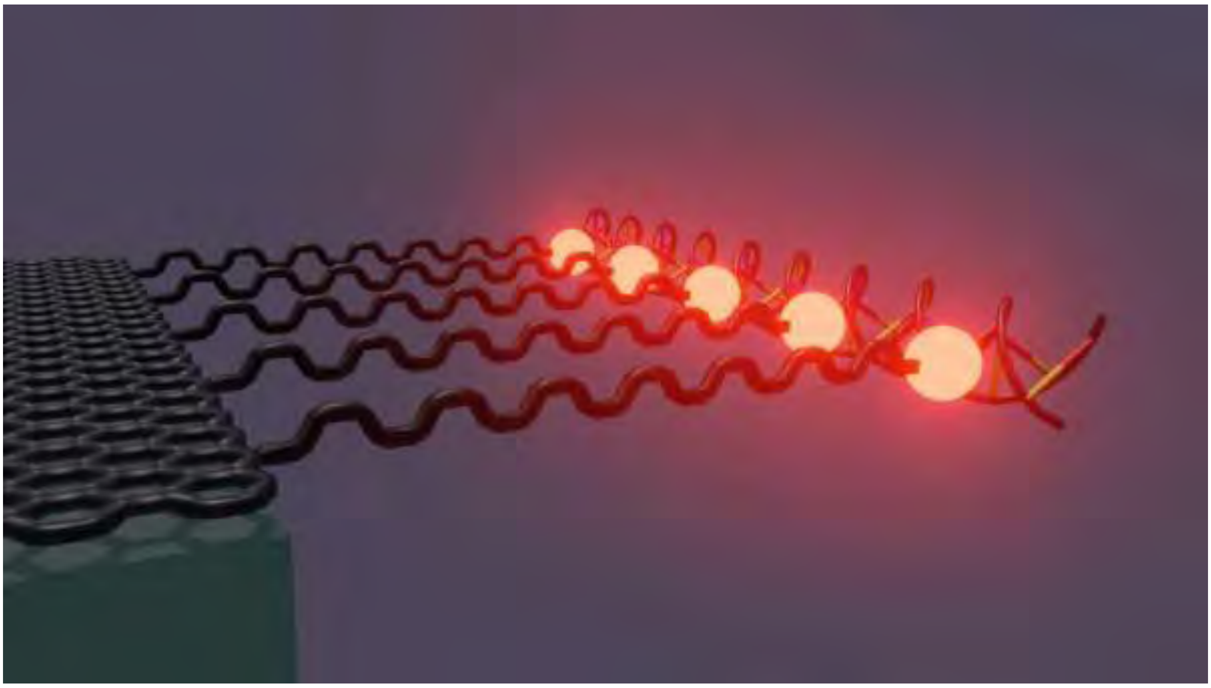
Devices that are aimed at using a tunnelling current to sequence DNA, with two graphene sheets lined up in a twisted configuration, cannot operate without a means to put the DNA strand at the graphene edge, where the tunnelling current is flowing. We aim to dock DNA and visualize the process at the same time, using a dual-action approach. We make use of two photochemical principles: on the one hand the so-called DNA light switch molecules, typically ruthenium complexes that light up when they bind to DNA, and on the other hand the fluorescence quenching effect of graphene, which is strongly dependent on the distance between the dye and the quenching species. By using both principles, we can design a platform that can dock DNA to a graphene edge through binding a ruthenium complex that is installed to the edge via a flexible linker, and show that the DNA is docked with fluorescence: as we can electrostatically change the distance between the edge and the ruthenium-DNA adduct, the fluorescence of this adduct will switch on and off, showing that the DNA is installed at the edge.

Figures



Electronic Properties of Metal-Phthalocyanine-Based 2D Conjugated Covalent Organic Frameworks

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Two-dimensional (2D) conjugated covalent organic frameworks (*c*-COFs) are emerging as a unique class of semiconducting 2D conjugated polymers for (opto)electronics and energy storage.[1,2] However, understanding the intricate interplay between structure and conductivity remains elusive. We have demonstrated two metal−phthalocyanine-based pyrazine-linked 2D *c*-COFs (MPc-pz, M = Cu or Zn) as *p*-type semiconductors with a band gap of ∼1.2 eV and charge mobility up to ∼5 $cm^2/(Vs)$.[3] Hall effect measurements and terahertz spectroscopy in combination with density functional theory calculations confirm that varying metal center from Cu to Zn has a negligible effect on the charge transport behaviors. After reversible *p*-type doping with I_2, the doping-defined 2D *c*-COF displays enhanced conductivity by 3 orders of magnitude, due to the elevated carrier concentration.[4] Remarkably, charge mobility also increased upon doping, which can be traced to increased scattering time for free charge carriers, indicating that scattering mechanisms limiting the mobility are mitigated by doping.

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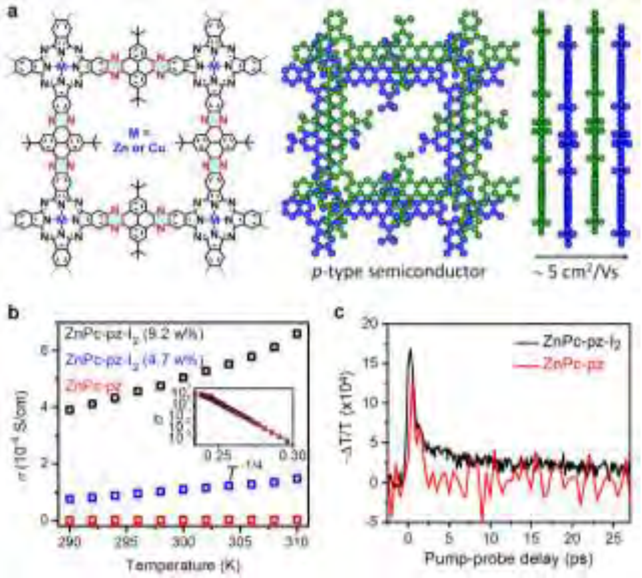

Figure 1: (a) Structural schematics of MPc-pz COF. (b) Variable-temperature conductivity of pristine and doped MPc-pz. (c) Terahertz spectroscopy.

Layer-Oriented 2D Conjugated Metal-Organic Framework Films Enabling Directional Charge Transport

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Layered two-dimensional conjugated metal-organic frameworks (2D *c*-MOFs), with strong in-plane conjugation and weak out-plane van der Waals force, have emerged as promising electrically conductive materials for organic electronics such as field-effect transistors (FETs) and spintronic devices. One of the key challenges faced by the scientific community is to synthesize 2D *c*-MOFs with control of layer orientation to dial-in desired electronic properties/devices. Here, we report the novel synthesis of unprecedented edge-on layer-orientated *p*-type semiconducting 2D *c*-MOF films by combining supramolecular chemistry and interface-assisted polymerization. We figure out the crystal structure and orientations of the 2D *c*-MOFs films ($Cu_2[PcM\text{-}O_8]$, M=Cu, Fe) with molecular precision, and demonstrate that the edge-on structure formation is guided by the pre-organization of metal-phthalocyanine ligands, whose basal plane is perpendicular to the water surface due to their π-π interaction and hydrophobicity. The synthetic $Cu_2[PcCu\text{-}O_8]$ film features with a thickness of ~20 nm and ~600 nm-sized crystal domains, and exhibits a room temperature conductivity of $\sim 5.6\times10^{-4}$ S cm^{-1} and a Hall mobility of ~4.4 $cm^2\,V^{-1}\,s^{-1}$ based on macroscopic van der Pauw pattern. Lateral and vertical measurements further reveal the directional charge transport feature in this edge-on 2D *c*-MOF film, i.e., the lateral conductivity is 2~3 orders of magnitude higher than the vertical one. The directional conductivity studies combined with theoretical calculation identify that the intrinsic conductivity of $Cu_2[PcCu\text{-}O_8]$ is dominated by charge transfer along the interlayer pathway. This work provides a state-of-art insight into the controlled synthesis of layer-orientated semiconductive 2D *c*-MOF films, allowing to dial-in lateral/vertical electronic devices and determine the intrinsic transport mechanism.

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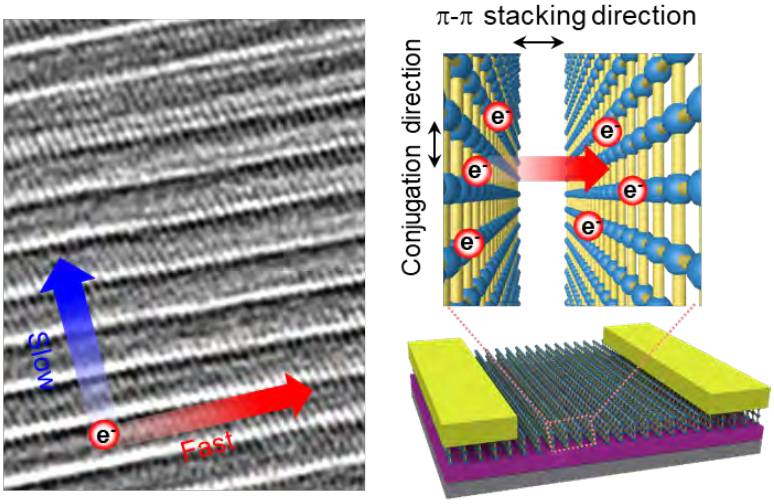

2D layered $CrPSe_3$-G-MWCNTs@NiB composite as a superior anode for high performance lithium storage

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Abstract

Energy storage based on electrochemical systems has made a surprising contribution to the well-being of our modern society. In particular, with the development of the electric vehicles (EVs) and storage energy stations, lithium-ion batteries (LIBs) due to their advantageous energy storage performance, low weight, and versatility not only have been given an excellent development opportunity but also have encountered a great challenge due to the huge demands of key markets, such as higher capacity [1]. Accordingly, the key solution to these issues is dependent upon the development of the new electrode materials with high energy and power densities [2]. Based on the considerations of attractive Li storage properties of two-dimensional (2D) layered chromium selenophosphate ($CrPSe_3$), as well as high conductivity and high specific surface area of carbon materials (graphite and multi-walled carbon nanotubes), we synthesized a 2D $CrPSe_3$ by one step high-temperature solid-phase synthesis [3]. After combining with graphite (G) and multi-walled carbon nanotubes (MWCNTs) by high-energy ball milling, the novel 2D/2D heterojunction of $CrPSe_3$-G-MWCNTs@NiB composite was successfully prepared. The XRD data of bulk $CrPSe_3$, $CrPSe_3$-G-MWCNTs, and $CrPSe_3$-G-MWCNTs@NiB materials are displayed in **Figure 1**, which exhibit similar diffraction peaks that can be well assigned to the $CrPSe_3$ phase (PDF no. 00-033-0403). Compared with the pristine $CrPSe_3$, the introduction of carbon materials can enhance its electronic conductivity, increase the interface contact area, and ameliorate the volume change during the repeated insertion/extraction of Li, thus contributing to fast ion/electron transport kinetics [4]. Following this trend, promising electrochemical performances in terms of low discharge-charge polarization, reversibility, cycling stability (660 mAh g^{-1} after 70 cycles), and capacity retention (89%) are observed (**Figure 2**). Thus, such a kind of 2D layered $CrPSe_3$-G-MWCNTs@NiB material is considered as a promising anode for high performance LIBs.

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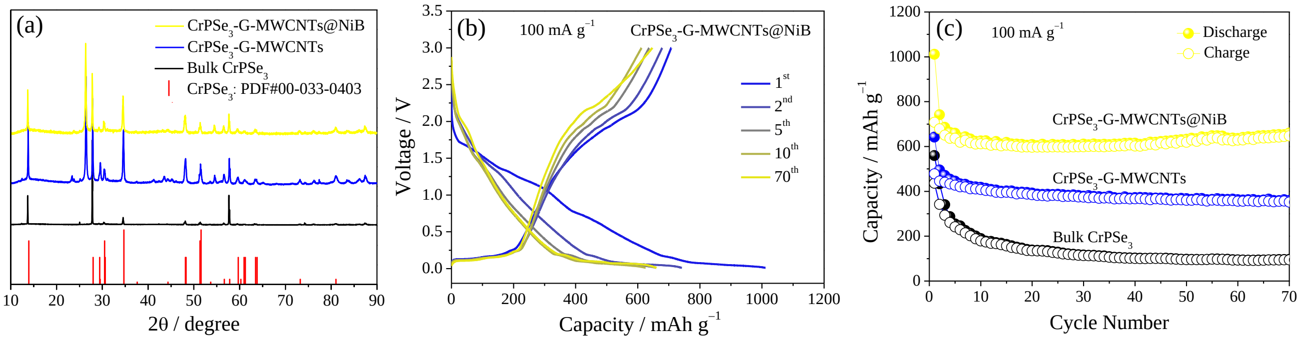

Figure 1: (a) XRD patterns of bulk $CrPSe_3$, $CrPSe_3$-G-MWCNTs, and $CrPSe_3$-G-MWCNTs@NiB composites; Cycling response of (b, c) bulk $CrPSe_3$, $CrPSe_3$-G-MWCNTs, and $CrPSe_3$-G-MWCNTs@NiB in two-electrode half-cell at 100 mA g^{-1} current density in terms of (b) voltage profiles of selected cycles and (c) cycling trend.

Grafting Ink for Direct Writing: Solvation Activates Covalent Functionalization of Graphene

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Covalent functionalization of graphene (CFG) is of interest to tune the electronic, mechanical, optical and thermal properties of graphene. However, facile, efficient, and large-scale CFG remains challenging. Herein, we present a diazonium-based grafting ink with high grafting efficiency. The grafting ink consists of only two components, i.e. the diazonium salt and the solvent dimethyl sulfoxide (DMSO). We discuss the mechanism and efficiency of the grafting in terms of the DMSO induced n-doping of graphene, in combination with solvation of the diazonium cations, promoting the electron transfer from graphene to reduce the diazonium cation, while stabilizing the diazonium salt in solution. The grafting density of CFG is controlled by the functionalization time and reaches very high levels of functionalization, up to the failing of the Tuinstra-Koenig (TK) relation,[1] while the functionalization layer remains at monolayer height. Additionally, the organic-addend group can be readily adjusted by using different diazonium cations in the grafting ink. The grafting ink can be used at ambient conditions and renders the covalent modification of graphene as easy as writing on paper. A combination of this approach with inkjet-printing would allow the direct and spatially selective functionalization of graphene or other 2D materials.[2]

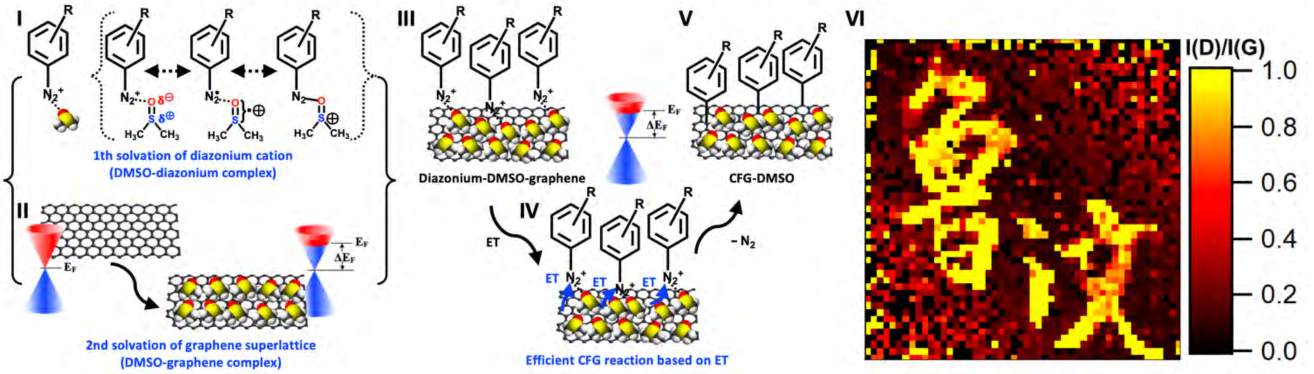

Figure 1. Solvation promotes ET for efficient CFG. I) Solvation of diazonium cation by DMSO based on dipole-ion interaction; II) Solvation of graphene lattice by DMSO based on dipole-induced dipole interaction; III-V) The aryl diazonium-DMSO-graphene interface promotes the EF for CFG; VI) Raman map of the spatially functionalized graphene/SiO_2/Si by direct hand-writing using soft Chinese brush dipped with the grafting ink at ambient condition. Scanning size 1 by 1 cm^2.

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Heptagon-Azulene Embedded Helical Bilayer Nanographene

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Twisted bilayer graphene and related nanographens exhibit outstanding electronic and physical properties [1]. However, the synthesis of structurally well-defined and defect bilayer nanographenes is still challenging. Here, a unique non-hexagonal helical bilayer nanographene has been synthesized. The heptagon and azulene embedded bilayer molecule represents the first non-hexagonal π−extended [10]helicene with a total of 35 fused rings. The folded bilayer structure was investigated theoretically and confirmed by single-crystal x-ray diffraction, revealing a highly twisted conformation and strong π−π interactions between the two layers. The enantiomers were separated, and their chiroptical properties were evaluated, showing the ECD responses of this novel chiral bilayer nanographenes. This non-hexagonal helical bilayer nanographene (**NHBNG**) could potentially serve as a seed for the preparation of structurally well-defined bilayer nanographene.

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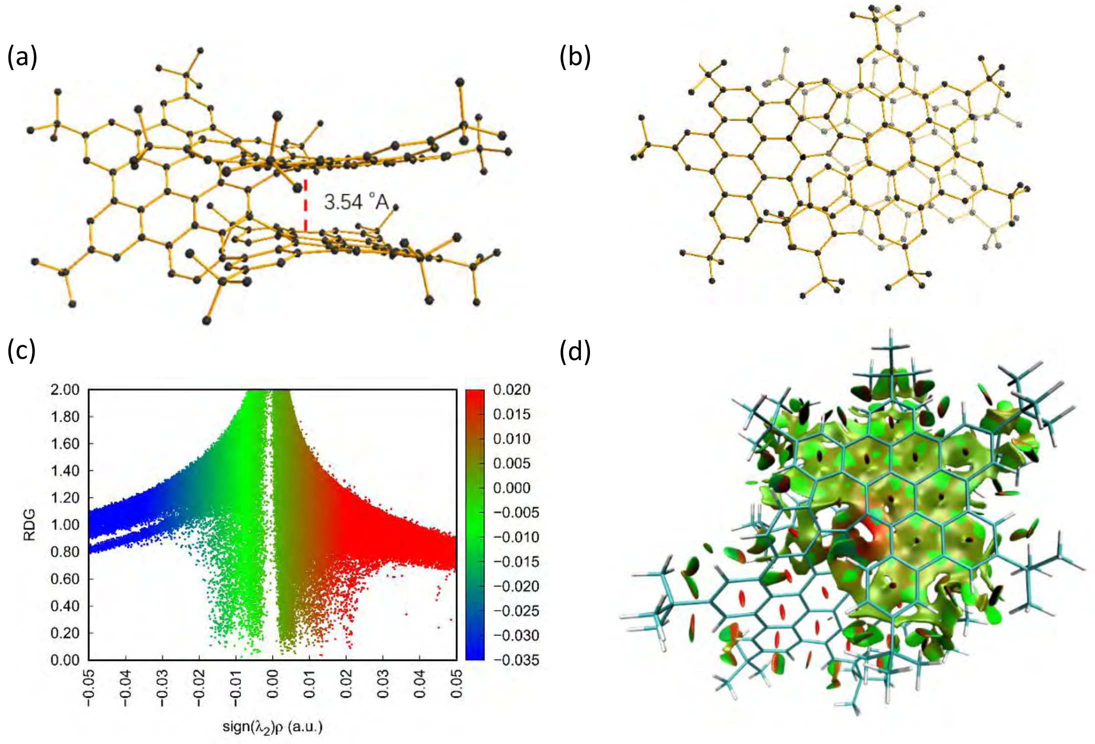

Figure 1: (a) side and (b) top view of **NHBNG 1**. The thermal ellipsoids are set at a probability level of 50%. (c) Graphical representation of the reduced density gradient(RDG) versus sign(λ2)ρ, in which the blue, green, and red color of the vertical scale represent the hydrogen bonding, Vandel Walls effect, and steric effect, respectively. (d) Plots of the reduced density gradient isosurfaces for compound **NHBNG 1**.

A nanoporous 2D membrane composed of graphene for direct methanol fuel cell

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Permselectivity of membranes is crucial in the design of high performance fuel cell which requires high permeability for charge carrier while preventing fuel crossover[1]. Functionalized graphene monolayer could trade off permeability and selectivity well owing to ultra-thin thickness which allows fast mass transport[2]. To integrate a nanoporous 2D membrane in a fuel cell, the challenges are three-fold: i) the need of high porosity with subnanometer pore ideally only allowing proton transport; ii) charged surface ensures high cation/anion selectivity; iii) proper support that allows easy fabrication of membrane electrode assembly (MEA)[3,4]. We prepared MEA for direct methanol fuel cell (DMFC) with sulfobenzendiazonium treated graphene monolayer supported by porous polycarbonate membrane and protected by a proton reservoir layer. For diazonium treatment, ~46% of ion pathways are selective to proton with respect to K^+ and trans membrane conductance reaches 180 S cm^{-2}. This also enhanced power output in DMFC by 102% comparing to Nafion 117. We attribute these to deformation of *SP*^{2} network of graphene with diazonium reaction which also introduce positive charge to the surface. Investigation of MEA with diazonium treated graphene offers opportunities to an utilization of graphene in separation membrane based on the control in nanoscale.

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Figures

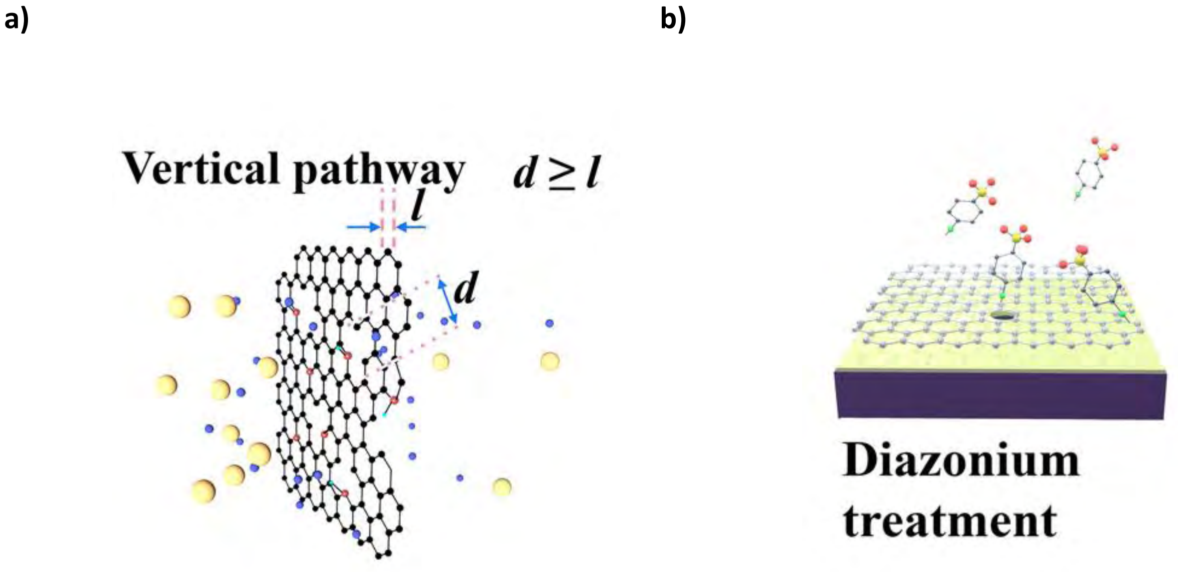

Figure 1: Illustrates of nanoporous graphene membrane. a) Vertical ion pathway through a nanoporous graphene membrane. b) Diazonium treatment of graphene on SiN/Si chip with 1 µm aperture.

Two-Dimensional Conjugated Framework Electrocatalyst

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Two-dimensional conjugated metal-organic frameworks (2D *c*-MOFs), with highly in-plane π-conjugation and weak out-plane π-π stacking, have emerged as novel generation of promising electrocatalysts, due to the intrinsic electrical conductivity, permanent pores, high surface area, and structural diversity. Herein, we developed a copper-phthalocyanine-based 2D *c*-MOF ($PcCu-O_8-Co/PcCu-O_8-Zn$) with square planar cobalt/zinc-bis(dihydroxy) complexes as linkage toward electrocatalysis oxygen/carbon reduction reaction (ORR/CO_2RR). $PcCu-O_8-Co$ 2D *c*-MOF mixed with carbon nanotubes exhibits excellent electrocatalytic ORR activity ($E_{1/2}$=0.83 V vs. RHE and j_L=5.3 mA cm^{-2}) in alkaline media owing to the synergistical contribution of 2D conjugated porous structure and dense CoO_4 sites with unique electric structure, which is the record value among the reported intrinsic MOF electrocatalysts. The $PcCu-O_8-Zn$ with carbon nanotube harvests high CO_2RR performance with high CO selectivity of 88%, long-term durability, and tunable molar H_2/CO ratio (1:7~ 4:1) toward syngas synthesis. The contrast results unveil a synergistic catalytic mechanism; the ZnO_4 complexes act as catalytic sites for CO_2 conversion while the CuN_4 centers promote the protonation of adsorbed CO_2 during the CO_2RR. Our works highlight the 2D conjugated MOFs with optimized the composition/architecture and electronic structure as effective electrocatalysts toward ORR and CO_2RR.

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Figures

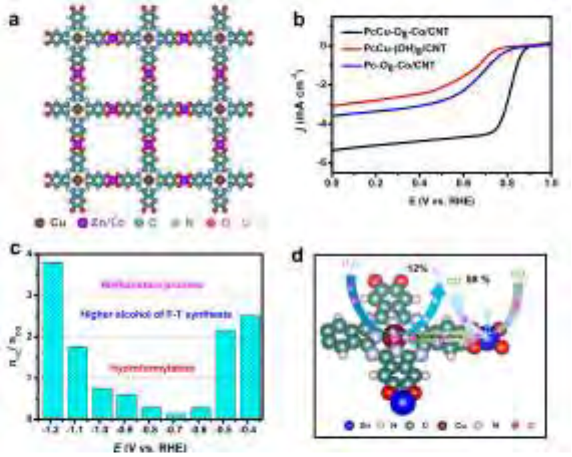

Figure 1: a. Schematic structure of 2D *c*-MOF. b. ORR polarization curves of 2D *c*-MOF/CNT. c. Molar H_2/CO ratio of 2D *c*-MOF/CNT from CO_2RR. d. Proposed CO_2RR process of 2D *c*-MOF.

Versatile Micromotors for Photocatalytic Environmental Remediation

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Environmental degradation issue is a global concern. Great efforts have been made to develop efficient and green approaches for wastewater treatment. Self-propelled nano/microrobots are the forefront of nanotechnology, holding great promise for environmental remediation. Visible light driven semiconductor photocatalyst would be the great catalyst to power such micromachines for environmental remediation. $BiVO_4$ has attracted researchers' great interest. However, its drawbacks such as significant recombination of photogenerated electron–hole pairs, poor electrical conductivity and slow hole transfer kinetics limit its applications. To enhance the photocatalytic efficiency, we elaborately develops light-responsive tubular micromotors with smart material design strategy: BiVO4 is robust visible light absorber; ZnO nanorod arrays act as electron transfer channel; reduced graphene oxide (rGO) films function as electron acceptor; and Co-Pi serves as hole acceptor and catalytic site. Herein, we established novel tubular Co-Pi/BiVO4/ZnO/rGO micromotors, studied the comprehensive performance of micromotors in the polluted water with three types of contaminant models (i.e. dye, explosive and bacteria model); and integrated abundant micromotors in 3DP-motor and demonstrate the pilot-scale test in artificial 5×5m2 pool for environmental remediation, as illustrated in Figure 1.

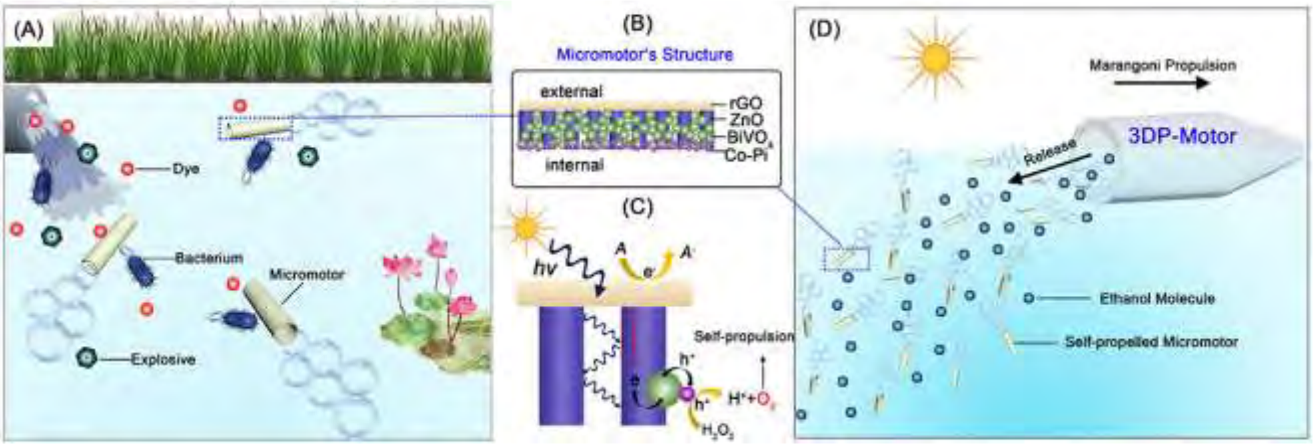

Figure 1: Schematic illustration of (A) versatile micromotors dynamically degrading dyes and explosives and killing bacteria in contaminated water, (B) structure of the designed micromotor, (C) design strategy of Co-Pi/BiVO4/ZnO/rGO: (i) increased light absorption and charge generation in both BiVO4 and ZnO through light trapping effect of the nanorods, (ii) electron injection into ZnO nanorods followed by prompt electron transport along ZnO nanorods, (iii) electron collection and storage in rGO for reduction reaction and (iv) hole transfer to Co-Pi for efficient water oxidation to generate oxygen bubbles for self-propulsion of micromotor, (D) 3D-printed millimeter-scale motor releasing micromotors and ethanol molecules.

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