Graphene Industrial Forum &2DM 2020 MAY 27

Organisers

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EXCELENCIA SEVERO OCHOA

FOREWORD

On behalf of the Organising Committee we take great pleasure in welcoming you for the 1st edition of the Graphene Industrial Forum (GIF2020) Online International Conference.

The one-day Graphene and 2DM Industrial Forum (GIF) online conference will present the most recent advances in technology developments and business opportunities in graphene and 2DM commercialization. Key representatives of Companies and key Research Institutes will share their market vision and business opportunities, but also present commercial showcases in all current market fields of graphene products.

This online INDUSTRIAL FORUM will be focusing on: latest developments in graphene and 2DM production methods towards wide scale commercialization, emerging opportunities for graphene-based materials, determining criteria for graphene and 2DM investment opportunities, revealing the latest updates application and commercialisation of graphene and 2DM based materials in electronics, energy storage, biohealth, composites, sensors, etc.

GIF2020 will be a one-day online event that means to gather the key players of the Graphene and 2DM Community and related sectors. This event is launched following the success of previous INDUSTRIAL FORUM editions (organised within Grapheneconf series) and considering that all major scientific and technological conferences are being cancelled or postponed worldwide until the end of 2020.

We are indebted to the following Companies for their help and/or financial support:
Oxford Instruments Plasma Technology (UK) and AMO GmbH (Germany)

We also would like to thank all the speakers and participants that join us this year.

We truly hope that GIF2020 serves as an international platform for communication between science and business.

Hope to see you again online in the next edition of the "Graphene Industrial Forum".

Graphene Industrial Forum (GIF2020) Organising Committee

PHANTOMS foundation

ICN2 Institut Català de Nanociència i Nanotecnologia — EXCELENCIA SEVERO OCHOA

INDEX

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Oxford Instruments Plasma Technology offers flexible, configurable process tools and leading-edge processes for the precise, controllable and repeatable engineering of micro- and nano-structures. Our systems provide process solutions for the etching of nanometre sized features, nanolayer deposition and the controlled growth of nanostructures.

These solutions are based on core technologies in plasma-enhanced deposition and etch, ion-beam deposition and etch, atomic layer deposition, deep silicon etch and physical vapour deposition. Products range from compact stand-alone systems for R&D, through batch tools and up to clustered cassette-to-cassette platforms for high-throughput production processing.

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

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

AMO is a worldwide sought-after partner of innovators who want to explore new and unconventional routes, translating the latest findings of research into new applications. As a service provider, AMO works in a tight feedback loop with its customers, ensuring short turnaround times and flexible process flow.

AMO's Graphene Pilot Line

Since 2018, AMO offers advanced graphene foundry services, including a first baseline process for fabricating back-gated graphene devices on 6-inch silicon wafers. Building on its 10 years of experience in graphene research and innovation, AMO carries on customer-specific prototyping and characterisation of graphene devices on customised substrates.

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Speakers/FlashPosters/ePosters list Alphabetical order

Speakers list
Alphabetical order

Flash Posters list
Alphabetical order

ePosters list
Alphabetical order

ABSTRACTS

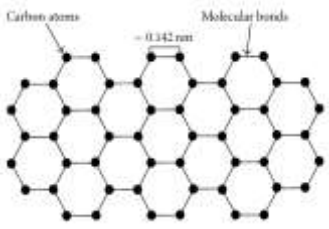
Graphene Application in Energy Storage

Sivasambu Bohm PhD, CChem, FRSC, FTSC
The Royal Society Industry Fellow
Imperial College London,
Department of Chemistry,
Molecular Science Research Hub,
White City Campus,
80 Wood Lane, London, W12 0BZ
s.bohm@ic.ac.uk

Abstract:

Graphene with its impermeable and conductive nature can replace currently used anticorrosive pigments in coating systems [1-3]. Further, with its considerable strength to weight ratio, graphene can be an essential component in next-generation surface coating additive. The current bottlenecks in using Graphene & Graphene oxide are the availability of cost-effective, high-quality graphene and its effective incorporation (functionalisation and dispersion) into anti-corrosion metal protective coating systems with inhibitors for industrial applications.

On overcoming these factors, protective coatings may prove to be significant demand drivers for graphene in terms of volume consumption. Graphene produced from industrially scalable and cost-effective top-down routes can be chemical / electrochemically / radiation treatment /mechanically the chemically tuned via functionalisation modified for use each Energy storage application, such "additive" Li-ion batteries and Bipolar plate(BPP) coatings for fuel cells – Polymer electrolyte membrane Fuel cells (PEMFC). Further highlights of a chemically tuning Graphene for each application is different.
Keywords: Graphene, Graphene Oxide, Graphene industrial application, Protective coatings, Batteries, Fuel cells



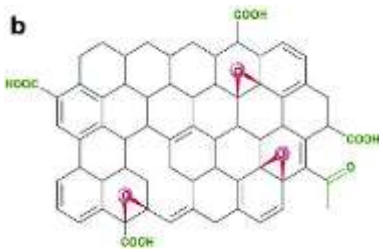


Figure a) Graphene **b) Reduced Graphene Oxide**

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Liquid phase production of 2D crystals for energy applications

Francesco Bonaccorso[1,2]
BeDimensional SpA, Via Lungotorrente Secca 3d, 16163 Genova, Italy
Istituto Italiano di Tecnologia, VIA morego 30, 16163 Genova, Italy

f.bonaccorso@bedimensional.it

Abstract

Graphene and related two-dimensional materials (GRMs) are entering several application areas, [1-5] improving the performance of existing devices or enable new ones. [1-5] A key requirement for the implementation of GRMs in the energy field is the development of industrial-scale, reliable, inexpensive production processes, [2] while providing a balance between ease of fabrication and final product quality.
In this context, the production of GRMs in liquid phase [2,6] represents a simple and cost-effective pathway towards the development of GRMs-based energy devices, presenting huge integration flexibility compared to other production methods. Here, I will first present our strategy to produce GRMs on large scale by wet-jet milling [7] of their bulk counterpart and then an overview of their applications for energy conversion and storage devices. [3,8-18]

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Perspectives of applications of 2D materials: Moore's and beyond CMOS view.

Paolo Bondavalli
Thales Research and Technology, *1, Av. Fresnel, 91767 Palaiseau France*
Paolo.bondavalli@tahlesgroup.com

Abstract

This contribution deals with the applications of 2D materials for applications dealing with energy, information storage and EMS and will present the vision on the next gen of applications in the field of Beyond CMOS. We have been working for around ten years on the implementation of Graphene and CNTs based mixtures to increase the power delivered by supercapacitors exploiting a deposition method based on spray-gun. We used the same technique to implement flexible ReRAM memories based on Graphene Oxide. Finally we developed new Electro-Magnetic Shielding layers based on thin Graphene layers able to reflect nearly 100% of electromagnetic wavelength. Now it is the time to move to Beyond CMOS applications with the new generation of 2D materials such as topological insulators, e.g. Stanene and Plumbene, which allow achieving devices reducing dramatically the energy consumption and thinking about a new generation of electronic circuits not based on transistors. We will introduce also the magic angle physics and the potential applications in industry.

Flexible monolayer Graphene-on-Insulator for biomedical applications.

Vincent Bouchiat, Marco Guerra, Andrej Tripsky, Antoine Bourrier, Cécile Delacour, Riadh Othmen
GRAPHEAL & Institut Néel , 25 rue des Martyrs , 38000 GRENOBLE, France.
Contact : vbouchiat@grapheal.fr

Graphene appear more and more as a very promising material for bioelectronics in vitro (1-4) as well as in vivo(5). It combines biocompatible, optical transparency and electrical conductivity. We have explored the use of graphene-on-polymer for enabling at the same time biosensing and tissue engineering.

The first-generation of our system is a graphene-based scaffold that looks like a very thin, transparent plaster. Based on that material, we are building an innovative bandage technology platform based on graphene-on - insulator film in order to better support chronic wounds. In particular, I will insist on the possibility to combine therapeutics (such as wound healing acceleration) with diagnostics features (such as infection detection) in the same device.

Following these properties, we have elaborated a graphene-based scaffold that looks like a very thin, transparent plaster (Fig 1) integrated in commercial bandage that is indented to be applied in direct contact with an open wound. We believe these films will have some impact in healthcare, as they target some important and poorly addressed diseases such as pressure ulcers and diabetic foot ulcers. I will present the preclinical results on animal studies and the perspectives of their commercial (1) use for wound-care, in particular in the treatment and diagnostics of chronic wounds that affect the diabetics and elderly.

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FIGURES

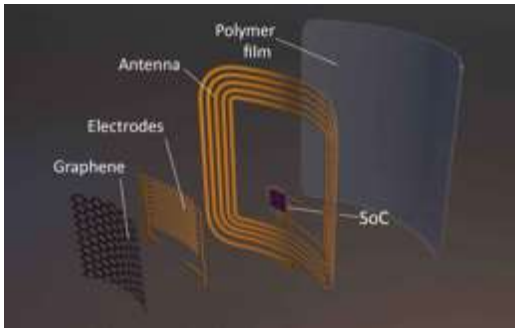

Figure 1: embedded graphene biosensors for wound care .

Correlated TERS, TEPL, & SPM measurements of 2D Materials

Marc Chaigneau
HORIBA FRANCE SAS, France
marc.chaigneau@horiba.com

Continuous and large research as well as industrial development have been carried out toward incorporating 2D materials in nanoelectronic devices and thereby in our daily life. With the great challenge of producing large areas of these materials and their integration with other material systems, comes the need of “structural control at the nanoscale”. An information-rich nanocharacterization technique becomes then necessary for further deployment of 2D materials-based applications.

In this talk, I’ll demonstrate how correlated TERS, TEPL & SPM measurements are possible using an AFM-Raman instrument. This means that co-localized information about the topography, the electronic properties and the structural quality can be obtained down to the nanometer scale with a single probe and without sample repositioning. I will present data on MoS2, WSe2, and WS2 as well as on a lateral WS2/WSxSe1-x/WSe2 heterostructure on SiO2/Si substrate. I’ll demonstrate that comprehensive Raman and Photoluminescence characterization at the nanoscale is crucial for understanding the composition and heterogeneities of 2D materials.

Challenges and progress in two-dimensional materials for industrial applications

Archana Venugopal† and Luigi Colombo‡
† Texas Instruments Incorporated, Dallas, TX
‡University of Texas at Dallas, Richardson, TX
a.venugopal@ti.com; lcolombo80@gmail.com

Abstract

Graphene has been studied intensively since 2004, yet the path to integration in standard semiconductor flows remains elusive. The many benefits of two-dimensional materials have been extensively investigated. While the specific benefits of the fundamental materials properties such as electron mobility, thermal conductivity and ambipolar behavior, for many applications have been presented, these materials are still to some degree in the incipient stage of development. Before these materials can be introduced in real device flows not only do the materials growth issues will have to be addressed but also the integration issues before any real use can be achieved in real device flows. The objective of this presentation is to discuss the potential for graphene and other two-dimensional materials for analog device applications as well as thermal dissipation.

A robust graphene platform for biorecognition

Mar Garcia-Hernandez [(1)]
Irene Palacio[(1)], Almudena Nañez[(2)], Carlos Briones[(2)], Pedro Alpuim [(3)] and Jose Angel Martín-Gago[(1)]

(1) CSIC, Instituto de Ciencia de Materials de Madrid, Sor Juana Ines de la Cruz,3, 28049 Madrid
(2) Centro de Astrobiología- INTA-CSIC, Torrejón de Ardoz, 28850 Madrid, Spain
(3) INL,Avda. Mestre Jose Veiga, Braga, Portugal

marmar@icmm.csic.es

Abstract
Technologically useful and robust graphene-based interfaces for devices require the introduction of highly selective, stable and covalently bonded functionalities on the graphene surface, whilst essentially retaining the electronic properties of the pristine layer. This work demonstrates that highly-controlled, ultra-high vacuum covalent chemical functionalization of graphene sheets with a variety of molecules, among them para-aminophenol and p-aminothiophenol [1]. These systems are subsequently used for the development of hybrid nanostructures by attaching metal nanoparticles and nuclei acid aptamers, as depicted in Figure 1. The impact of this controlled surface functionalization methodology on the electrical properties of graphene was evaluated by studying graphene solution-gated field-effect transistors (gSGFET), which were measured prior to and after functionalization with p-aminothiophenol.

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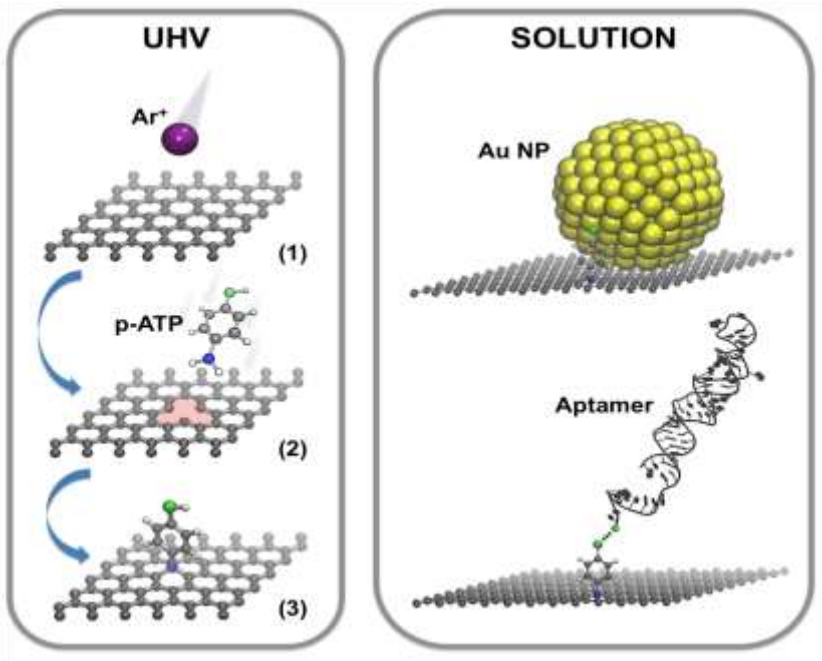

Figure 1: Left) Basic mechanism for the covalent functionalization with p-ATP that serves as a link to molecules of interest. It takes place in Ultra High Vacuum. Right) Example of linked molecules: gold nanoparticles and Aptamers . This second step takes place in solution

Commercial Scale Production of CVD Graphene and Graphene Quantum Dots

Byung Hee Hong
Department of Chemistry & Graphene Research Center, Seoul National University, Seoul, Korea
Graphene Square Inc. & BioGraphene Inc.
Advanced Institute of Convergence Technology, Suwon, Korea.
byunghee@snu.ac.kr

Recently, we demonstrated the continuous synthesis of graphene films using 500 mm-wide roll-to-roll processes that enables the production of > 100 m long graphene grown on Cu or Ni foils at a rate of max. 500 mm/min. The etching and transfer processes have been optimized for the applications that are close to markets, including car windshields, bullet proof vests, EUV pellicles, EMI shielding, and gas barriers. Now, *Graphene Square Inc.* is preparing commercial scale production as large as 200,000 m^2/year to be completed in 2022. In addition, we also developed a real-time assessment tool to examine coverage and quality of graphene on Cu surface, which are crucial for quality control and higher production yield. The scalable synthesis of graphene quantum dots also has been achieved for the massive use in therapeutic applications. In this talk, some emerging applications based on graphene quantum dots will be briefly discussed, targeting the applications to Parkinson's disease, colitis, and kidney diseases.

Transparent image sensor for eye-tracking and nanophotonic infrared photodetectors

Frank Koppens
ICFO
Barcelona (Castelldefels), Spain
Frank.koppens@icfo.eu

Integrating and manipulating the nano-optoelectronic properties of Van der Waals heterostructures can enable unprecedented platforms for photodetection, sensing and modulation. Many of the realized devices have already demonstrated competitive performances and proof-on-concept integration with Si-CMOS technologies has been demonstrated [1,2]. But many challenges remain, and there is still a clear need for competing photodetectors for the full spectral range from short-wave infrared, infrared and terahertz.

In this talk, we present
1) the first transparent camera, applied as an eye-tracking device
2) demonstrate several new photodetection concepts for infrared light.

Image sensors hold a pivotal role in society in their ability to digitize visual scenes. Currently, all commercial image sensors and therefore cameras are opaque. We present the first transparent camera based on an array of graphene photodetectors. These transparent image sensors can have a far-reaching impact on human-computer interfaces, smart displays, and eye-tracking for augmented and virtual reality. The operation of these devices presents a fundamental shift in how we think about image sensor, as these devices can be hidden in plain sight.

In the second part of the talk, we present several new photodetection concepts for infrared light. The first is a novel approach for highly responsive graphene-based photodetectors with orders of magnitude lower dark current levels, exploiting a metal-insulator-graphene diode structure . This detector takes advantage of the low density of states of graphene near the neutrality point, giving rise to a novel type of gain mechanism. We also present an infrared photodetector based on a plasmonic antenna coupled to hyperbolic phonon-polaritons in hexagonal-BN to highly concentrate midinfrared light into a graphene pn-junction. This novel approach explicitly benefit from the extraordinary nanophotonic properties of 2D materials and yields remarkable device performance featuring room temperature high sensitivity, hence achieving a combination currently not present in the state-of-the-art graphene and commercial mid-infrared detectors.

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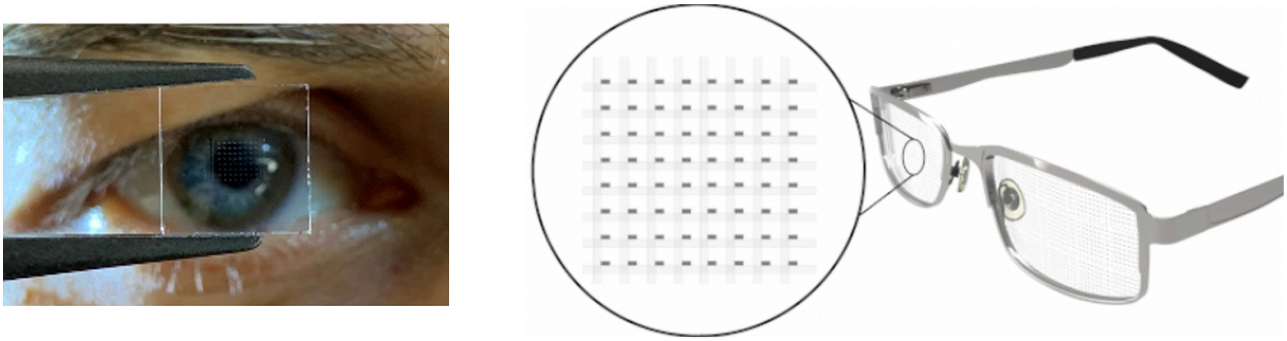

Figure 1: Left: transparent image sensor based on an array of graphene photodetectors. Right: eye-track device

Synthesis, properties and applications of free-standing monolayer amorphous carbon & nanoporous graphene foam

Barbaros Oezyilmaz

Department of Physics, National University of Singapore, Singapore 117551, Singapore.
Centre for Advanced 2D Materials, National University of Singapore, Singapore 117546, Singapore.
Department of Materials Science and Engineering, National University of Singapore, Singapore 117575, Singapore.
barbaros@nus.edu.sg

Environmental stability, synthesis cost and process compatibility are key challenges in commercializing 2D materials. I will discuss our approach in addressing these challenges for atomically thin amorphous carbon and nonporous graphene foam and their potential for applications.
Bulk amorphous materials have been studied extensively and are used widely. Amorphous thin films are for example essential for enabling device scaling, increase data storage densities and improve energy storage capacities. Yet their atomic arrangement remains an open issue. Although they are generally believed to be Zachariasen continuous random networks, recent experimental evidence favours the competing crystallite model in the case of amorphous silicon. In two-dimensional materials, however, the corresponding questions remain unanswered. Here I will discuss the synthesis, by laser-assisted chemical vapour deposition of centimetre-scale, free-standing, continuous and stable monolayer amorphous carbon, topologically distinct from disordered graphene [1]. Unlike in bulk materials, the structure of monolayer amorphous carbon can be determined by atomic-resolution imaging. Extensive characterization by Raman and X-ray spectroscopy and transmission electron microscopy reveals the complete absence of long-range periodicity and a threefold-coordinated structure with a wide distribution of bond lengths, bond angles, and five-, six-, seven- and eight-member rings. Direct measurements confirm that it is insulating, with resistivity values similar to those of boron nitride grown by chemical vapour deposition. Free-standing monolayer amorphous carbon is surprisingly stable and deforms to a high breaking strength, without crack propagation from the point of fracture. The excellent physical properties of this stable, free-standing monolayer amorphous carbon could prove useful for permeation and diffusion barriers in applications such as magnetic recording devices, copper interconnects and flexible electronics.

In the second part of my talk I will discuss the synthesis of nanoporous graphene foam, its properties and potential for supercapacitor applications.

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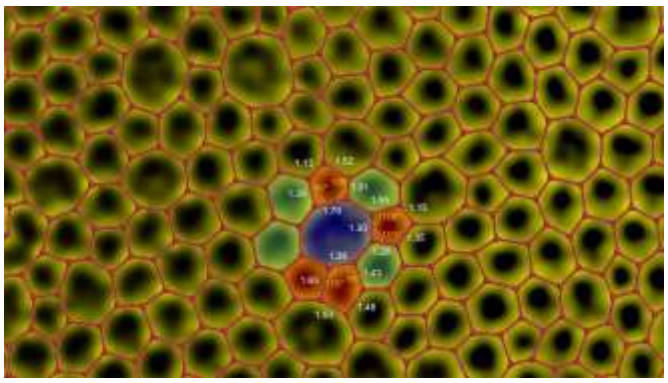

Figure 1: Atomic structure of MAC from TEM. Monochromated HRTEM image of MAC. The image contrast is inverted and false-coloured for better visibility. Colour overlay is added for identification of pentagons (red), heptagons/octagons (blue) and strained hexagons (purple for individual hexagons; green for crystallite regions) that are omnipresent. Crystallites (regions of green hexagons) separate the regions with non-hexagons.

From labs to pilot lines: Graphene and related materials device fabrication solutions

Dr Ravi Sundaram
Oxford Instruments Plasma Technology, North End, Yatton, Bristol, UK
Ravi.sundaram@oxinst.com

Abstract

Extensive efforts in the research and development of graphene-based technologies over the last 15 years has resulted in steady increase in technology readiness. Today, we see an emergence in efforts for development of graphene-based applications (such as modulators, detectors, gas and biosensors) at scale. For successful scaling up of prototypical applications demonstrated to date, robust technologies, and processes for large area device fabrication are required.

In this talk I will first give an overview of lab to fab technologies and processes developed at Oxford Instruments towards growth of Graphene, other layered materials and heterostructures by CVD and ALD followed by our developments in technology for device fabrication processes such as dielectric deposition by ALD and device pattern etching by RIE and ALE.

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Challenges and progress in two-dimensional materials for industrial applications

Archana Venugopal† and Luigi Colombo‡
† Texas Instruments Incorporated, Dallas, TX
‡University of Texas at Dallas, Richardson, TX
a.venugopal@ti.com; lcolombo80@gmail.com

Abstract

Graphene has been studied intensively since 2004, yet the path to integration in standard semiconductor flows remains elusive. The many benefits of two-dimensional materials have been extensively investigated. While the specific benefits of the fundamental materials properties such as electron mobility, thermal conductivity and ambipolar behavior, for many applications have been presented, these materials are still to some degree in the incipient stage of development. Before these materials can be introduced in real device flows not only do the materials growth issues will have to be addressed but also the integration issues before any real use can be achieved in real device flows. The objective of this presentation is to discuss the potential for graphene and other two-dimensional materials for analog device applications as well as thermal dissipation.

Derivatives of Graphene Oxide for different target applications

Rune Wendelbo
S. Eqtesadi, S. Etemadi, B. Gjoka, R. Gulla, M. Modarres, A. Motealleh, S. Santos
Abalonyx AS, Forskningsveien 1, 0373 Oslo, Norway
rw@abalonyx.no

Abstract

Graphene oxide is a very versatile material that can be modified in a range of ways, for example by deposition of metals and metal oxide nanoparticles on the surface. This makes it a candidate for as diverse applications as energy storage in batteries, supercapacitors, fuel cell membrane, solar cells and CO_2-capture [1, 2], water treatment [3], functional coatings, including anti-corrosion, anti-fouling and anti-bacterial coatings [4], wearable electronics and sensors [5], biomedical [6] as well as catalytic processes [7]. The combination of graphene oxide with TiO_2 nanoparticles (Fig. 1) from our lab shown as examples.
Unfortunately, most studies are performed on “home”-produced lab-scale graphene oxide, limiting the value of the results since it is not known exactly how similar samples from different labs are. We strongly recommend the graphene community to follow the practice of the Clay Mineral Society have a repository of well homogenized and fully characterized materials that are distributed to labs world-wide at low cost [8].

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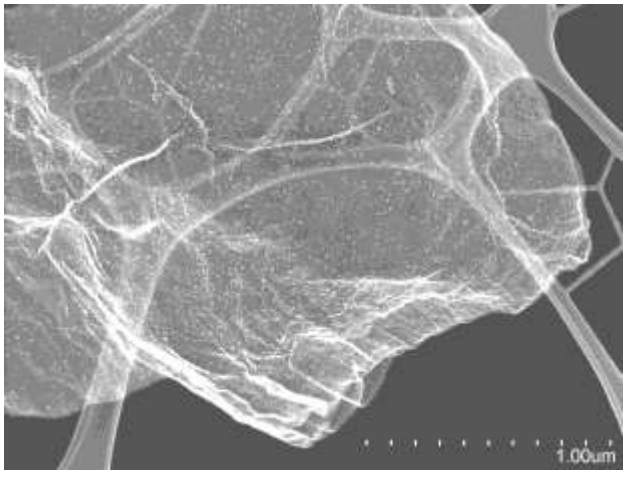

Figure 1: Abalonyx graphene oxide decorated with TiO_2 nanoparticles.

Developing a Graphene Industry

Amaia Zurutuza
Graphenea, Paseo Mikeletegi 83, Donostia-San Sebastian, 20009, Spain
a.zurutuza@graphenea.com

Abstract

Graphene alone or in combination with other materials such as quantum dots or silicon has shown to provide enhanced performance in many applications. However, in order to integrate graphene in semiconductor devices in a cost-effective manner, it will require combining it with CMOS technology while processing the graphene into functional devices. Indeed, graphene has been monolithically integrated with CMOS technology [1].

The fabrication of graphene at an industrial scale will require to overcome numerous challenges such as wafer scale uniformity with a high charge carrier mobility, presence of metal contamination, etc. However, wafer scale device fabrication is also critical for a successful graphene integration. At present, there is no commercial foundry able to process graphene in order to produce graphene devices (GFETs). As a consequence, we have recently launched a platform to commercialise graphene-based field effect transistor (GFETs) and thus help customers to focus on their applications rather than wasting time on graphene processing. At the same time, taking the first steps into providing a graphene commercial foundry service.

During this talk, I will cover current challenges related to wafer scale graphene growth, transfer and device fabrication.

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FIGURES

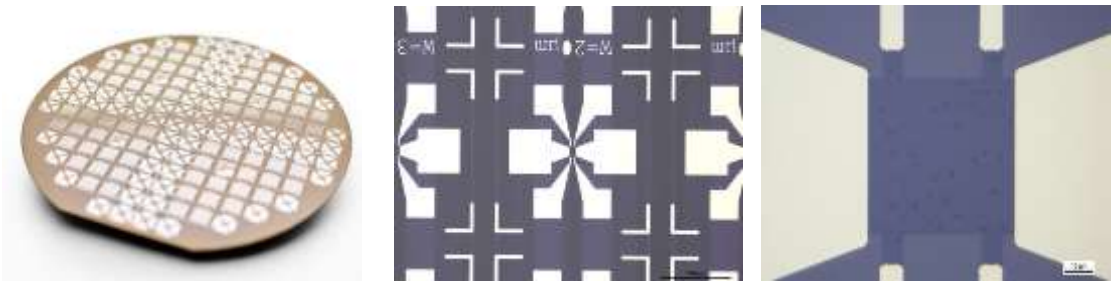

Figure 1: Wafer scale graphene field effect transistors.

Disordered Graphene Materials: Atomistic Characterization and Performances

Aleandro Antidormi[1]
Stephan Roche[1,2]
[1] *Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and BIST, Campus UAB, Bellaterra, 08193, Barcelona, Spain*
[2] *ICREA Institucio Catalana de Recerca i Estudis Avancats, 08010 Barcelona, Spain*
aleandro.antidormi@icn2.cat

Formidable progress has been recently achieved in the fabrication and characterization of disordered materials with unprecedented properties. In this context, particular forms of disordered graphene (reduced graphene oxides), obtained by chemical exfoliation techniques, have been found suitable to improve the performances of composite materials, with application in energy. Moreover, the recent demonstrated possibility to synthesize wafer-scale two-dimensional amorphous carbon monolayers, structurally dominated by sp2 hybridization has initiated a new platform of low-dimensional materials to explore as alternative forms of membranes with enhanced chemical reactivity which could serve as coating materials [1,2].
The excellent physical properties of the mentioned materials derive from the nature and degree of their disorder which, controlled at the fabrication level, represents the key ingredient to tune their physical/chemical properties for specific target applications. In this respect, new fabrication strategies to modify the degree of disorder and a systematic theoretical characterization of the impact of the material structural quality on the ultimate performance is urgent.
In this poster we present the results of our theoretical investigation on possible strategies to improve the (thermal) reduction process of graphene-oxides and the consequent possibility to recover the quality of pristine graphene [3]. Moreover, we present a systematic analysis of the structural and vibrational properties of amorphous carbon monolayers as a function of the structural quality of the material, showing how disorder results in a tunable thermal conductivity varying by more than one order of magnitude [4]. In particular, we identify how energy is dissipated in this material by a systematic analysis of emerging vibrational modes whose localization increases with the loss of spatial symmetries. Our simulations provide some recipe to design most suitable "amorphous graphene" based on the target applications such as ultrathin heat spreaders, energy harvesters or insulating thermal barriers.

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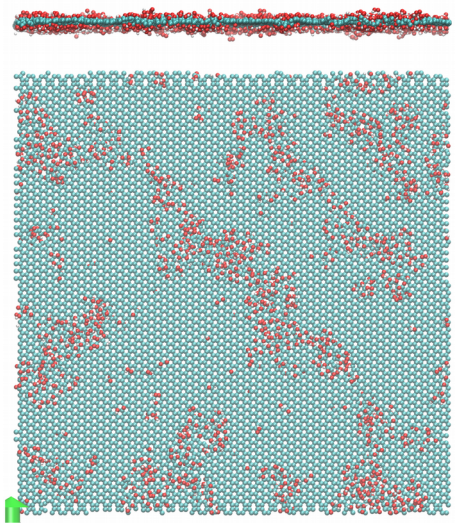

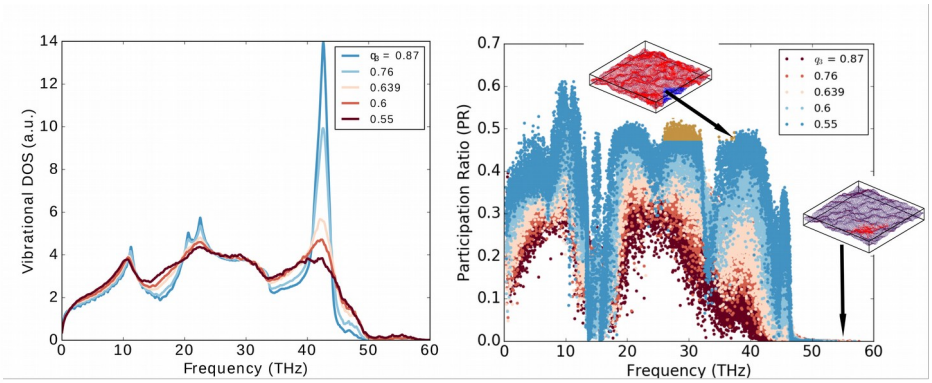

FIGURES
Figure 1: Side and top view of a GO sample before thermal reduction.
Figure 2: (Left) Vibrational DOS of Amorhous Graphene for different degrees of amorphousness. (Right) Participation Ratio of the samples and atomic displacements (insets)

Revealing supramolecular interactions in graphene-chitosan composites

Dr. Julio C. Chacón-Torres
Lorena Layana, Charlotte Berrezueta-Palacios, Lenin Andres Guerrero-León, Duncan John Mowbray, and Sarah Briceño
School of Physical Sciences and Nanotechnology, Yachay Tech University, Urcuquí 100119, Ecuador
jchacon@yachaytech.edu.ec

Graphene-chitosan composites have been developed to implement the use of graphene in bioapplications. For instance, the opto-electronic properties of graphene excel from many other materials in addition to its intrinsic structural strength. [1-3] On the other hand, chitosan excels as an excellent biocompatible material able to create film-coatings on the surface of the substrate material. [4] However, much less is known about the physico-chemical and supramolecular interactions between the graphene and chitosan acting as a bio-compatible organic composite.

Here have studied the physical, structural and electronic characteristics that interact along with the formation of a homogeneous graphene-chitosan composite material. We have conducted an experimental plus theoretical study of both systems to disclose the supramolecular influence between the graphene functionalization with the chitosan molecules to form the composite. The study includes a full panorama of the molecular interactions by means of Raman and Fourier transform infrared (FTIR) spectroscopies; atomic force (AFM), scanning electron (SEM) and transmission electron (TEM) microscopies; in addition to density functional theory (DFT) calculations that explain the functionalization mechanism in graphene-chitosan composites. Finally we deposited silver and gold nanoparticles on the graphene-chitosan surface revealing a preferential interaction of Au with the graphene-chitosan compound in contrast to the deposition of Ag. This nanostructured composite may serve to develop advanced materials that could be implemented in upcoming biomedical applications.

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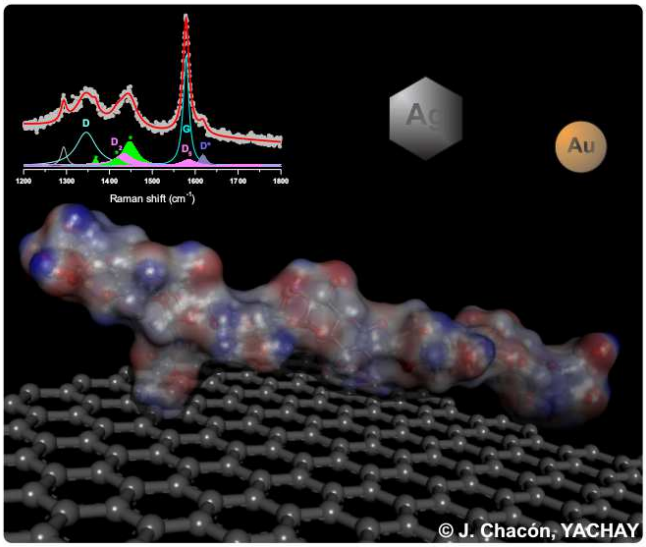

Figure 1: Schematic representation of the molecular interaction between a chitosan molecule on graphene when Ag and Au nanoparticles interact. The Raman spectrum represents the vibronic response of the chitosan-graphene composite.

Cost efficient washing and purification process for graphene oxide manufacturing at industrial scale

Erik Khranovskyy,
Mykhailo Zhybak
Grafren AB, Bobergsgatan 1, 58247, Linköping, Sweden
Department of Physics, Chemistry and Biology (IFM) Linköping University, 58183, Linköping, Sweden
ceo@grafren.se

Main approach for graphene oxide (GO) manufacturing remains still Hummers method, diversely modified in terms of process steps involved, deviation of conditions or chemicals used. However, still the most resources- and time-consuming step is washing of the as-synthesized sludge of GO and separation of pure graphene flakes from the possible waste of the chemical process. Producers are always faced with the contradictory choice between larger yield of graphene flakes and the quality of obtained material. Current methods for separation of pure GO are vacuum filtering or centrifugation, which proved to be applicable for small-scale academy research. However, none of these approaches is applicable for large industrial scale production of GO, due to complexity, low yield, and high labour costs.

We have developed the method [1] for washing of the as-synthesized GO paste, with step-by-step removal of i) acid, metals and other chemical contaminants ii) unreacted species of graphite (debris, rocks, 3D inclusions etc) and iii) flakes of GO thicker then 10 monolayers. The process involves dissolving and mechanical treatment of the GO paste, detaching the individual species from each other and separating them in space. Process is easily scalable (standard unit can be from current 10 g per batch to 1 kg) at low cost, has decent energy consumption and potentially may involve zero labour cost. Outcoming GO flakes are in dispersion, and the concentration can be tuned to the required level (e.g. from 0.01 20 mg/mL). Process depends negligible on the quality of incoming material and requires minor tuning of the system to supply the GO material accordingly to the ISO Standard on Graphene and Related Two-Dimensional (2D) Materials [2].

Figure 1 shows the SEM images of incoming GO paste in comparison to the purified GO flakes after the process as well as content of removed “waste”; bottom left image visualises the efficiency of the process in terms of GO purity before and after the process.

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FIGURES

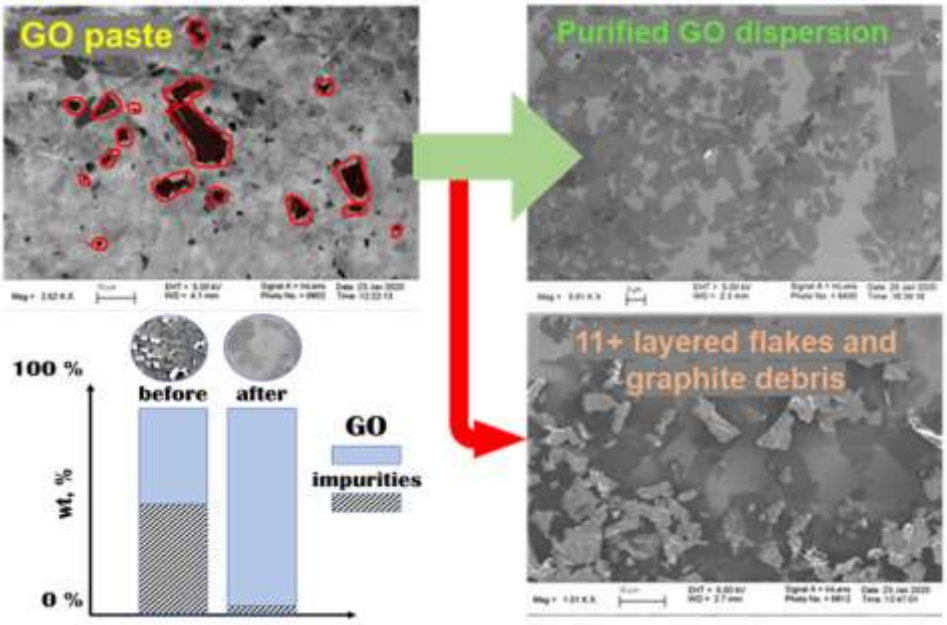

Figure 1: Illustration of the proposed method efficiency: SEM images of GO before and after the treatment, as well as separated “waste”.

Confocal Laser Scanning Microscopy as a Real-time Quality-assessment Tool for Industrial Graphene Synthesis

Dong Jin Kim[1,2,3,8], Chang-Won Lee[4,8], Yeonjoon Suh[2], Heejeong Jeong[5], Insu Jo[2], Joonhee Moon[6], Mina Park[2], Yun Sung Woo[3,7*], and Byung Hee Hong[2*]

[1] Program in Nano Science and Technology, Graduate School of Convergence Science and Technology, Seoul National University, Seoul 08826, Korea
[2] Graphene Research Center, Advanced Institute of Convergence Technology, Suwon 16229, Korea & Department of Chemistry, Seoul National University, Seoul 08826, Korea.
[3] Graphene Square Inc., Suwon 16229, Korea.
[4] School of Basic Sciences, Hanbat National University, Daejeon 34158, Korea
[5] Department of Physics, Faculty of Science, University of Malaya, Kuala Lumpur 50603, Malaysia
[6] Division of Analytical Science Research, Korea Basic Science Institute (KBSI), Daejeon 34133, Korea
[7] Department of Advanced Materials Application, Korea Polytechnics, Gyeonggi-do 13122, Korea
[8] These authors have contributed equally.
E-mail: krbyunghee@snu.ac.kr (B.H.H.), yunswoo@dankook.ac.kr (Y.S.W.)

For the industrial quality control (QC) of the chemical vapor deposition (CVD) graphene, it is essential to develop a method to screen out unsatisfactory graphene films as efficiently as possible. However, previously proposed methods based on Raman spectroscopy or optical imaging after chemical etching are unable to provide non-invasive and fast analysis of large-area graphene films as grown on Cu foil substrates. Here we report that the reflection mode of confocal laser scanning microscopy (CLSM) provides a high-contrast image of graphene on Cu, enabling the real-time evaluation on the coverage and quality of graphene. The reflectance contrast, RC, was found to be dependent on the incident laser wavelength, of which the maximum was obtained at 405 nm. In addition, RC decreases with increasing defect density of graphene. The dependence of RC on the graphene's quality and laser wavelengths were explained by the tight-binding model calculation based on the Fresnel's interference formula. Thus, we believe that the reflection mode CLSM would be a very powerful quality-assessment tool for the mass production of CVD graphene films grown on Cu.

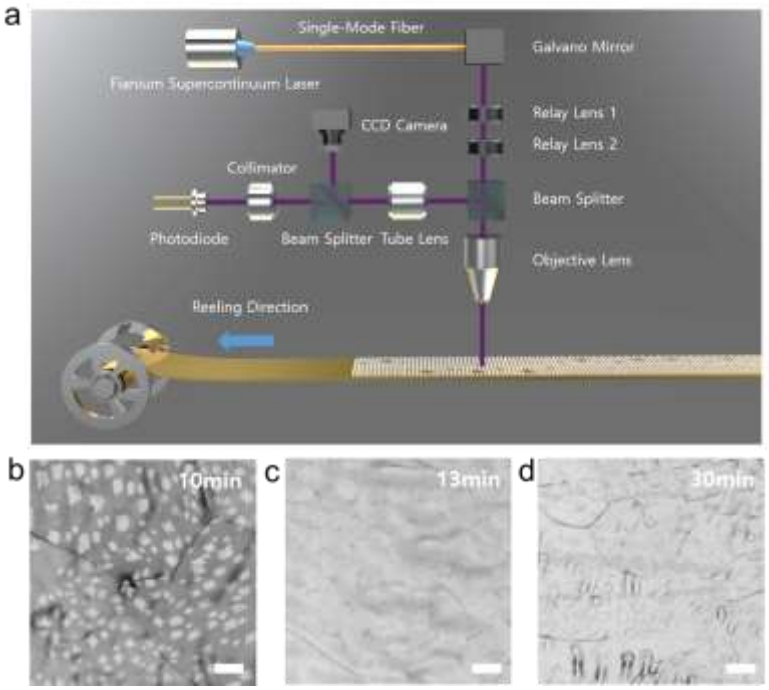

Figure 1: Concept of in-situ monitoring of the as-grown CVD graphene on Cu using CLSM. a) The concept of monitoring the as-grown CVD graphene on Cu foil during the continuous roll-to-roll synthetic process using the reflective mode CLSM. b)-d) The CLSM images of the CVD graphene with various coverage from sub-monolayer to fully covered on Cu foil controlled by growth time of 10, 13, and 30 min, respectively. High visibility of graphene on Cu in CLSM images of b)-d), in which the graphene domain is a bright region and Cu is a dark region, makes it possible to determine whether graphene growth is complete. Scale bar: 10μm.

Graphene Wafer Scale Integration

Sha Li
Zhenxing Wang[1], Oihana Txoperena[2], Mark Allen[3], Yinglin Liu[3], Ashley Rushton[3], Alexander Bessonov[3], Sami Kallioinen[3], Salla Kalaja[3], Chris Bower[3], Tapani Ryhanen[3], Amaia Zurutuza[2], Max C. Lemme[1,4], Daniel Neumaier[1,5]
[1] AMO GmbH, Advanced Microelectronic Center Aachen, Otto-Blumenthal-Straße 25, 52074 Aachen, Germany
[2] Graphenea, Paseo Mikeletegi 83, 20009, San Sebastián, Spain
[3] Emberion Limited, 151, Cambridge Science Park, Milton Road, Cambridge CB4 0GN, United Kingdom
[4] Faculty of Electrical Engineering and Information Technology, Chair of Electronic Devices, RWTH Aachen University, Otto-Blumenthal-Str. 2, 52074 Aachen, Germany
[5] School of Electrical, Information and Media Engineering, University of Wuppertal, Campus Freudenberg, Lise-Meitner-Str. 13, 42119 Wuppertal, Germany
li@amo.de

Graphene and other two-dimensional materials (2DM) have allowed prototyping devices with exceptional performances and potentially huge impact in electronics, photonics and sensor technology.[1,2] The next big challenge is the wafer-scale integration of 2DM, as success in real-world applications it requires not only outstanding performance at the single-device level but also, large-scale fabrication processes.[3] This abstract presents the successful integration of graphene fabrication technology on 150 mm silicon wafer platform as a needed unit for a new graphene imager product, including graphene growth and transfer, patterning, contacting and encapsulation. Statistics on graphene-on-wafer quality metrics show that the as-developed foundry process delivers good batch-to-batch reproducibility and high device yield. This technology development is promising for introduction of high-performing graphene-on-wafer at competitive cost, accelerating innovation for advanced 2DM-based electronics, and eventually creating a new imager product category. This work is funded by the European Union's Horizon 2020 research and innovation program G-Imager under grant agreement No. 820591.

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Functionalized Few-Layer-Graphenes: High Quality and Outstanding Processability without Compromises

Martin R. Lohe
Sixonia Tech GmbH, Pestitzer Straße 16, 01187 Dresden, Germany
mlohe@sixonia-tech.de

ABSTRACT
The process of electrochemical exfoliation and functionalization of graphene, developed at TU Dresden and patented by Sixonia Tech GmbH[1] creates the ability to functionalize few-layer graphenes deliberately and precisely, directly during their production. This versatility allows us to modify graphene solutions to suit selected substrates, intermediates or end compounds. Building the knowhow to tailor the graphene-solution-substrate systems enables us to achieve desired performance goals and meet particular application process requirements. By providing good scalability and yield, low production costs and the good processability, our mission is to unleash the currently limited potential of graphene in various fields.
The scalable and eco-friendly process technology opens up new possibilities and prospects for the applications of graphene, in the field of inks, composites, sensors, energy storage and energy conversion.

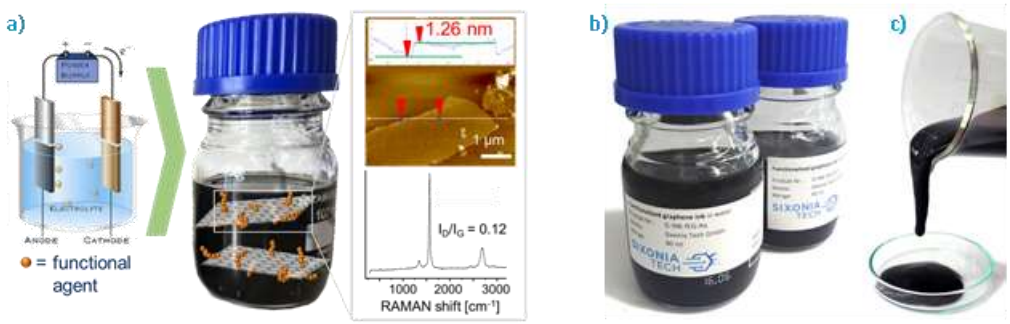

Fig. 1.: Surfactant-free aqueous dispersion of functionalized high-quality few-layer graphene (a), customizable conductive inks (b) and high viscosity formulations (c) based on our advanced E-Graphenes.

As an example, our E-Graphenes can be functionalized to be dispersible in water without the need for surfactants (Fig. 1a), while still maintaining an intrinsic conductivity that is at least one order of magnitude higher than that of commonly used reduced graphene oxide (rGO) materials. Sixonia Tech can help to identify the most suitable graphene for a given application and formulate it (Fig. 1b, c), to facilitate its integration into the desired applications.
Compared to other “graphene” products, E-Graphenes show a superior combination of tailorable properties within a single material, such as large flake-size in the µm-range, low thickness in the range of 1-10 layers and good processability. Unlike in GO, the defined functional groups can provide an improved processability while still maintaining high electrical conductivity and reasonable sheet size.

As an example, here are the specifications for our E-Graphene CSO in aqueous dispersion:

Physical Properties		**Chemical properties**	
Colour:	black	Odour:	odourless
Graphene concentration:	≥ 2 mg/ml	Solvent:	water
Additives/Binders:	none	pH:	(adjust. on demand)
Lateral Size (avg.):	1-2 µm	Zeta Potential:	-35 mV @ pH 3 to -60 mV @ pH 10
Thickness (avg.):	1-5 atomic layers		
Conductivity (bulk):	> 40 000 S/m	Raman D/G-ratio:	0.1-0.2
Resistivity (bulk):	< $2.5 \cdot 10^{-3}$ Ωcm	C/O ratio:	~20
Sheet resistance:	< 1 Ω/□ @ 25µm		

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Direct growth of graphene on MoS_2: Towards Van der Waals heterostructures

Roberto Muñoz Gómez
Elena López-Elvira, Carmen Munuera, Mar García-Hernández
Material Science Factory, Instituto de Ciencia de Materiales de Madrid (ICMM), C/ Sor Juana Inés de la Cruz nº 3, E-28049 Madrid. SPAIN
rmunoz@icmm.csic.es

Heteroepitaxial growth of thin layers of semiconducting materials conforming heterostructures represent the main foundations of numerous modern devices. Recently, 2D materials combined into van der Waals multilayers have emerged as an appealing option to conform valuable heterostructures, without the typical interfacial lattice-matching constraints encountered in conventional heteroepitaxial growth. The usual fabrication of these Van der Waals heterostructures relies on transfer processes that frequently limit the production yield. Therefore, a scalable method to directly growth 2D materials heterostructures is a priority in this field. To face this challenge, recently we devised new protocols to growth graphene on semiconducting oxides (SiO_2, TiO_2) at low temperature by using plasma-CVD [1, 2]. Now, we are extending our approach to synthesize graphene on transition metal dichalcogenides (MoS_2) exploring the feasibility of direct synthesis of van der Waals heterostructures [3]. In this contribution, we present our last developed protocols. The graphene films are characterized in terms of morphology (AFM)(Fig.1), chemical structure and composition (Raman). The role of the carbon precursors (CH_4 & C_2H_2), gas diluents (H_2 & Ar), temperature and other synthesis parameters used on the final properties on the film structure is discussed. We identify the substrate activation as the main limiting factor to improve the material quality and propose a new strategy to overcome this drawback. The methodologies shown are intrinsically pure, easily scalable and represent a step forward in the direct growth of van der Waals heterostructures.

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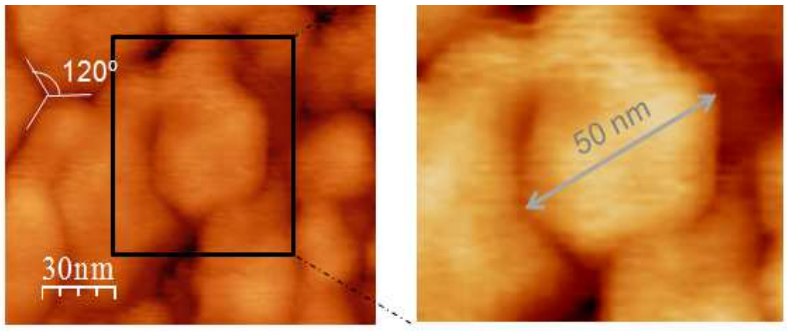

Figure 1: AFM images of graphene crystals (submonolayer coverage) grown on MoS_2.

Laser Processing optimization for 2D materials-perovskite solar modules

Stefano Razza
Antonio Agresti, Sara Pescetelli, Aldo Di Carlo
C.H.O.S.E., Department of Electronics Engineering, University Of Rome Tor Vergata, 00133, Rome, Italy
stefano.razza@uniroma2.it

Industrial applications for two-dimensional (2D) material-perovskite solar devices require optimized fabrication steps devoted to scale-up efficient lab-scale devices to large area modules. In this work, with the aim to get an efficient series interconnection between module constituting sub-cells, we employed a 10 ps laser (λ=355 nm) for all the ablation processes (namely P1, P2, P3), by carrying out a fully optimized device layout [1,2]. If, on one hand, the quality of P2 process has a strong impact on the module serial resistance, on the other hand a not fully optimized P3 process can lead to low parallel resistance value. In the present work, we show how the module performance can be improved by the optimizing P2 and P3 processes. The parameters used for each laser ablation step were set to obtain an efficient and fast process by retaining high process repeatability. As a matter of fact, laser fluence and process speed need to be optimized taking into account the presence of 2D materials and their depositions techniques, preventing the incomplete removal of the layers or the laser-induced active area degradation.

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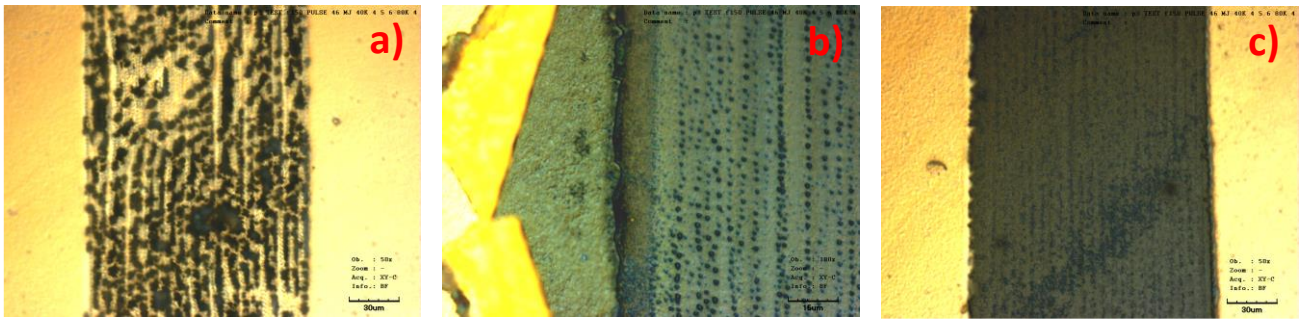

Figure 1: a) P3 scribe with electrical bridges due to a incomplete gold removal; b) gold delamination induced by using a very high fluence used during P3 process; c) optimized P3 scribe without gold residual particles in the scribed area and no delamination on the edge

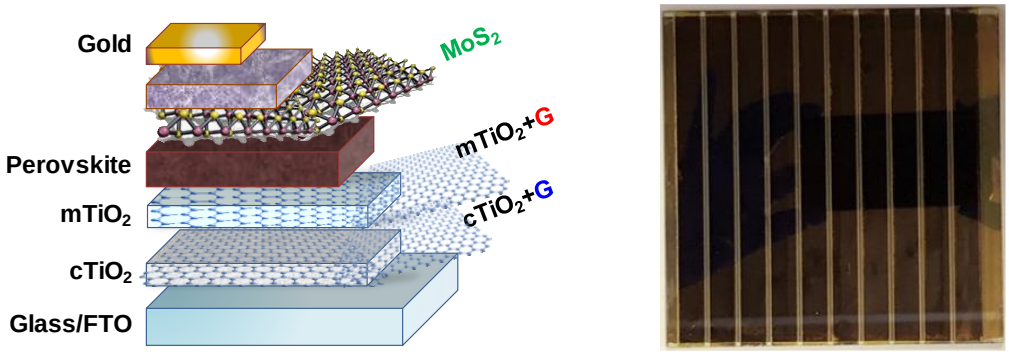

Figure 2: Cell structure and final module made realized by laser pattering of graphene, perovskite and 2D materials layers.

Water Filtration with Carbon Nanomembranes

Albert Schnieders
Nikolaus Meyerbröker, Polina Angelova, Henning Vieker
CNM Technologies GmbH, Morgenbreede 1, 33615 Bielefeld, Germany
albert.schnieders@cnm-technologies.com

Carbon nanomembranes (CNMs) are a molecular-thin 2D-sheet material made by cross-linking of self-assembled monolayers of aromatic molecules. Recently scientists at Bielefeld University demonstrated that CNMs possess an extremely high pore density of one sub-nm channel per square nanometre [1]. Thus, this 2D-material combines an exceptionally high permeance (~ 800 LMH) for water with close to full rejection of salts [2] and small organic molecules like urea. We have succeeded to implement nanometre-thin CNMs as active layers in large-area composite membranes consisting of a polymer support layer with pores in the micrometre-range giving access to the free-standing active CNM-layer (Figure 1). These composite membranes are mechanically stable and can be mounted in modules. Currently, we produce sheets with areas of up to 20 x 20 cm² in the laboratory. A concept for a pre-industrial pilot production with a capacity of up to several 10.000 m² is in place. We have demonstrated in laboratory experiments applications of our composite membranes as semipermeable membranes in forward osmosis for the cold concentration of watery solutions like juices, milk, beer, wine, urine etc. (Figure 2). Another possible application is in the provision of ultrapure water, where the membrane can filter last amounts of salt, heavy metals or small organic molecules from otherwise pure water.

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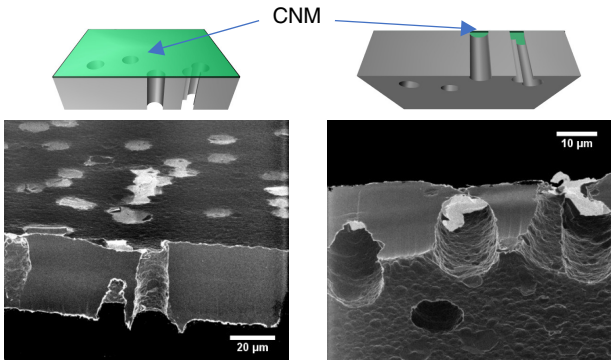

Figure 1: Helium ion micrograph of a cross section of a CNM-composite membrane.

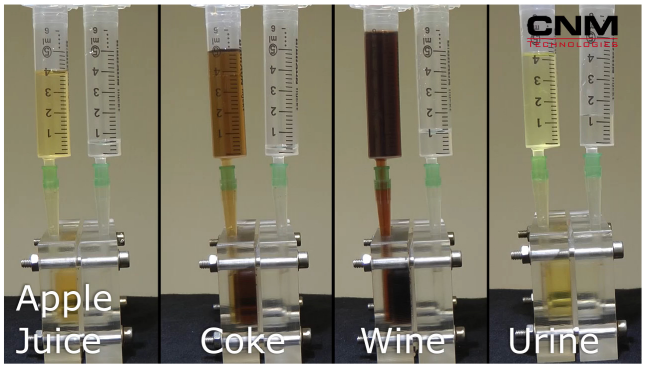

Figure 2: Cold concentration of watery solutions with CNM-composite membranes (for movie see http://www.cnm-technologies.com/en/applications/membrane-technology/osmosis.html).

MXene-based perovskite photovoltaics: a general approach for efficient and scalable devices.

Antonio Agresti
Sara Pescetelli, Hanna Pazniak, Danila Saranin, Alessia Di Vito, Stefano Razza, Aldo Di Carlo.
C.H.O.S.E., Electronic Engineering Department, University of Rome Tor Vergata, Via del Politecnico 1, 00133, Rome, Italy.
antonio.agresti@uniroma2.it

Recently, a new class of emerging bi-dimensional (2D) materials known as transition metal carbides, nitrides and carbonitrides (MXenes) was successfully employed in full inorganic or organic-inorganic halide perovskite (HP). In particular, $Ti_3C_2T_x$ MXenes have been tested as dopant for electron transporting layer (ETL), to improve the electron collection in planar devices [1] or as interlayer between inorganic perovskite and carbon counter-electrode (CE).[2] In this work we go further to the simple application of MXenes in a specific structure, by suggesting a general approach to boost device performance, suitable for both planar inverted and mesoscopic n-i-p device architectures, independent from the perovskite formulation and easily scalable to large area modules. In fact, as density functional theory predicts, MXenes WF can range from 1.6 eV (for OH-termination) to 6.25 eV (for O-termination), thanks to the surface termination (T_x) strongly influencing the density of states.[3] In addition, we experimentally and theoretically demonstrated perovskite WF tuning when MXenes are used as additive in perovskite precursor solution, for both mesoscopic n-i-p and p-i-n small area devices, without affecting other electronic properties. This approach resulted in strongly improved device power conversion efficiency (PCE) due to the dipole induced by the $Ti_3C_2T_x$ at the perovskite/ETL interface that changes the band alignment between these layers.[4] Moreover, the proposed approach can be applied even to the charge transporting layers, such as TiO_2 in mesoscopic n-i-p or PCBM in inverted PSCs, respectively. Finally, due to the easy solution-based fabrication of MXenes, the proposed approach is easily scalable on large area perovskite modules and panels.

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FIGURE

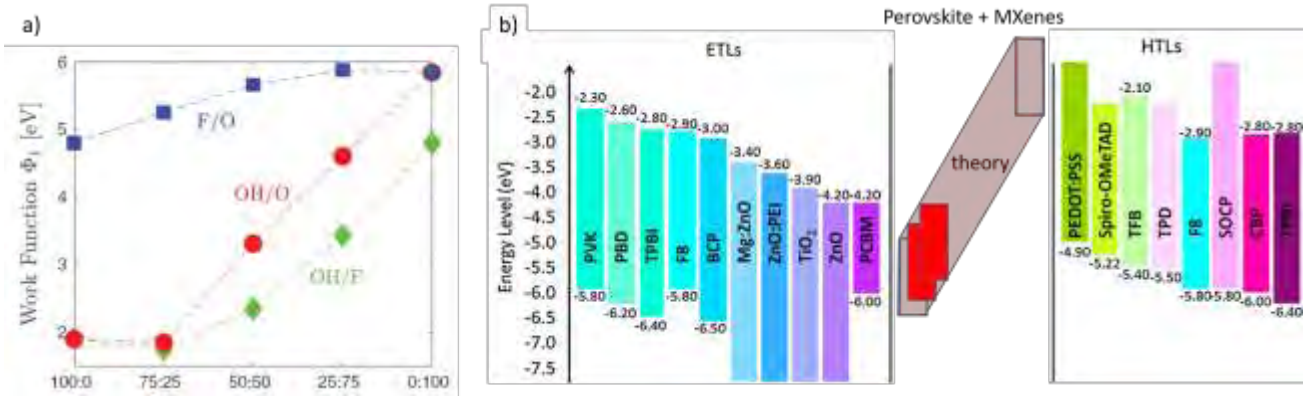

Figure 1: a) Work function values Φ1 derived from density functional theory calculations, for a mixture of OH, O, and F MXene surface terminations at the interface with perovskite (from ref. [3]); b) perovskite WF tuning theoretically predicted and experimentally verified and its energy level alignment with several electron (ETLs) and hole (HTLs) transporting layers (from ref. [4])

Graphene chemiresistors for gas sensing

Natalia Alzate-Carvajal[1]
Jean-Michel Guay[1], Ranjana Rautela[1], Samantha Scarfe[1], Petr Lazar[2], Michal Otyepka[2], Jean-Michel Ménard[1], and Adina Luican-Mayer[1]
[1] *Department of Physics, University of Ottawa, Ottawa, Ontario, Canada*
[2] *Regional Centre of Advanced Technologies and Materials, Faculty of Science, Palacky University Olomouc, Slechtitelu 27, Olomouc, Czech Rep.*
ealzatec@uottawa.ca

Graphene has demonstrated great promise for technological use, yet control over material growth and understanding of how material imperfections affect the performance of devices are challenges that hamper the development of applications.[1,2] In this work we reveal new insight into the connections between the performance of the graphene devices as environmental sensors and the microscopic details of the interactions at the sensing surface. Specifically, we monitor changes in the resistance of the chemical vapor deposition grown graphene devices as exposed to trace concentrations of ethanol. We perform thermal surface treatments after the devices are fabricated, use scanning probe microscopy to visualize their effects on the graphene sensing surface down to the nanometer scale and correlate them with the measured performance of the device as an ethanol sensor. Our observations are supported by theoretical calculations of charge transfers between molecules and the graphene surface. We find that, although often overlooked, the surface cleanliness after device fabrication is strongly correlated with the device performance and reliability. Moreover, we present a compact solution for field testing of our devices. These results further our understanding of the mechanisms of sensing in graphene-based environmental sensors and pave the way to optimizing such devices, especially for their miniaturization, since decreasing the size of the active zone will inevitably lead to an increased interference from surface contaminants.

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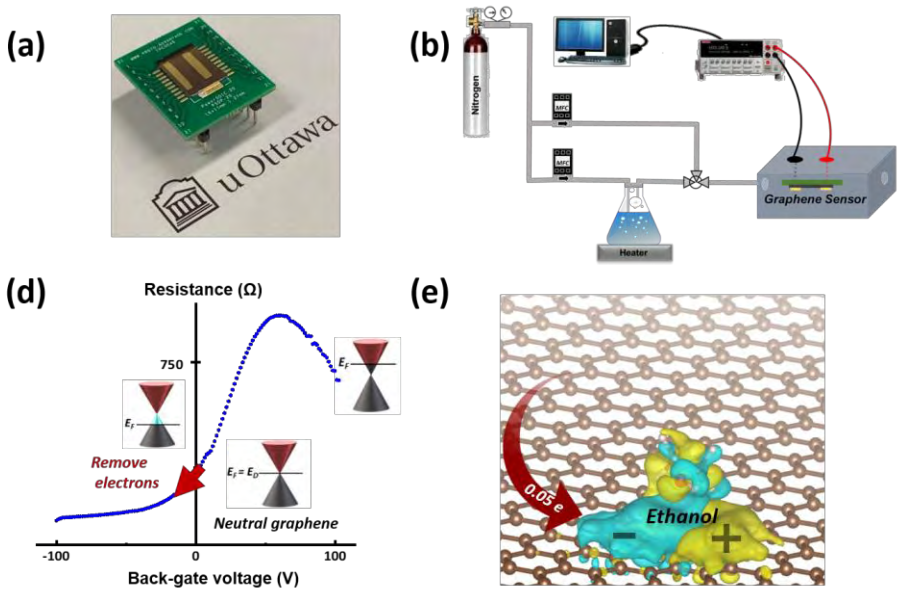

Figure 1: (a) Picture of the sensor geometry (b) Schematic of experimental setup for sensor testing (c) Working principle of graphene as a chemiresistor (d) Schematic of adsorbed ethanol molecule and the charge density distribution.

Multidisciplinary Research on Graphene Biosensors

Dobri Atanassov Batovski
Vincent Mary School of Science and Technology, Assumption University of Thailand, Bangkok, Thailand
dbatovski@au.edu

Abstract

Applications of graphene for the design of electrical biosensors face certain limitations that could be addressed by applying a multidisciplinary approach to describe the complexity of nanoscale systems. The sensitivity of functionalized graphene structures for virus detection is reduced due to the short Debye length in typical solutions like the phosphate-buffered saline (PBS) solution. Seemingly unrelated studies in ionic solutions and electrolytes analyse the Debye length from a different point of view. Graphene planar surfaces are seldom implemented in two-plate capacitor settings for bioresearch. There are some studies of the Debye length in parallel plate capacitors [1] that could be extended to graphene plates for a better understanding of long-range Coulomb interactions. An increase of the molarity in ionic liquid solutions follows to an increase of the electrostatic screening length after a certain threshold [2]. Efforts to design biosensors beyond the Debye length limit in high ionic strength solutions are reported in [3]. This topic becomes increasingly important as the research community puts a great effort to cope with the coronavirus disease 2019 (CoViD-19) pandemic. There are various technologies involving graphene that take part in the fight against CoViD-19 [4]. In order to reach a Debye length comparable with the expected size of a chosen antibody on the graphene surface (provided to bind the S1 subunit protein from COVID-19), a diluted 0.01xPBS solution of 1.6-Mm molarity and 7-nm Debye length is utilized [5]. Note that the size of the coronavirus is much larger than both the binding segment in a single S-protein spike and the Debye length. This makes it challenging to estimate statistically the number of binding events and the resultant electrical effect in the graphene sensor configuration. Further evaluation of the Debye length in ionic solutions between functionalised graphene plates with the application of ac voltage at different amplitudes and frequencies is the next logical step in understanding the optimal biosensor sensitivity. The optimal molarity for a given design is also to be determined. Since such empirical experiments could be costly and time consuming, the use of computational experiments and computer simulations with the involvement of researchers from diverse fields, not only in materials science and physical chemistry, but also in computer science and artificial intelligence (AI), is an essential part of the multidisciplinary research on graphene-based applications. Therefore, there is a specific niche in biosensing beyond the Debye screening. Said niche also involves graphene plasmonics. The unique properties of the two-dimensional graphene lattice result in the superior sensitivity of graphene biosensors. While new empirical works on testing various hybrid graphene sensors are reported daily, related theoretical and computational studies are less frequent. This could be attributed to the complexity arising from evaluating combinations of biological, physicochemical, and condensed matter phenomena. It should be noted that most experiments for commercial biosensors are performed at room temperature. The Debye length depends on the temperature as by definition it describes large thermodynamic systems of mobile charges. The thermal conductivity of graphene, graphene oxide (GO), and other graphene materials depends on the biosensing functionalization of its surface. Thus thermal conductivity is an additional useful characteristic for the design of graphene biosensors. In summary, this contribution provides a description of some proposed modifications for biosensor design and key points for performing computational studies involving the Debye length in ionic solutions at the surface of graphene structures.

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Investigating the quality of CVD-grown graphene on germanium using in-situ surface science methods

Andreas Becker
Jarek Dabrowski, Mindaugas Lukosius, Christian Wenger
IHP – Leibniz-Institut für innovative Mikroelektronik, Im Technologiepark 25, Frankfurt (Oder), Germany
becker@ihp-microelectronics.com

Germanium epitaxially grown on silicon has emerged as a relevant substrate for graphene growth because it is possibly compatible with established CMOS processing. Besides optimizing wafer-scale graphene growth on germanium template and subsequent transfer, we are exploring ways to directly integrate graphene growth into technological processing. However, major challenges are the relatively low quality of graphene on the standard orientation Ge(001) and the high required synthesis temperature. These challenges motivated an investigation of the growth process using a high-pressure preparation chamber for chemical vapor deposition that is connected to a surface science cluster tool. As a prerequisite for reliable graphene growth, we present a detailed study of the germanium substrate pre-cleaning and describe how to avoid etch pit formation. Furthermore, we investigated the influence of growth temperature on the quality of graphene on Ge(001), Ge(110) and Ge(111) using scanning tunneling microscopy, low-energy electron diffraction and Raman spectroscopy. We discuss graphene grain size and morphology, epitaxial alignment and intragranular defect density and conclude that the best graphene quality is obtained on Ge(110) at a growth temperature near the substrate melting point. Finally, we intend to bring up a discussion how enhancement of carbon etching might help improve the graphene quality.

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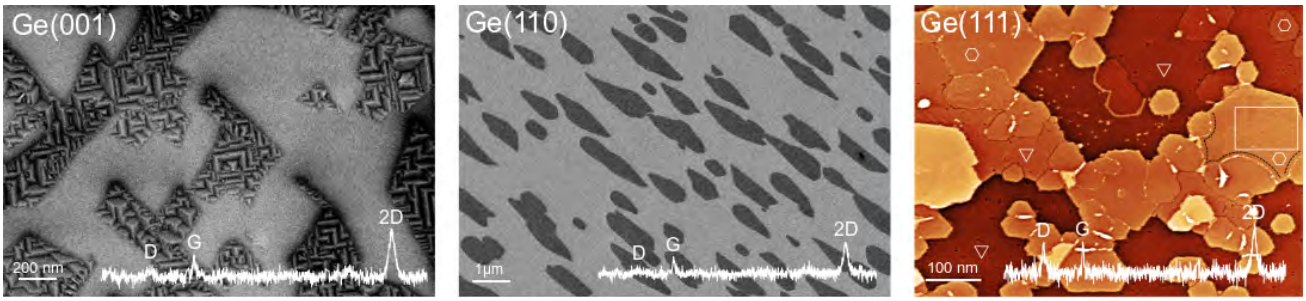

Figure 1: Scanning electron micrographs and scanning tunneling micrograph of graphene islands grown on different germanium orientations. Inset Raman spectra give an estimate of the island size and quality.

Non-volatile Resistive Switching in Nanocrystalline MoS_2 with Vertically Aligned Layers Enabled by Mobile Ions

Melkamu Belete[1], Satender Kataria[1], Thorsten Wahlbrink[2], Olof Engström[2] , Max C. Lemme[1,2]
[1] RWTH Aachen University, Chair of Electronic Devices, Otto-Blumenthal-Str. 2, Aachen, Germany.
[2] AMO GmbH, Otto-Blumenthal-Str. 25, Aachen, Germany.
melkamu.belete@eld.rwth-aachen.de

Two-dimensional (2D) layered materials are capable of providing bio-realistic ionic interactions that are needed for realizing energy-efficient artificial neural networks to emulate the functioning of the human brain[1]. Molybdenum disulfide (MoS_2) is a layered 2D transition metal dichalcogenide (TMD) material which is gaining considerable attention recently for exhibiting a memristive effect. However, the mechanism and origin of the effect still remains unclear. In this work, we provide experimental demonstrations on the presence and origin of a nonvolatile and bipolar resistive switching (RS) in nanocrystalline MoS_2 with vertically aligned layers (Figs. 1a and 1b). Electrical characterization results reveal that the RS process is forming-free and also has a stable endurance for at least 140 DC switching cycles and state-retention for at least 2500 s (Figs. 1c and 1d). Controlled switching tests carried out in ambient and vacuum conditions suggest that the observed RS is enabled by hydroxyl ions (OH^-) [2] that originate possibly from catalytic splitting of adsorbed water molecules in MoS_2 [3]. Experimental observations in combination with analytical simulations further suggest that the electric field-driven movements of the mobile OH^- ions along the vertical MoS_2 layers influence the energy barrier at the Si/MoS_2 interface [4]. The observed ion-based plasticity may be exploited in ionic-electronic devices based on TMDs and other 2D materials for memristive applications. Furthermore, the device fabrication process used in this work is fully scalable and semiconductor production compatible. This enables integration of such novel 2D materials-based memristors into existing Si technology for future neuromorphic applications.

Financial support by BMBF (NEUROTEC, 16ES1134) is gratefully acknowledged.

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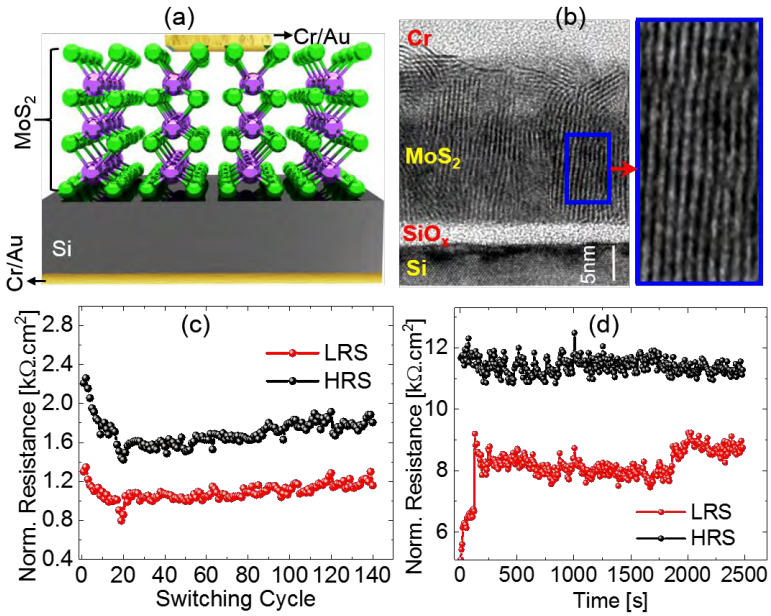

Figure 1: (a) Schematic diagram showing the structure of the investigated memristor device based on MoS_2 with vertically aligned layers and (b) a TEM cross-section image of the device structure revealing the nanocrystalline MoS_2 film with vertically aligned layers. Electrical characterizations of the present devices in ambient conditions indicating a resistive switching performance with stable: (c) endurance for at least 140 DC switching cycles and (d) state-retention for at least 2500 seconds.

Liquid-phase exfoliated GeSe nanoflakes for photoelectrochemical-type photodetectors

Gabriele Bianca[1,2]
Marilena Isabella Zappia,[3,4] Sebastiano Bellani,[1,3] Michele Serri,[1] Leyla Najafi,[1,3] Beatriz Martín-García,[1] Reinier Oropesa-Nuñez,[3] Tomáš Hartman,[5] David Sedmidubský,[5] Vittorio Pellegrini,[1,3] Zdeněk Sofer,[5] Anna Cupolillo[4] and Francesco Bonaccorso[1,3]

1 Graphene Labs, Istituto Italiano di Tecnologia, via Morego 30, 16163, Genova, Italy
2 Dipartimento di Chimica e Chimica Industriale, Università degli Studi di Genova, via Dodecaneso 31, 16146 Genoa, Italy
3 BeDimensional Spa., via Albisola 121, 16163 Genova, Italy
4 Department of Physics, University of Calabria, Via P. Bucci cubo 31/C 87036, Rende (CS), Italy
5 Department of Inorganic Chemistry, University of Chemistry and Technology Prague, Technická 5, 166 28 Prague 6, Czech Republic

gabriele.bianca@iit.it

ABSTRACT

Photoelectrochemical (PEC) devices represent powerful tools to convert the electromagnetic radiation into chemical fuels and electricity.[1] In particular, PEC cells, including water splitting ones, are emerging for the development of cheap, easily-fabricated, environmentally friendly self-powered photodetectors with high spectral responsivity (> tens of mA W^{-1} for UV-visible spectral region).[2] In this context, two-dimensional (2D) materials are attracting a huge interest as potential advanced photo(electro)catalysts,[3] and, recently, 2D group-IVA metal monochalcogenides have been theoretically predicted to be water splitting photocatalysts.[4] Among them, low-cost and environmentally friendly layered germanium selenide (GeSe), is a promising material candidate for optoelectronic devices due to its properties: tuneable electronic structure, strong visible-light absorbance, photoresponse, photoferroelectricity and environmental stability.[4] Here, we report the first experimental characterization of the photo(electro)catalytic activity of single-/few-layer GeSe flakes in different aqueous media, ranging from acidic to alkaline solutions: 0.5 M H_2SO_4 (pH 0.3), 1 M KCl (pH 6.5), 1 M KOH (pH 14). The PEC properties of the GeSe nanoflakes, produced by liquid-phase exfoliation (LPE) approach[5] in non-toxic solvents (e.g., 2-propanol) and deposited by spray-coating technique,[5] are used to conceive PEC-type photodetectors, reaching responsivity up to 0.32 AW^{-1} under 455 nm excitation wavelength, in acid electrolyte. The obtained performances are superior to those of several self-powered and low-voltage solution-processed photodetectors, approaching the ones of self-powered commercial UV–Vis photodetectors. Our results can open the way towards the use of 2D GeSe in innovative PEC systems.

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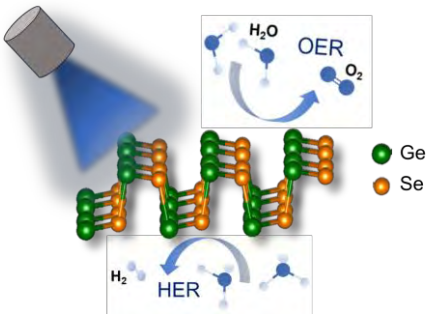

Figure 1: Schematic processes of photoelectrochemical water splitting on GeSe nanoflakes.

Short-Range Ordered Structure of Activated Carbons

Luca Cervini
John Griffin, Nathan Barrow
Chemistry Department, Lancaster University, Lancaster, LA1 4YB, UK
l.cervini@lancaster.ac.uk

Activated carbons are generally classified as amorphous, although there is long-standing evidence for a more ordered structure resembling graphite on a few nanometer length scale. Our recent results[1] have shown that water desalination occurs spontaneously in the smallest pores of PEEK-derived carbons (PDCs) activated at high temperature. It is therefore essential to describe the exact structure of such pores and their formation mechanism. A series of PDCs was characterized by PXRD and TEM, which showed graphene-like sheets organized in small graphitic domains. Raman microscopy studies revealed two types of regions with different levels of order. Gas adsorption analyses yielded a well-defined multimodal pore size distribution, and NMR allowed to deduce that all types of pores were in close proximity. These results were unified under a new supramolecular description of the structure that emphasizes the deterministic aspect of the porosity. The activation mechanism was then investigated by comparing samples activated at different temperatures. Figure 1 gives an example of activation mechanism. The results allowed to establish ways to manipulate the microstructure and properties of the material to better suit water desalination applications.

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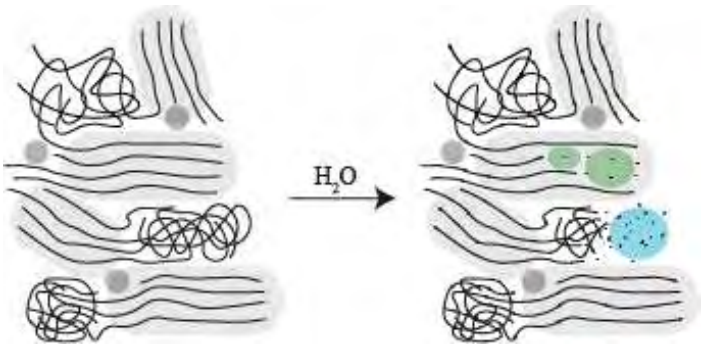

Figure 1: High-temperature steam-activation mechanism.

Photothermal cancer therapy with graphene-based materials and their drug conjugates

Raquel Costa-Almeida
Raquel Costa-Almeida [1,2], Diana Bogas[3], Licínia Timochenco[3], Filipa A. Silva[1,2], José R. Fernandes[4], João Meneses[3], M. Cristina L. Martins[1,2], Inês C. Gonçalves[1,2], Fernão D. Magalhães[3], Artur M. Pinto[1,2,3]
[1]i3S - Instituto de Investigação e Inovação em Saúde, Universidade do Porto, Porto, Portugal; [2]INEB - Instituto de Engenharia Biomédica, Porto, Portugal, [3]LEPABE, Faculdade de Engenharia, Universidade do Porto, Porto, Portugal; [4]CQVR – Centro de Química Vila Real, Universidade de Trás-os-Montes e Alto Douro, Vila Real, Portugal
rcalmeida@i3s.up.pt; arturp@i3s.up.pt

Oncological malignancies are the second leading cause of death globally, raising the need for novel treatment strategies. Photothermal therapy (PTT) may be applied as an effective non-invasive alternative treatment. Near-infrared (NIR) light energy can induce hyperthermia (39-47°C), inducing higher nanoparticle/drug uptake due to increased membrane permeability and tumor cell apoptosis. Graphene-based materials (GBM) present strong radiation absorption and possess large surface area, holding potential for synergistic biologic and drug release hyperthermia triggered effects [1]. Herein, GBM and GBM loaded with 5-fluorouracil (5-FU), an anti-cancer drug, are proposed as platforms for cancer PTT. Nano-sized graphene oxide (GOn) was produced through the modified Hummer's method [2] followed by ultrasonication through a custom-built industrial grade system, to assure the achievement of reproducible large-scale batches of nano-sized GBM. Following a one-step procedure, GOn was thermally reduced and functionalized with poly(ethylene) glycol (PEG) moieties to obtain stable aqueous dispersions (rGOn-PEG) [3]. GOn and rGOn-PEG (0.25 mg/mL) were mixed with 5-FU at a drug concentration varying between 0.25-5 mg/mL. GBM aqueous dispersions were irradiated with a LED source of 812.8±29.9nm (150 mW/cm^2) and temperature recorded using a thermocouple. The effect of GBM and NIR irradiation was evaluated by resazurin cell viability assay using a human skin carcinoma cell line (A431 cells, ATCC). GOn was obtained with mean lateral dimensions of 248 nm, as determined by TEM. GOn and rGOn-PEG dispersions showed colloidal stability with zeta potential values around -25.6±0.8 mV and -10.2±0.3 mV (pH=7), respectively. 5-FU was successfully loaded by simple molecular physiosorption on GOn and rGOn-PEG, with loading capacity being of 5.8±0.8 mg 5-FU/mg GOn and 3.6±1.2 mg 5-FU/mg rGOn-PEG. NIR irradiation increased rGOn-PEG temperature to 47ºC after 30 min, which is within temperature ranges of hyperthermia. rGOn-PEG in combination with NIR reduced A431 cells viability, in opposition to irradiated GOn or rGOn-PEG alone. This study opens new avenues for the development of GBM-based platforms for drug delivery and PTT of cancer.

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EMPIR GRACE - Good Practice Guides on the electrical characterisation of graphene using contact- and non-contact methods

*Alessandro Cultrera [1],
Félix Raso [2], Olga Kazakova [3], Amaia Zurutuza [4], Elena Taboada [5], Norbert Fabricius [6], Andrey Kretinin [7], Alexandra Fabricius [8], and Luca Callegaro [1].

[1] *INRIM Istituto Nazionale di Ricerca Metrologica, strada delle Cacce, 91, 10135, Torino, Italy*
[2] *CEM Centro Español de Metrología, Calle del Alfar, 2, 28760 Tres Cantos, Madrid, Spain*
[3] *NPL National Physical Laboratory, Hampton Rd, Teddington TW11 0LW, United Kingdom*
[4] *das-Nano, Poligono Industrial Talluntxe II, Calle M, 10, 31192 Tajonar, Navarra, Spain*
[5] *Graphenea, Mikeletegi Pasealekua, 83, 20009 Donostia, Gipuzkoa, Spain*
[6] *ISC International Standards Consulting, Rubensweg 11, D-32584 Löhne, Germany*
[7] *Uom University of Manchester, Oxford Rd, Manchester M13 9PL, United Kingdom*
[8] *VDE Association for Electrical, Electronic and Information Technologies Stresemannallee 15 60596 Frankfurt am Main Germany*

* a.cultrera@inrim.it

The GRACE project (2017-2020) [1] aims to an accurate approach to the electrical characterisation of graphene, through the development and comparison of both contact and non-contact methods (see Figure 1), with traceability to the electrical SI units.

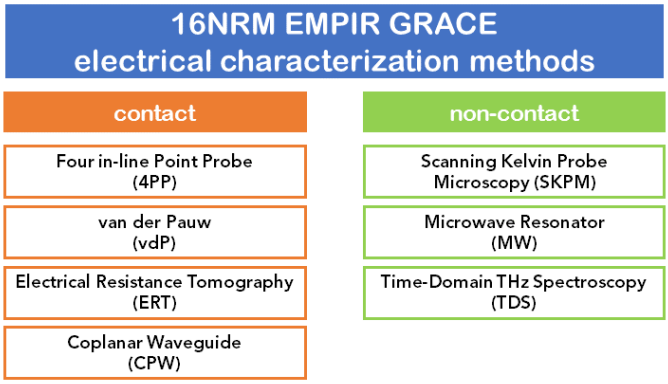

Figure 1: Characterization methods investigated by GRACE.

The GRACE consortium is also collaborating with standardization bodies, i.e. International Electrotechnical Commission Technical Committee 113, to develop new technical specifications that will enable the industry to harmonize the quality of the graphene-based future electronic products.
Within the GRACE project we developed validated electrical characterisation protocols specifically for large area graphene.

Chemical vapour deposited (CVD) graphene samples were produced by the industrial partners and circulated among the other partners during the project in order to test, on each sample, more than one of the above-cited characterisation methods and compare the measurements outcome.

The results of this inter comparison allowed to understand how to meaningfully implement different methods, and the gained experience is now collected in two Good Practice Guides, that will be presented at this Conference.

The GRACE Good Practice Guides are already available as open access documents on the project website [2].

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Temporal measurement of few-cycle laser pulses by third-harmonic dispersion-scan with optically improved graphene coatings

Tiago Gomes[1]
Miguel Canhota[1], Alexandre Carvalho[2], Bohdan Kulyk[2], Miguel Miranda[3], Bruno Jarrais[4], António José Fernandes[2], Cristina Freire[4], Florinda Costa[2], Helder Crespo[1]
[1]IFIMUP-IN and Dept. of Physics and Astronomy, Faculty of Sciences, University of Porto, Portugal

[2]I3N-Aveiro, Dept. of Physics, University of Aveiro, Aveiro, Portugal
[3]Sphere Ultrafast Photonics, S.A., Rua do Campo Alegre, 1021, Edifício FC6, 4169-007 Porto, Portugal
[4]REQUIMTE/LAQV, Dept. of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Portugal
up201504587@fc.up.pt

Graphene - a single atomic layer of carbon atoms - is a very promising material, mainly due to its extremely high and broadband nonlinear optical susceptibility [1] and the possibility of occurrence of interband transitions at all optical frequencies. Ultrafast third-harmonic generation (THG) in graphene allows not only the temporal characterization of the used ultrashort pulses but also the study of carrier dynamics in graphene. The possibility of obtaining an enhanced nonlinear signal when using multi-layer graphene [2] further adds to these capabilities. The new technique of dispersion scan (d-scan) developed by Miranda et al. [3] enables characterizing ultrashort light pulses using an unprecedentedly simple and fully inline optical setup. In this method, the spectrum of a nonlinear signal (in this case, THG) is recorded for different amounts of dispersion applied to a light pulse, creating a 2D d-scan trace from which the spectral phase of the pulse can be retrieved and, therefore, by inverse Fourier transform, provides the exact temporal intensity profile and phase of the pulse. The most common nonlinear signal for d-scan has been SHG. For very broadband octave-spanning lasers or mid-infrared systems, it is helpful to use higher-order nonlinearities, like THG [4]. Here we present several examples of THG d-scan measurements of broadband few-cycle laser pulses obtained in graphene coatings produced by different production techniques [5], which enable characterizing the used ultrashort pulses while providing insight on the electronic dynamics in graphene. A typical THG d-scan trace obtained in multilayer CVD-grown graphene by using a chirped mirror and glass wedge compressor, together with the corresponding retrieved femtosecond pulse, is shown below.

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FIGURES

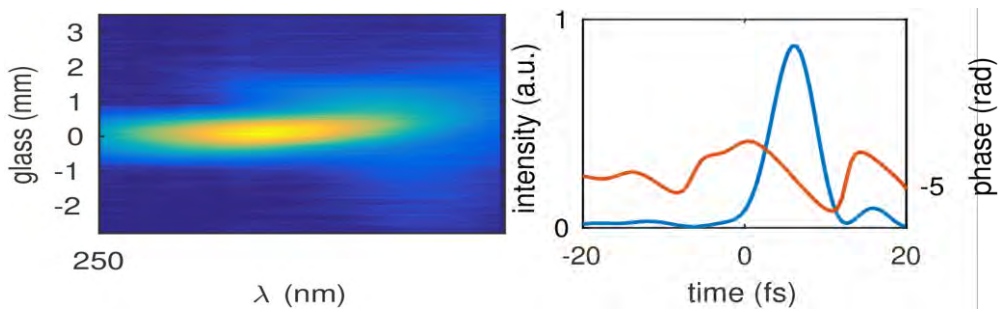

Figure 1: Typical measurement and reconstruction of a few-cycle laser pulse from a Ti:Sapphire oscillator – Third-harmonic signal as a function of dispersion (left) and temporal profile (blue) and phase (orange) of the retrieved few-cycle pulse (right).

A bio-inspired fractal designed breath sensors fabricated by graphene inks using extrusion 3D printing

Kamrul Hassan[1,2]
Tran Thanh Tung[1,2] , Nathan Stanley[1,2], Dusan Losic[1,2]*
[1]*School of Chemical Engineering and Advanced Materials, The University of Adelaide, Adelaide, SA 5005, Australia*
[2]*ARC Research Hub for Graphene Enabled Industry Transformation, The University of Adelaide, Adelaide, SA 5005, Australia*
kamrul.hassan@adelaide.edu.au, dusan.losic@adelaide.edu.au

Abstract

Despite a developing number of diagnostic devices in recent years, there are still significant demand for low-cost, fast and simple devices for personalized diagnostic for detection of most concerning human diseases such as cancer, respiratory syndromes, diabetes, obesity, astma etc. Breath analysis could play a significant role in this by providing non-invasive and on-demand human health data collected from abnormal biomarkers patterns from breath samples .[1] As a result, breath sensors can revolutionize medical diagnostics by monitoring and on-demand detection of health parameters in a personalized manner for many diseases. The aim of this work is to demonstrate the performance of extrusion 3D printed chemo-resistive patterned electrode inspired by the 'fern leaf' design with higher surface area to volume (SA/V) ratio for enhanced VOC detection where specially designed graphene ink is used. The concept is illustrated in Figure. 1. First, we have developed a graphene ink formulation that can be printed at room temperature via extrusion-based 3D printer. We adopt the 'Hilbert' design from natural fern leaf and printed the synthesized graphene ink on PET in continuous mode consisting of multiple lines with an average layer thickness of 12 µm overlayed onto printed silver connections, which enhanced the SA/V ratio of printed patterns ten times rather than normal planar/non-fractal design. Herein we demonstrate the bio-inspired 3D extrusion printed graphene ink based chemo-resistive sensors for detecting VOC biomarkers such as acetone, ethanol and methanol to analyse human breath. The as-fabricated sensor exhibits enhanced performance with a high level of tunable selectivity, fast response-recovery time (6/36 sec), as well as wide detection range (5-100 ppm) for ethanol during room temperature operation. This concept has the potential to make a beneficial contribution towards the development of low-cost, high-performing VOC sensors to monitor human health through metabolic breath testing. It could also be implemented in non-invasive biomedical diagnostics for personalised telehealth monitoring.

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FIGURES

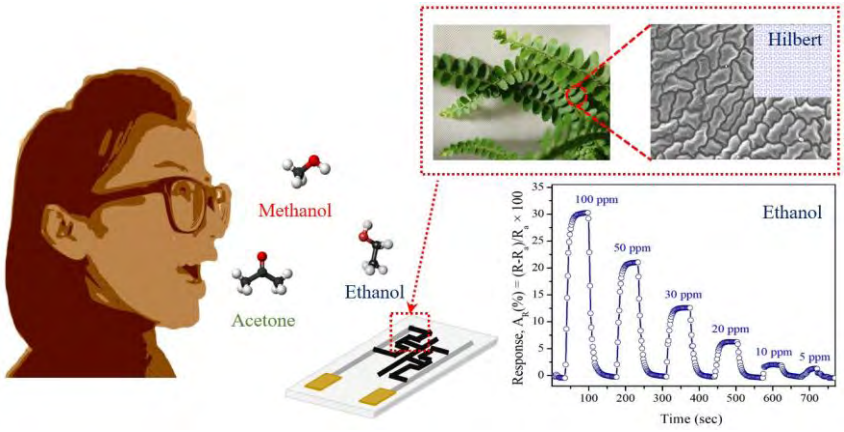
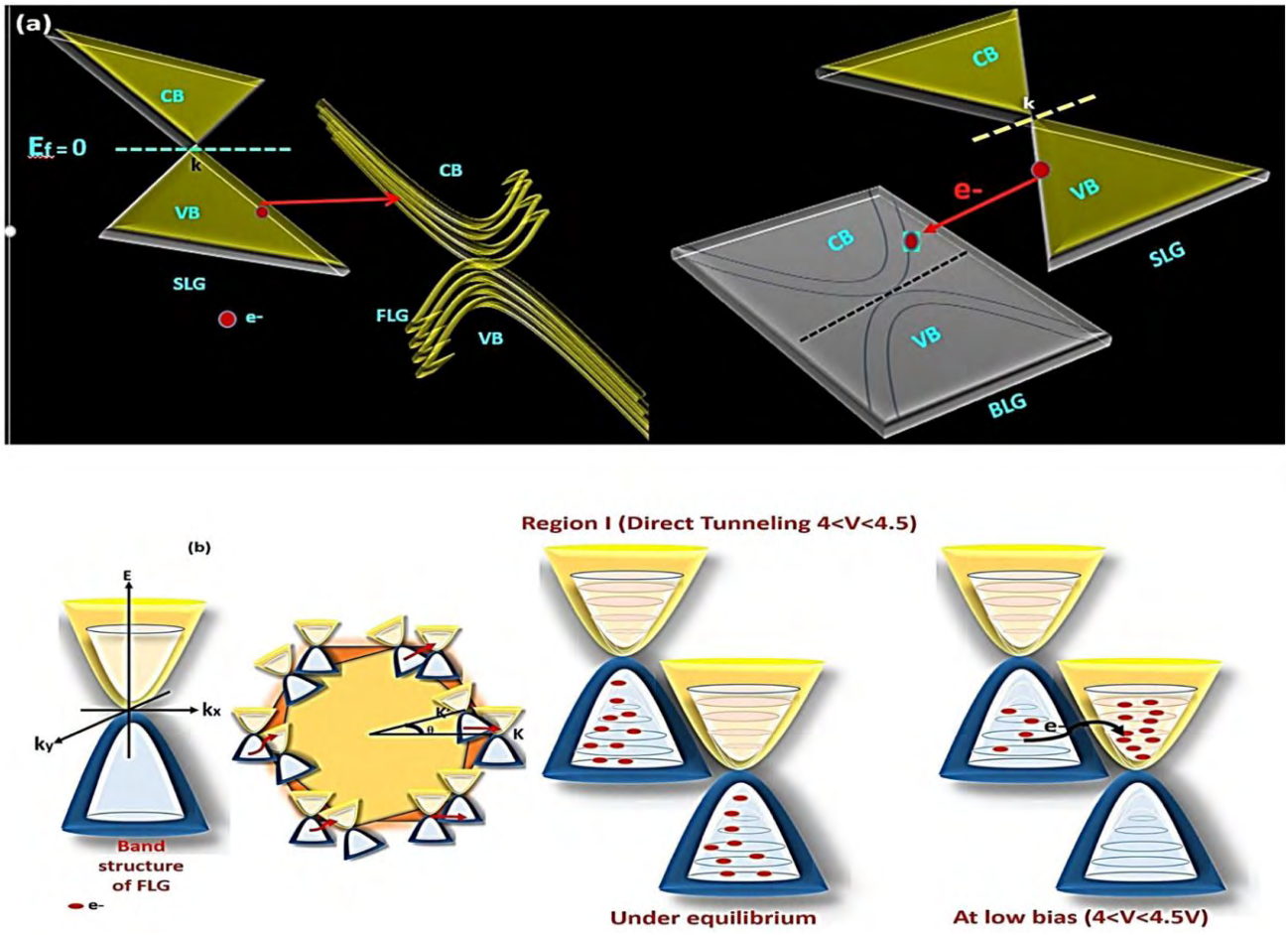


Figure 1: Overview of bio-inspired fractal designed graphene ink based extrusion 3D printed breath sensor.

Unveiling the tunneling phenomena in graphene-graphene homojunctions for emerging device applications

Presenting Author (Dr Amanpreet Kaur)
Ravi Chand Singh
Organization, Address, Department of Physics, Guru Nanak Dev University Amritsar-143002, India
akaur6765@gmail.com

Graphene, the 2D form of carbon based material exists as a mono layer arrangement of atoms in a honeycomb lattice, has sparked the science and technology sectors in view of its astonishing electrical and thermal properties, together with its elasticity and mechanical strength.
Motivated by the idea that high-quality graphene always produces innovative aspects of physics. In this outline, a novel class of two dimensional (2D) assembly namely thickness controlled homo-junctions with a configuration similar to graphene–insulator-graphene is introduced in this work. We demonstrate 2D-2D quantum tunneling between two graphene stacks in which van der Waals gap serves the purpose of tunneling barrier. The nonlinear I-V characteristics with improved current switching ratio (I_{on}/I_{off}) of ~10^6 coupled with counterclockwise current hysteresis which are the signatures of a memristive devices has been validated in the tunneling regime. It is the first time to report on revealing thickness modulated 2D homo junctions in exfoliated graphenic material and to disclose the involved tunneling mechanism for switching applications. This work promises well for the possibilities of graphene sheets for the realization of two terminal configured devices as a substitute of three terminal graphene based field effect transistors (GFETs) in the area of resistive switching memories. As graphene being a versatile candidate possessing durable future in nano-electronics, therefore understanding deep insights of its charge carrier transport mechanism under range of bias voltages is prerequisite. Strikingly, an unconventional approach for improving on/off ratio of graphene based resistive switching devices has been put forward.



(a) Pictorial representation of band to band tunneling of charge carriers in SLG-FLG, SLG-BLG (b) FLG-FLG configuration.

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A Novel Method to Form Carbon Nanocomposites

Professor, Yeuh-Hui Lin
Department of Greenergy Science and Technology, Kao Yuan University, Kaohsiung 840 Taiwan
lin@cc.kyu.edu.tw

Abstract: Carbon-coated nanocomposites have been synthesized by a self-heating detonation process using nitro-amine CHNO explosives of 1,3,5-trinitro-1,3,5-triazacyclo-hexane (RDX) providing the need of high temperatures, high shock waves, and parts of carbon sources in the presence of catalyst. The products of carbon nanomaterials are characterized by XRD, EDX and TEM techniques. In this work, various carbon nanostructures or metal nanocomposites can be efficiently obtained from the detonation of the desired molecular precursors. In summary, catalytic detonation of carbon-rich explosives can be designed as a simple method and with the potential application for the rapid production of nano-structured materials of graphitic carbon-encapsulated nanoparticles and carbon-nanotubes.

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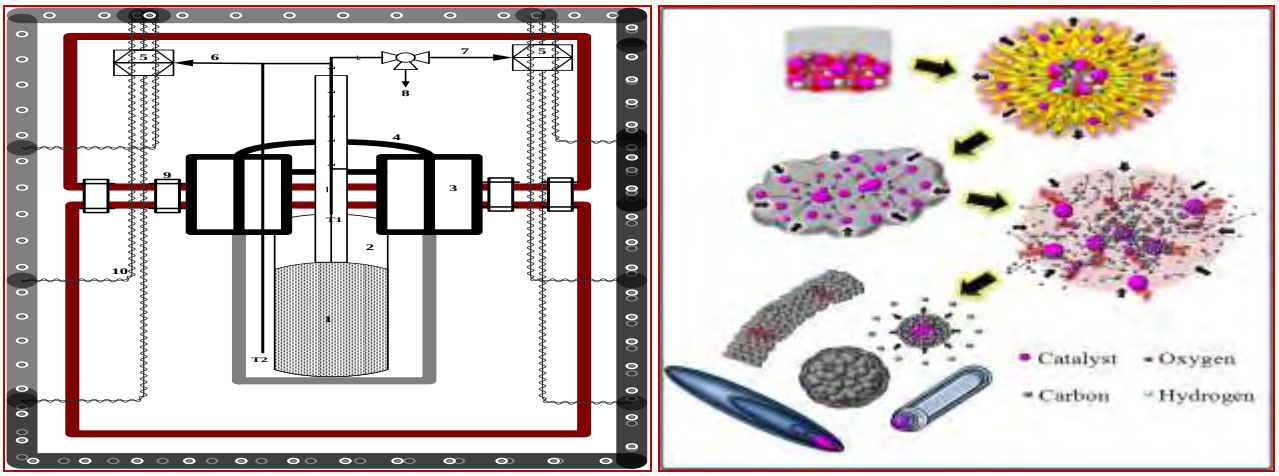

Figure 1: Schematic diagram (left) and reaction routes (right) of a novel reaction system for the detonation of CHNS energetic materials over different metal-catalysts for the assembly of various nanostructures.

Graphene-based electrocatalysts for the oxygen evolution reaction

Maximina Luis-Sunga
Gonzalo García
Elena Pastor
Departamento de Química, Instituto Universitario de Materiales y Nanotecnología, Universidad de La Laguna, PO Box 456, 38200, La Laguna, Santa Cruz de Tenerife, Spain
mluissun@ull.edu.es

The increasing global warming caused by the combustion of fossil fuels is leading to a search for alternatives environmentally friendly, accessible, and economically attractive. Hydrogen is considered a clean fuel for the future because it acts as a green energy carrier and provides a method for the storage and transport of energy. A variety of processes are available for H_2 production, based on conventional or renewable technologies. Water electrolysis offers a practical route for sustainable hydrogen production by utilizing a renewable electrical energy source for water splitting. The oxygen electrode in electrolyzers plays a central role as its catalytic activity and stability are conditioned by its slow kinetics under operating conditions [1,2].

Graphene-based electrocatalysts emerged as promising materials to improve efficiency in numerous electrochemical reactions since they are low-cost, abundant, and electrical conductors with tunable catalytic activity. Insertion of heteroatoms into graphene network may produce electronic and geometric distortions of the carbonaceous grid, and consequently, the activity toward several electrochemical reactions may be altered. Basically, two types of doping may occur in the graphene network depending on the interatomic distance between carbon-heteroatom compared to C-C. Thus, B-C, N-C and C-C have similar interatomic distance, and therefore, it is expected that after the heteroatom-modification the system will follow a similar modus operandi; on the other hand, P-C, Si-C and S-C show higher interatomic distance than C-C and their modification will display an exohedral doping, i.e., the heteroatom will be located above and/or below the graphene sheet. Another factor to take into account in the catalyst activity is the surface local acidity, which may be altered by the introduction of functional groups in the graphene network [3].

With the aim to solve the principal catalytic problems at the oxygen electrocatalysts in electrolyzers, S- and N-doped graphene-based materials were synthesized, characterized and tested toward the oxygen evolution reaction (OER) in alkaline medium. In-situ Raman spectroelectrochemistry, rotating ring-disk electrode (RRDE), cyclic voltammetry (CV) and linear sweep voltammetry (LSV) techniques were used to determine the catalytic activity of heteroatom-doped graphene catalysts toward the OER. Main results indicate that the OER is strongly influenced by the nature and amount of the doping agent in addition to the interaction with the electrolyte media, which also conditioned Raman signals such as the position of the D- and G-bands and the $Area_D/Area_G$ (A_D/A_G) ratio. Additionally, the percentage of molecular oxygen production is estimated by a novel procedure [1,2].

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Graphene-based counter-electrode for large area gold-free perovskite solar devices

Paolo Mariani,
L.Najafi[2,3], S.Bellani[2,3], M.I. Zappia[3,4], G.Bianca[2], N.Yaghoobi Nia[1], S.Pescetelli[1], A. Agresti[1], F. Bonaccorso[2,3] and Aldo Di Carlo[1,5]
[1]Department of Electronic Engineering, University of Rome "Tor Vergata", via del Politecnico 1 00133 Rome – ITALY / CHOSE- Centre for Hybrid and Organic Solar Energy, Viale Pietro Gismondi snc 00133 Roma- ITALY
[2]Graphene Labs, Istituto Italiano di Tecnologia, via Morego 30, 16163 Genova, Italy
[3] BeDimensional Spa., Via Albisola 121, 16163 Genova, Italy
[4] Department of Physics, University of Calabria, via P. Bucci cubo 31/C, 87036 Rende, Cosenza, Italy
[5] Istituto di Struttura della Materia, CNR-ISM, via Fosso del Cavaliere 100, 00133 Roma, Italy
paolo.mariani@uniroma2.it

Gold films are typically used as the back electrode of the most efficient certified perovskite solar cells (PSCs) [1], arising severe concerns for industrialization purposes. In fact, on one hand, both gold cost and deposition through energy-consuming vacuum evaporation negatively affect the levelized cost of energy (LCOE) of the mesoscopic PSC technology. On the other hand, gold ion migration toward either the hole-transporting layer (HTL) or the perovskite causes severe instability effects under operating conditions, decreasing the PSC lifetime [2]. In this work, we report solution-processed electrically conductive adhesive (ECAs) based on graphene flakes to replace the gold in PSC back electrode without altering the underlying structure of the traditional mesoscopic devices. Our ECAs are formulated by mixing carbon nanomaterials with different topological morphologies, including wet-jet milling-produced pristine (not oxidised) single-/few-layer graphene flakes. Thanks to the peculiar properties of pristine graphene, our ECAs show optimal electrical properties (sheet resistance < 20 Ω/sq for thickness < 30 μm) and mechanical strength. The ECAs are deposited in form of counter-electrode for large-area PSCs. By optimizing the thickness of spin-coated graphene-based ECAS, we have increased the photovoltaic performance of our PSCs by 30%. In particular, optimal ECA thickness of ~40 μm resulted in a sheet resistance of ~10 Ω/sq. Afterwards, we investigated the ECA deposition through blade coating technique, aiming to scale-up our PSC technology [7]. Beyond to provide an effective method to fabricate large-area PSCs, blade coating efficiently reduce material waste compared to other depositions techniques, such as spin-coating. Our preliminary tests proved that our graphene-based PSCs can overcome the performances obtained with market-ready c carbon pastes.
Our ECAs are currently implemented in advanced mesoscopic PSCs [3,4] and perovskite solar modules (PSMs) [5], using graphene-doped TiO_2 electron-transporting layers (ETLs) and two-dimensional (2D) transition metal dichalcogenides interlayers [6] to surpass the "gold" PCE and reach the state-of-the-art performance through viable large-scale manufacturing processes.

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FIGURES

Figure 1: on the left, J-V curves of graphene-carbon based PSCs. On the right: blade coating equipment

Review of Graphene Oxide for anti-bacterial and anti-viral functions

Maryam Modarres
Abalonyx AS, Forskningsveien 1, 0373 Oslo, Norway
mm@abalonyx.no

Abstract
The recent Covid-19 pandemic as a global health crisis has triggered intense R&D to find vaccines, detection methods and personal protection. Research groups around the world are now focusing on providing products to confront COVID-19. Graphene based materials such as graphene oxide (GO) have been identified as a promising candidate in biomedical applications due to their unique properties such as biocompatibility, hydrophilicity, high surface area, dispersity as well as antibacterial/antiviral properties [1,2]. The interaction mechanism between graphene oxide and various pathogen leads to inhibit the bacterial and viral growth. Graphene oxide has high potential to help in the war on Covid-19 virus, by novel and cost-effective technologies with high efficiency being prepared for virus prevention. Recently, graphene oxide nanocomposites have also been used for anti-bacterial coatings [3], sensors [4], and other biomedical [5]. Antibacterial and antiviral coating with graphene oxide nanocomposites have great potential in health care to control microbial and viral infection. The combination of nanoparticles such as silver, titanium dioxide and magnetite nanoparticles with graphene oxide can be considered for personal protection equipment to decrease the transmission of viruses increases effective, increases surface area and prevent from the aggregation of graphene oxide nanosheets [6]. Graphene oxide nanocomposites can be used as face mask filter due to remarkable antibacterial/ antiviral properties for health protection. The biomedical application of graphene oxide nanocomposites is schematically illustrated in Fig. 1.

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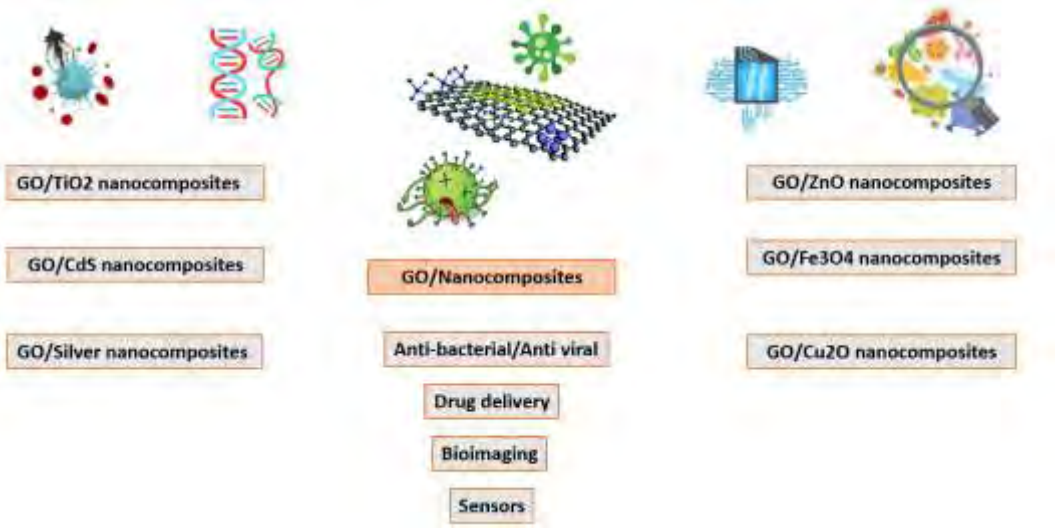

Figure 1: Schematic overview of applications of graphene oxide nanocomposites for anti-bacterial / -viral.

2D Van der Waals Lateral Spin Valve

Aybey MOGULKOC[1]
Yesim MOGULKOC[2], Mohsen MODARRESI[3] and Alexander RUDENKO[4,5,6]
[1]Faculty of Science, Department of Physics, Ankara University, Ankara, Turkey.
[2]Faculty of Engineering, Department of Engineering Physics, Ankara University, , Ankara, Turkey.
[3]Department of Physics, Ferdowsi University of Mashhad, Mashhad, Iran
[4]School of Physics and Technology, Wuhan University, Wuhan 430072, China
[5]Radboud University, Institute for Molecules and Materials, Heyendaalseweg 135, 6525 AJ Nijmegen, Netherlands.
[6]Theoretical Physics and Applied Mathematics Department, Ural Federal University, 620002 Ekaterinburg, Russia.

mogulkoc@science.ankara.edu.tr

Abstract
A 2D Van der Waals spin valve in monolayer blue phosphorus sandwiched between two half-metallic ferromagnetic (FM) CrN monolayers is proposed based on the density functional theory calculations together with Boltzmann transport theory. We studied the electronic, structural and spin-dependent transport properties of monolayer CrN, P/CrN and CrN/P/CrN systems. Among the different possible stacking patterns between monolayer blue phosphorus and monolayer CrN, AA stacking is only one to be dynamically stable.
Moreover, we calculated the exchange interactions and single-ion anisotropy parameters to estimate the Curie temperature within the random phase approximation, which is found to be to be well above the room temperature for CrN/P/CrN which is promising feature for a spin-valve device. The alteration of magnetic ordering (FM and AFM) modifies electronic transport causing magnetoresistance of up to 12% in the low-doping regime. [1]

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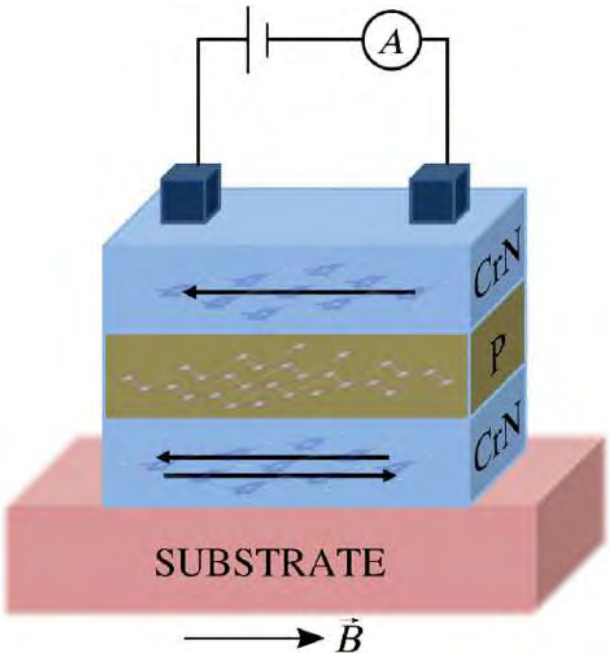

Figure 1: A lateral spin-valve device based on CrN/P/CrN. [1]

Graphene-based dispersions for touch sensor fabrication

Miguel Monteiro
Sergey Tkachev, Pedro Alpuim, Andrea Capasso
International Iberian Nanotechnology Laboratory, Braga, Portugal
Andrea.capasso@inl.int

Graphene-based and two-dimensional materials are approaching the industrial production stage with a sustained pace [1]. These materials can be processed in solution and deposited by several techniques to make components for many technologies, such as flexible electronics [2, 3]. However, graphene-based dispersions are currently rather expensive and face some issues, such as a limited compatibility with substrates or the need for post-processing treatments. Here, we propose an approach to produce graphene-based dispersions with high yield and control on the material properties. Our approach is based on the use of a combination of two solution-processing techniques (*i.e.*, shear mixing and ultra-sonication) for the efficient exfoliation of natural graphite into graphene flakes. The dispersions and the dispersed materials (upon deposition and drying) were carefully characterized by Raman and optical spectroscopy, scanning and transmission electron microscopy, and x-ray photoelectron spectroscopy. The dispersions were deposited by several techniques (*i.e.*, spray coating, inkjet and screen-printing) on various substrates to fabricate films with desired levels of transparency and conductivity. As a proof-of-concept test, we fabricated a capacitive touch sensor by spray coating highly concentrated graphene dispersions in *green* solvents (Figure 1). When interfaced with the electronics and tested, the sensor showed high signal-to-noise ratio and featured multi touch detection.

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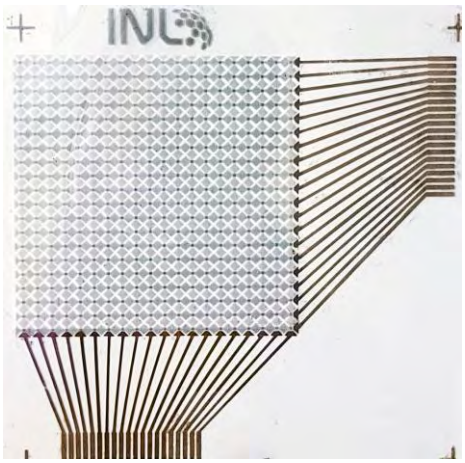

Figure 1: Graphene-based 10×10 cm^2 touch sensor with external contacts fabricated by spray coating.

Graphene Processing on Wafer Scale for Microelectronic Applications

Himadri Pandey[1]
A. Esteki[1], S. Sawallich[2], B. Conran[3], C. McAleese[3], S. Krotkus[4], S. Kataria[1], M. Nagel[2], M. Heuken[4] & M. C. Lemme[1,5*]
[1]Chair of Electronic Devices, RWTH Aachen University, Otto-Blumenthal-Str. 2, 52074 Aachen, Germany
[2]Protemics GmbH, Otto-Blumenthal-Str. 25, 52074 Aachen, Germany
[3]AIXTRON SE, Dornkaulstr. 2, 52134 Herzogenrath, Germany
[4]AIXTRON Ltd, Buckingway Business Park, Anderson Road, Swavesey, Cambridge CB24 4FQ, United Kingdom
[5]AMO GmbH, Advanced Microelectronics Center Aachen, Otto-Blumenthal-Str. 25, 52074 Aachen, Germany
Email: lemme@amo.de

Abstract

Large area chemical vapor deposited (CVD) graphene has shown immense potential for future electronic device applications [1]. However, one major problem often encountered today is the poor reproducible quality of such CVD grown layers. We report on the progress made in the GIMMIK project, where we aim to address this problem. Wafer scale graphene is grown on sapphire substrate, and quality assessment is systematically done by fabrication and characterization of electronic devices. The aim of this ongoing research project is to evolve graphene technology for electronic devices from lab to industrial levels. The weak points in the relevant processing steps are identified and ways to eliminate/minimize the sources of error are being developed. In addition, the transfer of the key graphene properties to electronic devices is continuously tested by integration into a material environment. State of the art characterization methods like tera-Hertz time domain spectroscopy (THz-TDS) are also being employed to ensure a consistent high quality graphene. Till date, Graphene sheets grown on 4" Sapphire wafers with average carrier mobility of 1700 cm^2/Vs have been demonstrated. By employing CMOS compatible Nickel edge contacts to graphene [2], contact resistance values as low as 500 Ω.µm and decent sheet resistance values in the range of 800 – 1350 Ω/□ have been observed. Lessons learnt in these steps will then be implemented on 200 mm Industrial quality wafers in future.

Support from BMBF (GIMMIK, 03XP0210) is gratefully acknowledged.

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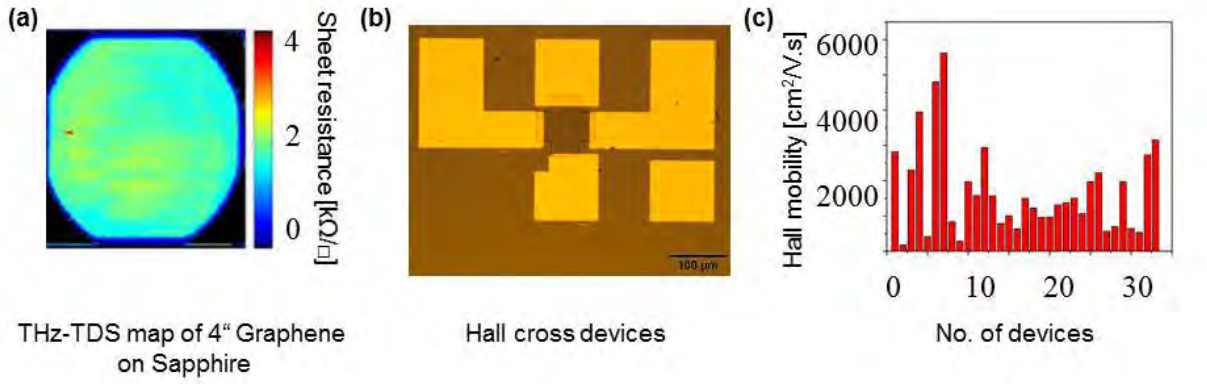

Figure 1: (a) THz-TDS assessment shows wafer scale uniform growth of Graphene on Sapphire with decent sheet resistance. (b) A typical test device used in this work. (c) These Graphene devices demonstrated average Hall mobility of 1700 cm^2/Vs. Graphene used in this project was grown on 2" and 4" Sapphire wafers till date.

Perovskite solar panels: an innovative highlight achieved by 2D materials

Sara Pescetelli
Antonio Agresti, Stefano Razza, Paolo Mariani, Sebastiano Bellani, Francesco Bonaccorso, Enrico Leonardi, Marco Pierro, Cristina Cornaro, Aldo Di Carlo
C.H.O.S.E., Electronic Engineering Department, University of Rome Tor Vergata, Via del Politecnico 1, 00133, Rome, Italy.
sara.pescetelli@uniroma2.it

Perovskite solar cells (PSCs) represent nowadays the forefront of innovative photovoltaic technologies due to their high efficiency and low fabrication costs. At the same time, during the last few years, 2D layered materials have attracted a great deal of interest due to their fascinating optoelectronic, chemical, and mechanical properties and unique structure. Recently, the exploration of a wide range of novel 2D materials for use in PSCs has seen considerable progress, but despite the rapid development of this cutting-edge technology still a lot remains to be done regarding scalability.
Herein, we combine the use of graphene and emerging 2D layered materials in large area perovskite solar modules (PSMs) and in perovskite solar panel (PSPs) by retaining good power conversion efficiency (PCE) and stability. In fact, passing from solar cell to module i) the increasing of contact series resistance, ii) the difficulty in controlling perovskite morphology and uniformity, iii) the interfacial charge recombination strongly limits the final PCE and the stability. Moreover, passing from module to panel, the main constrain is represented by the organic selective layer, degrading at standard lamination temperatures (140°C), even for a limited time. In this work we demonstrate highly efficient large area perovskite solar module (11x11 cm^2) by employing 2D interface engineering strategy together with the use of stable polymeric hole transporting material (HTM).[1] Indeed, the addition of graphene within the electron transporting layer (ETL) as well the insertion of functionalized MoS_2 interlayer at perovskite/HTM interface allowed to achieve PCE exceeding 15.7% over more than 80 cm^2 active area and an excellent stability at 85°C after 1000 h of prolonged stress test.[2] Finally, we developed a standardized procedure for the high-throughput and large number production processes suitable for the fabrication of large-area modules. In this way, 40 perovskite-2D materials modules based on the structure FTO/cTiO_2+graphene/mTiO_2+graphene/perovskite/fMoS_2/PTAA/gold have been realized and laminated in a 0.5 m^2 panel. The outdoor measurements performed at STC demonstrated power conversion efficiency output above 10%. Moreover, the performance ratio (PR) was computed by showing higher values under overcast conditions than those measured under clear sky conditions, proving that 2D material-perovskite solar panels working are efficient even in case of diffuse irradiance.

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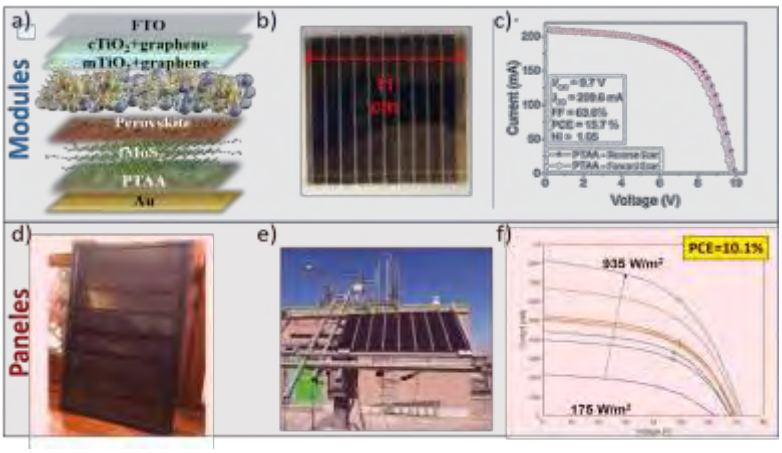

Figure 1: a) 2D interface engineering structure; b) module 11x11 cm^2 picture; c) I-V curve of best module under 1 SUN illumination; d) Perovskite-2D material solar panel; e) panel on the tracker station of ESTER laboratory of Tor Vergata University; f) I-V curve of tested panel at different outdoor irradiance conditions.

Solution-processed Layered Double Hydroxides for Energy Applications

Marco Piccinni[1,2]
Sebastiano Bellani[1], Gabriele Bianca[1,2], Marilena Zappia[3,4], Leyla Najafi[1], Francesco Bonaccorso[1,4]

[1] *Dipartimento di Chimica e Chimica Industriale, Università degli Studi di Genova, via Dodecaneso 31, 16146 Genoa, Italy*
[2] *Istituto Italiano di Tecnologia, via Morego 30, Genoa, Italy*
[3] *Department of Physics, University of Calabria, Via P. Bucci cubo 31/C 87036, Rende (CS), Italy*
[4] *BeDimensional Spa., via Albisola 121, 16163 Genova, Italy*
marco.piccinni@iit.it

Layered double hydroxides (LDHs) are a class of anionic clays consisting of positive charged brucite-like layers spaced by water molecules and counterbalancing anions[1]. In particular, transition metals LDHs have drawn attention for energy storage and conversion applications[2] because of their electrocatalytic properties for water splitting[3], and pseudocapacitive behaviour[4][5]. Contrarily to other layered materials, LDH layers are held together by electrostatic forces and a dense network of hydrogen bonds[6]. For these reasons, a careful choice of solvent is pivotal for an efficient exfoliation of the LDHs. One of the most effective is formamide[1][7]. However, due to formamide toxicity and its high boiling temperature, other solvent options are recommended for the processing of LDHs[8][9]. Although dispersions of LDH nanoplates in water or alcohols are stable, they result in an ineffective material exfoliation[1]. To overcome the aforementioned issues, we will report the treatment with aqueous acetate solution of NiFe-LDH hexagonal nanoplatelets, synthesized with Jaśkaniec's method[10], to produce a stable dispersion in ethanol (see Figure 1). Transmission electron microscopy (TEM) analysis reveals the exfoliation of the LDH nanoplatelets, whilst the ultraviolet-visible light spectroscopy (UV-Vis) measurements suggest that the presence of the acetate plays a key role for the stability of LDH ethanol dispersion. The as-produced LDH dispersion can be deposited onto conductor substrates (*e.g.*, graphite paper, nickel foam) to form catalytic films for electrochemical applications. Finally, LDHs are combined with graphene-based materials and/or transition metal dichalcogenides to create composites or hybrid superlattices with superior electrochemical properties compared to single component materials[2].

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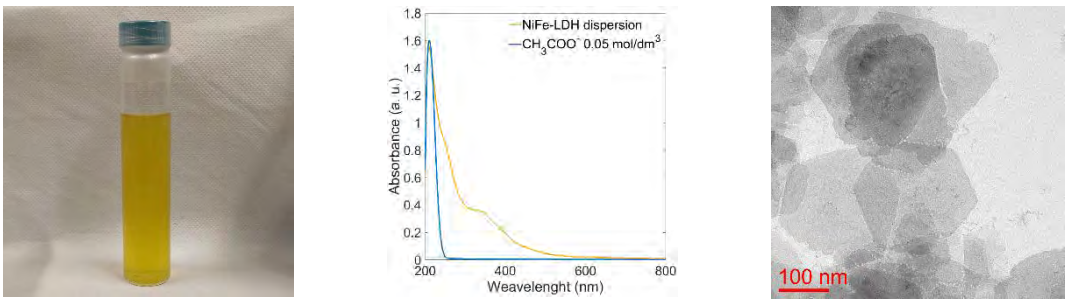

Figure 1: A picture of the NiFe-LDH dispersion in ethanol (left). Comparison between UV-Vis spectra of the LDH dispersion and a sodium acetate solution in ethanol (middle). TEM image of LDH hexagonal flakes (right).

Few-layers graphene-based cement composites

Salvatore Polverino[1,2]
Antonio Esau Del Rio Castillo[2,3], Luigi Marasco[2], Renata Morbiducci[1] and Francesco Bonaccorso[2,3]

[1]*Dipartimento di Architettura e Design, Università degli Studi di Genova, Stradone Sant'Agostino 37, 16123 Genoa, Italy*
[2] *Graphene Labs, Istituto Italiano di Tecnologia, via Morego 30, 16163, Genoa, Italy*
[3] *BeDimensional Spa., via Lungotorrente secca 3d, 16163 Genova, Italy*

Salvatore.polverino@edu.unige.it

Abstract

Cement composites are widely exploited materials worldwide, with a consumption of more than thirty billion tons per year and with continuous demand growth. [1]
The production processes for the Portland cement involve significant carbon emissions and consequently, it has a significant impact on the environment. [2] One possible solution to this environmental problem is to improve the mix-design to enhance the performance by the addition of special nano additives (*e.g.,* SiO_2 or TiO_2 nanoparticles).[3] The nano additives can increase the durability of cement composites, thus reducing future degradation and commercial demand. Moreover, they can add new properties and functions to the concrete *e.g.*, photocatalytic, electrothermal or self-sensing properties[4], thus transforming the cement composites into smart concretes. The carbon-based nano additives, graphene in particular, stand out among the wide variety of available nano additives. Nevertheless, the production of graphene is still a bottleneck for triggering the commercialisation of its cement composites. [5,6]
We exploit a high-pressure homogeniser, specifically the wet-jet milling, for the production of few-layers graphene at semi-industrial rates, *i.e.* kg per day (**Fig 1a**).[7] The high production rate enables the testing of new graphene-based cement composites, with the view of future commercialisation. The few layer graphene-based mortars produced (**Fig 1b**) demonstrated an improvement of the physical performances. In particular, we achieved an enhancement of ~25% for both the flexural and compressive strength.

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Figure 1: a) Examples of graphene dispersions produced by the wet-jet milling process. b) Raman mapping image of the fracture surface of a few layer graphene-based cement mortar sample.

Beyond the lab: Scalable production of electrochemically exfoliated graphene / transition metal oxide hybrids for wearable energy storage

Adrián Romaní Vázquez
Ali Shaygan Nia, Martin R. Lohe, Carsten Gröber, Andreas Röpert, Xinliang Feng
Technische Universität Dresden, Mommsemstr. 4, 01069 Dresden (Germany)
Adrian.romani_vazquez@mailbox.tu-dresden.de

The remarkable properties of graphene give this 2D-material the potential to be a competitive material for a broad range of industrial and commercial applications. Some of these characteristics are a high theoretical capacitance and electrical conductivity, giving graphene great potential for energy storage. However, large-scale production is still a key challenge to overcome in the path to commercial viability. The electrochemical exfoliation method has been described as a facile, scalable and green approach to producing a high amount of low-defect, large-lateral-size graphene (EG) [1]. The large lateral size and high aspect ratio make this graphene ideal for use in wearable thin-film supercapacitor devices. Additionally, the process can be modified to functionalize the graphene flakes [2]. In this work, we describe a simple modification to the electrochemical exfoliation process to decorate the EG flakes with manganese oxide to improve the energy storage performance. The material is produced in large scale by Sixonia Tech GmbH technology, with the developed inks/pastes having been used by our industrial partner (Elmeric GmbH) to fabricate series of supercapacitor devices. These were then integrated by Interactive Wear AG into a thermoregulatory shirt to power an embedded climate monitoring and control system.

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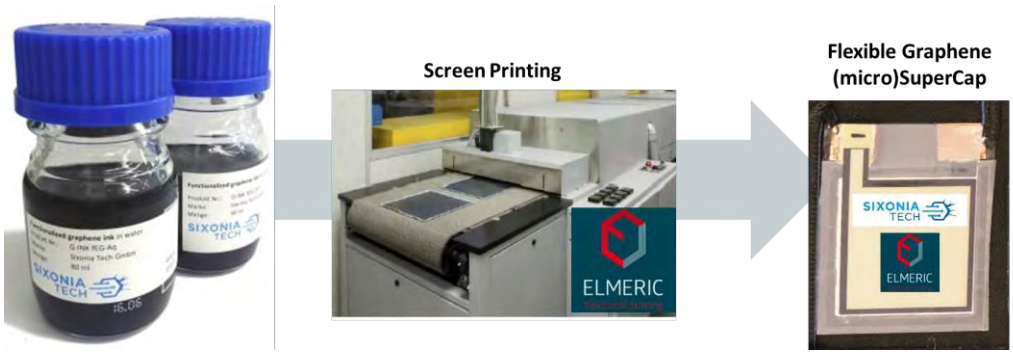

Figure 1: Simple diagram of EG\TMO supercapacitor production process

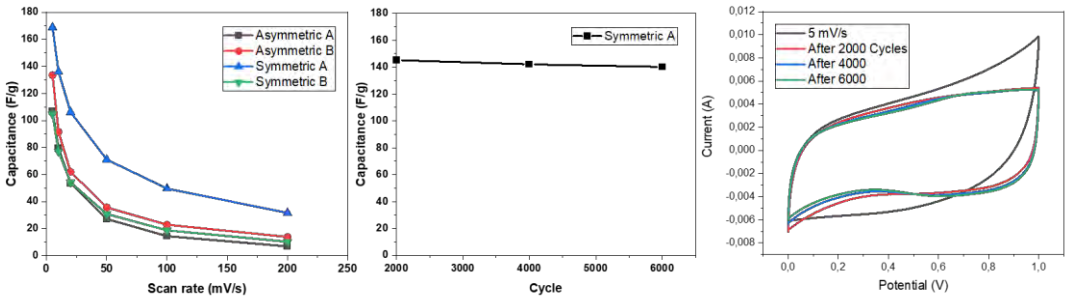

Figure 2: Performance of screen-printed EG\TMO supercapacitor devices

Effective approach for graphene electron structure characterization

Maxim Rybin
Vera Islamova, Alexander Tonkikh, Ivan Kondrashov, Evgeniy Guberna, Elena Obraztsova
A.M. Prokhorov General Physics Institute, 38 Vavilov str., Moscow, Russia
Moscow Institute of Physics and Technology, Moscow, Russia
rybmaxim@gmail.com

The paper presents a simple and effective approach for analyzing the electronic structure of graphene using a combination of two methods: measuring sheet resistance and measuring the thermoelectric effect (Seebeck coefficient). To use graphene in microelectronics or optoelectronic devices, it is necessary to know its electronic structure. As you know, graphene is a material with a zero bandgap and its Fermi level is located at the contact points of the valence and conduction bands. However, particles are adsorbed from the atmosphere on graphene, due to charge transfer, the Fermi level of graphene changes, and after thermal annealing in vacuum, particles can be desorbed. Thus, the Fermi level of graphene is very sensitive to surface charge. This paper presents the results of the synthesis of graphene by chemical vapor deposition with transfer of graphene onto a dielectric substrate and the modification of its properties by the deposition of molecules from the gas phase. Iron chloride was used as an electron acceptor, and cobaltocene as an electron donor, shifting the Fermi level in graphene to either the valence or conduction bands, respectively. In the course of the work, the graphene surface was functionalized and its electrophysical characteristics were measured. Charts were built to quickly determine the electronic structure of graphene and the position of its Fermi level.

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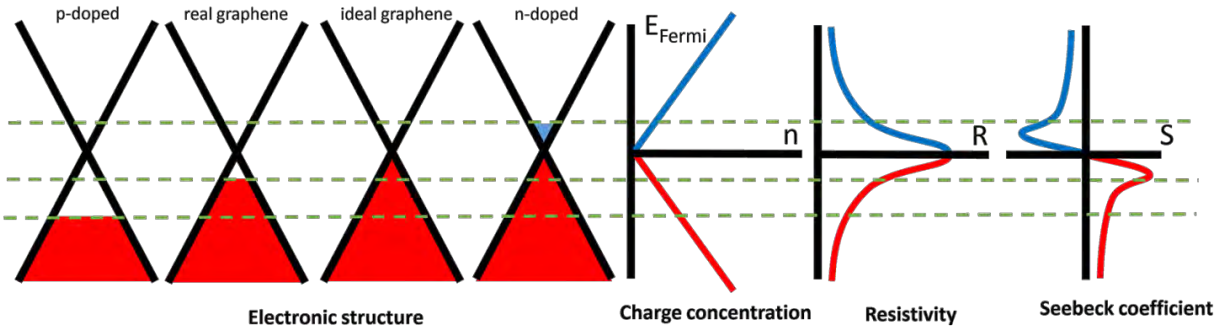

Figure 1: Scheme of electronic structure of graphene and its electronic characteristics vs Fermi energy.

One-step Self-assembly for Producing Graphene and Carbon Nanocapsules

Jin-Wei Shi and Yeuh-Hui Lin
Department of Applied Greenergy, Kao Yuan University, Kaohsiung 840 Taiwan
lin@cc.kyu.edu.tw

Abstract: The 2D graphene and 3D carbon nanocapsules (CNCs) structures of extreme strength may offer excellent protection to their encapsulated nanomaterials for applications. This interest has been driven by the potential applications of the filled nanocapsules, which lie in areas as diverse as optical, electronic, magnetic recording materials and nuclear medicine. Graphene and carbon encapsulated nanocapsules have been synthesized by a self-heating detonation process using an energetic explosive for providing the need of high temperatures, high shock waves, and parts of carbon sources in the presence of metallic-containing catalysts. The detonation synthetic system can provide a unique environment and this gives a survival of the pre-fed catalyst and simultaneously a ready generation of the Cn species. The experimental results show that the metal compounds can be converted into metallic nanoparticles due to the fast decomposition with a reduction reaction after the detonation and this will play an important role for the growth of grapheme related to different structures of carbon nanocapsules. The systematic of experiments indicate that the nanoparticles encapsulated in concentric layers of graphitic carbon. Additionally, these results experimentally used in this study show that it is possible for a cheaper process with simple one-step and can be as an alternative compared to these high energy and hardware intensive processes to prepare these nanomaterials.

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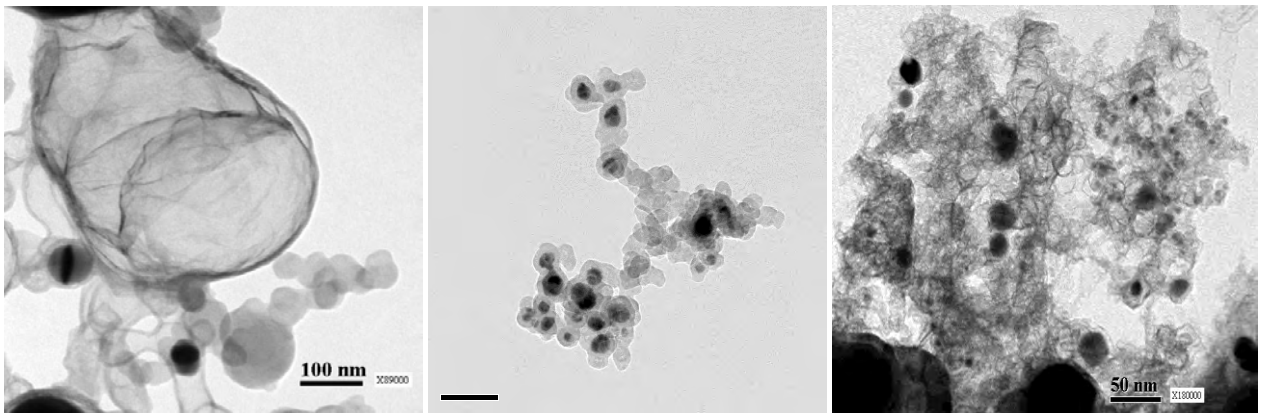

Figure 1: TEM image for one-step detonation of energetic materials to form grapheme and carbon encapsuled nanomaterials.

Chemical Tuning of Specific Capacitance in Functionalized Fluorographene

Smita Talande
Eleni C. Vermisoglou, Petr Jakubec, Aristides Bakandritsos, Martin Pykal, Vojtěch Kupka, Radek Zbořil, Michal Otyepka
Regional Centre for Advanced Technologies and Materials, Department of Physical Chemistry, Department of experimental Physics, Faculty of Science, Palacký University Olomouc, 17. listopadu 1192/12, 771 46 Olomouc, Czech Republic
Smita.talande01@upol.cz

Abstract

Supercapacitors (SCs) play an important role in the energy storage landscape due to their high power density and long cyclic stability. However, due to the ever-growing demand on portable energy, it is crucial to further enhance the energy which can be stored SCs. Graphene is known as a promising electrode material due to its high conductivity, large surface area[1]. Although, the restacking of graphene layers during electrochemical cycling restricts the ion diffusion hence reduce the capacitance and cyclic stability. The covalent functionalization of graphene with suitable organic molecules is a promising strategy for bypassing the restacking of the layers. Moreover, non-agglomerated organic molecules bonded with the single sheet of graphene may enlarge the interlayer spacing which can enhance the ion diffusion[2]. On this basis, we developed a covalent functionalization of graphene with a zwitterionic organic moiety through the nucleophilic substitution reaction of fluorographene with 5- aminoisophthalic acid by adopting facile, one-step and up-scalable synthetic procedure[3]. The amount of covalently grafted functional groups and density of the sp2 carbon is smartly balanced to boost the performance of the full supercapacitor cell built from this material.

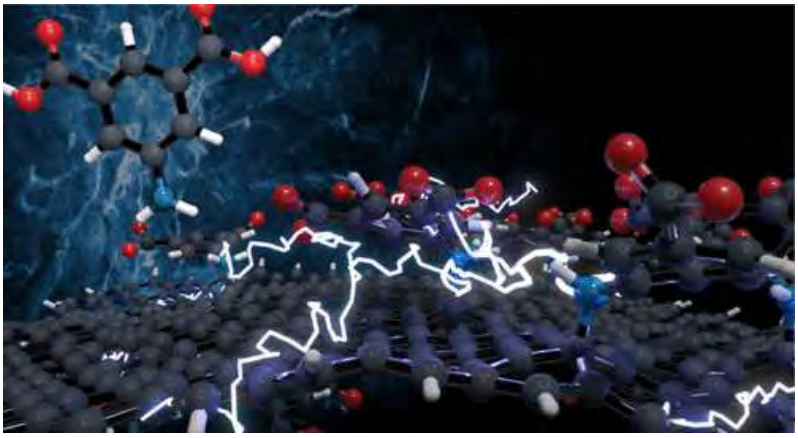

Figure 1: Covalently functionalized graphene schem

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Ultrafast electro-absorption graphene modulators with a 2D-3D integration of hBN and a high-κ dielectric.

Bernat Terrés[1]
H. Agarwal[1], L. Orsini[1], A. Montanaro[2], V. Sorianello[2], M. Pantouvaki[3], K. Watanabe[4], T. Taniguchi[4], D. van Thourhout[3], M. Romagnoli[2] and F. H. L. Koppens[1,5]
[1] ICFO — Institut de Ciencies Fotoniques, The Barcelona Institute of Science and Technology, 08860 Castelldefels (Barcelona), Spain
[2] Consorzio Nazionale per le Telecomunicazioni (CNIT), Photonic Networks and Technologies National Laboratory, via Moruzzi 1, 56124 Pisa, Italy
[3] Photonics Research Group, Department of Information Technology, Ghent University-IMEC, Sint-Pietersnieuwstraat 41, Gent, 9000 Belgium
[4] National Institute for Materials Science, 1-1 Namiki, Tsukuba 305-0044, Japan
[5] ICREA — Institucio Catalana de Recerca i Estudis Avancats, Barcelona, Spain.
bernat.terres@icfo.eu

Abstract

Electro-absorption (EA) waveguide-coupled modulators are essential building blocks for on-chip optical communications. Compared to state-of-the-art silicon (Si) devices, graphene-based EA modulators promise smaller footprints, larger temperature stability, cost-effective integration and high speeds [1]. However, combining high speed and large modulation efficiencies in a single graphene-based device has remained elusive so far. In this work, we overcome this fundamental trade-off by demonstrating the first 2D-3D dielectric integration in a high-quality encapsulated graphene device. We integrated hafnium oxide (HfO_2) and two-dimensional (2D) hexagonal boron nitride (hBN) within the insulating section of a double-layer (DL) graphene EA modulator (Fig. 1a). This novel combination of materials allows for a high-quality modulator device with record high performance: a bandwidth (BW) beyond 40GHz (Fig. 1c) with a three-fold increase in modulation efficiency (Fig. 1b) compared to previously reported high-speed modulators. This first demonstration of 2D-3D integration paves the way to a plethora of electronic and opto-electronic devices with enhanced performance and stability, while expanding the freedom for device designs.

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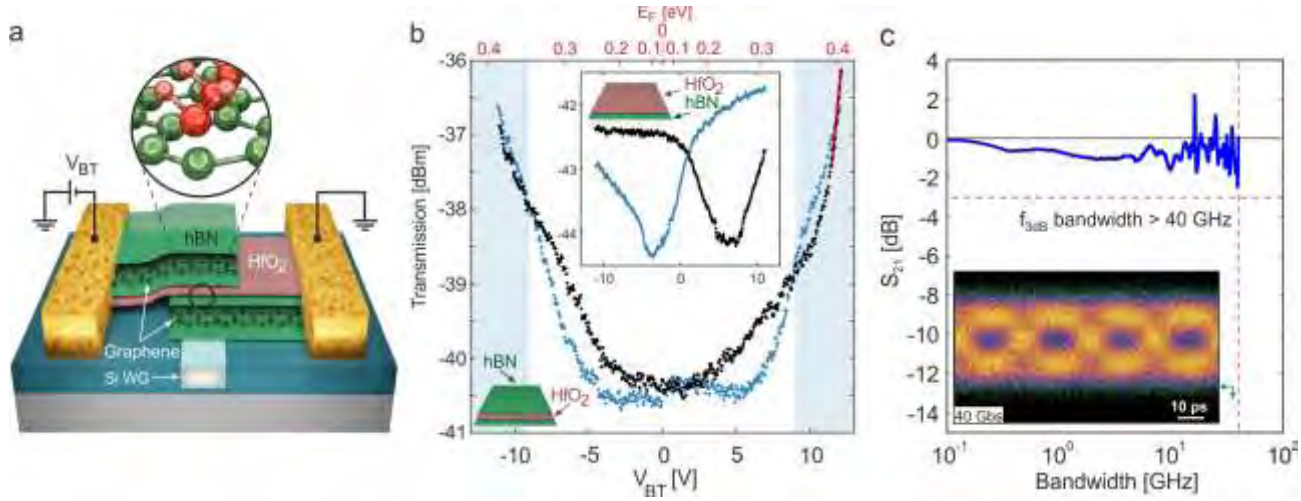

Figure 1: a) Sketch and connections of the EA modulator with a hBN-HfO2-hBN dielectric. b) Transmission as a function of the applied voltage V_{BT}. The forward and backward voltage sweeps are indicated in black and blue. The red line is a linear fit to the data within a 0.5V voltage span (slope: 2.2 dB/V). The inset shows the transmission of a modulator with a hBN-HfO2 dielectric. c) Frequency response of the modulator and eye diagram measured at 40Gbps. The green arrow indicates the 0W power baseline.

Gate-tunable graphene-based Hall sensors on flexible substrates with increased sensitivity

Burkay Uzlu [1,2*], Zhenxing Wang[1], Sebastian Lukas[1,2], Martin Otto[1], Max C. Lemme[1,2] and Daniel Neumaier[1]

[1]*Advanced Microelectronic Center Aachen (AMICA), AMO GmbH, 52074 Aachen, Germany*
[2]*Chair of Electronic Devices, RWTH Aachen University, 52074 Aachen, Germany*
https://doi.org/10.1038/s41598-019-54489-0

Hall sensors are widely used in application fields like consumer electronics and automotive for position precision and switching applications. Key parameters of Hall sensors are the current related (S_i), the voltage related (S_v) sensitivities and the magnetic resolution (B_{min}). Graphene, because of its very high mobility μ and low charge carrier concentration n ($S_v \approx \mu$ and $S_i \approx 1/n$) as well as its mechanical flexibility, appears to be an ideal material for Hall sensors. Previously, graphene based Hall sensors outperforming all other technologies on flexible substrate were demonstrated. However, the sensitivity of flexible graphene Hall sensors is not yet outperforming rigid Hall sensors based on conventional semiconductors, at least if the graphene Hall sensor is fabricated with a scalable approach. [1,2]

In this work, we demonstrate a novel concept for operating graphene-based Hall sensors using an alternating current modulated gate voltage, which provides two important advantages compared to Hall sensors under static operation: 1) The sensor sensitivity can be doubled by utilizing both n- and p-type conductance. 2) A static magnetic field can be read out at frequencies in the kHz range, where the 1/f noise is lower compared to the static case. Sensitivity up to 0.55 V/VT and B_{min} down to $290\ \mathrm{nT}/\sqrt{\mathrm{Hz}}$ at 2 kHz gate frequency were found for Hall sensors fabricated on flexible foil. This significantly outperforms state-of-the-art flexible Hall sensors and is comparable to the values obtained by the best rigid III/V semiconductor Hall sensors.

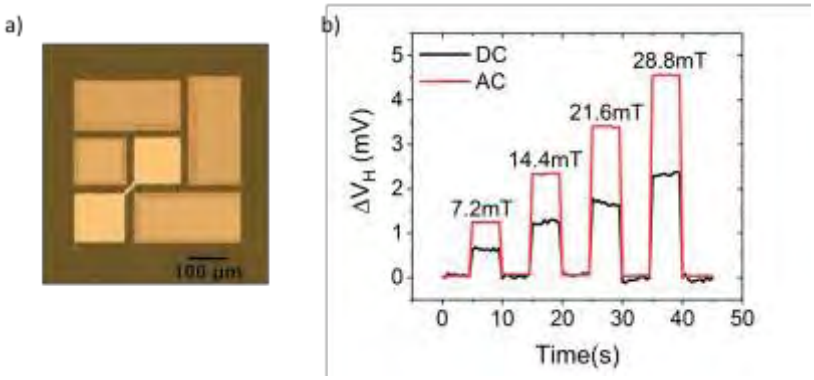

Figure 1: a) Microscope image of the top gated graphene Hall sensor on flexible substrate. b) Hall voltage under DC (black) and AC (red) operation.

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Multithiol Functionalized Graphene Bio-Sponge for Efficient Removal of Heavy Metal Ions in Water

Pei Lay Yap[a,b]
Kamrul Hassan[a,b], Farzaneh Farivar[a,b], Diana N.H. Tran[a,b], Jun Ma[b,c,d], Dusan Losic[a,b]
[a]School of Chemical Engineering and Advanced Materials, The University of Adelaide, Adelaide, SA 5005, Australia
[b]ARC Hub for Graphene Enabled Industry Transformation, The University of Adelaide, Adelaide, SA 5005, Australia
[c]Future Industries Institute, University of South Australia, Mawson Lakes, SA 5095, Australia
[d]School of Engineering, University of South Australia, Mawson Lakes, SA 5095, Australia
peilay.yap@adelaide.edu.au

Abstract

Efficient water purification technologies are still highly sought-after owing to the uncontrollable widespread of heavy metals in water bodies. This work presents a sustainable modification of a graphene bio-sponge for heavy metals adsorption consisting of alginate bio-polymeric network encapsulated with magnetic reduced graphene oxide (mrGO) and functionalized with multithiol precursor via photoinitiated thiol-ene click chemistry.[1] The multithiol functionalized graphene bio-sponge (SH-Graphene bio-sponge) is well-engineered with bountiful of oxygen functionalities and high density of sulfur-containing groups (10.2 at % S) for capturing Cd (II) and Pb (II) ions. SH-functionalized graphene bio-sponge exhibited excellent adsorption capacity for Pb (II): 101.01 and Cd (II): 102.99 mg/g, outperformed commercial and literature reported adsorbents in highly competitive selectivity studies using co-existing heavy metal ions (Cu, Co, Pb and Cd) spiked- sea water. The multithiol modified bio-sponge was highly recyclable and showed remarkable stability with only 0.015 mg/L Pb (II) detected, meeting the strict US EPA maximum contaminant level (MCL) for lead, after five repeating adsorption-desorption cycles using mixed heavy metal ions solution and acidic eluent. The outcomes from this work contribute promising solution towards the development of scalable, energy-efficient and sustainable adsorbents for efficient water purification technology.

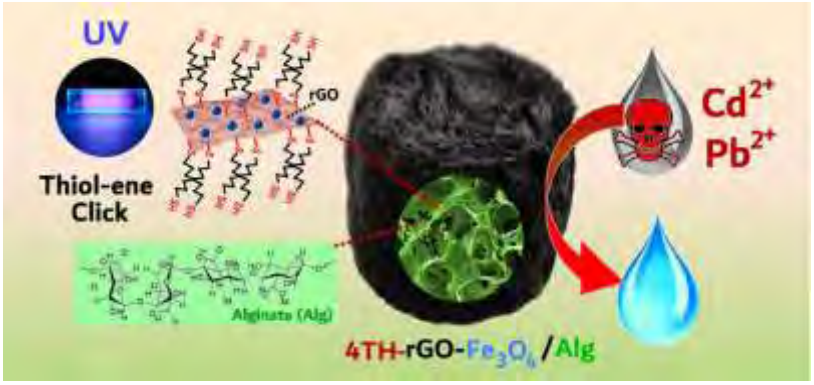

Figure 1: Multithiol functionalized graphene bio-sponge via photoinitiated thiol-ene click approach for efficient removal of Cd(II) and Pb(II).

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Solution-processed GaSe nanoflake-based films for photoelectrochemical water splitting

Marilena Isabella Zappia[1,2]
Gabriele Bianca,[3,4] Sebastiano Bellani,[1,3] Michele Serri,[3] Leyla Najafi,[1,3] Reinier Oropesa-Nuñez,[1] Beatriz Martín-García,[3] Daniel Bouša,[5] David Sedmidubský,[5] Vittorio Pellegrini,[1,3] Zdeněk Sofer,[5] Anna Cupolillo[2] and Francesco Bonaccorso[1,3]

[1] Bedimensional Spa., via Albisola 121, 16163 Genova, Italy
[2] Department of Physics, University of Calabria, Via P. Bucci cubo 31/C, 87036 Rende (CS), Italy
[3] Graphene Labs, Istituto Italiano di Tecnologia, via Morego 30, 16163, Genova, Italy
[4] Dipartimento di Chimica e Chimica Industriale, Università degli Studi di Genova, via Dodecaneso 31, 16146 Genoa, Italy
[5] Department of Inorganic Chemistry, University of Chemistry and Technology Prague, Technická 5, 166 28 Prague 6, Czech Republic

m.zappia@bedimensional.it

Gallium selenide (GaSe) is a van der Waals (vdW) layered material, which can be exfoliated in two-dimensional (2D) form due to its low cleavage energy (typically < 0.5 J m^{-2}) [1]. 2D GaSe has been theoretically proposed as a photocatalyst for water splitting reactions [2]. In fact, its 2D nature intrinsically guarantees that the charge carriers are directly photogenerated at the interface with the electrolyte, where redox reactions take place before their recombination [2]. Moreover, the 2D GaSe electronic structure can be tuned by controlling the number of the layers to fulfil the fundamental requirements for a water splitting photocatalysts, *i.e.*: 1) conduction band minimum (CBM) energy (E_{CBM}) > reduction potential of H^+/H_2 ($E(H^+/H_2)$); 2) valence band maximum (VBM) energy (E_{VBM}) < reduction potential of O_2/H_2O ($E(O_2/H_2O)$) [3]. In our work,[4] we have investigated for the first time the photoelectrochemical (PEC) properties of GaSe nanoflakes, produced by scalable liquid-phase exfoliation [5] in a green solvent (2-propanol) [6]. We report the remarkable photoelectrocataytic properties of the GaSe nanoflakes for hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) in both acidic (0.5 M H_2SO_4) and alkaline (1 M KOH) media. In 0.5 M H_2SO_4, the GaSe photoelectrodes show the best PEC performance, reaching a cathodic photocurrent density at 0 V vs. RHE ($J_{0V\ vs\ RHE}$) of −9.3 μA cm^{-2}, a ratiometric power-saved metric for HER ($\Phi_{saved,HER}$) of 0.09%, an anodic photocurrent density at +1.23 V vs. RHE ($J_{1.23V\ vs\ RHE}$) of 83.4 μA cm^{-2} and a ratiometric power-saved metric for OER ($\Phi_{saved,OER}$) of 0.25%.

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FIGURE

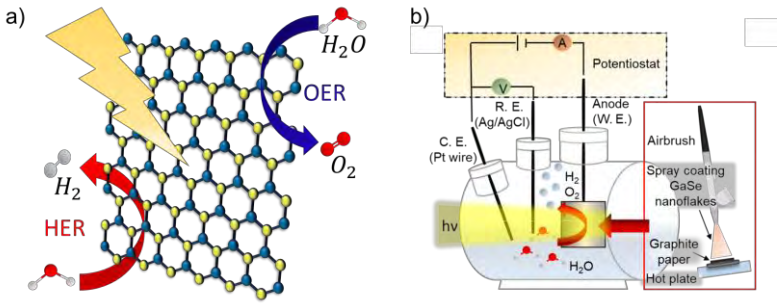

Figure 1: a) Schematic diagram of HER and OER processes. b) Schematic illustration of the experimental setup for electrochemical characterization of the GaSe photoelectrodes.

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Edited by

Phantoms Foundation

Alfonso Gomez 17
28037 Madrid – Spain

info@phantomsnet.net
www.phantomsnet.net