ABSTRACT BOOKLET

Advances and applications in carbon related nanomaterials: From pure to doped structures including heteroatom layers

2023, Jan 09 -- Jan 13

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ORAL
CONTRIBUTIONS

A RETRO-ENGINEERING DEMONSTRATION OF THE EXISTENCE AND ROLE OF A LIQUID PHASE WHEN DEPOSITING GRAPHENES FROM METHANE ONTO CARBON NANOTUBES AT 1400°C

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The results of experiments aiming at depositing pyrolytic (graphenic) carbon onto carbon nanotubes by means of a chemical vapor deposition (CVD) process at 1400 °C are compared to the literature dealing with the physics of wetting strings by liquids. The comparison demonstrates that carbon deposition mechanisms involve the transient formation of a liquid phase (here organic), and that the wetting physics is still able to apply in spite of the high temperature and the nanoscale, i.e., far beyond the condition range usually investigated in wetting science. This was unexpected, because the high temperature makes all the involved physical and chemical processes transitory, including the fact that the liquid turns itself into solid carbon because of the ongoing carbonisation process. The observations provide an estimate of the time scales of the processes involved, as they have to be short enough to complete in spite of the high temperature conditions. From a practical point of view, as the resulting material is a solid, graphenic carbon, the work demonstrates that using wetting physics in high temperature CVD can be a way to dramatically modify the surface energetics and the nano/microscale morphology of carbon nanofilaments, here forming carbon nanotube-supported complex morphologies which include all-graphene carbon nanocones [1]. The statement is assumed to also apply to other chemical systems. This work was recently published in [2].

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Atomic scale mapping of electrostatic field and potential in MBE grown TMD layers by DPC-CoM

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Structural anomalies in 2D materials have been known as the key to locally modify the electrical, optical and magnetic properties. In order to tailor the material properties and to explore their functionalities, the ability to survey the structural configuration at the atomic scale is essential. Today, low-voltage Scanning Transmission Electron Microscopy (STEM) stands out as one of the most powerful techniques for structural and chemical analysis of 2D materials at atomic scale by Z-contrast imaging as well as EDX and EELS spectroscopies. Recently, a new imaging technique called Differential Phase Contrast – Center of Mass (DPC-CoM) sensitive to local electrostatic field was demonstrated in STEM [1-2] Analyzing the deviation of the transmitted beam position gives access to the local electric field in a sample with atomic resolution, and to the electrostatic potential and the charge density through Poisson's equation [3-4]. However, the lack of quantitative understanding and interpretation of DPC-CoM images are the main reason that this imaging mode is not yet used for the study of 2D materials.

In this work, we explore the use of DPC-CoM for the atomic scale mapping of local electrostatic field and potential in TMD monolayers. The experimentally obtained E-field and potential maps are compared to the DFT-based multislice STEM image simulations [5] taking into account the influence of important microscope parameters such as: convergence angle, defocus, aberrations. The developed analytical process was applied to investigate the local potential around single V dopant in WSe2.
This DPC technique is still exploratory and far from being used in a standard way to study synthesized 2D materials. The methodology highlighted here will open the use of electron microscopy to provide atomic scale multiple information on structure, chemical and electric characteristics appearing in 2D layers and their heterostructures.

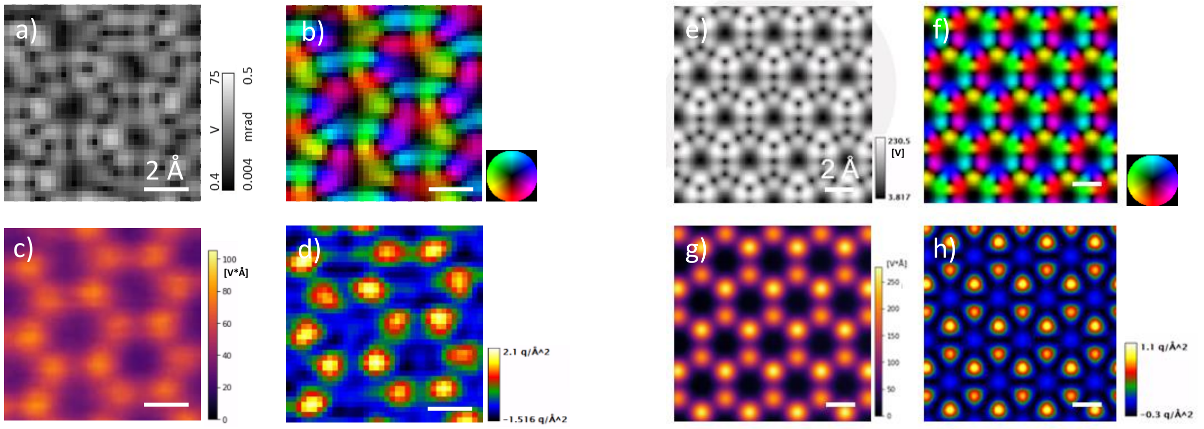

Figure: a-d) Experimental projected electric field magnitude, orientation, potential and charge density of MBE grown WSe_2; e-h) Simulated projected E-field magnitude, orientation, potential and charge density of WSe_2 for an aberration-free electron probe.

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ATOMIC SCALE OBSERVATIONS OF OXYGEN INTERACTIONS WITH 2D MoS2 AND MoTe2

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Oxidation in ambient conditions can cause serious degradation in 2D materials affecting their structure and properties, critical to their use in technological applications. In this study we focus on understanding the oxidation process in 2D transition metal dichalcogenides comparing MoS_2 and $MoTe_2$. Using high resolution scanning transmission electron microscopy operated at controlled low pressure oxygen environments, we directly observe the surface dynamics at the atomic scale [1]. Our results show clear evidence of the oxidation related chemical etching and reveal the effect of hydrocarbon contamination commonly found on all surfaces. We explore the oxidation pathways and the energetics by density functional theory calculations. The two materials react very differently to oxygen. In $MoTe_2$ the interactions lead to vacancy and pore formation at pressures above $1x10^{-7}$ torr ($1.3x10^{-7}$ mbar). The damage formation is observed outside of the continuous imaging area, thus minimising electron beam induced changes. The etching is accelerated by the presence of hydrocarbon contamination by up to a factor of forty. In comparison, MoS_2 is inert to oxygen at all the measured partial pressures within the timescale of the study. Thus, all observed structural changes in MoS_2 are caused by the interactions with the electron beam. Our computational analysis reveals a possible mechanism for the oxygen mediated degradation in MoTe2, explains the observed differences between the two materials, and explores the role of the hydrocarbon contamination in the etching process. The study fits in the "Functionalization, surface modification, and chemistry of nanomaterials", "Advanced characterization/spectroscopic studies" and the "Multiscale modeling and computation" themes of the HeteroNanoCarb23 meeting.

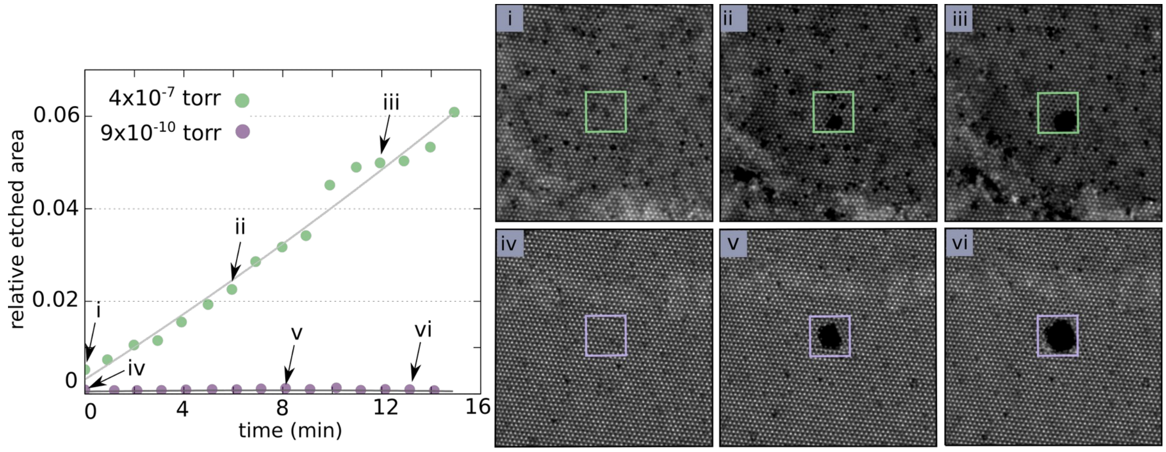

Figure 1 – Relative etched area in $MoTe_2$ when oxygen is introduced into the microscope objective area (green) and without oxygen (purple). STEM HAADF images of the sample surface correspond to the points marked with arrows in the plot. The green and purple squares denote the continuous imaging area excluded from the analysis. The surrounding area (20x20 nm) is scanned once per minute to minimise the effects caused bv the electron beam.

[1] E. H. Åhlgren et al. "Atomic-Scale Oxygen-Mediated Etching of 2D MoS_2 and $MoTe_2$", Adv. Mater. Interfaces, 2022, 2200987. https://doi.org/10.1002/admi.202200987

Bending and Flexing in Carbon and BN

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In this talk I will explore an interesting family of 1D-defects, local folds: in graphene, h-BN, SW- and MWNTs. Folding can occur through a number of mechanisms - mechanical deformation, thermal contraction, dislocation pile-up and nanotube collapse amongst others. Once present, folds can significantly alter the local behaviour of the host material, modifying the electronic and vibrational structure, both through curvature effects and symmetry breaking. I will look at how axial folds can form in arc-electric MWNTs [1], the effects of folding on the electronic structure of h-BN [2], and on the vibrational behaviour of graphene and collapsed SWNTs [3], and if there is time, discuss comparison with local dislocation-induced disorder in graphite [4].

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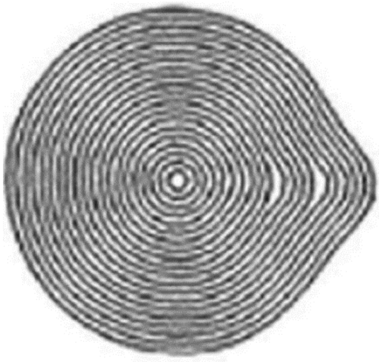
https://doi.org/10.3390/c8010010



[2] 'Electronic structure of folded hexagonal boron nitride',
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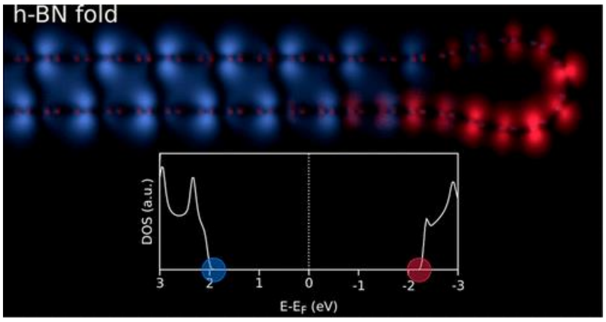

[3] 'Intense Raman D Band without Disorder in Flattened Carbon Nanotubes',
E. Picheau, A. Impellizzeri, D. Rybkovskiy,
M. Bayle, J.-Y.Mevellec, F. Hof, H. Saadaoui,
L. Noe, A. Dias Torres, J.-L. Duvail,
M. Monthioux, B. Humbert, P. Puech, C. Ewels,
A. Penicaud, ACS Nano, 15 (1), 596-603 (2021)
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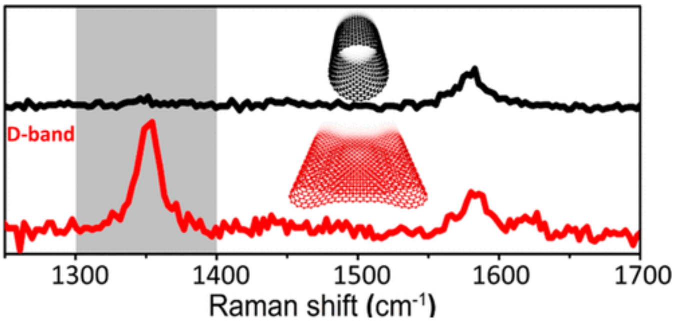

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J. G. McHugh, P. Mouratidis, A. Impellizzeri,
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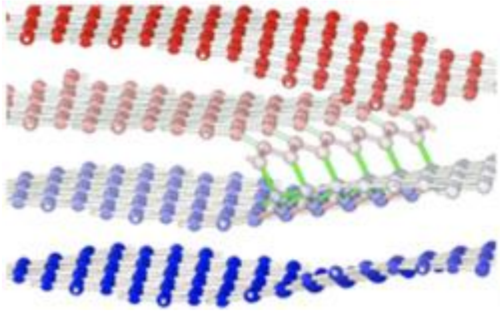

[5] Full publication list with links at
https://chrisewels.github.io/ewels.info/

Abstract Heteronanocarb 2023

Biomedical applications of devices based on surface-functionalized monolayer graphene

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Graphene appears more and more as a very promising material for biomedical applications for both in- vitro and in-vivo applications. Indeed it combines in a single film biocompatibility ,mechanical flexibility, optical transparency and high mobility semiconductivity, enabling Field effect transistor in-vivo biosensing. We have explored the use of graphene-on-polymer for enabling at the same time biosensing and tissue engineering with integration to RFID component to enable direct smartphone connectivity. I will show the application of graphene surface functionalization based as pyrene non-covalent chemistry to implement sensitive biosensors. Finally, I will show prospect for consumer applications that unlock new use cases for wearable and in-vitro diagnostics.

Carbon and B/N doped Nano Onion for biomedical applications

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There are many issues associated with free drug delivery including: adverse side-effects, multi-drug resistance, premature drug degradation, lack of tissue penetration, and non-specific toxicity. Targeted delivery, which utilizes nanocarriers as payload delivery vesicles, has the potential to address and alleviate these prominent issues. Specifically, it involves nanomaterials functionalized with targeting agents, allowing for the selective uptake of these nanocarriers by cells overexpressing specific receptors. This approach explicitly increases the drug concentration in the target cell of interest whilst minimizing the exposure of healthy cells to the therapeutic agent.

In this presentation, carbon nano-onions (CNOs) will be discussed as a potential vesicle for nanocarrier-type drug delivery systems.[1] CNOs, or multi-layer fullerenes, consist of multiple concentric layers of sp^2 hybridized carbon and are emerging as platforms for biomedical applications because of their ability to be internalized by cells and low toxicity. [2]

In my research group we have developed a synthetic methodology for the synthesis of pure, monodispersed CNOs and various chemical functionalization strategies for the introduction of different functionalities (receptor targeting unit and imaging unit) onto the surface of the CNOs. The modified CNOs display high brightness and photostability in aqueous solutions and are selectively taken up by different cancer cell lines without significant cytotoxicity. Supramolecular functionalization with biocompatible polymers is an effective strategy to develop engineered drug carriers for targeted delivery applications. We reported the use of a hyaluronic acid-phospholipid (HA-DMPE) conjugate to target CD44 overexpressing cancer cells, while enhancing solubility of the nanoconstruct. Non-covalently functionalized CNOs with HA-DMPE show excellent *in vitro* cell viability in human breast carcinoma cells overexpressing CD44 and are uptaken to a greater extent compared to human ovarian carcinoma cells with an undetectable amount of CD44. In addition, they possess high *in vivo* biocompatibility in zebrafish during the different stages of development suggesting a high degree of biosafety of this class of nanomaterials. [3]

We recently synthesized Boron/nitrogen co-doped carbon nano-onions (BN-CNOs) [4] and examined their interactions with biological systems. Our study on the toxicological profiles of BN-CNOs and oxidized BN-CNOs in vitro in both healthy and cancer cell lines, as well as in vivo on the embryonic stages of zebrafish (*Danio rerio*) demonstrate that these new class of carbon nanoparticles have high cyto-biocompatibility and a high biosafety [5]. Non covalent functionalization of BN-CNOs with HA-DMPE gave dispersions with long term aqueous stability. [6]

Our results encourage further development as targeted diagnostics or therapeutics nanocarriers.

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CARBON NANORIBBON FORMATION BY *IN-SITU* TEM MANIPULATION OF A $C_{59}N$ DITHIOLANE DERIVATIVE ENCAPSULATED INTO SWNTS

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The creation of new types of functionalized carbon nanostructures is, with no doubt, one of the main pillars of solid-state physics research due to the wide range of potential applications that it can yield [1]. Electron irradiation within a TEM is a great tool for *in-situ* studies on these structures while they are being formed, providing a study of this phenomenon as it is happening at the nanoscale [2].

In this context, carbon 'peapods' (fullerenes encapsulated inside of single-walled nanotubes (SWNT) [3] continue to amount interest regarding the controlled formation of nanostructures. A good case of this nanostructure formation are graphene nanoribbons (GNRs) templated by the encapsulated fullerenes upon heating or beam irradiation [4]. Functionalized C59N-derivatives using dithiolane molecules, containing both sulphur and oxygen [5] may give rise to the creation of fine S, O, N or S-O-N co-doped GNRs within SWNTs under beam irradiation.

In this work, these derivatives (C59N-DT) have been introduced into SWNTs and irradiated *in situ* within a TEM. Results seem to point out to the formation of passivated GNRs. In order to discern their edge passivation, DFT calculations on these structures have been performed to discern the energetic viability of different GNR edges. Preliminary results seem to show that stoichiometrically favourable configurations, such as S-O co-doped edges, are more energetically stable than S-doped edges, contrary to what has been shown in the literature [3].

Further insight on these nanostructures is key to fully understand their structure, behaviour and possible future applications.

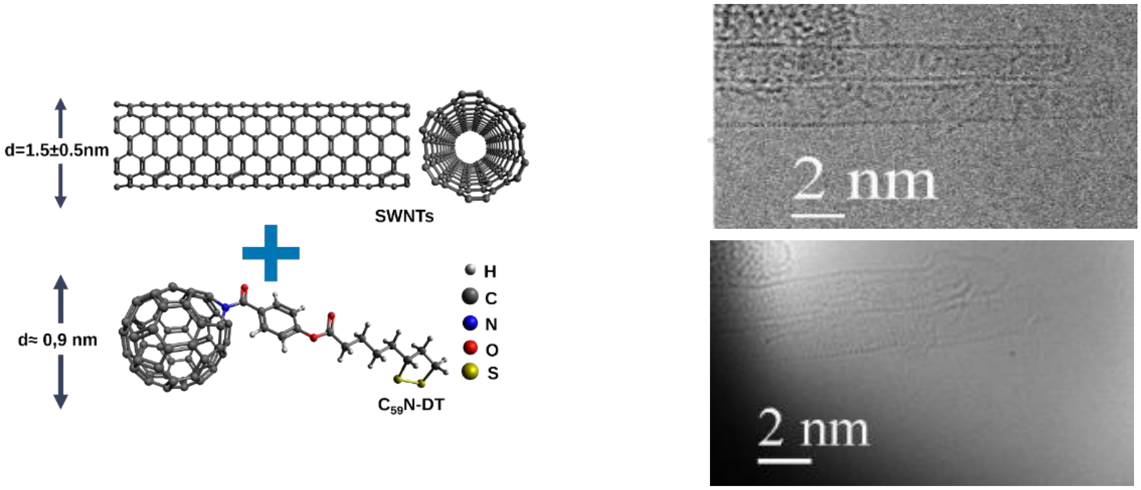

*Figure SEQ "Figure" * Arabic 1 – Left: structure of the different components of the DT-C_{59}N@SWNT. Right: TEM images of DT- C_{59}N@SWNT before (top) and after (bottom) irradiation, showing the formation of*

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Carbon nanostructures towards metal-free photocatalysis

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The advancement of low-cost photocatalysts from abundant materials is one of the key stepping-stones towards the development of hydrogen as renewable and sustainable energy vector [1]. The use of ZnO or TiO_2 as semiconductors coupled with sensitizers such a metal-organic framework [2] or SnO_2 [3] have shown great promise towards this endeavour. Nonetheless, the ultimate goal is a metal-free catalyst completely based on carbon materials.

For this, the initial step consists on using use of carbon-based sensitizers instead of metallic ones. In this sense, nanoscale carbon materials (Fig. 1a) such as graphene quantum dots or polymeric carbon dots [4] have risen as ideal candidates owing to their easy processing and tunable properties.

Similarly, the metal-based semiconductors can be fully substituted for conducive polymers such a poly(3-hexylthiophene) (P3HT) or poly(3,4-ethylenedioxythiophene) (PEDOT). Their operation is critically dependent on the aggregate structure of their polymeric chains, which determines the dominant charge transfer pathway. Careful tuning of this aggregate structure and its influence on the operational behaviour of these conductive polymers can be achieved by integrating them with planar carbon nanomaterials such as graphene oxide [5] or carbon nitride. These planar materials provide an ideal conductive platform upon which the properties of the polymer can be tailored while drastically improving the charge transfer of the photocatalysts. Thus, it is possible to obtain metal-free, carbon-based efficient photocatalysts enable by the presence of these planar carbon nanostructures.

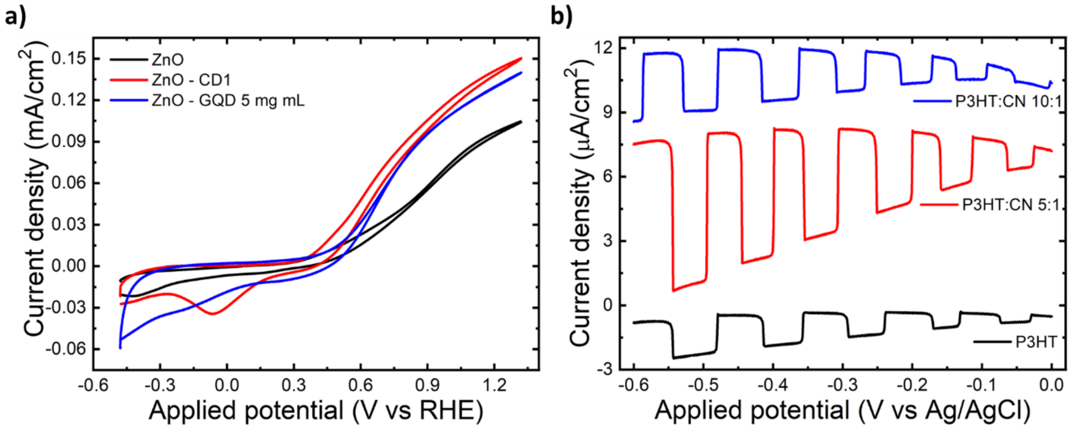

Fig. 1. *Photoelectrochemical response of* ***a)*** *CD/GQD sensitized ZnO nanowires and* ***b)*** *P3HT:CN hybrids.*

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Acknowledgements: Financial support from Spanish MICINN/AEI under projects Margarita Salas RSU.UDC.MS21, PID2019-104272RB-C51/AEI/10.13039/501100011033 and the regional Government of Aragón under project DGA T03_20R (Grupo Reconocido) is acknowledged.

Charge distribution and dynamics of graphene oxide characterized with Kelvin Probe Force Microscopy

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Pristine GO has a non-stoichiometric, disordered structure where both sides of the carbon basal plane are randomly and inhomogeneously decorated with oxygen functionalities that locally change the characteristic graphene sp^2 hybridization to a sp^3 one. It is precisely the inherent functionalization-induced disorder, and the singular sp^2 and sp^3 bonding distribution what confers GO its unique electronic and optical properties. The facility of tailoring these properties, controlling the oxidation degree and the functional group chemistry, together with the possibility of being processed from aqueous solutions, makes GO an attractive new “green” platform with application in a large variety of fields, ranging from optoelectronic, energy storage, biophysics, biomedical or catalysis

Here, we resolve the GO charge distribution as well as the charge dynamics of individual flakes by means of Kelvin probe force microscopy (Figure 1 (a)-(c)) [1]. Experimental measurements are compared with “electron glasses” theoretical simulations, allowing us to verify the existence of slow relaxation times as well as fast fluctuations, confirming the presence of different timescales within the material [2]. Furthermore, we are able to resolve individual charge domains with a charge of around ± 1e and with a radius of about 25 nm, which is of the order of the correlation length of electrons in the material (~15 nm). The observed correlation length is larger than the localization length of electrons in the material and as such, Efros-Shklovskii conduction is expected to take place [2]. In addition, we performe out of equilibrium charge injection experiments. Monitoring the charge spread evolution together with theoretical modeling, we explore GO’s conducting properties.

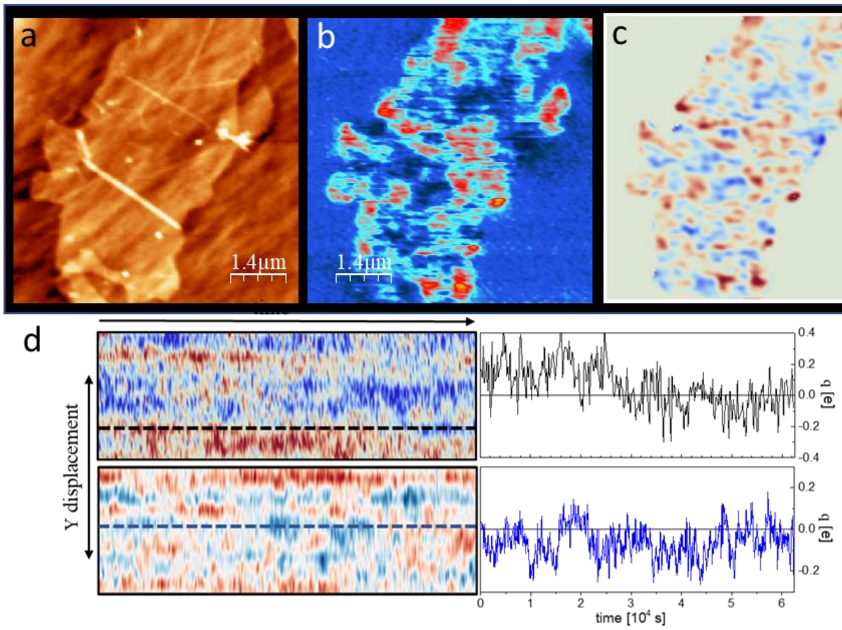

Figure 1: Individual GO flake a) topography b) surface potential distribution, c) real charge distribution .d)) experimental and simulated charge time evolution

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Chemical and structural TEM analyses on carbon and related nanomaterials - 3D information: what for?

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Carbon and related nanomaterials are very promising nanostructures for potential applications due to their attractive electronic, optical and mechanical properties (among others). Transmission electron microscopy (TEM) techniques (structural and analytical modes) have provided major advances in the study of these materials, including, very rich information at the atomic scale [1]. Among these TEM techniques, electron tomography offers the possibility of the 3D investigation of the nano-world. In this contribution, I will present a selection of recent works concerning the 3D study of the atomic structure & configuration of carbon and related nanostructures [1-7]. These works will illustrate the excellent capabilities offered by electron tomography for getting a full knowledge of the morphology, structure and composition of these nano-objects in three dimensions.

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[5] We acknowledge the collaboration of different groups: O. Ersen (IPCMS, France), F. Peiro & S. Estrade (U. Barcelona, Spain) and F. de la Peña (U. Lille, France).
[6] Funding from the following institutions & programs is acknowledged: Spanish MICINN (PID2019-104739GB-100/AEI/10.13039/501100011033), Government of Aragon (project DGA E13-20R) and EU-H2020 “Graphene Flagship” (881603), “ESTEEM3” (823717), MSCA-Promises (889546) and Margarita Salas (MICINN).

Chemical functionalization of 2D materials

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Abstract:

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

Keywords: 2D materials; chemical functionalization; organic chemistry

Acknowledgement

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Colloidal stability over months of highly crystalline hydrogenated nanodiamonds in water

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Two main processes are used to synthesize nanodiamonds (NDs): (i) by detonation (DND) giving rise to 5 nm mono-dispersed but highly defective nanoparticles, or (ii) by milling of bulk diamond (natural or synthetic) into polydispersed nanoparticles (MND). The latter preserves the crystallinity of bulk diamond and similar semi-conductor properties suitable for energy related applications. Able to host NV or SiV color centers, these MND are also currently under study for nanomedecine or quantum applications[1]. These applications imply a fine control of colloidal properties, especially for a hydrogenated surface chemistry. Hydrogenated DND colloidal stability is well understood but its hydrogenated MND counterpart still needs further comprehension for stability over time.

In this study, MND synthesized from HPHT diamonds were successfully hydrogenated using different conditions. Hydrogen treatments were performed at high annealing temperature up to 750°C, and under hydrogen pressures ranging from 10 to 1000 mbar. Moreover, their colloidal stability and spatial organization were monitored over a 2 months period.

FTIR and XPS measurements showed the optimal hydrogenation conditions to minimize the carbon/oxygen bonds and sp^2/amorphous carbon at MND surface. HR-TEM images display clean crystalline particles with sharp edges. The colloidal stability was studied through DLS and zetametry and the spatial organization of the particles through Cryo-TEM. The latter revealed a particular formation of chain-like structures extending over micron range only for hydrogenated MND. Furthermore, the residual amount of sp^2 carbon at the surface, the role of the facets and the evidence of a surface conductivity are discussed to tackle the reasons for the H-MND colloidal stability.

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Continuous, macroscopic fibres of carbon nanotube intercalation compounds

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This presentation describes progress on the synthesis and study of continuous fibres of carbon nanotube intercalation compounds (CNTIC). They consist of macroscopic, continuous fibres of aligned carbon nanotubes with intercalated species ordered between the CNTs, forming long-range domains of periodic intercalation of $FeCl^3$ or Br, respectively.[1,2] The first part focuses on the determination of their structure through direct imaging by HRTEM and 2-dimensional X-ray (wide-angle X-ray scattering), as well as DFT simulations. This analysis shows the importance of CNT polydisperisity and bundling to form CNTICs, and the lack of commensurability between the graphitic surfaces and the intercalate lattice.

The introduction of either of these intercalants involves electron transfer from the CNTs to the intercalant, observed through various spectroscopic methods, which increases the density of free carriers in the CNTs. As a consequence of intercalation the bulk fibre electrical conductivity increases by up to an order of magnitude, approaching the level of copper or aluminium on a mass basis. Through low-temperature transport measurements we show that this improvement is largely due to the intercalate reducing the tunneling-dominated resistance associated with transport between adjacent CNTs, rather than exclusively acting as a dopant that increases CNT conductance.

Finally, this work demonstrates that by preserving the separation between CNTs, intercalation of small species retains the exceptional mechanical properties of the CNT fibre host. The combined tensile strength above 2.46 GPa, conductivity of 10.68 MS/m and density of 2.34 g/cm^3, makes intercalated CNT fibres attractive lightweight conductors with combined properties superior to metals and graphite intercalation compounds.

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Diameter-dependent single- and double-file stacking of squarilium dyes inside single-wall carbon nanotubes

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By using the structure and size as a tunable parameter, novel nanohybrid materials can be designed in which the functionalities of the individual building blocks couple and yield new, fundamentally different properties. Particularly interesting in this perspective are single-wall carbon nanotubes (SWCNTs), that allow to tune the dimensions of such supramolecular assemblies into one dimension. The filling of SWCNTs with dyes has therefore become a novel path to add and create new functionalities through the mutual interaction between the confined dyes and host SWCNTs. In particular cases, the encapsulated dyes form strongly interacting molecular arrays that result in severely altered optical properties of the dyes.[1-3]

In this work we report the combination of such dye-filled SWCNTs with extensive diameter sorting of the large-diameter, filled SWCNTs[4], leading to the isolation of nearly single chirality dye-filled SWCNTs as shown in the photoluminescence-excitation (PLE) maps presented in Figure 1.

For each dye@SWCNT combination we observe a different absorption wavelength of the confined dyes, originating from the different dye stacking driven by the diameter of the surrounding SWCNT. This diameter-dependent dye absorption is experimentally determined through the measurement and detailed fitting of PLE maps of different chirality-sorted dye-filled SWCNT samples, where for each dye@SWCNT combination a different energy transfer peak is observed.

Combined with a simple molecular model of dye stacking inside a cylinder with a particular diameter, we demonstrate that the diameter of the SWCNT is a lever to tune optical properties of the hybrids, paving the way for future applications in optoelectronics. The comparison with molecular models provides access to the possible different stacking configurations of the dyes inside the hollow space of SWCNTs with different diameters.[5]

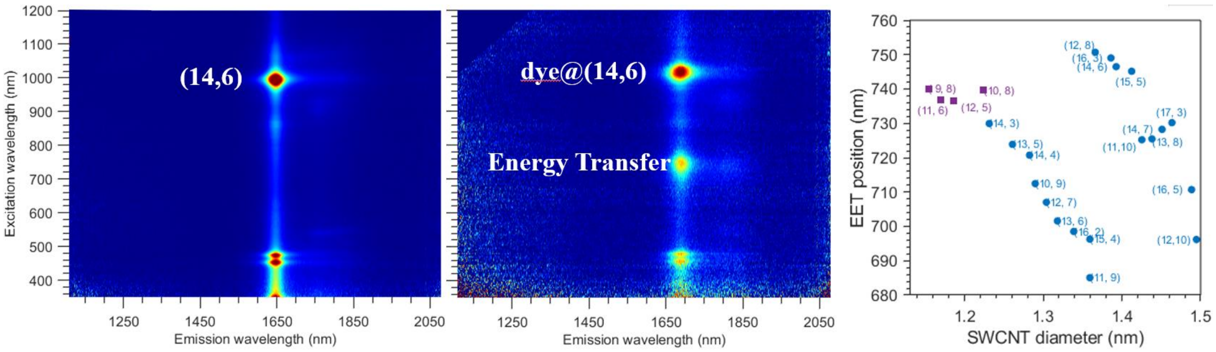

Figure 1 Example PLE maps of (left) an empty (14,6) SWCNT and (middle) a dye-filled (14,6) chirality, clearly showing the energy transfer peak. (right) dye energy transfer absorption wavelength for different SWCNT chiralities as a function of SWCNT diameter.

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Electronic properties of twisted multilayer graphene

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Around specific magic twist angles, twisted multilayer graphene exhibit correlated insulating phases and superconductivity, thus boosting the new field of "twistronics" where strong electron-electron interactions play a dominant role on its electronic properties.

In this work, atomistic calculations using the Green's function techniques are developed to solve the tight-binding Hamiltonian for low-angle multilayer graphene, whose atomic structures have been previously optimized [1].

Below a threshold twist angle θ_c~1.1°, the twisted bilayer graphene superlattice undergoes lattice reconstruction, leading to a periodic Moiré structure which exhibits a slight-corrugation that is found to strongly modify both its electronic structure [2] and its vibrational properties [1,3].

In twisted multilayer graphene [4], the dependence of the local electronic properties on the twist angle and on the stacking configuration are also investigated in order to fully taking into account atomic reconstruction effects.

At last, the moiré superlattice formed by a bilayer graphene aligned with boron nitride (*h*-BN) is investigated [5]. Although this superlattice should inherit from the hexagonal lattice a 60° periodicity with the layer alignment, the symmetry is found to be broken between the 0° and 60° alignments, creating non-identical moiré twins with different electronic properties.

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EMPLOYING REDOX-ACTIVE ADDITIVES FOR ENHANCED CHARGE POLARIZATION AND 200 % HIGHER ENERGY DENSITY IN SUPERCAPACITOR

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Achieving high energy density and power density has been the holy grail of energy storage devices. This mutual tradeoff is all the more challenging in solid-state devices where the dynamics of ion migration through solid-state electrolytes become an important bottleneck for achieving both high energy storage and high-power delivery. Here, we demonstrate the use of a redox-active additive in the form of sodium molybdate (Na_2MoO_4, i.e., NM) into a polymeric gel-electrolyte combination of methyl-cellulose (MC) as the matrix and 1-Butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide [BMI][TFSI] as the ionic conductor. The inclusion of sodium molybdate results in a two-fold increase of specific capacitance (0.009 F/cm^2 to 0.018 F/cm^2), along with significantly improved polarization and charge transport at the solid-solid electrode-electrolyte interface. This provides a 200 percent upgrading in energy density (0.76 µwhcm^{-2} to 1.7 µwhcm^{-2}) without compromising power density (160 Wcm^{-2}) and long-term cycling stability (nearly 2.5-fold increment in cyclability and 93% retention over 10,000 cycles). The existence of the electrochemically active center ($Mo^{4+} \leftrightarrow Mo^{6+}$) with Na^+ in the transport channel of ionic liquid enables charge relay and hopping-based charge transfer leading to lower charge transfer resistance (R_{ct}) and enhancing the ionic conductivity by five times. This favorably accomplishes the five times lowering of relaxation time constant (τ = 2.7 s to 0.96 s) as well as high scan rate operability up to 10 V/s. Notably, the supercapacitor's power density and non-Faradic charge storage remain unaltered, resulting in performance that outperforms numerous solid-state and liquid electrolyte-based supercapacitors. Electrode materials also play an important role in controlling the power-delivering capacity of the supercapacitor. Here three-dimensional hard-carbon-based nanocarbon florets (NCF) with high accessible surface area (950 m^2/g), graded porosity (5 nm average pore size), and through-plane electrical conductivity (50 S/cm) function as an excellent solid-state supercapacitor electrode. The elegantly designed marigold-like shape with continuous, open-ended channels extending outward from the center promotes quick ion diffusion and works in concert with its chemical characteristic to function as an excellent capacitive electrode. This solid-state supercapacitor integrates the advantage of redox active additive (Na_2MoO_4) with the randomly distributed turbostratic graphitic domains of NCF, establishing a strong structure-property-performance relationship for hard carbon (*Figure 1*).

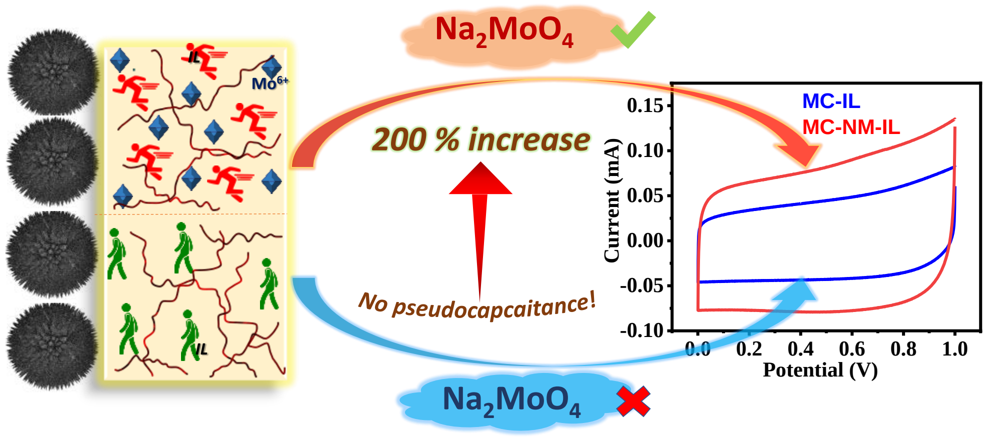

Figure 1: Schematic to explain two hundred percent enhancement in the supercapacitor performance

ENERGY TRANSFER FROM ENCAPSULATED STRUCTURES TO CARBON NANOTUBE HOSTS

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The advances on the science and application of carbon nanotubes within the last three decades have brought to reality the production of materials approaching the theoretical predictions. Single-walled carbon nanotubes (SWCNTs), in particular, have outstanding electronic and optical properties. For instance, enhancing the photoluminescence of SWCNTs can bring to reality more than one ground breaking application in fields like biology and optoelectronics. However, the optical properties of these materials are strongly related to their morphology and intrinsically to their diameter. A potential way to gain control of properties like PL is the encapsulation of molecules or nanostructures in the tube´s hollow core but there are very small diameter tubes where this is not straightforward. In this presentation, I will show how new hybrids composed by SWCNTs and confined linear carbon chains have been developed inspired on the possibility to extract SWCNTs from their double-walled counterparts. We will discuss the optical response of these materials and I will describe how a diameter-dependent enhancement of the PL induced by energy transfer can be induced. Also, graphene nanoribbons with a defined chirality will be in the focus of this presentation and we will see how to study their specific Raman active modes independently from non-encapsulated fragments of ribbon-like molecules.

Engineering of quantum states in atomically precise graphene nanostructures

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Graphene provides an ideal platform to tune its electronic properties by rational control of its nanoscale structure. Quantum confinement effects in graphene nanoribbons for example can be exploited to tune their electronic band gap and specific edge and hetero-junction topologies can lead to localized in-gap sates showing π-electron magnetism. However, atomically precise synthesis of these graphene-derived nanostructures is the key to fully control their electronic properties.

Here, I will briefly review the concept of on-surface synthesis as a versatile tool to create nanographene materials previously inaccessible via wet-chemistry routes due to insolubility or reactivity of the final structures. Next, I will discuss the concept of localized topological states in GNRs, which can occur at their ends, hetero-junctions or edge extensions. By creating well defined periodic sequences of these topological electronic modes, one-dimensional electronic bands can be created, which are described by the Su-Schrieffer-Heeger (SSH) Hamiltonian representing the dimerized atomic chain [1]. A strategy to realize small-band gap 1D GNR and polymers using the concept of a topological phase transition in a GNR structure family as well as their experimental realization and characterization by scanning tunneling microscopy and spectroscopy of such chains will be presented [2,3]. Finally, I will discuss the magnetic properties of localized π-electron states [4,5].

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Epitaxial growth of transition metal dichalcogenide monolayers and heterostructures for large area device applications

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Wafer-scale epitaxial growth of semiconducting transition metal dichalcogenide (TMD) monolayers such as MoS_2, WS_2 and WSe_2 is of significant interest for device applications to circumvent size limitations associated with the use of exfoliated flakes. Epitaxy is required to achieve single crystal films over large areas via coalescence of TMD domains with the same crystallographic direction.

The prospects and challenges associated with the epitaxial growth of wafer-scale TMD monolayers and heterostructures for the development of large area 2D devices will be discussed. Metalorganic chemical vapor deposition (MOCVD) has emerged as an enabling growth technology for TMDs due to its ability to achieve a combination of high growth temperatures ($>700^{o}C$) and large chalcogen overpressures which are needed to obtain stoichiometric epitaxial films. The unique aspects of van der Waals epitaxy of TMDs on sapphire substrates will be presented including the effects of crystallographic orientation of the substrate on nucleation density and domain orientation and the role of surface passivation and steps on domain alignment and defects. Techniques for wafer-scale 2D layer transfer for device integration will be reviewed and applications for wafer-scale TMD monolayers in nanoelectronics, sensing and photonics will be presented.

Fe doped 1T/2H MoS_2/reduced graphene oxide for hydrogen evolution reaction

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Abstract

The metallic-phase 1T-MoS_2 has received broad concern in hydrogen evolution reaction (HER) due to its good conductivity. Here, we synthesize Fe-doped molybdenum disulfide/reduced graphene oxide (Fe-MoS_2/rGO) composites with high 1T-MoS_2 content as HER catalyst via a facile hydrothermal process. Fe atoms are successfully doped into MoS_2 crystal lattice, causing partial phase transition from 2H to 1T. Meanwhile, well-dispersed vertically aligned petaloid-like 1T/2H-Fe-MoS_2 nanostructures are in-situ grown on the surface of rGO, increasing the specific surface area and providing extra electrical conductivity. Because of the unique morphology, existence of 1T metallic phase and intimate integration with rGO, the 1T/2H-Fe-MoS_2/rGO composites present excellent HER activity and persistent stability, providing a low overpotential of 197 mV at 10 mA cm^{-2} and a Tafel slope of 53 mV dec^{-1}. The result offers a new phase engineering strategy for designing 1T-MoS_2 based electrocatalysts for increasing HER activity.

Graphene-based Conformal Coating: How to Avoid Hot Spots?

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A printed circuit board (PCB, Figure 1a) is an essential component of nearly all forms of commercial electronics, where conformal coating over the PCB and the attached electronic components is widely used to protect the electronics from the external environment, e.g., moisture, dirt, electromagnetic interference (EMI) and thermal stresses. The highly dense electronic components in modern PCBs result in elevated operating temperatures (hot spots) that directly affect the performance of the device, i.e., reduced operation speed and life-time shortening. Conventional heat removal solutions (e.g., metal-based heat sinks) may partially solve the heat accumulation challenge, but are heavy and large, and do not provide shielding against shocks, vibrations and corrosive agents for the electronic devices when located outdoors. Heat can be removed by coupling the heat source (resistor) to thermally conductive *polymer composites*, as a replacement for the *metallic* heat-sink when lighter weight and easier processing (workability) are required. Unfortunately, polymers possess low thermal conductivity (TC, ~0.2 W $(m K)^{-1}$) and hence cannot provide heat dissipation. Our approach is to employ the existing conformal polymeric coating approach as a platform for solving heat dissipation by loading it with high conductivity filler(s) to form a composite, i.e., graphene nanoplatelets (GnP, Figure 1b) and boron nitride nanoplatelets (BNNP). The GnPs contribute significantly to the TC of the composite while BNNP inhibit the electrical conductivity to avoid short circuits. We showed that GnP-based conformal coating **reduced the hot spot temperature drastically (~30°C)** by increasing the TC of the coating. The use of a commercially available polymer material, GnP, and BNNP, along with a simple but highly effective dispersion method, constitutes a timely and relevant approach for thermal management applications.

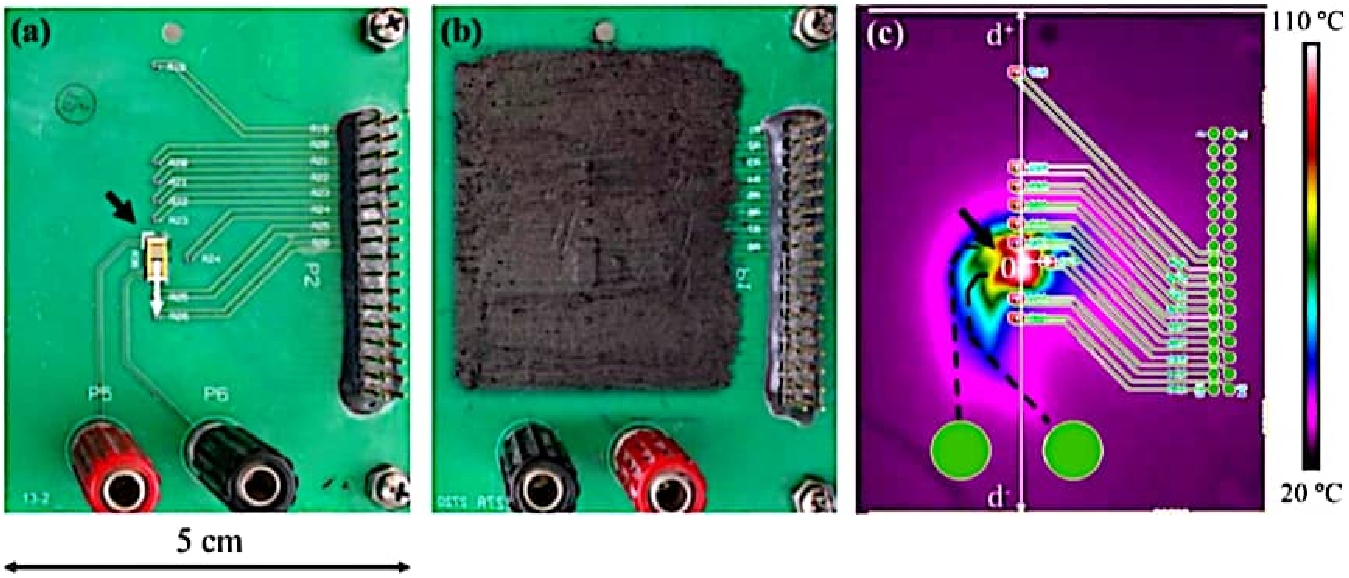

Figure 1. A floating resistor (black arrow) model PCB: (a) uncoated, a white arrow indicates the distance of temperature indicators from the hotspot, (b) conformally coated with GnP-loaded (15 wt%) acrylic-based composite. (c) IR temperature map of pristine PCB (filler-free). The power is supplied by the sockets in the lower part of the PCB model.

GRAPHENE OXIDE: MORE SURPRISES

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Graphene oxide (GO) is a fascinating nanoscale building block. Its electronic properties are essentially controlled by the presence of different types of oxygen functional groups on the basal plane of individual GO sheets, as studied by a broad set of electron microscopy studies [1-3]. Furthermore, charge domains and charge interactions, accompanied by short range fluctuations of jumping electrons and long-term relaxation times, observed by Kelvin Probe Force microscopy [4], reveals hopping transport between charge domains, typical for an electron glass. Despite its electrically insulating nature, its ease of processing in aqueous dispersions, offers unique possibilities to establish novel nanohybrid materials with highly promising and superior charge-transfer interface interactions of great interest for the development of optoelectronic device structures [5-8]. In this presentation we will provide insights on our latest findings on the extraordinary and still surprising behavior of graphene oxide.

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Graphite-GnP-salt composite: Thermal properties enhancement for energy storage applications

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Thermal energy storage is required in the renewable energy field due to the increasing global demand for energy, alongside finite available resources of fossil fuels. Thermo-solar energy is stored during daytime and used at night. The storage principle of phase change materials (PCM) is based on the heat of fusion and solidification-melting transitions of PCM, e.g., salts, which demonstrate high thermal energy storage density. Salts are also completely green compared to fossil fuels, and are already integrated in existing industrial systems, such as thermo-solar power plants. However, the thermal conductivity of *salt* - crucial for the energy storage process - is rather low (<1 W/mK). We aim at enhancing its thermal conductivity by loading it with high thermal conductivity fillers, such as carbon-based materials, such as graphite, leading to the formation of a composite. We found that the molten salt treatment exfoliates the graphite to graphene nanoplatelets (GnP, <100 nm thick), hence enhancing the thermal conductivity of the salt-based composite.[1] The exfoliation of graphite in molten NaCl–KCl salt (@750 °C) yielded a homogeneous composite, from which salt-free GnP could be easily and completely separated. The produced GnP displayed relatively large-size particles (12 µm, TEM, SEM, laser diffraction) and low defect density (Raman, XPS), indicating the superiority of the molten salt approach over conventional liquid-phase exfoliation. Moreover, the large-size and low defect density GnP obtained in the molten salt are directly applicable in enhancing the thermal properties of the composite: in the GnP-salt composite, the thermal conductivity is enhanced by more than one order of magnitude (up to ~44 W/mK, Figure 1a, squares) compared to the neat salt matrix (~0.6 W/mK, Figure 1a, diamond). Our developed GnP-loaded molten salt could be used as a high thermal conductivity PCM for high-temperature thermal energy storage applications, where the filler is both produced and directly dispersed in the salt matrix (Figure 1b).

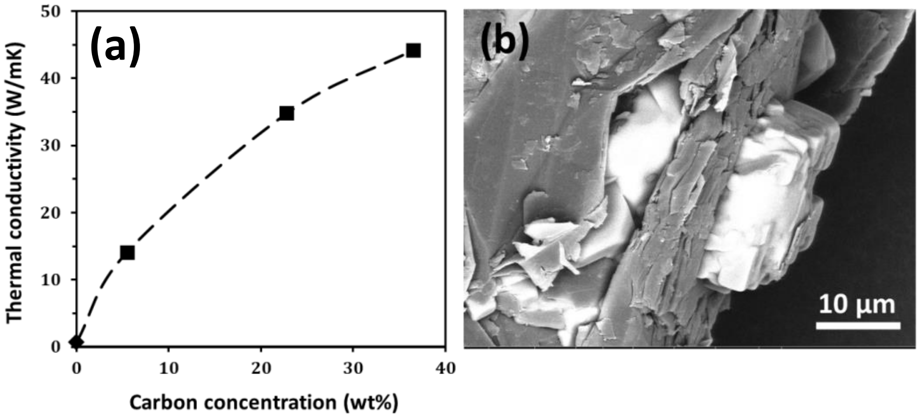

Figure 1. (a) Thermal conductivity of the graphite-GnP-salt composite loaded with various initial graphite concentrations in NaCl–KCl salt. Diamond - neat salt. The error bars are smaller than the marker size (b) SEM micrograph of the composite, where salt crystals (white) exfoliate the graphite.

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Greener Approach towards Rapid Water Evaporation and Space Heating with Nanostructured Hard-Carbon

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Solar-thermal based water evaporation has currently gained wide attention since it utilizes green energy to address challenges based on water-energy nexus. Solar-thermal conversion has been highly dependent on the material and the technologies utilized. So, recent development in material aspect for thermal management gives us an opportunity to deal with water crisis occurring globally in a most sustainable manner. For effective usage of solar energy, a material with high broadband absorption (200-2500 nm) ability is needed. Herein, a new three dimensional dendritic porous hard-carbon material developed via template-driven approach called Nanostructured Carbon Florets (NCF) is introduced which by morphology resembles a marigold flower. They exhibit open-ended lamellae originating from the center, where each lamella behaves as an optical microcavity and intrinsic structure depicts presence of both short-range order and long-range disorder. The conical architecture of each lamella can undergo multiple internal reflection leading to broadband absorption while the hard-carbon arrangement effectively leads to high solar-thermal energy conversion via phonon-induced photon thermalization. The thermal conductivity being lower prevents heat dissipation which in-turn causes effectual heat delivery. The synergistic combination of both the property drives the solar-thermal based water evaporation in an expeditious manner. The coating of arbitrary substrate with the NCF via easy spray-coating technique has bring out its versatileness to study space-heating application.

Hyperspectral Detection of the Fluorescence Shift between Chirality-Sorted Single-Wall Carbon Nanotube Enantiomers

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Abstract: Single-wall carbon nanotubes (SWCNTs) have remarkable chirality-dependent optical and electronic properties, which are very sensitive to any interaction with their surrounding and inner environment. For instance, the fluorescence (PL) of the SWCNTs will redshift depending on the filling of the SWCNTs [1,2]. While this sensitivity to the environment could be highly applicable in ultrasensitive sensor applications, these interactions are not identical for different SWCNT chiralities, and it is difficult to resolve them on an ensemble level due to a comparable inhomogeneous broadening and magnitude of these shifts. Therefore, a technique is needed that can study SWCNTs at a single-tube level, yet at the same time allowing for sufficient statistics on multiple SWCNTs to be simultaneously acquired. Here, we present a hyperspectral fluorescence microscopy setup that is capable of both spatially and spectrally resolving the PL along the length of individual SWCNTs [2]. Moreover, we combine this setup with automated SWCNT structure recognition through principal component analysis to acquire information from thousands of individual tubes to obtain a statistically significant data set for further analysis. With this setup not only can we determine the water-filling-induced redshift in PL for individual SWCNTs and study its inhomogeneity across different SWCNT species but we can also study the shift in PL for left- and right-handed SWCNTs. This shift, which is otherwise inaccessible on the ensemble level, arises from the different interaction of both enantiomers with the chiral surfactant that is used to solubilize the SWCNTs.

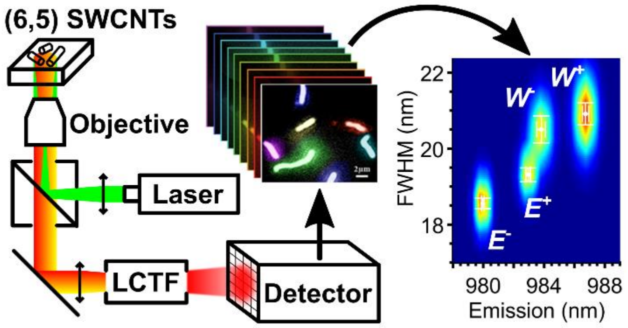

Figure1. A laser excites the SWCNTs and the emitted PL is hyperspectrally projected on a 2D detector by a tunable filter with each pixel containing a PL spectrum.

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Inorganic nanotubes: From WS_2 to "misfit" compounds

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Update on the synthesis and characterization of new inorganic nanotubes from 2D compounds, like $W(S,Se)_2$ [1] will be given. The strong coupling between optical cavity modes confined in the nanotube and the exitonic transitions have been studied in some detail [1,2]. Virtually recently, an “artificial recording eye” combining vison, storage and writing power has been established by a 4x4 array of WS_2 nanotubes. [3] Recent progress in mechanically reinforcing different polymers, will be briefly discussed. Different nanotubes from quaternary “misfit” layered compounds (MLC) have been realized in recent years. In one recent case, the strong chemical affinity of the RE atoms towards sulfur atoms and that of selenium towards the tantalum atoms, led to the synthesis of highly anisotropic nanotubes, like RES-$TaSe_2$ and RE-$(TaSe_2)_2$ (with RE=La, Sm) with extremely large (local) dipole moment. [4] Such nanotubes offer unique behavior, like 1D superconductivity, etc., suitable for quantum technologies. Generally speaking, nanotubes like any other nanoparticles, are a metastable phase. The mechanism of nanotubes decomposition at elevated temperatures will be discussed in brief.

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Mid-infrared electrochromics enabled by intraband modulation in carbon nanotube network

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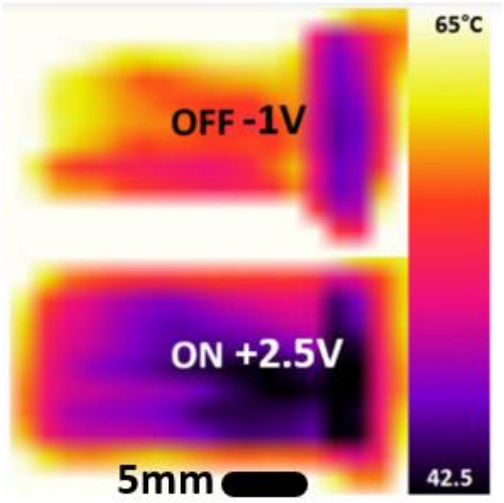
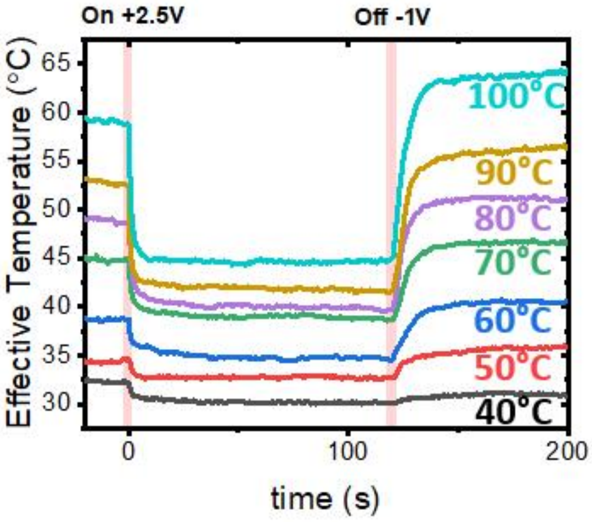
Tuneable infrared properties, such as transparency and emissivity, are highly desirable for a range of applications, including thermal windows and emissive temperature control. Here, we demonstrate the use of spray deposited carbon nanotubes networks spray deposited either side of an ionic liquid-infused membrane to fabricate devices with electrochromic modulation in the mid-infrared spectrum, facilitating control of emissivity and apparent temperature. Such modulation is enabled by intra-band transitions in unsorted single-walled carbon nanotube networks without the need for purification, allowing the use of scalable nanotube inks for printed devices. These devices are optimised by varying film thickness and sheet resistance, demonstrating emissivity modulation (from ~0.5 to ~0.2) . These devices and understanding thereof opens the door to selection criteria for infrared electrochromic materials based on the relationship between band structure, electrochemistry, and opto-thermal properties to enable the development of large-area solution-processable large-area coatings for widespread thermal management applications.





Multi-scale analysis of epitaxially grown TMDs using 4D-STEM

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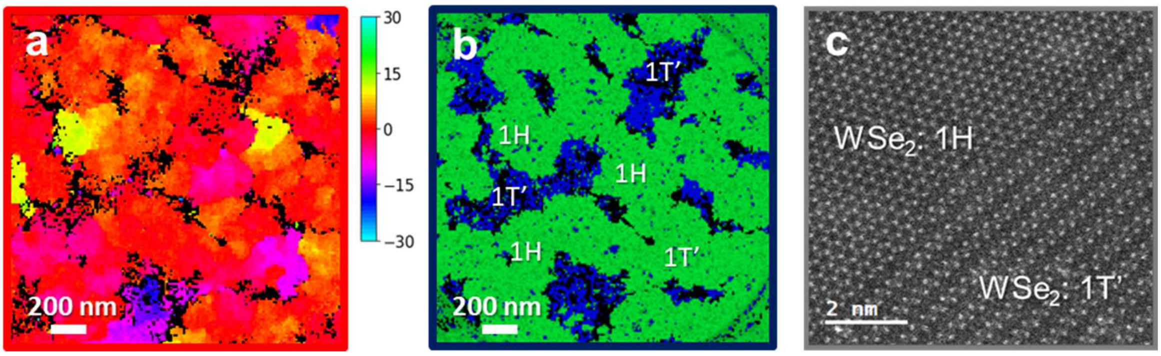
Epitaxial growth is a route to achieve highly crystalline continuous 2D layers. In recent years, wafer scale epitaxial growth of graphene and various transition metal dichalcogenides (TMDs) have been demonstrated by many research groups. However, highly crystalline layer production with expected electrical properties is still challenging due to the absence of covalent bonding between substrate and grown layers. Slight mis-alignement and symmetrical crystal inversion in neighboring nucleation sites result in a large amount of atomic defect structures at the stage of coallescence and which drastically degrades materials quality. The presence of polymorphe, such as 2H and 1T‘ in the TMDs, also modifies their electronic properties. In order to control growth process and to predict properties of grown materials up to wafer scale, multidimensional and multiscale structural analysis should be accessible in routine way. X-ray diffraction (XRD) gives a precise information on material quality regarding the crystallinity and the orientation distribution at mm scale, while scanning transmission electron microscopy (STEM) imaging offers today the capability to study the detailled local atomic structures such as vacancies, grain boundaries as well as the associated chemical composition at atomic scale. However these techniques do not reveal complete material characteristiques because of the gap in scale between the information obtained by different techniques. Four dimensional (4D)-STEM is a new acquisition technique allowing to simultaneously record 2D images in real and recoprocal spaces.[1] Multiple information, from structure to electric field,[2] at different scales can be reconstructed from signals appearing in diffraction pattern acquired at each pixel of the beam scan.

In this work, we demonstrate the use of 4D-STEM to study 2D materials epitaxially grown in both laboratory and industrial scales. Orientation, polarity and phase maps in various TMD monolayers are reconstructed at micron scale and directly correlated with both large scale XRD analysis and related atomic defect structures. In addition, the local electric field around the identified structural anomalies were also investigated at atomic scale by measuring the displacement of the centre of mass (CoM) of the transmitted beam recorded in the reciprocal space. The results show the capacity to construct an overview of synthesized materials from large scale down to atomic scale with multiple information on structure, chemistry and electric character, collected in statistical and quantitative way.



Figures: Example of multi-information mapping: WSe_2 monolayer grown on mica substrate by MBE; (a) orientation and (b) phase maps reconstructed by 4D-STEM and (c) detailed atomic structure at interface between 1H and 1T' phases.

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Nano structures self-assembled at graphite surfaces by ion-beam-irradiation

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Low energy (< 10 keV) ion beam irradiation has proven to be a versatile and facile tool to fabricate various nanostructures at surfaces of most materials, including graphite.[1] If ion beam of noble gases such as Kr is incident on graphite surface with its ion energy (E_{ion}) not enough to form structural defects at surface, some Kr ions still pass through residual defects such as grain boundaries and atomic vacancies at surface and become trapped just below the surface graphene layer. Continued ion beam irradiation leads to the formation of the encapsulated Kr nano bubbles mediated by transient mobility of the trapped ions. (Fig.1a) The density and mean size of the bubbles can be controlled by the ion irradiation time.[2] Encapsulated atoms are expected to have different properties compared with their free counterparts due to the high-pressure environment in GPa range imposed by the modified surface graphene layer and the confinement effects. For example, encapsulated He atoms are found to show 2d superfluidity.[3]

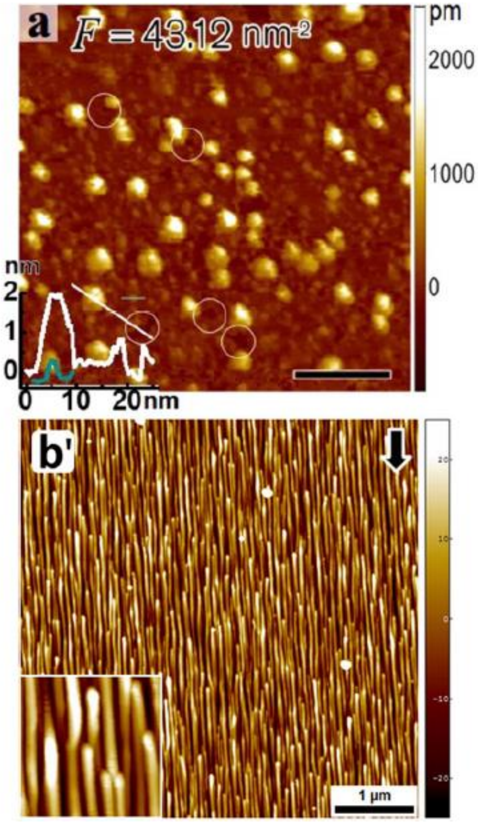

Figure 1a. STM image of Kr nano bubbles encapsulated by a graphene layer.

1b. ripple pattern formed at graphite surface by Ar ion beam irradiation at grazing angle.

If ion-beam-irradiation with E_{ion} large enough to displace surface carbon atoms is extended for several tens of minutes, despite its stochastic nature, nanoscale pattern forms at graphite surfaces. If ion beam is irradiated at grazing angle, the motif of the pattern changes from dot to ripple as irradiation time increases. (Fig.1b) [4] If the substrate rotates during the irradiation, the motif changes from dot to holes.[5] If the substrate azimuthally swings during the irradiation, patterns of hierarchical structures develop.[6] Sizes of the abovementioned motifs are easily scalable by adjusting the irradiation time. Those observations indicate various motifs of pattern can be fabricated by simply varying irradiation conditions, allowing fabrication of carbon nanostructures on demand. The presentation is completed by discussion on the mechanism for the pattern formation.

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Nanotubes from Ternary $WS_{2(1-x)}Se_{2x}$ Alloys: Stoichiometry Modulated Tunable Optical Properties

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Abstract:

Nanotubes of transition metal dichalcogenides (TMDs) such as WS_2 and MoS_2 offer unique quasi 1D properties and numerous potential applications. Replacing sulfur by selenium would yield ternary $WS_{2(1-x)}Se_{2x}$ ($0 \leq x \leq 1$; WSSe) nanotubes, which are expected to reveal strong modulation in their absorption edge as a function of selenium content, x_{Se}. Solid $WO_{2.72}$ oxide nanowhiskers were employed as a sacrificial template to gain a high yield of the nanotubes with a rather uniform size distribution. Though sulfur and selenium belong to the same period, their chemical reactivity with oxide nanowhiskers differed appreciably. Here, the closed ampoule technique was utilized to achieve the completion of the solid-vapor reaction in short time scales instead of the conventional flow reactor method. The structure and chemical composition of the nanotubes were analyzed in detail. X-ray and electron diffractions indicated a systematic modulation of the WSSe lattice upon increasing the selenium content. Detailed chemical mapping showed that the sulfur and selenium atoms are distributed in random positions on the anion lattice-site of the nanotubes. The optical excitonic features and absorption edges of WSSe nanotube do not vary linearly with the composition x_{Se}, which was further confirmed by density functional theory (DFT) calculations. The WSSe nanotubes were shown to exhibit strong light-matter interactions forming exciton-polariton quasiparticles, which was corroborated by finite-difference time-domain (FDTD) simulations. Transient absorption analysis permitted following the excited state dynamics and elucidating the mechanism of the strong coupling. Thus, nanotubes of the ternary WSSe alloys offer strong bandgap tunability, which would be useful for multispectral vision devices and other optoelectronic applications.

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M. B. Sreedahara et al., Nanotubes from Ternary $WS_{2(1-x)}Se_{2x}$ Alloys: Stoichiometry Modulated Tunable Optical Properties, ***J. Am. Chem. Soc.*** **2022**, 144, 23, 10530–10542.

Title: Novel van der Waals compounds and their potential for optical biosensing

Presenter: Shengxi Huang

Abstract:

Emerging 2D van der Waals compounds have gained increasing attention due to their unique electronic and optical properties, and have shown promise in sensing applications. The realization of sensing devices using these materials still faces several challenges. For example, it is critical to gain clear understandings of (1) the fundamental light-matter interactions and their relations to the atomic structures, which govern many key material properties and device performances; and (2) the coupling with other nanostructures and molecules, which is a required structure for sensing devices and systems. This talk introduces new discoveries and pioneering works on these critical challenges, and novel applications of these materials in biochemical sensing. The first part of this talk presents light-matter interactions and techniques to augment material performance, such as 2D Janus transition metal dichalcogenides. The second part of this talk focuses on the interaction of 2D materials with organic molecules and related sensing applications. In particular, a novel enhancement effect of molecular Raman signals on 2D surface was discovered, which offers a new paradigm of biochemical sensing with high specificity, high multiplexity, and low noise. The selection rule for the 2D material substrates has been revealed, which is critical for device design. Two sensing applications for Alzheimer’s disease and respiratory viruses will also be discussed. Overall, the works presented in this talk are significant in fundamental quantum science, and offer important guidelines for practical applications in sensing and quantum technologies. The methodologies used here also provide a framework for the future study of many emerging materials and sensing scenarios.

Photocatalyzed acylation of single-walled carbon nanotubes with tetrabutyl ammonium decatungstate

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In this contribution, we will present the decatungstate-photocatalyzed acylation of semiconducting (7,6)single-walled carbon nanotubes (SWCNTs) by employing alkyl, aromatic and organometallic aldehydes. The success of the newly developed functionalization methodology was confirmed by complementary spectroscopic, thermal, microscopy imaging and redox techniques. We will discuss the mechanism oft he catalytic acylation process by considering the generation of acyl radicals which subsequently add to activated (7,6)SWCNTs by electron transfer from the decatungstate complex (Figure 1). Given the mild reaction conditions required and the vast availability of starting aldehydes, the presented methodology is also considered ideal from the vantage point of industries and can be extended to modify other two-dimensional nanomaterials.

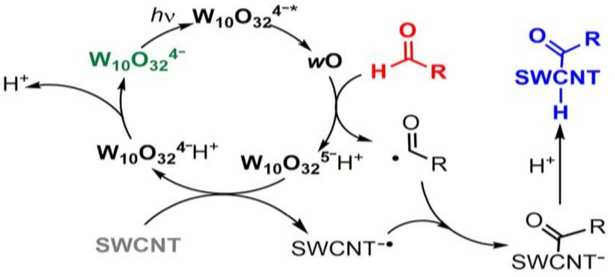

Figure 1. Mechanism of the decatungstate-photocatalytic acylation of (7,6)SWCNTs.

Probing the interaction between 2D materials and tectomers

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Heterostructures of 2D materials such as graphene and MoS_2 exhibit unprecedent optical and electrical properties which enables the fabrication of sensing and phototransistor devices. These hybrid systems are more intriguing when coupling with nanosheets which emulate biomolecules such as oligoglycine self-assemblies (tectomer). It is found that tectomer sheets modulate the physiochemical properties of 2D materials by electrical doping and mechanical straining, opening the avenues for graphene- and MoS_2- based sensor applications for the detection of biomolecules such as DNA-protein complexes. Here we present a systematic approach using Raman spectroscopy to deconvolute the mechanical strain and electrical doping of 2D materials by tectomer adsorption. We also demonstrate functionalised scanning probe technique to understand the interaction and the binding affinity between tectomer and 2D materials. These studies provide insights into attractive soft-chemistry strategies as well as the development of future biochemical and surface sensors.

$PtSe_2$ films grown by molecular beam epitaxy for high frequency optoelectronics

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$PtSe_2$ is a promising 2D material for high frequency IR optoelectronics [1], its bandgap varying from 1.2eV (monolayer) to 0.2eV (bilayer) [2]. We have grown 2D $PtSe_2$ films on sapphire substrates by molecular beam epitaxy. In particular, we studied the impact of the Se flux for a growth temperature of 544°C with/without a post-growth anneal at 704°C on the full width at half maximum (FWHM) of the $PtSe_2$ E_g Raman peak (Fig.1). A small FWHM value is an indicator of crystalline and electronic quality [3]. We characterized the films using grazing incidence X-ray diffraction, transmission electron microscopy and their transport properties were evaluated using Van der Pauw experiments.

To fabricate optoelectronic devices, we synthesized a 15 layers thick $PtSe_2$ film on a 2 inches sapphire substrate. In particular, coplanar waveguides integrating a 4x4 µm $PtSe_2$ channel were realized to perform high frequency photodetection and optoelectronic mixing. The channel was illuminated with a 1.55 µm laser beam modulated in intensity at frequencies varying between 2 and 67 GHz. Our $PtSe_2$ photodetector exhibits a record 3dB bandwidth of 60 GHz (Fig. 2). Moreover, high frequency optoelectronic mixing has been performed and device performances will be compared to those obtained with graphene [4]. These results show that $PtSe_2$ is a highly promising material for high frequency optoelectronics.

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Figures

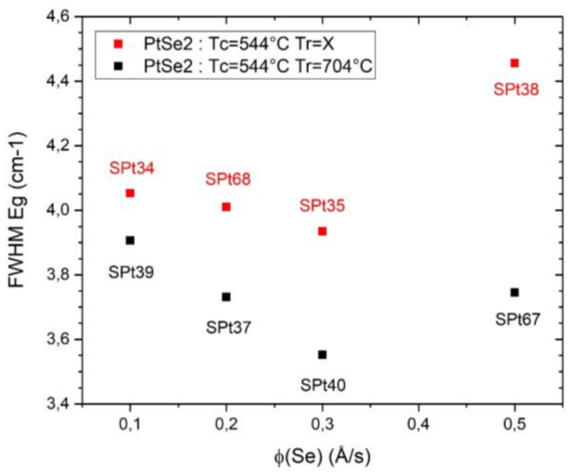

Figure 1: FWHM values of $PtSe_2$ E_g Raman peak for various growth conditions. A small FWHM value is an indicator of crystalline and electronic quality [3]

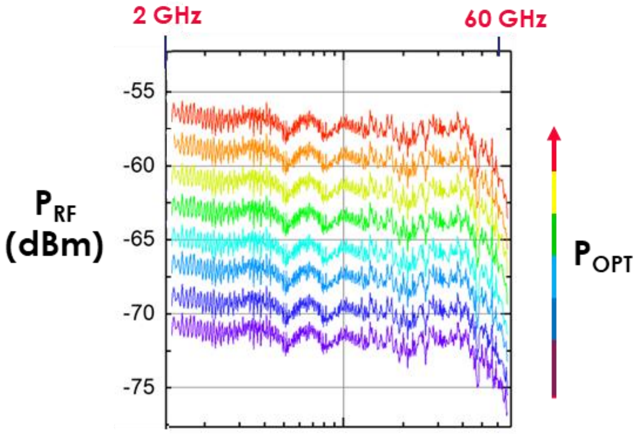

Figure 2: High frequency 1.55 µm photodetection with a $PtSe_2$ channel inserted in a coplanar waveguide. A 60 GHz bandwidth photodetector is demonstrated.

Shaping 1D Nanostructures with Surfaces

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The large-scale assembly of 1D nanostructures, such as nanotubes, nanowires, nanoribbons and nanofins, with controlled orientation on surfaces remains a challenge toward their integration into practical devices. During the last decade, we have reported the growth of perfectly aligned nanotubes, nanowires and nanofins of various materials with controlled crystallographic orientations on different substrates. The growth directions and crystallographic orientation of the nanowires are controlled by their epitaxial relationship with the substrate, as well as by a graphoepitaxial effect that guides their growth along surface steps and grooves. We demonstrated the massively parallel self-integration of nanowires into circuits via guided growth and the production of optoelectronic nanosystems, including phototransistors, photodiodes and photovoltaic cells. Recently developed a kinetic model for the surface-guided growth of nanowires, and tested it by observing their growth in real time under by *in situ* SEM. This talk will present the evolution of surface-guided growth o 1D nanostructures and its future prospects from both fundamental and practical points of view.

Single and multi-layers of alkali metal atoms inside graphene and MoS_2 bilayers as well as their heterostructures: a systematic first-principles study

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Contrary to a wide-spread belief that alkali metal (AM) atoms intercalated into layered materials form single-layer structures only, recent experiments [1,2] provide evidence that multi-layer configurations of lithium are possible. Using state-of-the-art first-principles calculations, we systematically study the intercalation energetics for various AMs (Li, Na, K, Rb, Cs) into bi-layer graphene and MoS_2. We consider not only single- but also multi-layer configurations of AM atoms. We show [3] that, in view of the previous experimental data on lithium, a multi-layer of Na might therefore form, while it is well-known that single-layers of Na in graphitic hosts are energetically very unfavorable. In MoS2, multi-layer structures are considerably higher in energy than the single-layer ones, but the formation of the former can still occur, especially for the AMs with the lowest electro-negativity. As stacking various two-dimensional materials in van der Waals heterostructures is an effective approach to design new systems, we further study heterostructures as host materials which can accommodate AM atoms to tune their electronic properties or store energy. We systematically investigate the intercalation of the most wide- spread AMs (Li, Na, K) into a graphene/MoS2 heterostructure. We assess the intercalation energetics for various concentrations of AM atoms, calculate charge transfer from AM atoms to the host system, and show that although intercalation of AMs as single layer is energetically preferable, multi-layer configurations can exist at high concentrations of AM atoms. Our findings should help to better understand the behavior of heterostructures upon AM atom intercalation and may stimulate further experiments aimed at the tailoring of heterostructure properties and increasing the capacity of anode materials in AM ion batteries.

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SINGLE-WALLED CARBON NANOTUBES CHARGE MANAGEMENT BY CONTROLLED FUNCTIONALIZATION

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Managing the density of charges in carbon nanotubes opens new ways to tune their optical response, their transport properties, and their physico-chemical features. Charge transfer from molecules adsorbed onto the sidewall or filled within the hollow cavity of the nanotubes has already been demonstrated, yet a fine-tunable control of the surface coverage/filling fraction (and thus the amount of transferred charge) remains challenging to achieve. Alternatively, we developed an optically nonperturbing covalent functionalization technique based on the inclusion of a triazine derivative into the carbon network [1]. The nitrogen atom sustaining the attached group becomes an integrated part of the pi-conjugated network and contributes with its lone electron pair to uplifting the position of the Fermi level of the tube. Since the density of attached groups can be varied by adapting the synthetic conditions, this technique offers the advantage of controlling the amount of charge injected into the tubes. Additional groups attached onto the other end of the triazine moiety, moreover, are able to inject charge into the tubes as well. This, for example, allowed us to modulate the photoluminescence of the tubes, switching their emission on and off through the attachment of the switchable spiropyran/merocyanine system [2]. Here we focus on a class of charge-transfer agents that either donate or withdraw electrons depending on the arrangements of their building units [3] and how their decoration affects the properties of the tubes.

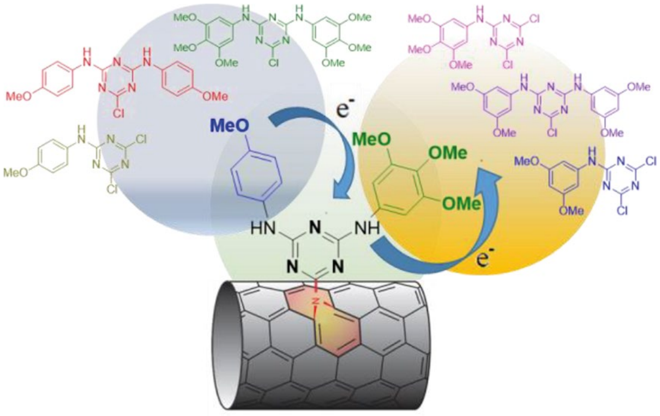

Figure 1 – : Different number of methoxy groups can be attached onto aniline at different positions, resulting in compounds that can either donate or withdraw electrons from the tubes they are attached onto [3].

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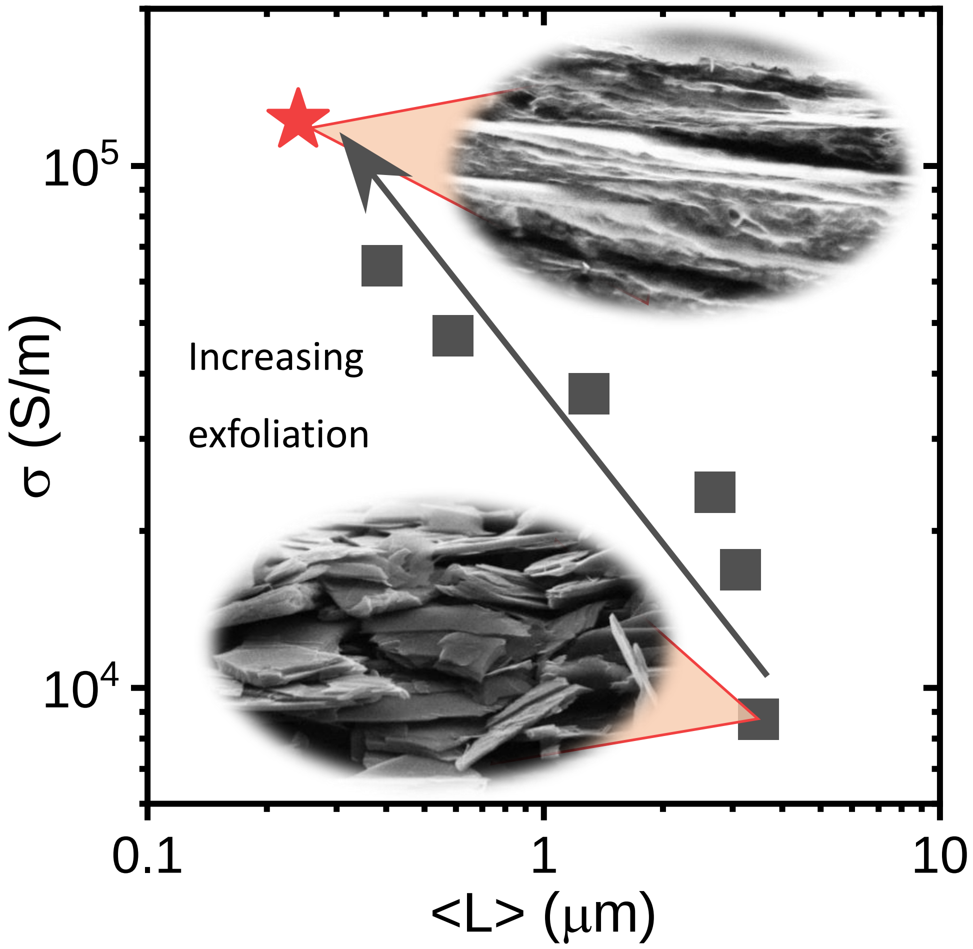
Size-dependent packing in nanosheet networks yields record-high electrical conductivities

Here, it is demonstrated that the size selection of liquid-exfoliated nanosheets leads to high electrical conductivities despite both the surfactant residue within the networks, and the junction effects associated with networks of small nanosheets. Size-dependent electrical conductivity is observed, with the smallest nanosheets of the pristine graphene system achieving a record-high conductivity in excess of 10^5 S/m. Given the high electrical conductivity of these networks despite a high density of inter-sheet junctions (hence a relatively low thermal conductivity), this process shows promise in thermoelectric applications, with a high power factor of 127 $\mu W/mK^2$ realised in these graphene networks. These high values are attributed to the influence of nanosheet packing as it is observed that networks of the smallest nanosheets exhibit the least porosity and display a high degree of alignment. With our understanding of graphene as a model system, we propose that a range of promising materials can be optimised for printed electronics and thermoelectric applications using this size selection approach.



Size-dependent porosity defines conductivity in liquid-exfoliated nanosheet networks

Transition metal dichalcogenides such as molybdenum disulfide (MoS_2) are layered materials of great interest due to their interesting thickness-dependent properties and potential for optoelectronic devices. MoS_2 can be prepared in dispersion by liquid phase exfoliation, size selected by liquid cascade centrifugation and deposited by vacuum filtration, spray deposition and printing techniques. Here, the dependence of the electrical conductivity of MoS_2 nanosheet networks on the average lateral size is investigated. Size-selected dispersions are characterised by statistical atomic force microscopy and UV-visible extinction spectroscopy using established metrics. We find that network conductivity increases as nanosheet size decreases, suggesting that nanosheet packing dominates over the increasing density of inter-nanosheet junctions. The conductivity in the networks of the smallest nanosheets reaches 10^{-3} S/m, a thousandfold increase on that of the larger nanosheets reported in the literature. This conductivity enhancement is understood in terms of nanosheet packing and porosity, enabling their development towards applications in printed optoelectronic devices.

STRONGLY CORRELATED ELECTRONIC GROUND STATE IN THE FLAT SURFACE BAND OF RHOMBOHEDRAL GRAPHITE

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In crystalline solids the interactions of charge and spin can result in a rich variety of emergent quantum ground states. A prime example is twisted bilayer graphene, where measurements have demonstrated the presence of superconductivity, ferromagnetism, and Mott insulator quantum states due to the enhanced correlation effects of the partially filled flat bands. Rhombohedral graphite (RG) is perhaps the simplest and structurally most perfect condensed matter system to host a flat band, which is also protected by the symmetry [1]. In this talk we provide detailed investigation of the flat band in RG by using low temperature Scanning Tunneling Microscopy (STM) measurements combined with electronic structure calculations [2]. We measured the flat surface band of 8,10 and 17 layers of RG at various charge densities and found correlated behavior up to a temperature of 20K. At charge neutrality we also identified a degenerate ground state, forming a competing domain structure between a sublattice antiferromagnetic insulator and a gapless, correlated paramagnet. Our density-matrix renormalization group (DMRG) calculations explained this observation by revealing a degenerate ground state of the system and demonstrate the important role of the correlation effects. Our work establishes RG as a platform to study many-body interactions beyond the mean-field approach, where quantum fluctuations and entanglement dominate.

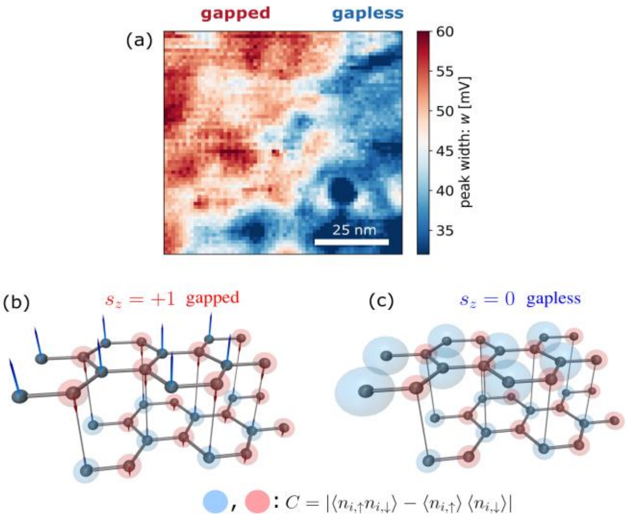

Figure 1 – (a) Gapped and gapless domains measured by STM over an 80×80 nm area of the sample. (b-c) DMRG calculations of the sublattice antiferromagnetic and correlated paramagnetic states. Colored arrows show the distribution of magnetic moments, while the radius of the opaque spheres is proportional to the local electronic correlation C values.

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STRUCTURE AND ELECTRONIC PROPERTIES OF COBALT OXIDE BASED MISFIT NANOTUBES

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One possibility to stabilize meta-stable CoO_2 is by intercalation in misfit-layered compounds (MLCs) [1,2]. Here, we present the in-depth analysis of nanotubes made of Sr,Co,O based MLCs synthesized by a novel method based on a crystal conversion process of bulk material under hydrothermal conditions [3]. In contrast to common synthesis techniques, the nanotubes synthesized by this method are not formed from the pure elements or a parent bulk with the identical structure, but a bulk material with different crystal structure is destabilized and transforms to the desired structure in nanotube form. The resulting product is studied by electron microscopy and spectroscopy and related techniques. The electronic properties of the nanotubes are analyzed in detail on the individual nanotube level. They show a Sr_xCoO_2 – CoO_2 misfit structure, which is Sr-deficient compared to the previously studied MLC [2] and thus are mainly composed of Co and O. EELS and XPS indicate a high valence state of up to Co^{4+}.

The nanotubes possess a high electrical conductivity (1.3 10^4 S cm^{-1}), an extremely high ampacity (10^9 A cm^{-2}) and an extraordinary breakdown power per channel length (P/L 38 W cm^{-1}). The values are highest for inorganic oxide-based materials and compete with hBN coated C nanotubes. These properties make them a highly interesting candidate as interconnect material. [4]

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[4] Funding by the EU's Horizon 2020 MSCA grant agreement No 889546 and "ESTEEM3" (grant # 823717) as well as by the Spanish MICINN (PID2019-104739GB-100/AEI/10.13039/501100011033) is acknowledged.

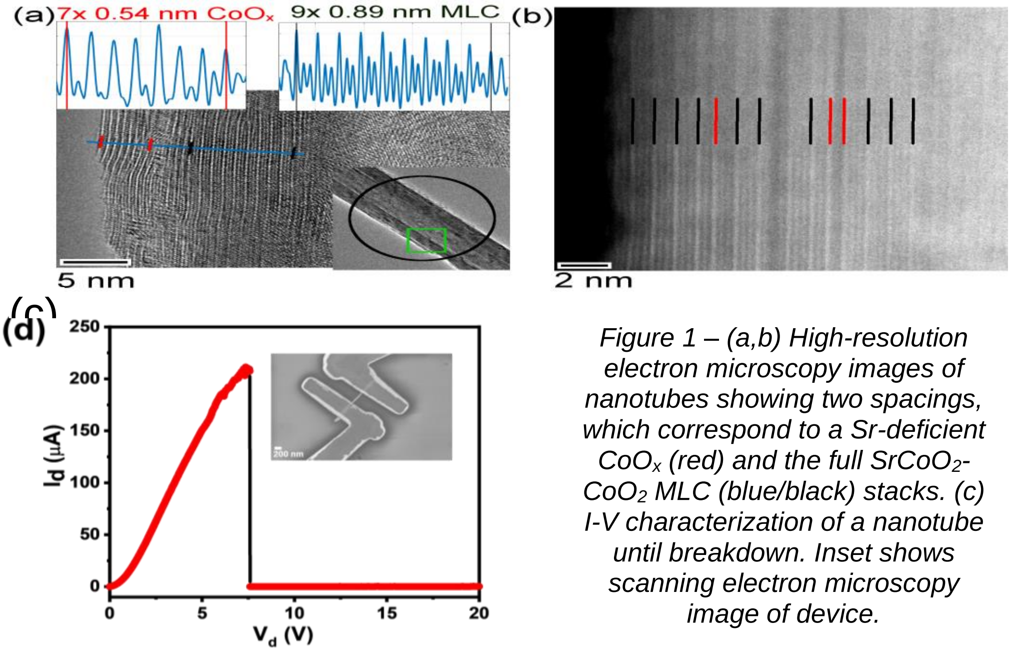

Figure 1 – (a,b) High-resolution electron microscopy images of nanotubes showing two spacings, which correspond to a Sr-deficient CoO_x (red) and the full $SrCoO_2$-CoO_2 MLC (blue/black) stacks. (c) I-V characterization of a nanotube until breakdown. Inset shows scanning electron microscopy image of device.

Synthesis and Characterization of Colloidal Nitrogen-Doped Graphene Quantum Dots as Biomarkers

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Natural low-cost and biocompatible chitosan was converted by microplasma system into nitrogen-doped graphene quantum dots (NGQDs) with adjustable sizes. NGQDs were characterized by Photoluminescence (PL) and Raman scattering. The nucleation, growth, and simultaneouse N doping of GQDs were achived [1]. The appearance of NGQDs with diameter of 4-6 nm and graphene-like nuclei has been confirmed by a high resolution transmission electronic microscopy (HRTEM). The QDs with 4 different diameters have been investigated. Then the PL maps (emission vs excitation) have demonstrated a size-dependent position of resonant PL signal. The size-dependent Raman signals were registered with excitation by radiation of He-Cd laser (325 nm). There was a strong PL background in the spectrum under excitation with longer-wavelength radiation. This effect confirms a 0-dimension structure of the material formed. The synthesized NGQDs can be used for facile and sensitive pH detection with a broad range pH (1.25-13.56) using PL, UV-Visible absorbance and Raman spectroscopies. With adjusting the pH condition during detection, a rapid screening system for biomarkers, multiple biomolecules (including uric acid (UA), folic acid (FA), epinephrine (EP), and dopamine (DA)) can be formed. The detection can be performed simultaneously with the high selectivity and sensitivity, simultaneously using a single material only. This work opens a new approach for biomedical applications of NGQDs as well as for the early detection and diagnostics of diseases and for the development of new drugs. *The work was supported by RSF/MOST Grant no. 20-42-08004 (110-2628-E-011).*

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Synthesis of boron doped diamond core-shell particles grown by MPCVD

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In this study, we report an innovative approach that aims to grow a Boron Doped Diamond (BDD) coating onto monodisperse silica particles seeded with nanodiamonds to obtain SiO_2@BDD core-shell particles by microwave plasma chemical vapor deposition (MPCVD). After removal of the silica core, hollow BDD nanoparticles could be used in the development of new electrode architectures, towards promising application of diamond-based material for (photo)electrochemical production of hydrocarbon fuels from CO_2 [1]. Currently, BDD particles are only obtained by grinding massive BDD films, an expensive process that produces in small amounts highly polydisperse particles.

We first dedicated our work to improve the crystalline quality and the morphology of diamond coatings grown on silica particles. For this purpose, seeding parameters like the nature of diamond seeds (milled or detonation nanodiamonds) and their density on silica spheres were optimized. Second, MPCVD growth conditions (methane concentration in H_2, reactor design) were adjusted to obtain the highest crystalline quality in our diamond coating. The best experimental conditions were then used for boron doping adding Trimethylboron (TMB) in the gas phase at varying concentrations.

The morphology of BDD coatings was characterized by scanning electron microscopy (SEM). Results showed that the lower initial seeds density of milled nanodiamonds and methane concentration, the larger grain size we obtain with faceted structure. Raman measurements on BDD coatings allowed us to compare diamond crystalline quality and sp^2 to sp^3 carbon ratio. We also noticed a downshift and a broadening of the diamond Raman peak that can be attributed to a Fano effect, signature of boron incorporation in diamond lattice [2]. To access the diamond microstructure, transmission electron microscopy (TEM), coupled with EELS and EDS spectroscopies were realized on SiO_2@BDD cross-sections obtained by Focused ion beam (FIB). Finally, electrochemical behavior of these BDD coating was evaluated and compared to bulk BDD material.

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Tailoring confined carbyne

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Carbyne is the elusive carbon allotrope with sp^1 hybridized carbon, leading, to an infinite linear chain of carbon atoms. Theoretically, it is a true 1D nanomaterial with unique electronic and mechanical properties, for example it is predicted to be the world's strongest material [1]. The length and interaction with the environment of carbyne allow tunable band gaps [2]. However, the instability of polyynes (short linear carbon chains) and carbyne impedes effective synthesis, characterization and application of these materials. Based on our breakthrough of the discovery of long linear carbon chains inside double walled carbon nanotubes, we have made great progress in the tailored synthesis of confined carbyne [3] and in the understanding of the growth precursor and mechanism [4,5]. Here, I will present recent results using metallicity sorted SWCNTs as precursors. I will also present progress in understanding the interaction of the carbon chain with the nanotube host.

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Taxonomy of 2D carbon allotropes

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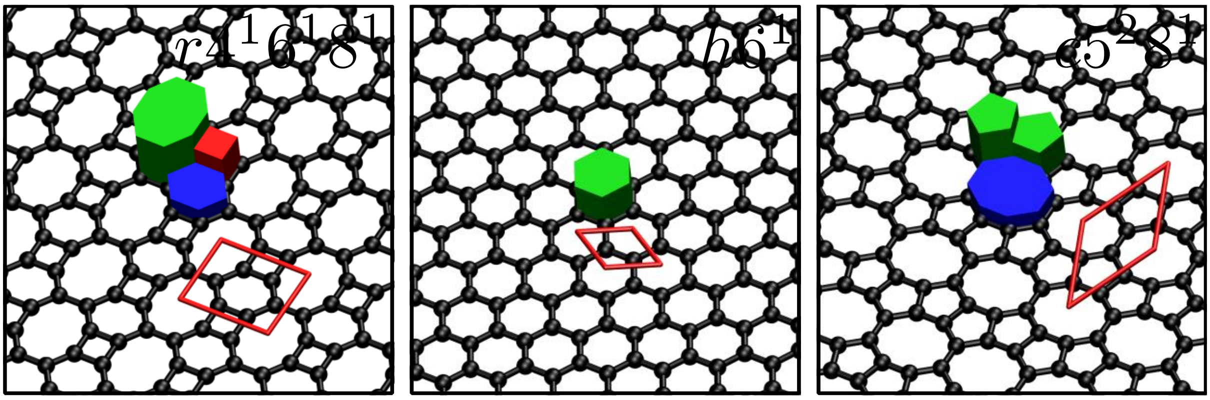
A unified taxonomy for sp2 nanocarbon allotropes in two dimensions (2D) is proposed where structures are assigned a unique symbol associated with the geometry of each allotrope. The naming scheme will be demonstrated for all the structures described in the literature and is further illustrated for a number of other topology-allowed carbon sp2 systems. The symbol is easy to use and gives a direct access to geometrical features such as the number of polygons and their arrangement. It facilitates the classification of structures reported in the literature, where many such structures are found to have been assigned a name based on each author's somewhat arbitrary choice. The naming scheme can be applied to 1D systems and has the potential to be expanded to mixed sp2-sp3 carbon system as well as non-carbon nanostructures in 2D.



HeteroNanoCarb 2023 | Advances and applications in carbon related nanomaterials:
From pure to doped structures including heteroatom layers
2023, Jan 09 -- Jan 13, Benasque, Spain

Tuneable synthetic reduced graphene oxide scaffolds elicit high levels of glioblastoma interconnectivity *in vitro*

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Three-dimensional tissue scaffolds have utilised nanomaterials to great effect over the last decade. In particular, scaffold design has evolved to consider mechanical structure, morphology, chemistry, electrical properties, and of course biocompatibility – all vital to the performance of the scaffold and how successful they are in developing cell cultures. We have developed an entirely synthetic and tuneable three-dimensional scaffold of reduced graphene oxide (rGO) that shows good biocompatibility, and favourable mechanical properties as well as reasonable electrical conductivity. Our synthesis procedure has lots of opportunities to tune the resulting scaffold properties - such as pore size distribution, specific surface area, mechanical stiffness, and more. Importantly, the synthesis is scaleable and suitable for producing scaffolds of any desired geometry and size, and we observe a high level of biocompatibility and cell proliferation for multiple cell lines. In particular, one of the most devastating forms of malignant brain cancer, glioblastoma (GBM), grows especially well on our rGO scaffold in vitro, and without the addition of response-specific growth factors. We have observed that our scaffold elicits spontaneous formation of a high degree of intercellular connections across the GBM culture. This phenomenon is not well documented in vitro and nothing similar has been observed in synthetic scaffolds without the use of response-specific growth factors – which risk obscuring any potential phenotypic behaviour of the cells. The use of scaffolds like ours, which are not subject to the limitations of existing two-dimensional substrate technologies, provide an excellent system for further investigation into the mechanisms behind the rapid proliferation and success of cancers like GBM. These synthetic scaffolds can advance our understanding of these malignancies in the pursuit of improved theranostics to treat them.

Water Processable P3HT Nanoparticle/carbon nanomaterial hybrids as active phase in photocathodes for hydrogen production

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Poly(3-hexylthiophene) (P3HT) is a widely used material in organic optoelectronic and photovoltaic devices. Similarly, P3HT architectures can also be used as photocathodes for direct photoelectrochemical hydrogen evolution reaction (PEC-HER) [1]. In a parallel effort, the need to eliminate environmentally dangerous solvents has put water-processable materials in the spotlight. In this sense, P3HT nanoparticles and its hybrids with carbon nanostructures are becoming of increased interest [2,3].

Since P3HT on itself is unable to sustain effective charge separation and charge transfer processes, its application in photoelectrochemical reactions requires the development of a complex layer-by- layer electrode architecture. This involves the use of electrocatalytic, electron transport, and hole transport layers, in addition to the presence of electron acceptors in the active phase.

In this work, we present the effect of several carbon nanomaterials, such as C_3N_4, DMF-dots or N-doped graphene quantum dots, as electron acceptors, in the performance of water processable P3HT NP-based photocathodes for PEC-HER. Those carbon nanomaterials induce structural and electronic changes in the P3HT NPs, thus improving the performance of the electrode, and paving a promising way for their future use in green hydrogen production.

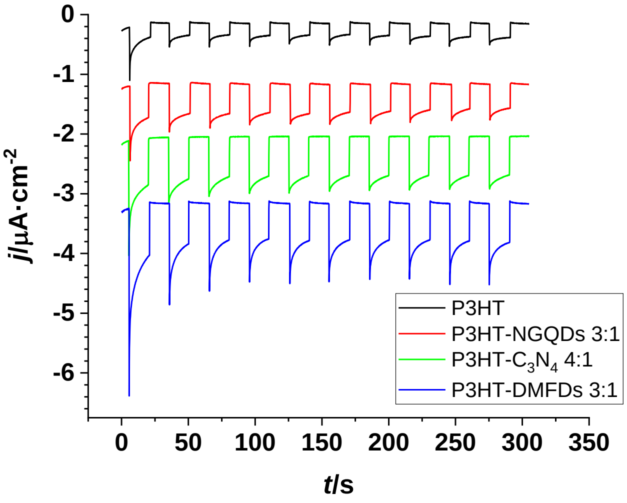

Figure 1. *Photocurrent (0 V vs. RHE, 0.5 M H_2SO_4) for several hybrid material.*

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WETTING STUDIES USING ATOMIC FORCE MICROSCOPY TECHNIQUES: COMPLEXITY ON THE NANOSCALE

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For some applications a precise understanding of the structure-function relation of interfaces is still an open issue [1]. For the case of wetting, it is far from clear how nanoscale chemistry and structure determine macroscopic wetting. In this field Nature is still ahead of “first principles calculations and theory”: if surfaces with well-defined and robust wetting properties are to be designed, it is still more effective to “look” at what Nature offers, than to rely on theoretical modeling. The Lotus and the Rose Petal effect are two striking examples of how Nature fine-tunes nanoscale chemistry and physics to obtain an appropriate function on the macro-scale.

In the present work, we use Atomic Force Microscopy (AFM) to simultaneously measure nanoscale topography and chemistry of Rose Petals [2]. We found two extraordinary features linked to their peculiar wetting properties: (i) surface roughness is concentrated on the nanoscale and fractal-like, and (ii) the surface has an extreme nanoscale chemical variability. While high roughness is generally accepted to be the origin of peculiar wetting (super-hydrophobicity) the role of nanoscale chemical variability is usually not really a topic of discussion; most probably because -up to now- it could not be “seen”. Both, extreme roughness and chemical variability are, in our opinion, the basis for the Rose Petal Effect. From our data, we conclude that a liquid drop will strongly adhere to nanoscale hydrophilic patches, and detach from all the other hydrophobic parts of the surface, since the combined effect of roughness and chemical (nanoscale) wetting properties will induce a high effective local contact angle (=nanoscale wetting parameter). This explains the surprising and in principle antagonistic properties associated with the Rose Petal Effect: high contact angle and high drop adhesion.

Although this work is focused on rose petals, the fundamental mechanism by which Nature is able to generate high contact angle and drop adhesion will apply to other surfaces. In addition, the application of this fundamental mechanism will trigger the development of new functional surfaces by “learning from Nature”. In particular we will discuss how our findings might affect wetting of surfaces on which 2D materials are used to modify the nanoscale chemistry of an solid-liquid interface. This case of surface modification using 2D materials can be considered an extreme case of controlled modification of wetting using only (nanoscale) chemical variability and essentially no surface roughness.

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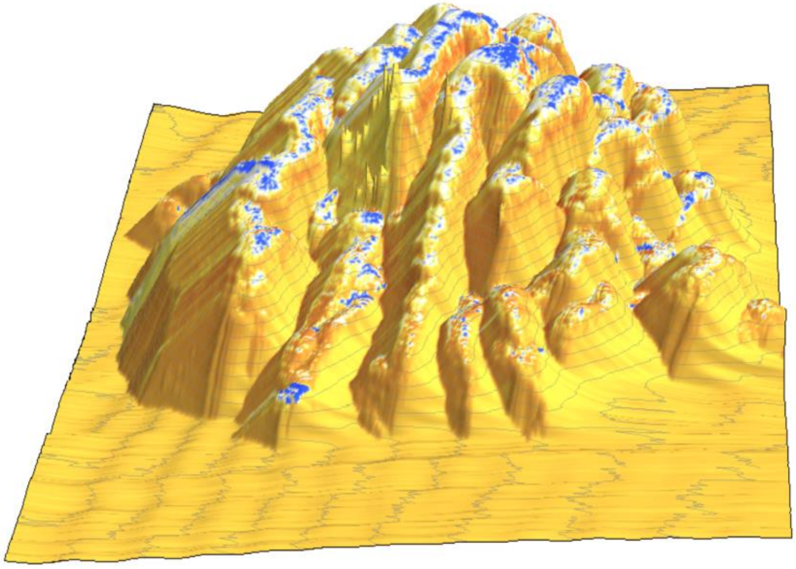

AFM images showing topography (vertical scale, 3d representation) and wetting properties coded as the color of surface. blue: hydrophilic, red: hydrophobic.
Note that the more hydrophilic regions tend to be at the highest regions of the surface. Lateral scale: 12.5 mm, vertical z-scale (height) about 4 mm.

WS_2 & MoS_2 from 3D to 1D structures: Curvature and chirality induced properties of nanotubes

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Inorganic nanotubes (INTs) of WS_2, a member of the 2D transition metal dichalcogenide (TMD) family, demonstrate unique properties due to their nanosize, closed-cage arrangement of the layers into chiral tubes and mechanical strength. Wide investigation of this nanomaterial, became possible due to the breakthrough in their vapor-gas-solid (VGS) synthesis, resulting in pure phase and macroscopic amounts [1]. Recent theoretical calculations demonstrated that mechanical properties of MoS_2 are superior to that of WS_2, as well as their excitonic emission. An advance in extremely complicated synthesis of INT-MoS_2 by VGS of Mo oxides with H_2/H_2S gases [2] will be reported here. The availability of MoS_2 semiconductive 1D nanocrystals will enable their wide investigation as well.

Bulk photovoltaic effect (BPVE) was recently discovered in INT-WS_2 [3]. The photocurrent in the nanotube-based device was orders of magnitude larger than in other BPVE materials. The BPVE does not require p–n junctions of traditional photovoltaic effect (PVE) for generation of electric current, and occurs due to the intrinsic properties of INT-WS_2: small band gap (1.4-2.1 eV), broken inversion symmetry and polar structure. This progress is particularly important for environmentally benign energy harvesting because the efficiency of traditional PVE has been almost reached the theoretical limit. An exponential increase of the resistivity with tensile strain was demonstrated [4] up to a recorded elongation of 12 %, thereby making INT-WS_2 suitable for piezoresistive sensor applications. (3) Low temperature cathodoluminescence of single-wall few nm diameter WS_2 nanotubes, produced by high-power plasma irradiation of multiwall WS_2 INTs, demonstrates blue shift, evidencing quantum confinement and strain effect [5]. Bandgap engineering via size and number of layers control in these INTs will be discussed. An artificial vision system based on the memory effect produced by sliding ferroelectricity in multiwalled tungsten disulfide nanotubes will be presented [6].

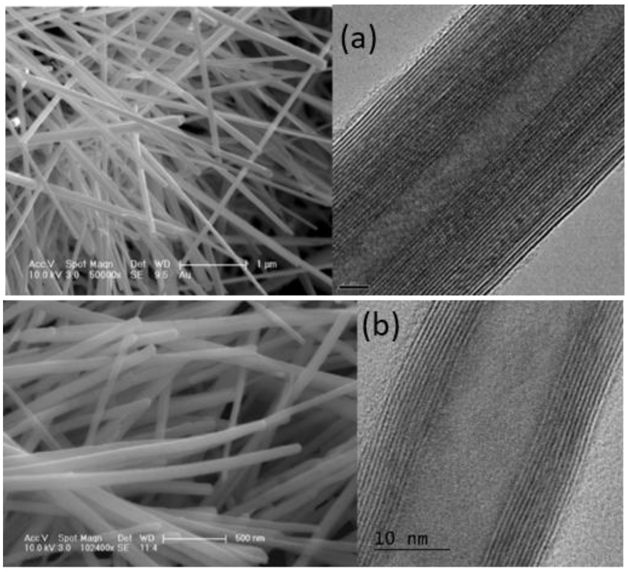

Fig. 1. *SEM and TEM images of (a) WS_2 nanotubes, (b) MoS_2 nanotubes, (scale bar 10 nm).*

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POSTER CONTRIBUTIONS

ANALYSIS OF IRON-OXIDE BASED NANOPARTICLES BY ELECTRON MICROSCOPY AND SPECTROSCOPY

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Iron-oxide based nanoparticles (NPs) are promising for several applications, especially if they are synthesized in a core-shell form, which allows fine-tuning their properties[1-3]. These macroscopic or ensemble properties are strongly dependent on the actual structure, shape and the local composition of the individual NPs. One way to elucidate this nanoscopic structure is by electron microscopy in scanning transmission mode (STEM) and spectroscopy (EELS), which allows to analyze structure and chemistry below the nanoscale.

Here we present results obtained on various NP samples. The first study was performed on core-shell NPs with a magnetite $Fe_3O_{4-\delta}$ core and a $CoFe_2O_4$ shell, where the influence of Co on the Fe-L and O-K EEL edge and the best way to analyze the NPs is discussed in detail (Figure 1)[1]. These results serve as reference for the additional project presented, where similar NPs were used as active material in the Oxygen evolution reaction (OER) and the change in morphology and composition was analyzed[2]. Furthermore, an example of a pure iron-oxide NP with valence-state variations within, shows that these changes, invisible in pure composition maps, can be visualized by mapping details of the Fe-L and O-K edge intensity.

Together, the studies show that an in-depth analysis by STEM-EELS data provides a way to reveal the structure, composition and chemistry of NPs at the local scale, prerequisite for understanding their properties.

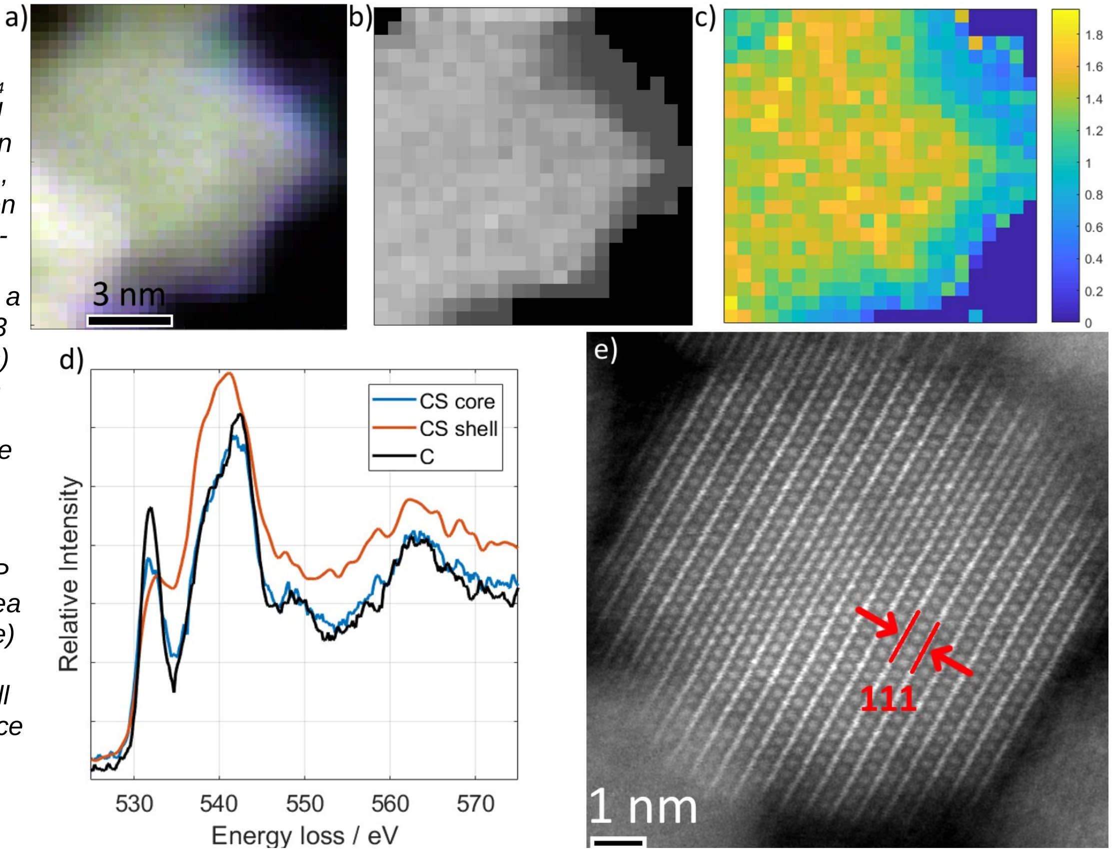

Figure 1 – In-depth analysis of $CoFe_2O_4$ @$Fe_3O_{4-\delta}$ core-shell NPs. (a) Composition map with Fe (green), Co (blue) and Oxygen (red) revealing a Co-rich shell. (b,c) The shell is also visible in a map of the (b) Fe-L3 peak position and (c) intensity ratio of the pre-peak and the following valley of the O-K edge. (d) Comparison of EEL spectra of the O-K edge from a core NP and the shell/core area of a core-shell NP. (e) HAADF-HRSTEM image of a core-shell NP with lattice distance marked.

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An Attempt to Produce Graphene in Large Scale by a Low-Cost Method-A High School Experiment

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Graphene is a material with unprecedented application possibilities owing to its unique optical, electronic and mechanical properties. However, industrial application requires a large scale, low-cost production method for graphene which is one of the main aims of the researchers around the globe involving in the synthesis process of this wonder material. In 2014, Jonathan Coleman *et. al*., found a graphene production method that could be adapted to be carried out in a low-cost way.[1] The current experiment is an effort by a high-school student to produce high-quality graphene using the same method but with a regular kitchen mixer, standard detergent powder and raw graphite rods. Some of them were subjected to heat treatment to attain an improved results in terms of quality/quantity. The samples were examined extensively using different experimental techniques i.e., scanning electron microscopy, aberration-corrected transmission electron microscopy, Raman and X-Ray photo-electron spectroscopy to understand the quality of the graphene produced by this process. The raw graphite has a high number of defects as seen from the Raman experiment. Raman measurement also showed formation of multilayer graphene which closely resembles with the high-resolution TEM (HRTEM) experiments. The HRTEM showed formation of some long-range order due to the heat treatment of the samples in addition to the formation of some fullerene like particles, which is also confirmed by the I_D/I_G ratio from the Raman analysis.[2-3] XPS measurement revealed increment in the O content for the samples annealed in air due to the formation of oxides. However, an increased thermal conductivity was observed for the heat-treated samples when they are deposited on a commercial can. Overall, the graphene was not observed to be formed in single layer and a sufficient modification in the synthesis process is needed to improve the quality of the graphene obtained. But, overall, this is a commendable effort from a high school student to develop the idea and to execute it.

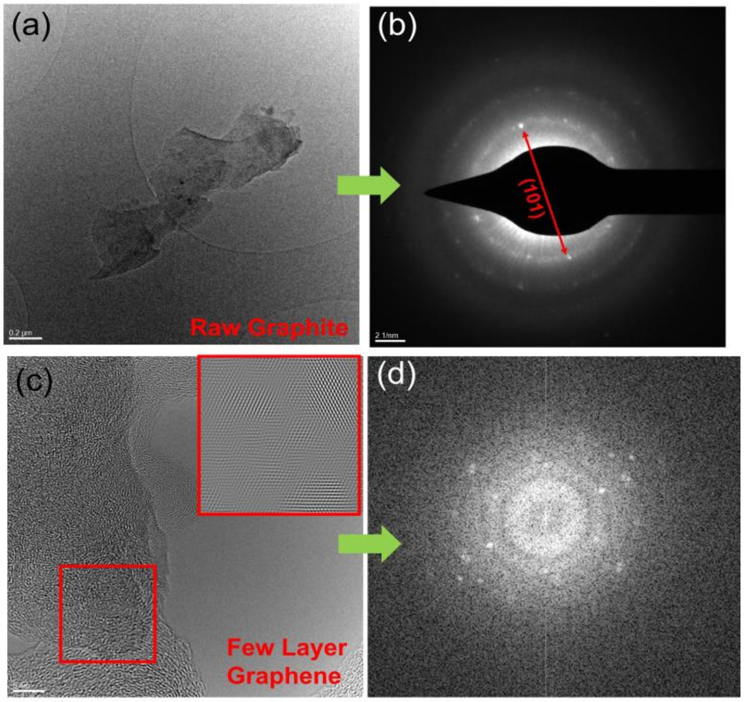

Figure 1. *(a) Bright-field TEM (BF-TEM) image of Raw Graphite Flake. (b) SAED pattern from the flake showing amorphous crystalline pattern. (c) BF-TEM image of few layer graphene (inset showing the inverse fast Fourier transform (IFFT) pattern from the red square)(d) FFT pattern from the red square in (c) showing hexagonal FFT pattern corressponding to graphene.*

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AN OPTICAL ABSORPTION APPROACH TO UNRAVEL THE OPTICAL BANDGAP OF GRAPHENE NANORIBBONS INSIDE SWCNTS

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Semiconducting nano-structures such as single wall carbon nanotubes (SWCNTs) and graphene nanoribbons (GNRs) are becoming more and more important for nanoelectronics and other technologies but in order to use them to their full potential we need to be ably to properly control and understand their electronic and optical properties. GNRs are 1-dimensional strips of graphene with a defined width and edge structure which together determine a large part of their characteristics.

In order to synthesize GNRs with the best possible precision, we have used endohedral functionalization of SWCNTs by inserting the terrylene dye molecule. Like this, we have synthesized ultra-narrow graphene armchair nanoribbons (5-AGNRs) inside SWCNTs that served as nanoreactors. These 5-AGNRs belong to the N=3p+2 family, and are expected to have small but non-vanishing bandgaps making them ideal for electronic applications due to their high carrier mobility and strain resistance.[1] The bandgap of this material has never been measured using optical characterization techniques to the best of our knowledge. To better understand the properties of this one-dimensional material we have performed Fourier Transform Spectroscopy (FTS) on a broad energy range from 0.2 to 2.5 eV[2]. We have found both a reduction and a shift of the E11 excitation of the SWCNTs as a result of the interactions between the two materials. We have determined the GNR bandgap to be around 0.19 eV close to the theoretical predictions of a bandgap around 100 meV for long GNRs[3].

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Compression-enhanced thermal conductivity of carbon loaded polymer composites

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The miniaturization, integration and compatibilization of electronic devices dictate the need for efficient thermal management to prevent heat accumulation, which may reduce the operation speed and shorten their life time. Addressing this challenge requires the development of novel polymer-based composite materials with enhanced thermal conductivity. Here, we report a compression-based (25-250 bars) approach for the preparation of polymer composites loaded with carbon-based hybrid fillers, i.e., graphene nanoplatelets and graphite flakes. The carbon-based fillers contribute significantly to the thermal conductivity of the composite while a boron nitride nanoparticles provide the desirable inhibition of the electrical conductivity to avoid short circuits. An optimal thermal conductivity of 27.5 W/(m·K) is obtained, for the compressed system (measured under atmospheric pressure) for epoxy polymer loaded with 30 wt% graphene nanoplatelets and 40 wt% graphite flakes compared to 0.2 W/(m·K) of the neat thermoset polymer.

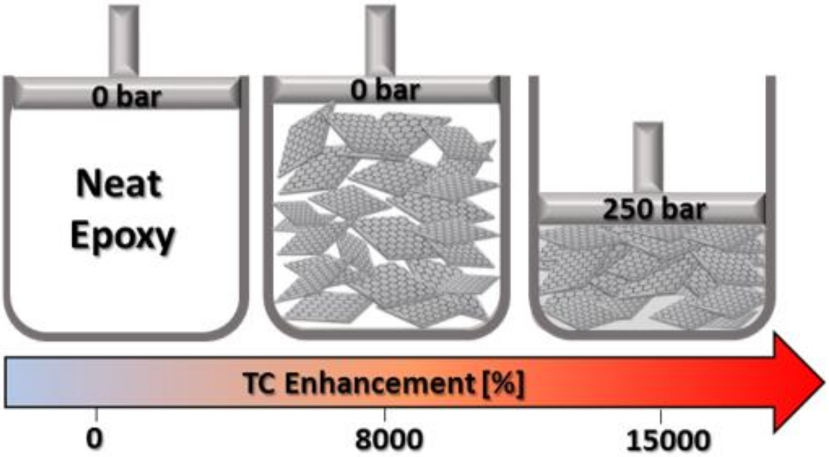

Figure 1. Illustration of filler loading and compression effect on composite thermal conductivity enhancement.

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Covalentlymodified MoS_2 with zinc phthalocyanine for managing photoinduced charge-transfer phenomena

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We present the covalent incorporation of zinc phthalocyanine (ZnPc) carrying an 1,2-dithiolane oxide linker onto exfoliated semiconducting molybdenum disulfide (MoS_2) and evaluate the efficiency of the newly derived hybrid material ZnPc-MoS_2 in photoinduced charge-transfer reactions. The structure of ZnPc-MoS_2 was fully assessed by complementary spectroscopic, thermal and microscopy imaging techniques. A bi-directional electron transfer leading to $ZnPc^{\bullet+}$-$MoS_2^{\bullet-}$ charge separated state was revealed by direct band-gap excitation of MoS_2 or from $^1ZnPc^*$. Systematic studies performed by femtosecond transient absorption revealed involvement of excitons generated in MoS_2 in promoting charge transfer phenomena, while such charge transfer was also possible when ZnPc was excited, signifying their potentiality in light energy harvesting devices.

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Explosive percolation yields highly-conductive segregated network nanocomposites

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Explosive percolation is an experimentally-elusive phenomenon where network connectivity coincides with onset of an additional modification of the system; materials with correlated localisation of percolating particles and emergent conductive paths can realise sharp transitions and high conductivities characteristic of the explosively-grown network. Nanocomposites present a structurally- and chemically-varied playground to realise explosive percolation in practically-applicable systems but this is yet to be exploited by design. Herein, we demonstrate composites of graphene oxide and synthetic polymer latex which form segregated networks, leading to low percolation threshold and localisation of conductive pathways. *In situ* reduction of the graphene oxide at temperatures of <150˚C drives chemical modification of the polymer matrix to produce species with phenolic groups, which are known crosslinking agents. This leads to conductivities exceeding those of dense-packed networks of reduced graphene oxide, illustrating the potential of explosive percolation by design to realise low-loading composites with dramatically-enhanced electrical transport properties.

FLUORESCENCE MICROSCOPY ON SINGLE WALL CARBON NANOTUBES OF SPECIFIC CHIRALITY

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Single wall carbon nanotubes (SWCNTs) are one dimensional nano-scaled materials that have unique optical and electronic properties directly related to the geometrical configuration of the carbon atoms in their walls. They can be either metallic or semiconducting and the one dimensional quantum confinement is revealed in the van Hove singularities in the density of states. The last years of research on these materials have enabled the production of SWCNTs with a high purity and in batches of chirality sorted species. Such materials are very promising for applications where a tunable control of the electronic and optical properties is desired. For instance, all semiconducting tubes absorb in the visible excitation range, while they emit in the near infrared, and this is extremely useful for photonic and bio imaging applications. Despite the tremendous advances in separation by metallicity and chirality-sorting of SWCNT, to date, only relatively low fluorescence efficiency is obtained. Isolated SWNTs tend to be affected from the presence from remainings of surfactant in the sample after sorting. On the other hand, bulk amounts are generally composed of mixed metallicity tubes where quenching of the fluorescence via the metallic species is inevitable. The quantum yield and efficiency need to be optimized. This works focuses on the study of metallicity sorted nanotube material that has been produced for these specific purposes. The level of purity is studied here in order to understand the real influence of external agents to the fluorescence of single-chirality nanotubes. Different series of experiments have been performed. I will show our progress toward using fluorescence spectroscopy in frequency and time domains for the disclosing of quantum yield and radiative lifetime. Time-correlated single photon counting has been performed. Estimating the radiative lifetime of pristine single chirality nanotubes is one of the main focuses of this work. Furthermore, preliminary studies on fluorescence imaging will be presented.

FLUORESCENCE OF FULLERENES: TADF AND CARBON-13 ISOTOPE EFFECT

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Thermally Activated Delayed Fluorescence (TADF) has a unique temperature dependence and a duration typical of phosphorescence. In the last decade, there was a surge of interest in TADF owing to its application in 3rd and 4th generation OLEDs [1-3]. Two different types of TADF were identified by us: One-way and two-way TADF [4,5]. Fullerenes, usually very weakly fluorescent, were shown by us to display a strong TADF under appropriate conditions, thereby increasing their fluorescence quantum yield by orders of magnitude [6,7]. The unique carbon-13 isotope effect observed in the photophysics of fullerenes [8] will also be described in detail and shown to be a nuclear mass effect [9].

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FROM GO TO rGO: CHARACTERIZATION OF ELECTROSTATIC PROPERTIES AT THE NANOSCALE

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Graphene oxide (GO) is a 2D flake-like material in which the familiar sp^2 network of graphene has been modified by the addition of a high number of different oxygen functional groups that decorate its carbon basal plane and edges. These functional groups cause the material to become highly disordered and non-stoichiometric. Unlike pristine graphene, this material can be easily dispersed in common polar solvents such as water. These oxygen groups can be removed through well known reduction techniques to drastically increase the conductivity of the resulting material, reduced graphene oxide (rGO).

Atomic Force Microscopy (AFM) related techniques have been proven to be ideal to explore the different properties of these materials. In particular, the electronic and conducting properties of both GO and rGO with varying degrees of reduction can be probed with the aid of Kelvin Probe Force Microscopy (KPFM). This technique allows for the mapping of surface potentials and for the estimation of the dielectric constant of a given material with nanoscale spatial resolution.

In Fig.1 a) we show the topography image of a collection of GO and rGO flakes. With the aid of KPFM we are able to efficiently discriminate between GO and rGO flakes in a noninvasive way (Figs.1 b), c)). In the 2w electrostatic channel (Fig. 1b)) some of the flakes can be clearly seen while the others remain invisible due to the increase in dielectric constant of the reduced flakes. Additionally, the reduction process is not uniform over the flake and patches with varying degrees of reduction spanning hundreds of nanometers can be differentiated.

The situation is different on the surface potential channel (Fig. 1c)), the flakes that were invisible on the 2w electrostatic channel now show bright and dark domains that evolve with time. These domains are associated with localized charges hopping between localized states in the bandgap of the material. These charge domains can't be observed in highly reduced rGO.

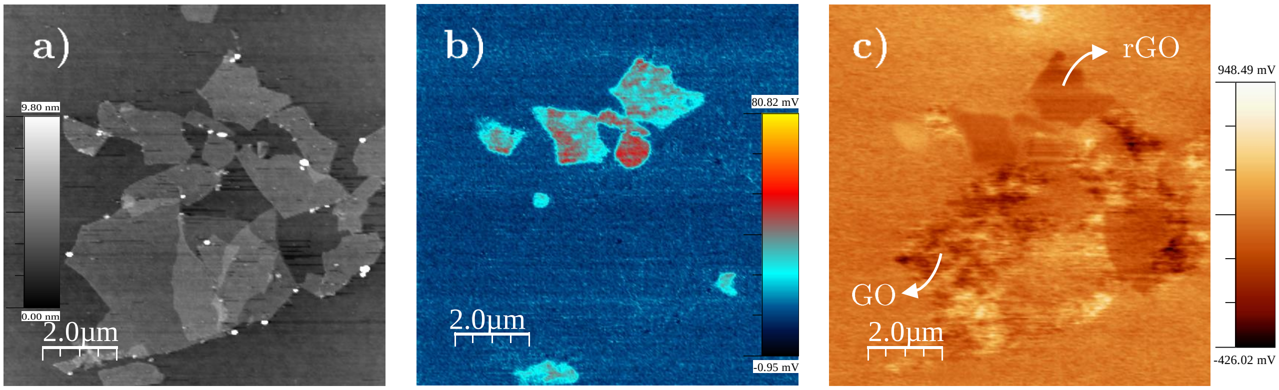

Fig1. a) Topography, b) 2w electrostatic channel, c) Surface potential image

By studying partially reduced GO we can see that the 2w electrostatic patches have a correlation with the surface potential image (Figs.2 a), b)) and, unlike those of GO, they are do not originate from localized charges as they do not move. From these measurements we extract the electrostatic fingerprints of GO and rGO, the presence of localized charge domains within the flake that move and evolve with time and lower permittivity for GO and an overall higher permittivity and correlation between then 2w electrostatic channel and surface potential channel for rGO.

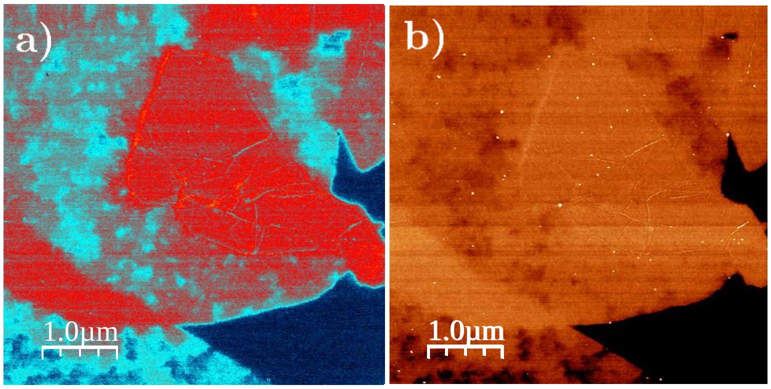

Fig 2. a) 2w electrostatic channel, b) Surface potential image

GRAPHENE OXIDE: THE SPRING-DANCE OF ELECTRONS

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The electronic properties of graphene oxide (GO) are largely determined by the presence of basal-plane oxygen functional groups organized in nanoscale domains [1-4]. In this work shine light on the nanoscale charge density and dynamics of isolated GO nanosheets. Being probed by Kelvin Probe Microscopy (KPFM) [5] we visualize the existence of charge-domains with respective charge interactions. We further reveal short range fluctuations of jumping electrons and the existence of very long-term relaxation times. The experimental findings are consistent with theoretical simulations, emphasizing that graphene oxide can be understood in terms of an electron glass revealing hopping transport between charge-domains.

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PID2019-104272RB-C52/AEI/10.13039/501100011033,
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LOW DOSE TEM IMAGING ON SENSITIVE COLLOIDAL COVALENT-ORGANIC FRAMEWORKS

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Covalent-organic frameworks (COFs) are currently acquiring an increasing research interest due to their tunability and many possible applications, which range from gas storage to optoelectricity or catalysis[1]. Within this realm, recently single-crystal colloidal COF suspensions have been first synthesised, thus opening a new realm of possibilities for these materials[2].

The characterisation of these COFs, most notably their dispersion, morphology and crystallinity, is vital for the development of this research. However, TEM characterisation in these samples presents a great challenge due to the sensitivity of such samples to the electron beam. In this sense, colloidal COF nanoparticles (NPs) have already been imaged using TEM [2,3], but this imaging has consistently been performed in CryoTEMs in order to lower the beam damage on the samples.

A different path to lower this beam damage is the employment of direct detectors in the TEM. Novel studies[4] show that the usage of said detectors, like TIMEPIX3,, allow for much lower doses when imaging.

These works show the possibility to image colloidal COFs in a regular TEM. This imaging has been performed at low doses using a cryoholder and a TIMEPIX3 detector. Results will be discussed with respect to previous studies, as well as the potential role of the TIMEPIX detector in the imaging of sensitive samples.

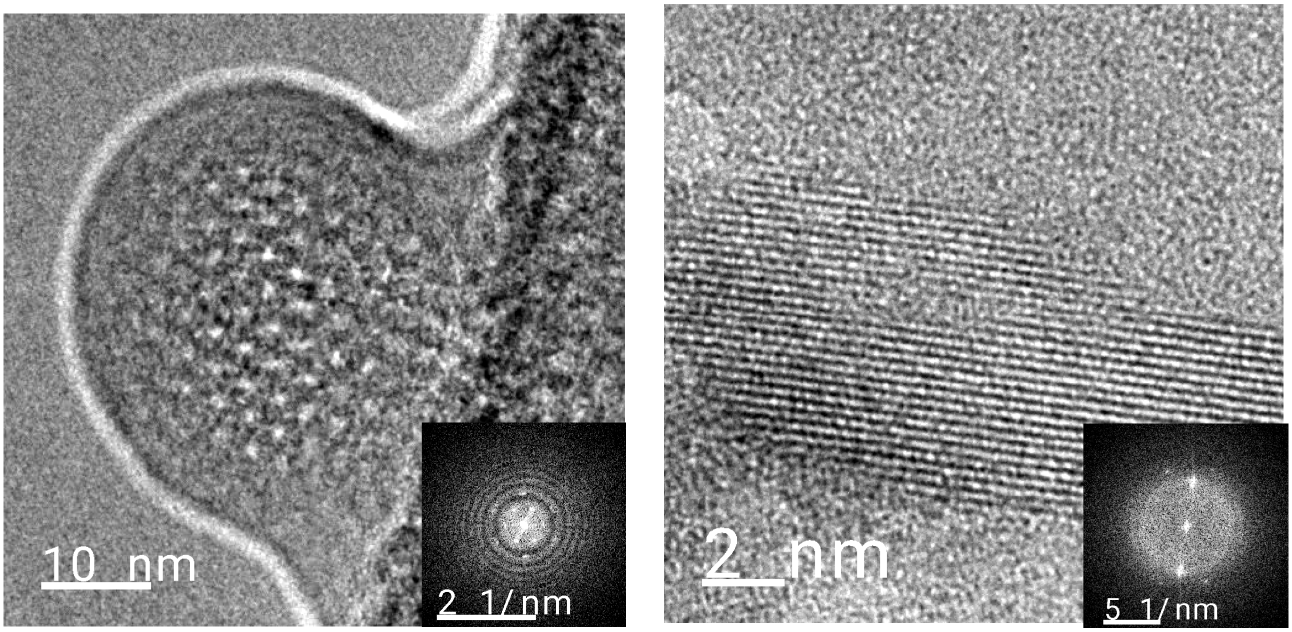

Figure 1 – Two different TEM images of a COF in two different orientations taken by a TIMEPIX3 detector.

[1] S.-Y. Ding and W. Wang, Chem. Soc. Rev. 42, 548 (2013).
[2] A. M. Evans et al, Science 361, 52 (2018).
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NEXT-GENERATION NANOCOMPOSITE SILICONE STRAIN SENSORS

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We are developing the next generation of nanocomposite strain sensors utilising liquid-phase exfoliated graphene nanosheets and commercially available silicones. We structure the graphene network via emulsification to produce graphene-coated silicone droplets, which can be used as filler material, enabling high conductivity at relatively low graphene loadings. When combined with highly elastic, highly flexible silicone matrix, we demonstrate excellent electromechanical properties with a robust exponential response to applied strain. Moreover, these composites exhibit minimal hysteresis when deposited on a substrate during cyclic strain, providing real-world application potential.

Rational Design of Ir-doped NiMoP-NiMoPxOy/CNTs Heterostructure for Water Splitting

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Efficient and robust electrocatalysts for water splitting have been explored in H_2 production. In this study, doping Ir atoms into both phase of an amorphous NiMoPxOy and crystalline of NiMoP phase generates enriched active sites with high intrinsic activity. The catalyst material coating on the CNTs-Gr/Cu foam (CF) serves as an electron transport pathway, improving surface area and protective layer (Ir-(NiMoP-NiMoP_xO_y)/CNTs-Gr/CF). The designed material has outstanding electrochemical water splitting properties. The optimized Ir-(NiMoP-MoNiP_xO_y)/CNTs-Gr shows with an overpotential of 90 mV at 10 mA cm^{-2} for the hydrogen evolution reaction and 220 mV at 20 mA cm^{-2} for the oxygen evolution reaction. Long-term stability of Ir-(NiMoP-NiMoPxOy)/CNTs-Gr/CF in 1.0 M KOH is demonstrated by a cell voltage of 1.72 V at 50 mA cm^{-2} after 150 hours. Our result suggests an attractive electrocatalyst with low cost and high catalytic activity for bifunctional water splitting.

Resistiance converting by the simultaneous formation of oxygen vacancies and conductive nano-filaments in memory devices based on TiO_2/a-IGZO bilayers

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Abstract: We fabricate resistive memory devices using the bilayer 2 nm of TiO_2 and 20 nm of a-IGZO thin film, which are annealed at various temperatures. Indium-tin-oxide is used as a bottom electrode as it is frequently applied in transparent electronic devices and makes it possible to integrate the ReRAM with other circuit elements. The thickness of the TiO_2 layer is decreased to improve the device conductivity, as it has been shown for metal oxide-based devices, that the switching thickness is expected to be less than 2 nm. Based on the observations, we propose a possible switching mechanism by virtue of the drift of oxygen ions under the large electric fields. The practical characteristics of the optimized ReRAM devices is studied by performing multiple forward and reverse sweeps to determine the appropriate SET, RESET, and READ voltages.

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