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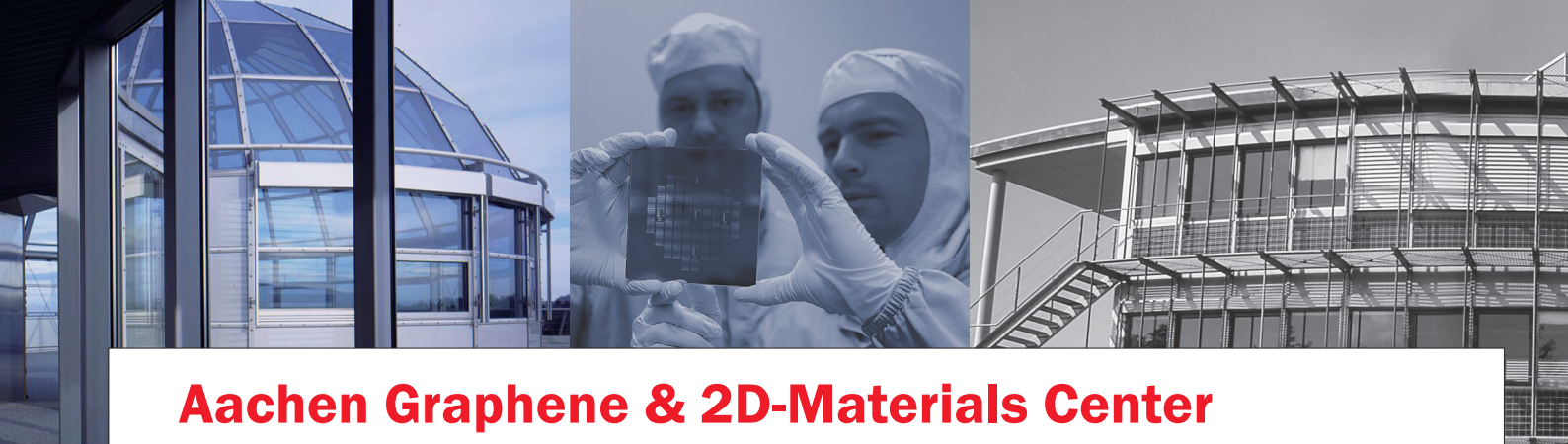


Graphene Industrial Forum & 2DM 2021



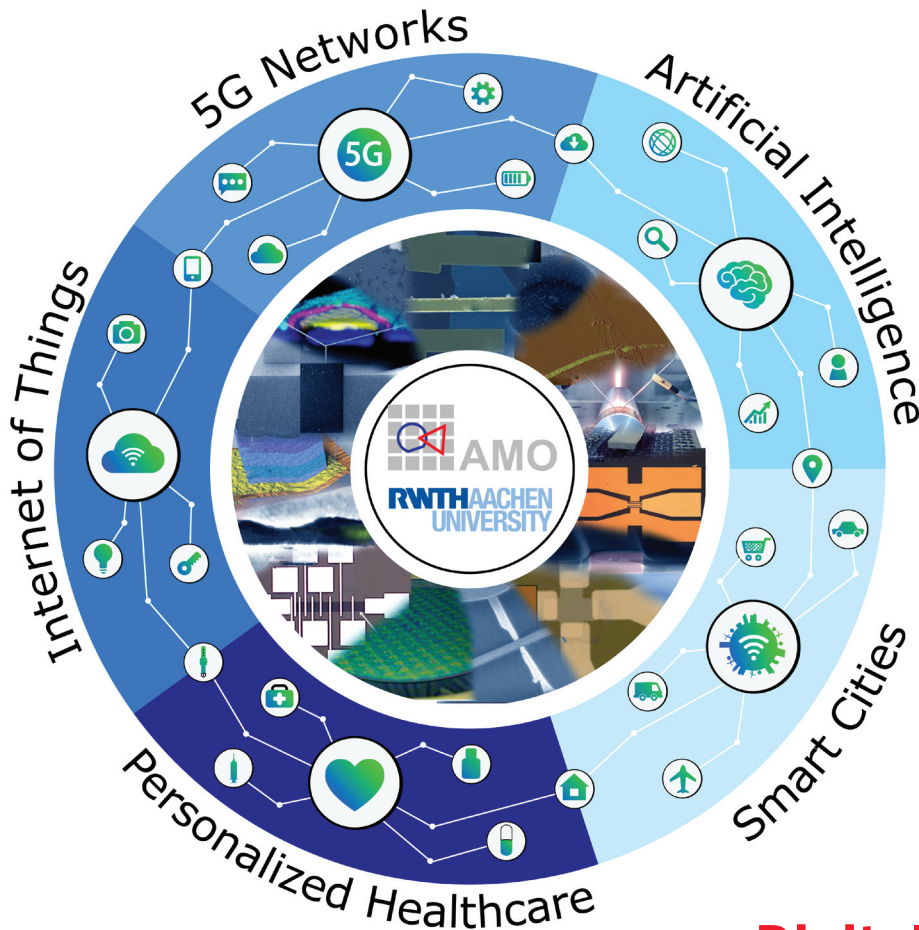
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F OREWORD

On behalf of the Organising Committee we take great pleasure in welcoming you for the 2nd edition of the Graphene Industrial Forum (GIF2021) Online International Conference.

The two-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.

GIF2021 will be a two-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 GIF2020 and previous INDUSTRIAL FORUM editions (organised within Grapheneconf series) and considering that all major scientific and technological conferences are being postponed worldwide until middle of 2021.

We are indebted to the following Companies for their help and/or financial support: AMO GmbH (Germany) and CMC Microsystems (Canada).

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

We truly hope that GIF2021 serves as an international platform for communication between science and business.

Hope to see you again in the next edition of the "Graphene Industrial Forum", online or in-person within the Graphene2021 International Conference (Grenoble, France: October 26-29, 2021).

Graphene Industrial Forum (GIF2021) Organising Committee



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Graphene Industrial Forum (GIF2021) Jan 26-27, 2021

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Towards inline electrical metrology of graphene

Peter Bøggild¹

Patrick Whelan¹, Abhay Shivayogimath¹, Jie Ji¹, Binbin Zhou², Amaia Zurutuza³, Alex Jouvray⁴, Camila Coletti⁵, Peter Uhd Jepsen²

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As monolayer graphene films made by CVD growth are becoming available at competitive price point and quality, the list of attractive applications grow within electronics and photonics. There is a strong need for large-scale, non-destructive characterisation techniques as traditional field-effect device are cumbersome and ineffective in providing spatial information on the electric properties on a large scale. While lithographic processing to some extent destroys the fragile graphene film, scanning probes that rely on physical contact with the graphene film also lead to unwanted scratches and contamination. Since the terahertz absorption of graphene is directly linked to its electrical conductivity, terahertz time-domain spectroscopy allows to extract not only the conductivity, but also carrier density, carrier mobility and even Fermi velocity from a graphene film, without physical contact. In the talk, I will overview our efforts towards making THz-TDS a viable metrology technique. In early 2021 we publish an International Electrotechnical Commission (IEC) metrology standard and a comprehensive review article that overviews selected exemplary cases from our numerous collaborations on graphene on polymer substrates, silicon carbide, silicon, and sapphire, as well as encapsulated graphene. I will show how useful insights into the impact of imperfections and non-uniformity on the electrical properties and the spatial uniformity can be extracted from THz-TDS maps. The talk will highlight the strengths and weaknesses of the technique and discuss what is needed to realise high speed inline electrical characterisation in a production environment.

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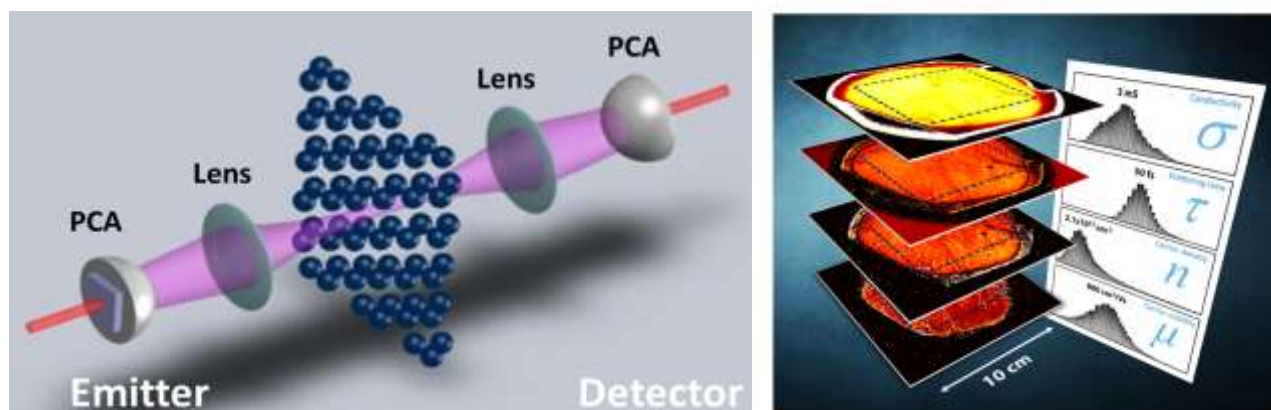


Figure 1: Thz-TDS measures the absorption of terahertz radiation by graphene. From the frequency dependent conductivity, the DC conductivity, scattering time, carrier density and carrier mobility can be extracted.

Perspectives and challenges in printable and flexible electronics based on two-dimensional materials

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The extraordinary mechanical and electrical properties shown so far by graphene and related two-dimensional materials (2DMs), are pushing their exploitation towards new directions and applications [1-3].

Printable and flexible electronics is one of the fields where 2DMs could be the game changer, and they could represent much needed enabling technology in order to reach the desired goal of obtaining distributed systems with various functionalities on flexible and wearable substrates.

In this talk, I will discuss the points of strength of this technology, and I will highlight the weaknesses and the problems that still need to be solved, while trying to provide an overview of the perspectives and challenges that have to be tackled.

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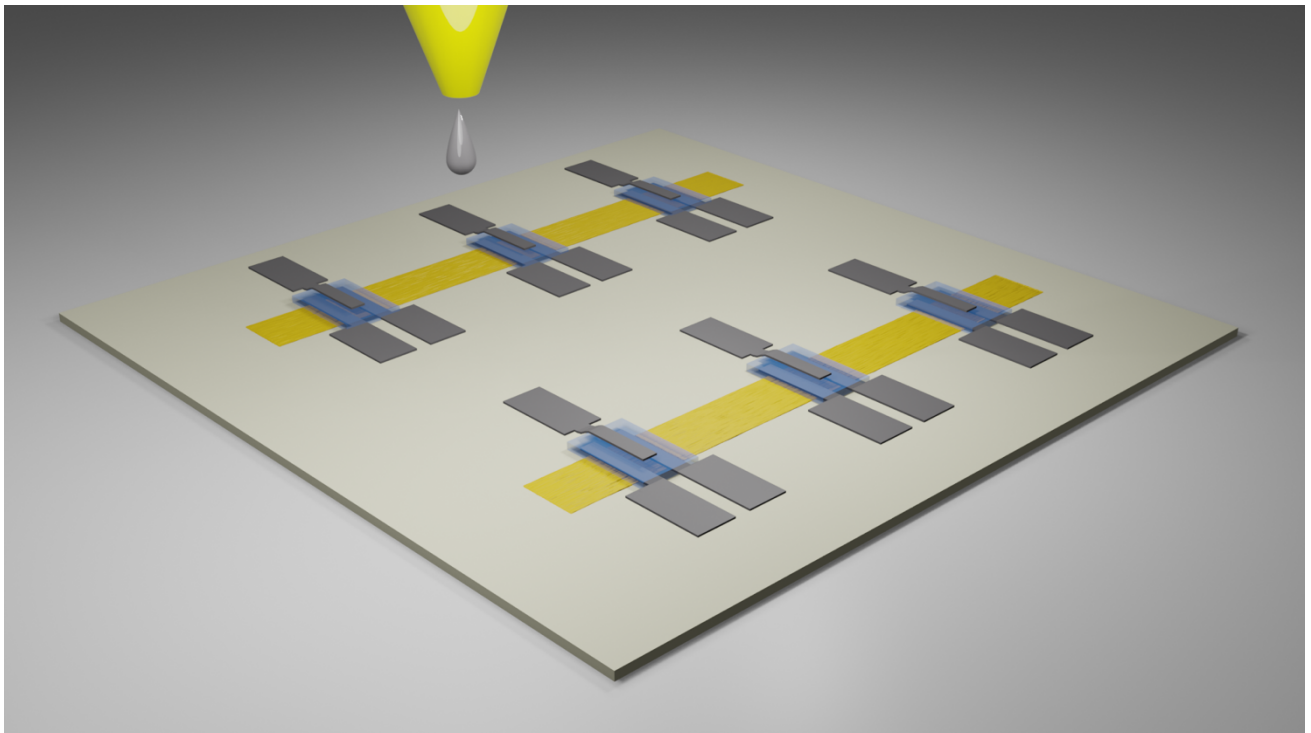


Figure 1: Sketch of printed devices on a flexible substrate

Graphene composites; current status and new perspectives towards commercial applications

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Over the last decade, Graphene and Related 2D materials (GRMs) have emerged as ideal inclusions for the development of a whole range of advanced composite materials with enhanced multifunctionality. This is due to the exceptional mechanical, electrical, thermal and impermeable properties of GRMs. In fact, these remarkable properties of GRMs can be imparted to composite material systems in various forms such as fillers, coatings or continuous sheets depending on desired function and cost considerations. Furthermore, GRMs can be integrated in all type of matrices such as metals, ceramics and polymers giving rise to diverse industrial applications in the fields of aerospace, automotive, electronics, renewable energy, biomedical and consumer goods. More specifically, to support wide spread diffusion of GRMs in the plastics industry, low cost, quality controlled and tailor made GRM masterbatches (MBs), *i.e.* polymeric pellets containing high concentrations of GRMs, have been developed at an industrial scale [1]. Integration of GRMs in FRPs (fibre-reinforced plastics), has enabled the development of mechanically enhanced and/or multi-functional integrated system components in industries such as the aerospace and automotive. Low content GRM fibre reinforced plastics (FRPs) have demonstrated notable enhancements [2] in properties such as damping, fracture toughness, impact damage resistance, etc. Likewise, in elastomeric materials, GRMs can bestow a number of physical enhancements [3] (e.g. chemical resistance, thermal stability etc) that has given rise to a multitude of new applications (e.g. smart seals, wear-resisting tires, thermal interface materials, fire retardant elastomers, etc.). Regarding continuous CVD graphene sheets embedded in polymers, recent work [4] has shown the resulting nanolaminates can outperform conventional laminates in certain aspects of mechanical behaviour and most importantly in EMI shielding effectiveness per unit weight. Furthermore, GRM composites containing inorganic components (e.g. metallic powders, nanoparticles or nanofibers) have a significant impact in the thermal and electrical efficiency of conductors, tribological characteristics (e.g. switches) and environmental protection of coatings, thus, enabling enhancements in the thermo-electrical properties and life-cycle of the components and reductions in assembly time and cost. As manufacturing goes digital and the industry is striving for more sustainable solutions, GRM composites can significantly contribute towards this goal. For example, GRM composites can substitute poor performing materials presently utilized in additive manufacturing processes (e.g. 3D printing), and thus, enable to produce functional products rather than simple replicas. . They can also readily attain sustainability key drivers, such as reductions in weight, energy savings, system integration, longer service life, lower maintenance, assembly costs and others. The future of graphene composites still faces important challenges. Widespread adoption by the industry would inevitably require further developments in the scaling-up of graphene production, especially if graphene were to be used for example as reinforcement – even at low loadings - in construction applications. Finally, standardization of graphene composites is an issue that is not only limited to maintaining the quality of graphene in large quantities, but also improving product identification amongst different suppliers regarding number of layers, oxygen content, densities, lateral sizes, aspect ratios, etc.

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Opportunities and Challenges of Graphene Technology in Medtech

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Graphene and graphene-related materials display a combination of properties that make them very attractive for a broad variety of applications, among them biomedical and medtech applications [1]. During the last years we have witnessed an increasing amount of evidence demonstrating that prototype devices based on these materials can surpass the performance and technical specifications of the state-of-the-art technology [2,3]. However, the demonstration of an improved technical performance does not guarantee a successful translation to a clinical product; in the field of medtech, regulatory hurdles, for instance, are particularly penalizing for novel materials.

In this presentation I will discuss on the opportunities and challenges of graphene technology for biomedical and medical applications, with a particular focus on devices that are intended to interface with the nervous system, such as implantable devices to monitor and modulate brain activity for diagnosis or therapy purposes. Clinical applications of these devices are, for instance, the treatment of brain disorders such as Parkinson's disease or epilepsy, or the development of brain-machine interfaces to help patients with sensory or motor disabilities.

I will review recent developments in the field, with a particular attention to the technical and scientific grounds of these developments. Further, I will also discuss other non-technical challenges that these technologies will have to overcome to be eventually translated into medtech products.

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Wafer-scale integration of two-dimensional materials in high-density memristive crossbar arrays for artificial neural networks

Mario Lanza¹

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During the last decade, memristors have attracted enormous interest due to their excellent capability to store digital information, and they are being considered to be a key element to build future artificial neural networks for bio-inspired neuromorphic computing systems [1-5]. Recent works have shown that memristors made of layered two-dimensional (2D) materials can exhibit performances that traditional memristors (made of transition metal oxides) do not show, such as excellent transparency and flexibility, high-temperature stability, and unique controllability of the conductance potentiation, depression and relaxation [6-10]. However, all studies on 2D materials based memristors focused on single devices, and system level performances like yield and device-to-device variability have never been analyzed in depth. Furthermore, several basic properties of 2D materials based memristors (such as switching time, write energy, I-V non-linearity, and scalability) have never been investigated. In this talk, I will present the first wafer-scale statistical analysis of high-density memristive crossbar arrays made of 2D layered materials. By using chemical vapor deposited multilayer hexagonal boron nitride (h-BN) sheets, we have fabricated metal/h-BN/metal memristive crossbar arrays not only exhibit outstanding performance, but also high yield ~98%, and low device-to-device variability. These findings may accelerate the use of 2D materials for building wafer-scale and high-density electronic memories and artificial neural networks.

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Wafer-scale manufacturing of graphene based electronic and sensor devices

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Abstract

Graphene based electronic, photonic and sensor devices have attracted significant interests because of their outstanding properties. However, for commercializing these devices, large volume production, i.e. wafer-scale processing, needs to be developed and mastered. While wafer scale growth of graphene and related 2D materials has been demonstrated by means of chemical vapor deposition or similar methods, the transfer of such grown 2D layers to target substrates still faces severe challenges related to contamination, mechanical stress and reproducibility. In addition, defining and controlling quality, yield and reproducibility of (opto-)electronic devices is at a very early stage.

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

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FIGURES

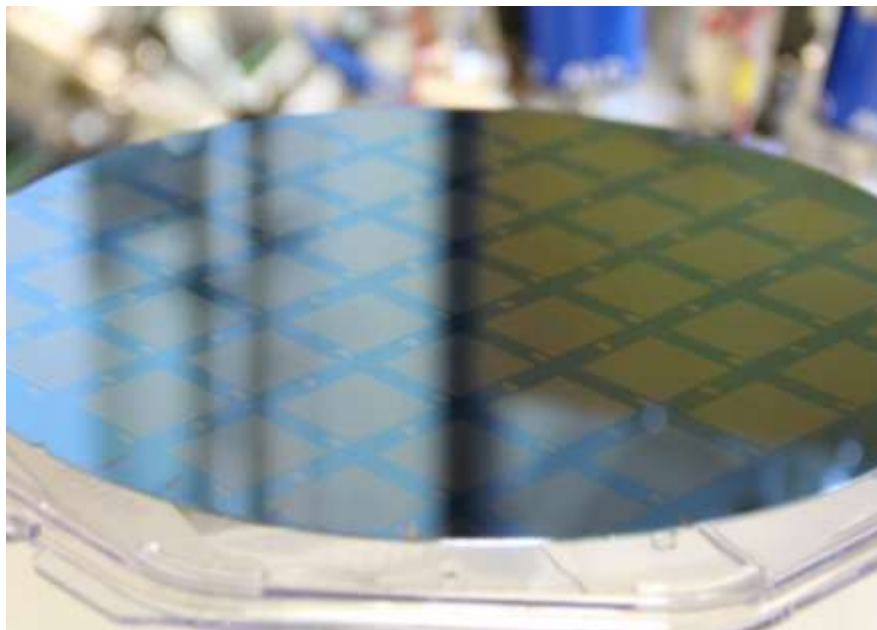


Figure 1: 8 inch wafer containing graphene based sensors.

Effect of Foaming on the Electrical and Thermal Conductivities of GnP Composites

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Abstract:

Recently, multifunctional, lightweight, and low-cost polymer-composites incorporating graphene nanoplatelets (GnP) have demonstrated great promise as next-generation materials for energy management and storage, electromagnetic interference (EMI) shielding, heat dissipation components in electronic industries. However, the practical underpinning needed to economically manufacture graphene-based polymer composites is missing. Our research has demonstrated how critical challenges for efficient manufacturing of functional polymer composites, can be overcome by using supercritical fluid (SCF)-treatment and physical foaming technologies.

Our research has developed an in-depth understanding of the effects of cellular structures, GnPs' orientation, arrangement, and exfoliation on the thermal/electrical conductivity, percolation threshold, dielectric performance, and EMI shielding effectiveness of the polymer/GnP composites. We have demonstrated how SCF-foaming can significantly enhance thermal conductivity of polymer/GnP composites (Figure 1a) [1]. This technique can exfoliate the layers of graphene in situ [2] and microscopically tailor the composites' structure [3] to substantially increase the electrical conductivity, EMI shielding effectiveness and can decrease the percolation threshold of the polymer/GnP composites [4] (Figure 1b). We have also presented a facile technique for manufacturing a new class of ultralight polymer/GnP composite foams with excellent dielectric performance by generation of a unique parallel-plate arrangement of GnPs within a microcellular structure [5]. (Figure 1c-d)

Our research presents new routes to microscopically engineer the structures and properties of conductive polymer composites for EMI shielding, energy storage and heat management in microelectronic packaging.

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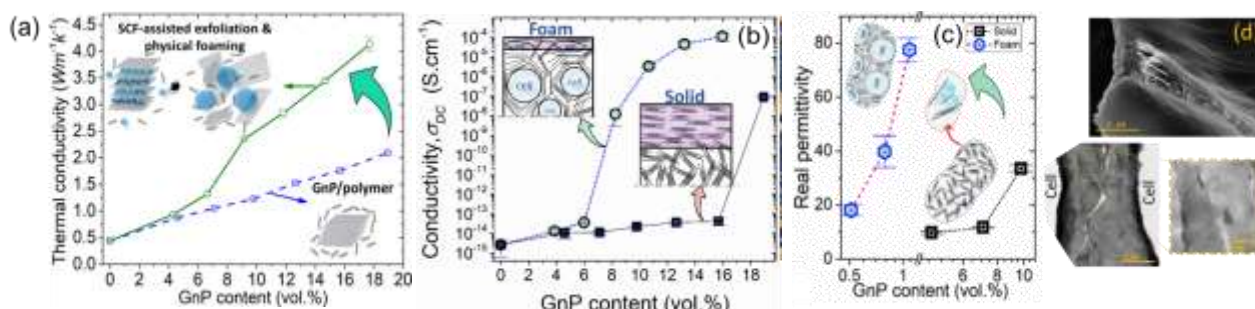


Figure 1: a) Thermal conductivity [1]; b) electrical conductivity [4]; and c) dielectric constant of the polymer/GnP composites [5]. d) SEM and TEM images of polymer/GnP foams [5].

Graphene as a new material for Li-ion batteries

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Abstract

In this talk I will discuss how graphene can be employed as a new material in the production of Li-ion batteries. I will first highlight market needs and opportunities [1] and then discuss the challenges related to the material production and quality certification [2]. I will present and discuss our activities, obtained in the framework of the European Graphene Flagship, leading to a hybrid anode material for lithium-ion batteries, encompassing silicon nanoparticles embedded onto graphene and synthesized via a scalable wet-jet milling method [3,4,5]. This synthesized composite, reinforced by a network of conductive carbon black exhibited electrochemical behavior that significantly supersedes the performance of a Si-dominant electrode structures [6].

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INVITED

Graphenovation - Graphene Industry in Malaysia

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Abstract

The National Graphene Action Plan 2020 (NGAP2020) created an ecosystem of international materials supply chain, domestic innovators and industry up-takers focusing on rubber and plastic additives, conductive inks, energy storage, nanofluids and electronic devices. Over 40 companies are participants of the action plan generating approximately commercially viable 30 intellectual property rights joint-developed with NanoMalaysia and research collaborators from universities. For the period 2021-2025, NGAP2020 has evolved into Graphenovation with greater focus on levelling up graphene based solutions and products to reach national economy of scale relevant to focus industry sectors under the 12th Malaysia Plan.

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Graphene products for micro and macro-electronics

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Abstract

Graphene-based and two-dimensional materials are approaching the industrial production stage at a sustained pace [1]. These materials can be obtained by bottom-up and top-down approaches like, for example, chemical vapor deposition (CVD) and liquid phase exfoliation (LFE), respectively. While CVD is particularly suitable for growing high-grade single-layer graphene (on a metal catalyst) for microelectronics, LFE methods allow for the direct deposition of multi-layered films low cost that are compatible with a wide range of large-area substrates for macro-electronics [2]. CVD graphene's atomically-thin nature, high carrier mobility, and chemical stability allow fabricating relatively simple, label-free, highly sensitive biosensors based on different types of devices. Here, we show a microelectronics biosensing platform based on liquid-gate graphene field-effect transistors achieving detection of DNA hybridization down to attomolar concentration while being able to discriminate a single nucleotide polymorphism (SNP) [3].

To date, graphene LFE dispersions present some limitations, particularly the use of efficient yet hazardous solvents with limited substrate compatibility, high boiling point, and toxicity, which are all undesirable features for industrial production. We propose a novel approach, with high yield and control on the material properties that uses a green carbon solvent – Cyrene, to replace toxic and hazardous solvents such as NMP and DMP in the exfoliation process. Using a combination of shear mixing and ultra-sonication with tuned conditions (such as time, frequency, and power), we obtained stable graphene dispersions with concentrations above 4 mg/mL (with lateral size of the graphene flakes between 30 and 500 nm). The dispersions were then deposited by spray coating on flexible PET substrates to successfully fabricate, as a proof of concept, a macro-electronics 20x20 channel multi-touch screen prototype.

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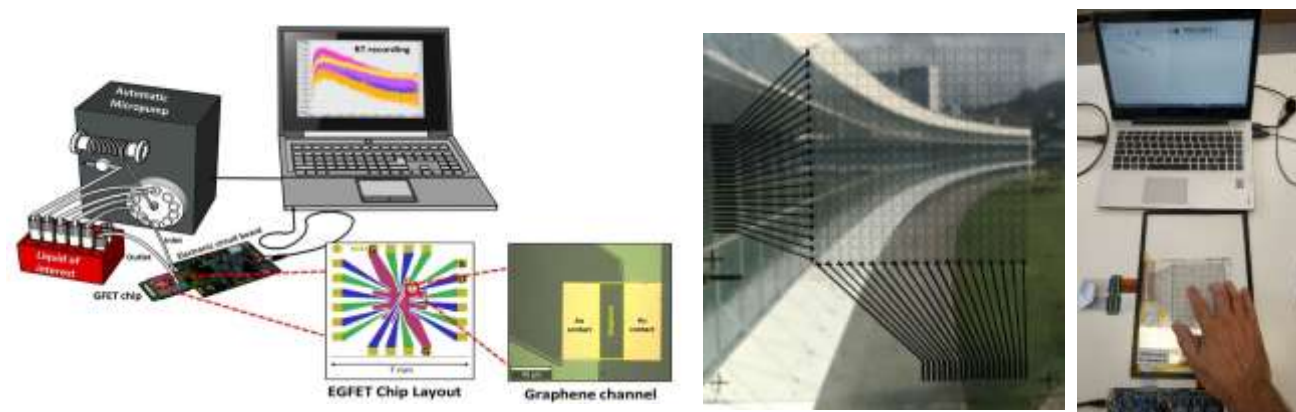


Figure 1: (left) The integrated portable system with automatic micropump and electronic reader of the graphene transistors chip; (right) graphene 20x20 channel multi-touch screen fabricated on PET.

Emerging properties in amorphous forms of novel materials

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

The excellent physical properties of the mentioned materials derive from the nature and degree of their disorder which, controlled at the fabrication level, represents the key ingredient to tune their physical/chemical properties for specific target applications. In this respect, new fabrication strategies to modify the degree of disorder and a systematic theoretical characterization of the impact of the material structural quality on the ultimate performance is urgent. Even more importantly, the search for new disordered materials for novel applications appears as an extremely promising way.

In this talk we present a systematic analysis of the structural, vibrational and electronic properties of amorphous carbon monolayers as a function of the structural quality of the material.

We hence show how disorder results in a tunable electrical conductivity and mean free path. In addition, a strong variation of thermal conductivity varying by more than one order of magnitude is found [3].

Finally, we present the results of the newly demonstrated synthesis of a thin film of amorphous Boron Nitride showing extremely low dielectric characteristics: high breakdown voltage and likely superior metal barrier properties [4]. The fabricated material aims at replacing current interconnect insulators in the next-generation of electronic circuits. We discuss the experimental setup and present the results of our calculations which have contributed to the understanding of the structural morphology of the amorphous material. We conclude discussing the resulting thermal and electronic properties [5].

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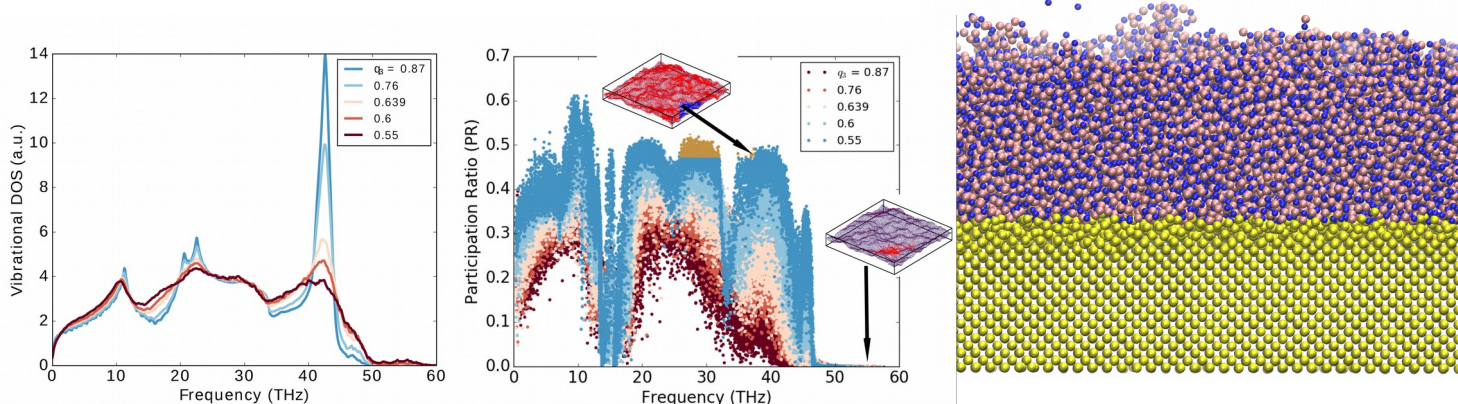


Figure 1: (Left) Vibrational DOS of Amorphous Graphene for different degrees of amorphousness. (Right) Participation Ratio of the samples and atomic displacements (insets)
Figure 2. Atomistic sample of Amorphous Boron Nitride.

Graphene and advanced 2D materials: immune-based applications

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Two dimensional materials such as graphene and Mxenes are destined to leave an indelible mark in many application areas including biomedicine. In particular, due to a multitude of exceptional intrinsic properties, these materials offer new perspectives for the development of advanced tools for therapeutic delivery approaches, imaging, cancer theranostics, and tissue regeneration or engineering.

For any biomedical applications, the immune system plays a fundamental role. Understanding whether and how immune cells respond to nanomaterials by immune activation or immunosuppression might allow taking advantage of both of those selected intrinsic immune properties. For example, immuneactivation could be useful to stimulate the immune system against malignant cells in cancer immunotherapy or as vaccine adjuvants. On the other hand, immunosuppression may find applications for overactive inflammation in allergic reactions, chronic inflammation, autoimmune disorders, and organ transplantation. Here we present our “Nanoimmunity-by-design concepts” (figure 1.) as well as published and unpublished data on the immune-based applications of graphene, Mxenes and other advanced 2D materials.

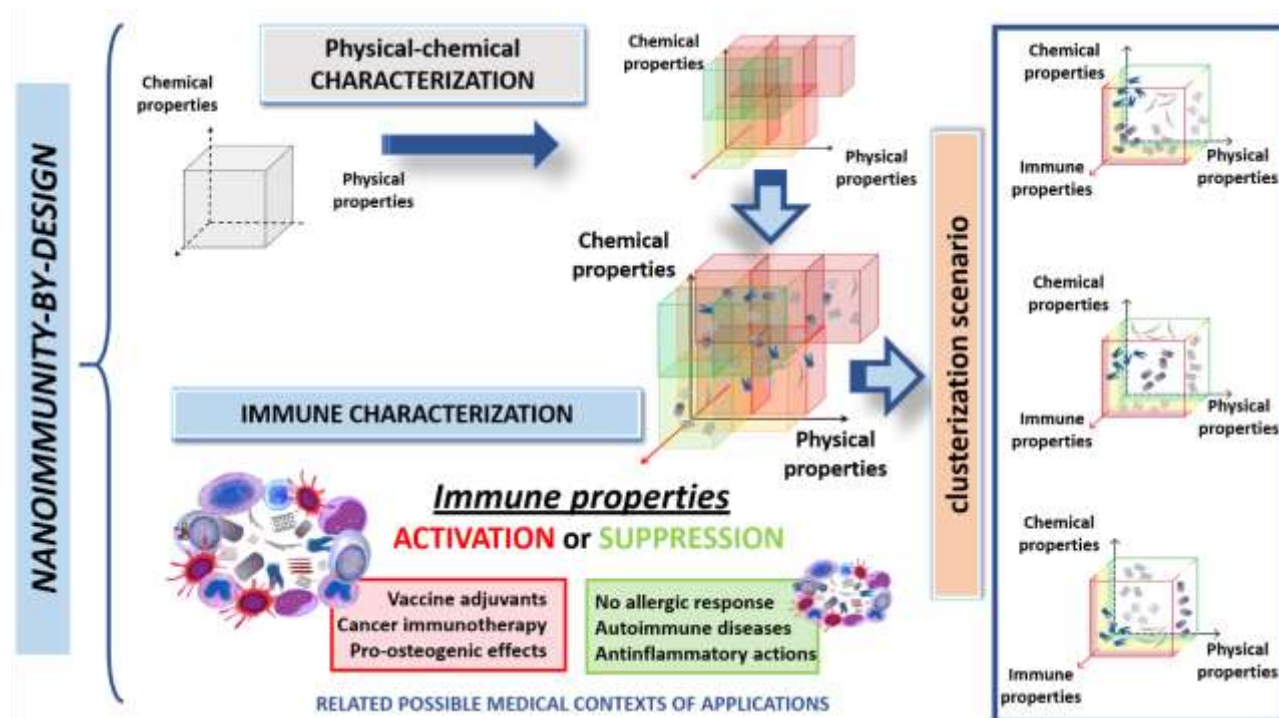


Figure 1. Schematic representation of the Nanoimmunity-by-design concept

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Market Trends of Graphene in China 2020

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Since the graphene was exposed to the public sight, it attracts lots of interests both in academic research and business circle. China as the second largest economy by nominal GDP and the world's largest economy by purchasing power parity, also raise the interests in graphene since 2010. Especially in the graphene commercialization process.

Till April 2020, China has more than 13,999 companies registered which are all labeled with "Graphene". China keeps a real high increasing speed of new born "Graphene company" every year since 2010. However, we found not every of those companies are doing real graphene business. The new born labeled graphene companies are much more than the real new born graphene companies. A huge bubble occurred since 2016, and reached to the peak at 2018. Which match to the Gartner TRL expectation curve perfectly.

To understand the "Death Valley" of graphene industry is coming will be much helpful for the top-level design and market understanding. In this talk, I will introduce the newest research regarding on the recent graphene market in China and summarize the industry process of graphene to share the possible business chance with global partners.

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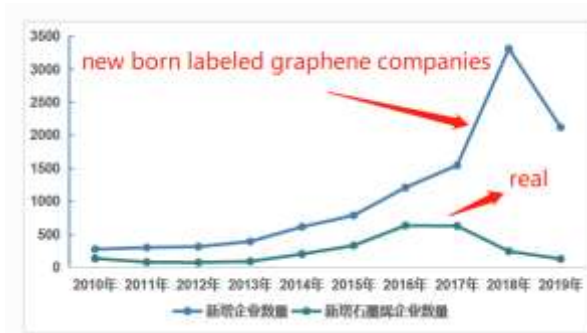


Figure 1: Fig.1 New born "labeled" graphene companies per year in China compare with the real increased graphene companies per year

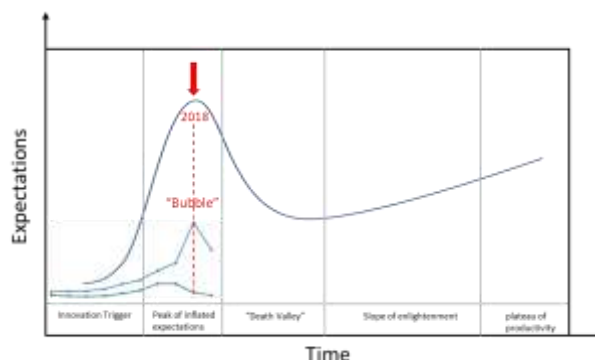


Figure 2: Fig.2 Bubble occurred since 2014 but reached to the peak at 2018. Death Valley will come soon
GRAPHENE AND 2DM INDUSTRIAL FORUM (GIF2021)

Graphene Oxide Derivatives: Opportunities for New Applications

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Graphene oxide (GO) can be considered as an oxidized single sheet of graphite containing oxygen functionalities on the basal plane and on the edges. Abalonyx produces GO in Kg-quantities using a safe, cost effective and reliable process. Besides having many remarkable chemical and physical properties itself which make it suitable for applications in fields including environment, energy, biomedicine, graphene oxide also serves as a convenient intermediate for large scale production of graphene-like materials such as reduced graphene oxide (rGO). [1][2] To improve the electrical and thermal conductivity of rGO, both chemical and thermal reductions have been performed in this work. Thermal reduction of graphene oxide has shown superior results in terms of the degree of reduction (C/O ratio) compared to chemical methods. However, the restoration of the honeycomb lattice, necessary to increase the electrical conductivity of the reduced material, still remains a challenge. For each method applied, the scalability of the process was explored and optimized together with the chemical and physical properties of the modified material. Additionally, to expand the possibilities of graphene oxide-like materials and show versatility in terms of chemical modification, covalent functionalization with amine groups was performed. Such amine-based GO materials have found use in many fields such as composites, catalysis, electronics and water treatment. [3][4] These chemical modifications were implemented not only to enhance and modulate the properties of graphene oxide, but also to provide scalable and reproducible functionalized graphene oxide materials, in view of large-scale production. Additionally, modifications will provide better dispersion in different organic solvents and as example in Figure 1 is reported a general procedure to obtain reduced and functionalized graphene oxide material. Analytic techniques, such as FT-IR, XRD, XPS; FT-Raman and TGA, were combined to better characterize the graphene oxide modified derivatives.

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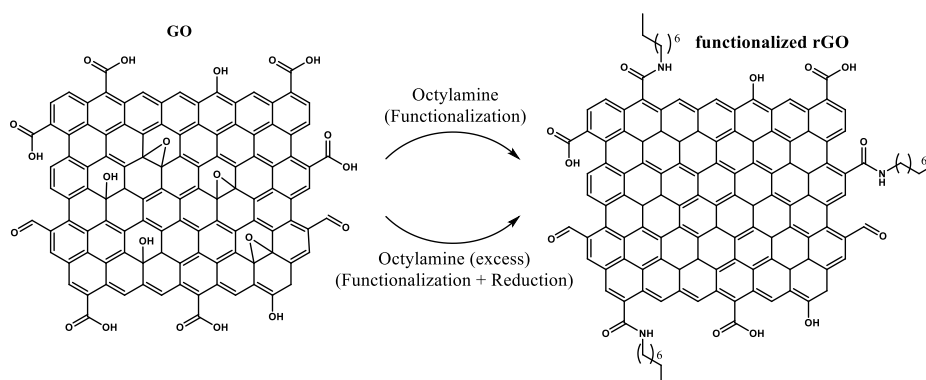


Figure 1: General scheme for reduced graphene oxide functionalized with amine using different procedures.

Enabling a world of enhanced perception

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Qurv develops wide spectrum image sensors that capture previously hidden information. Either information that was hidden by ambient light interference or information that is not available in the visible light spectrum. More information allows improved decision making for machines.

The human eye only sees red, green and blue light. Ubiquitously available CMOS image sensors see visible and near infrared light up to 1 μm . Qurv image sensors based on nanomaterials are sensitive to visible, near infrared and short wave infrared light: from 300 nm up to 2 μm and in the near future beyond 2 μm .

Qurv's image sensor technology targets bringing enhanced computer vision applications to everyday life. The technology has a high manufacturability potential and can thus reach low cost products. Key to achieve high manufacturability is Qurv's waferscale back-end-of-line (BEOL) process. A proof of concept wide spectrum image sensor shows the validity of this BEOL process.

Qurv's wide spectrum image sensor BEOL process is CMOS technology agnostic. Furthermore, all Qurv image sensors will be designed for AI.

Electromagnetic interference shielding and absorption with 2DM polymer nanocomposites

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Abstract:

With the rapid development of the portable technologies and telecommunication systems such as 5th generation wireless systems, the electromagnetic pollution has become a serious issue. The electromagnetic interference (EMI) issues resulted from electromagnetic induction effects can cause system failure, data misinterpretation/loss and can even lead to harmful health effects. Thanks to their attractive combination of properties, the polymer nanocomposites of emerging 2D materials such as graphene and MXene have shown great promise to efficiently shield/absorb the electromagnetic (EM) waves [1–4].

In our research studies we have developed hybrid polymer composites of 1D materials (e.g. carbon nanotubes (CNT) and SiC-nanowire (SiCnw)) and 2D materials (e.g. graphene and MXene $Ti_3C_2T_x$) for efficient EMI shielding/absorption. For instance, the synergism between the CNTs and graphene resulted in a high shielding effectiveness (SE) of 36.46 dB in the poly(vinylidene fluoride) (PVDF)/CNT/graphene films with the thickness of 0.25 mm [4]. We have also demonstrated that the incorporation of SiCnw into the PVDF/graphene nanocomposites can significantly increase the dielectric loss of the composites by 4 orders of magnitude as compared with the neat PVDF resulting in high EMI SE of 32.5 dB at 1.2 mm thickness [3].

Recently we have developed heterogeneous nanostructures of SiCnw/MXene within a PVDF matrix to develop excellent electromagnetic wave absorption materials. The nanostructured assembly of the 2D MXene nanosheets and 1D SiCnws generated large heterogeneous interfaces in the polymer matrix. This unique structure (Figure 1) led to superior electromagnetic wave absorption properties with an effective bandwidth of 5.0 GHz over the measured frequency range of 12.4–18.0 GHz [1].

Thus, our research works present facile techniques for manufacturing a new class of efficient, flexible, and lightweight electromagnetic wave absorption materials with a tailored nanostructure.

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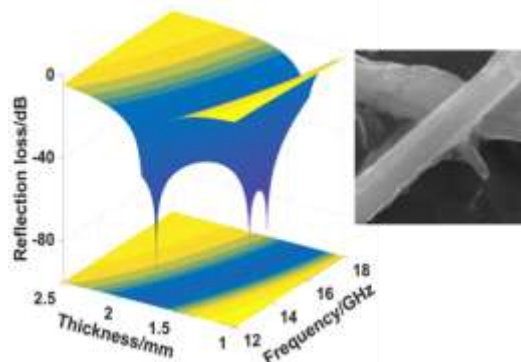


Figure 1: 3D representations of the EM wave absorption performance of polymer/SiCnw/MXene shown in the SEM image.

Development of ground-breaking graphene products in AirMembrane

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Abstract

AirMembrane Corporation is a venture company established in July 2017 that manufactures graphene and develops applications. By using high-speed graphene synthesis method [1] and high-quality graphene transfer technology developed by AIST we develop, manufacture, and supply graphene products. In this talk, we will introduce the features of our graphene synthesis technology and some ground-breaking products.

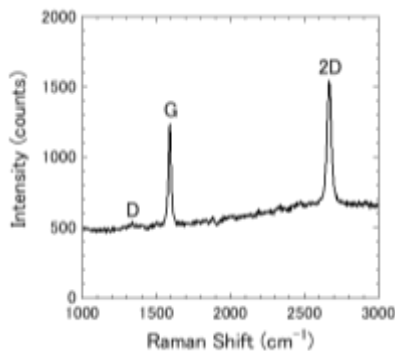
Bilayer graphene TEM grid (see Figures)

Bilayer graphene TEM grid [2] utilizes high-purity CVD-synthesized bilayer graphene free-standing film over grid holes which has high durability against electron beam irradiation. It is an ideal sample support film for TEM observations of ultrafine particles, viruses, etc. Our bilayer graphene TEM grid is strong against hydrophilic treatment using UV irradiations. Very thin vitreous ice layer with uniform thickness, which is indispensable to cryo-TEM observations, can be formed by applying hydrophilic treatment.

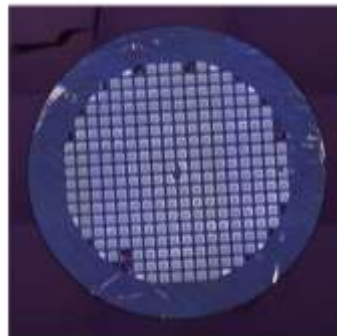
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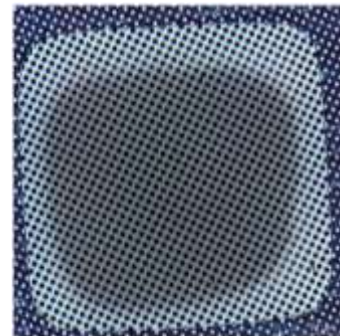
FIGURES



Raman spectrum of bilayer graphene (Laser 532 nm)



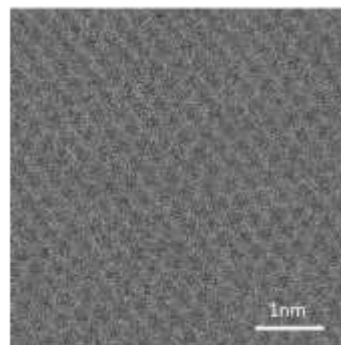
Graphene TEM Grid (Diameter 3mm)



One square of mesh



Free standing graphene on grid hole (Diameter 1.2 μm)



Atomic image of graphene (monolayer)

UVC LEDs Based on Nanowires and Graphene

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The need for efficient disinfection and purification has accelerated the growth of the UVC illumination market, with LEDs positioned to take increased market-shares from conventional lamp technology due to using less energy and having non-toxic and more environmentally friendly materials. UVC LED devices based on traditional planar technology faces many challenges and limitations, most significantly because of high defect densities caused by lattice mismatch between the LED layers and the substrate[1]. By combining nanowire growth and a graphene substrate, some of these fundamental challenges can be addressed, as graphene has a low sheet resistance combined with transparency for all wavelengths[2]. We are developing UVC LEDs (275 nm) for the water disinfection market, based on high percentage aluminum AlGaIn nanowires grown on a graphene substrate.

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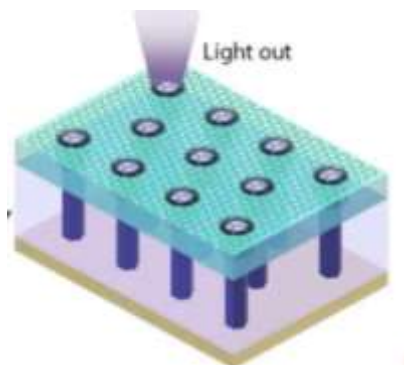


Figure 1: UV LED utilizing graphene as substrate and transparent electrode.

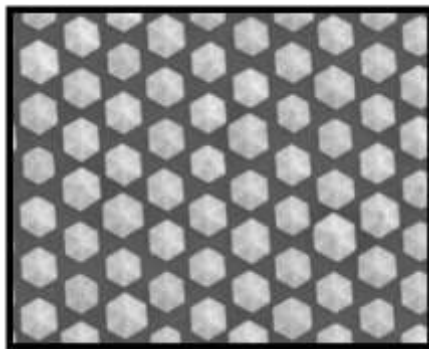


Figure 2: Position-controlled AlGaIn nanowires grown on graphene substrate.

Setting up the ecosystem for 2D materials integration with Silicon technology

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The continual scaling of Si-based transistors has revolutionized the world through continuous breakthroughs in electronics. The Si scaling roadmap is challenged by short channel effects that limit further gate length scaling. Field-effect transistors (FETs) with semiconducting transition metal dichalcogenides (MX₂, such as WS₂ or MoS₂) as the semiconductor channel promise however to be relatively immune to these short channel effects. FETs with 2D semiconductor channel owe this promise to the ability to make atomically thin channels combined with the theoretical ability to maintain higher carrier mobility – independent of channel thickness. These two properties give the gate voltage a better electrostatic control over the channel.

Besides this prospect of continuation of the scaling roadmap, Graphene and related 2D materials offer a heterogeneous platform for enhanced non-computational functionality monolithically integrated with silicon technology [1].

Several years ago, imec started pathfinding work on 300mm integration of both graphene modulators and MS₂-FET devices – a key requirement for industrial adoption. This work has resulted in unique 300mm test vehicles for 2D-FETs, allowing the fabrication of functioning devices with gate lengths down to 18nm [2].

These flows are used to study the impact of various processing conditions, such as the channel deposition and transfer process as well as other remaining challenges, including 2D growth quality, formation of the gate dielectric, doping and contact resistance.

This talk will give an overview on how we work out solutions in the lab which can be upscaled in the fab towards a 300mm compatible 2D technology which is compatible with the semiconductor standards.

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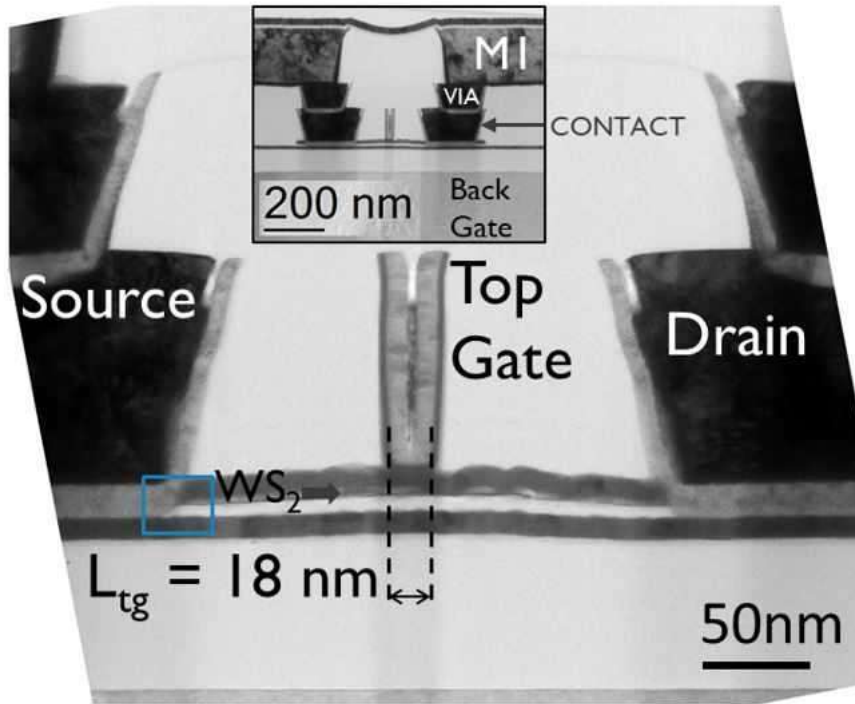


Figure 1: TEM image of 2D device fabricated with 300mm processes (imec web site).

International standardisation for graphene and related 2D materials

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Abstract

From the past 15 years several international expert groups (Technical Committees) have been working on the development of standards for nanotechnology and nanomaterials. Some 168 standard documents were developed [1] by organisations such as ISO TC229, IEC TC113, CEN TC352 and ASTM E56 up to now with over 130 new or updated documents in development. Coherent and reliable approach to new technologies, measurement techniques and novel materials provide a reference for industry as well as regulatory and policy oversight. This update will focus on developments in Graphene and 2D materials standards from terminology to measurements methods and material specifications. Standards provide a sustainable path to growing market needs in graphene and advanced materials in general.

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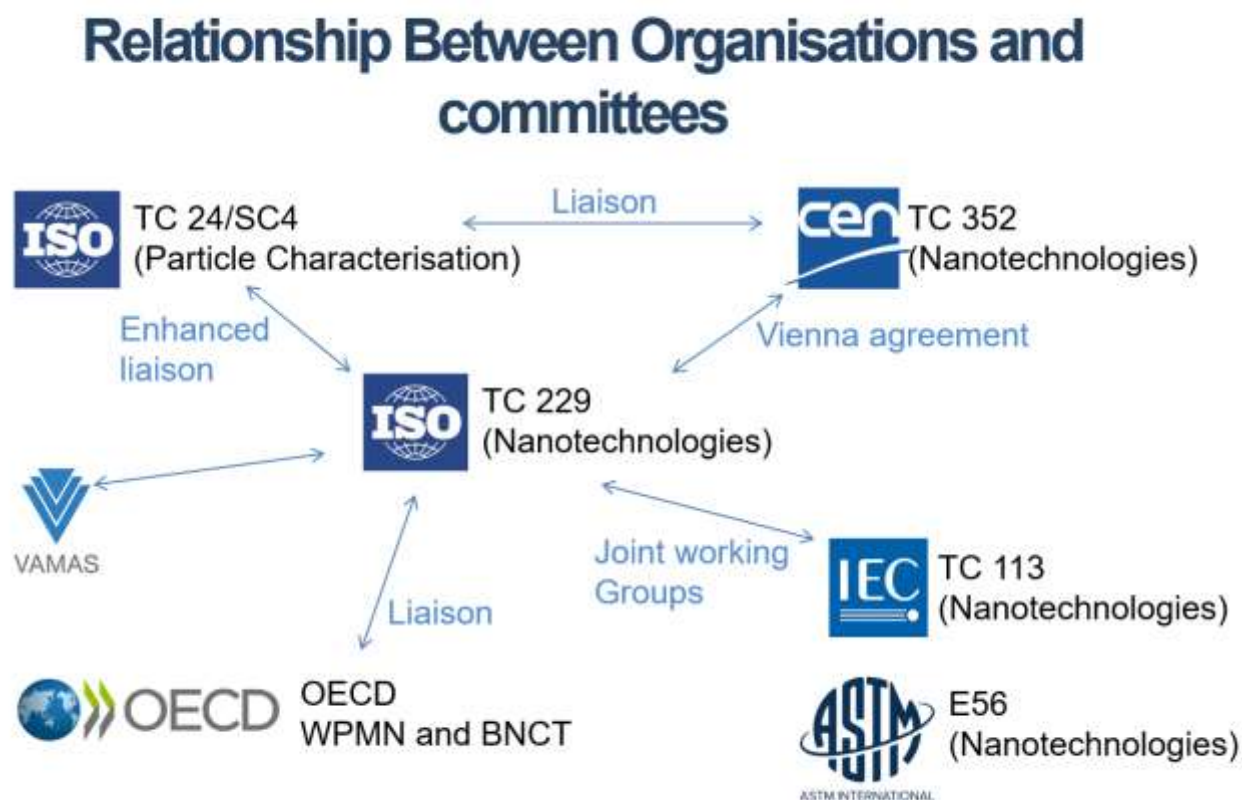


Figure 1: Relationship between key standardisation committees for nanomaterials and Graphene

Interactions of Graphene and Other 2D Materials with Biological Molecules: A Focus on Viral Infections

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2D materials, including graphene, display unique physicochemical properties and have generated a high interest for biological applications. They have been exploited for photothermal therapy, in drug delivery, tissue engineering, and biosensing. Functionalization enables to impart novel properties and also to modulate their interactions with biological molecules. In this talk, I will show the impact of the functionalization of graphene family nanomaterials on their interactions with nucleic acids for gene therapy,^[1] with immune cells allowing to increase their biocompatibility,^[2] and with enzymes to enhance their biodegradability.^[3] I will also give an overview of the literature on the interactions of 2D materials, mainly graphene family nanomaterials, with viruses, focusing on the main factors governing these interactions.^[4] An emphasize will be given on how functionalization can endow the materials with selectivity. Different strategies for the development of 2D-material biosensors for the detection of viral infections will be presented, including the sensing of viruses, viral nucleic acids, and antibodies (Figure 1). I will critically detail the advantages and drawbacks of 2D materials, and provide insights for the development of future biosensors for virus detection. Some suggestions will be given to stimulate research that could help in designing advanced systems for preventing virus-related pandemics.

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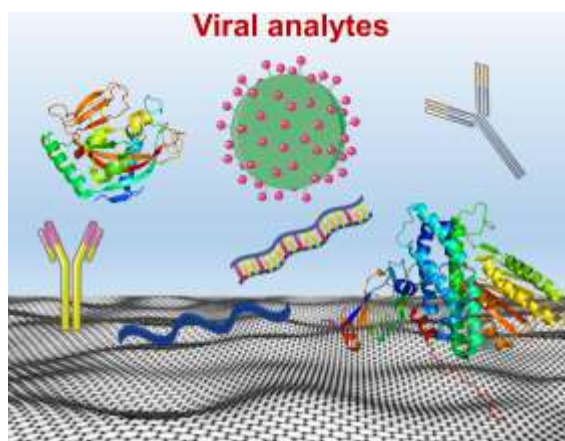


Figure 1: Biosensors incorporating two-dimensional materials.

Black flakes with green value proposition – graphene polymer composites for sustainability

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Since the discovery of graphene and its impressive mechanic, thermal and electrical properties, major materials research efforts have been made towards harnessing these properties for the development of polymer composites with unprecedented performance. While this research has shown that some of the bolder expectations for their properties will probably not be achievable for reasons from basic physics, substantial progress has been made in the production of composites with more down-to-earth property improvements.

At the same time, the production of graphene related materials (GRM) has made great progress with respect to available quantities, cost and resource efficiency that pragmatic applications of graphene as just another functional filler for polymer composites has become economically and ecologically viable.

The value proposition of graphene in applications flame retardance, thermal conductivity or mechanical reinforcement may not lie in beating the performance of conventional fillers in these fields but in avoiding negative side effects of the conventional fillers such as

- introduction of “foreign” elements into the polymer
- embrittlement of the material by large volume fractions of filler
- increase of density due to large fractions of inorganic fillers
- abrasive properties of the melt

While such properties are not necessarily “flashy”, they nevertheless may greatly help the polymer industry on the way of to a more circular and resource-efficient economy

Perovskite Solar Panels with Graphene. An industrial perspective

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Perovskite solar cells (PSCs) have raised research interest in the scientific community due to their high efficiency comparable to traditional commercial solar cells (i.e., amorphous Si, GaAs, and CIGS). Apart from that, PSCs are lightweight, can be flexible, and have lower production costs. Recently, graphene and 2D materials have been used as a novel material for PSC applications due to their excellent optical, electrical, and mechanical properties. For example, Graphene and its derivatives have been used as interface layers or dopant to improve charge transfer¹, to increase mobility², to improve band alignment, to tune the work-function and to limit the ion diffusion³. Moreover, recently more usages of the graphene for the fabrication of Perovskite solar Modules (PSMs) have been demonstrated.⁴ By exploring the application of graphene in PSCs, a new class of strategies can be developed to improve the device performance and stability before it can be commercialized in the photovoltaic market in the near future. We have experimented several of these techniques within an industrial environment and we have verified the benefits of a graphene interface engineering in our perovskite solar devices. In this talk, we will discuss the points of strength of this technology, and we will propose the following prospects:

- i) Front and rear electrodes composed of graphene materials in order to be compatible with perovskite absorber layer fabricated under low temperature. Replacing the gold rear electrode with multi-layer graphene materials would allow to save about 30% on the final cost of the solar modules.
- ii) Widespread adoption by the industry would inevitably require further developments in deposition techniques to uniformly deposit graphene-material on a large area, we are working on large area deposition technique of graphene and graphene doped ETLs suitable with PSMs technology.

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Silicon/graphene composites for high-energy batteries

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Within the last decade, extensive efforts have been made in the field of electrochemical power sources, to meet the increasing demands of numerous industries and applications for more powerful, long-lasting, safer and greener energy storage. Above all, energy storage market is undoubtedly driven by the automotive industry and the prospective electrification of the power train, which lead to the development of novel, large cell designs with 20-50 times higher energy content than common mobile phone batteries. (1) Simultaneously, the beginning of the so-called carbon age, meaning particularly the discovery of carbon nanotubes and graphene in 1991 and 2004 (2) offered exciting new possibilities for the tailoring of micro- and nano-sized applications and triggered an almost exponential growth in scientific publications in this field (3). Since then, pioneering developments have been reported especially in the area of flexible, portable and wearable electronics (4).

For energy storage systems in general and especially for lithium ion batteries, the demand for high-energy and high-power applications can only be fulfilled by the development of new generations of electrochemically active materials. Here, the use of silicon as active material on the negative electrode is most promising, since silicon offers exceptional high volumetric and gravimetric lithium storage capabilities as well as low charging/discharging potentials. However, this high storage capability is accompanied with high volume changes during lithium insertion/extraction, which causes a rapid decay in dimensional stability of the host material (5). The use of graphene-related materials can help to overcome these crucial problems, as graphene offers a highly conductive and mechanically stable matrix that can suppress or buffer this large volume expansion (6) (7). Consequently, graphene-related materials improve the cycling stability by retaining the native structural integrity as well as the electrode porosity.

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Graphene Membranes for Pressure and Gas Sensors

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Suspended layers of graphene are the thinnest membranes known to mankind. This results in very high flexibility, surface-to-volume ratio and strength, while at the same time having a very low mass. These features have the potential to extend the performance of current pressure and gas sensors, offering higher sensitivity and dynamic range, and also enabling new sensing modalities. In this presentation, recent advances in using graphene for pressure and gas sensing applications will be shown, and an overview [1] of the performance and challenges in implementing various pressure and gas sensing concepts will be given with a focus on innovative concepts like squeeze-film pressure sensing (Fig. 1, [2]) and permeation-based gas sensing (Fig. 2, [3]).

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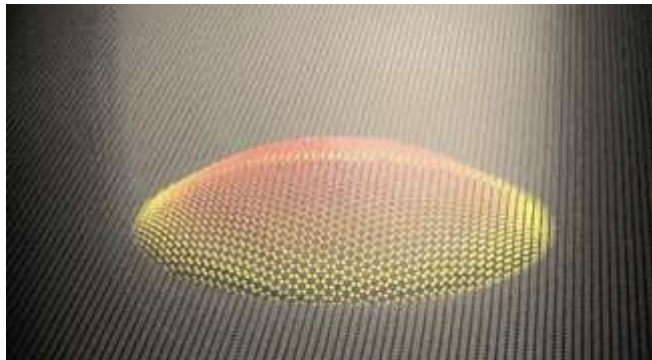


Figure 1: Graphene membrane pressure sensor with optical readout [2]

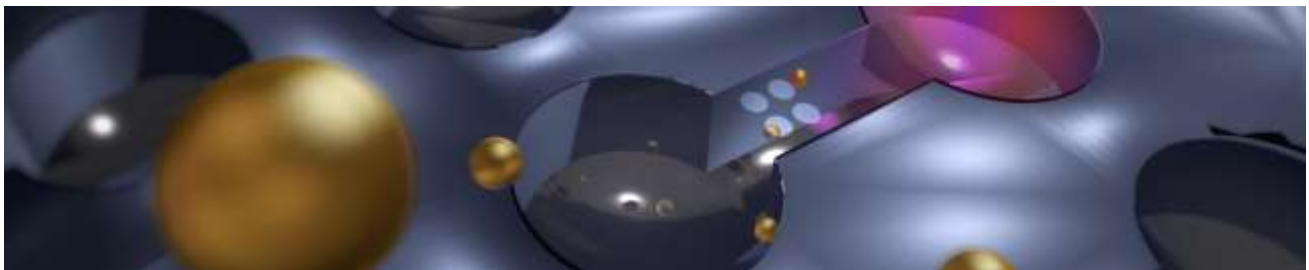


Figure 2: Nanopores are engineered in graphene membranes to enable permeation-based gas sensors [3]

Graphene Electro-mechanical Bio-sensors

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We present a sensitive and low-cost immunoassay, based on a customized open-source quartz crystal microbalance coupled with graphene bio-interface sensors (G-QCM), to quantify antibodies in undiluted patient serum. We demonstrate its efficacy for a specific antibody against the phospholipase A2 receptor (anti-PLA2R), which is a biomarker in idiopathic membranous nephropathy, a progressive kidney disease. A novel graphene-protein bio-interface was constructed by adsorbing a low concentration of denatured bovine serum albumin (dBSA) on the reduced graphene oxide (rGO) sensor surface. The dBSA film prevents the denaturation of the protein receptor on the rGO surface and serves as the cross-linker for immobilization of the receptor for anti-PLA2R antibodies on surface. The detection limit and selectivity of this G-QCM biosensor was compared with a commercial QCM system. The G-QCM immunoassay exhibited good specificity and high sensitivity toward the target, with an order of magnitude better detection limit (of 100 ng/ml) compared to the commercial system, at a fraction of the cost and with considerable time saving. The results obtained from patient sera compared favourably with those from enzyme-linked immunosorbent assay (ELISA), validating the feasibility of use in clinical applications. The multifunctional dBSA-rGO platform provides a promising bio-functionalization method for universal immunoassay and biosensors. With the advantages of inexpensive, rapid and sensitive detection, the G-QCM sensor and instrument form an effective autoimmune disease screening tool.

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FIGURES



Figure 1: Schematic for functionalization of rGO surface to detect the antibodies starting with BSA adsorption, amine activation with EDC/NHS, immobilization of the receptor NC3 (in red) via amine covalent cross-link and blocking with ethanolamine.

Graphene in Sensors

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Abstract

Graphene being a monolayer of carbon atoms exhibits some remarkable electronic and mechanical properties that make it an ideal candidate to be applied in various types of sensors. The sensors' market is extremely large since we are dealing with the automotive, electronics and healthcare industries among others. Therefore, it is an excellent starting platform for graphene applications. For example, the current COVID-19 pandemic has demonstrated the urgent need for fast diagnostics in order to minimise and control its effects, here, biosensors based on graphene field effect transistors (GFETs) have shown great potential as a platform for future diagnostics, Figure 1. Since graphene has unique properties such as high carrier mobilities and electrical conductivity, flexibility, biocompatibility, facile chemical functionalisation, and large specific surface area, allowing the immobilisation of high density of bioreceptors, leading to increased sensitivity.

During this talk, I will cover the use of graphene in various types of sensors including MEMS [1,2] ion sensors (ISFETs) [3-5], gas sensors [6] and biosensors. Depending on the type of sensor, the graphene requirements including the transfer and characterisation vary considerably.

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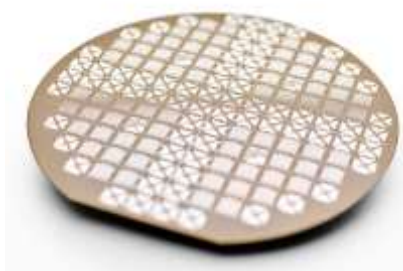


Figure 1: Graphene field effect transistors (GFETs) at wafer scale.

ORAL

Two – Dimensional GaSe and GeSe Nanoflakes for Photoelectrochemical Water Splitting and (PEC)-Type Photodetectors

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Aqueous-based photoelectrochemical (PEC) devices, such as self-powered photodetectors and water splitting cells, represent powerful tools to convert the electromagnetic radiation into chemical fuels and electricity.[1] In this context, two-dimensional (2D) materials are continually attracting utmost interest as potential advanced photo(electro)catalysts,[2] and recently, group-III and group-IV transition metal monochalcogenides. These layered materials can be exfoliated in 2D form due to their low cleavage energy (typically $< 0.5 \text{ J m}^{-2}$), being theoretically predicted to act as photocatalysts for water splitting.[3] Among them, layered gallium selenide (GaSe) and germanium selenide (GeSe), are promising material candidates for optoelectronic devices due to their tuneable electronic structure, strong visible-light absorbance, photoresponse and environmental stability.[4] However, the evaluation of their photo(electro)catalytic properties was still incomplete until last years, pointing out the need of experimental trials and validation. Here, we report the first experimental evidence of the PEC water splitting activity of single-/few-layer flakes of GaSe and GeSe produced in inks form by scalable liquid-phase exfoliation approach in non-toxic solvent (*i.e.*, 2-propanol).[5] The PEC behaviour of monochalcogenides(MCs)-based photoelectrodes, obtained by spray coating approach,[6] were evaluated in different aqueous media, ranging from acidic to alkaline solutions and under different illumination wavelengths, *i.e.*, 455, 505 and 625 nm. The obtained performances (responsivity and external quantum efficiency up to 0.32 A/W and 86.3%) are superior to those of several self-powered and low-voltage solution-processed photodetectors, approaching the ones of their commercial UV–Vis counterparts. Finally, we demonstrate the use of MCs-based photoelectrodes as photoanodes or photocathodes for water splitting reactions under simulated sunlight.

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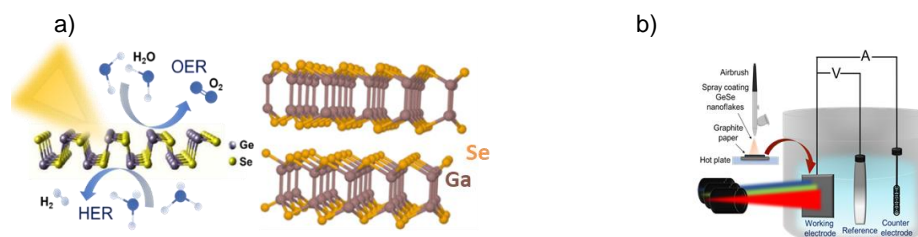


Figure 1: a) Crystal structure of monochalcogenides and schematic processes of photoelectrochemical water splitting; b) experimental setup for photoelectrochemical characterization.

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Optimization of Graphene Photothermoelectric Detectors

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Owing to its unique properties, graphene is a promising material for a wide range of applications [1]. Particularly promising are applications that utilize several of graphene's unique properties in a single system or device. A perfect example of such devices are photodetectors based on the photothermoelectric effect (PTE) in graphene, which combine a broadband and fast photoresponse with high signal-to-noise ratio and minimal power consumption [2-5]. There are many design parameters impacting the performance of these devices, including the light profile, the device geometry, and the material quality.

In this talk, I will discuss the impact that these design parameters have on the performance of PTE-based graphene photodetectors, and I will demonstrate how their performance may be optimized. Careful tuning of the light profile and device geometry can improve the photoresponse by more than one order of magnitude. Detector performance can also be improved with higher graphene material quality, but only to a point. When material quality is too high, Peltier cooling can degrade the photoresponse, indicating an upper bound on device performance and suggesting that ultraclean graphene may be unnecessary for, and actually detrimental to, the performance of these detectors.

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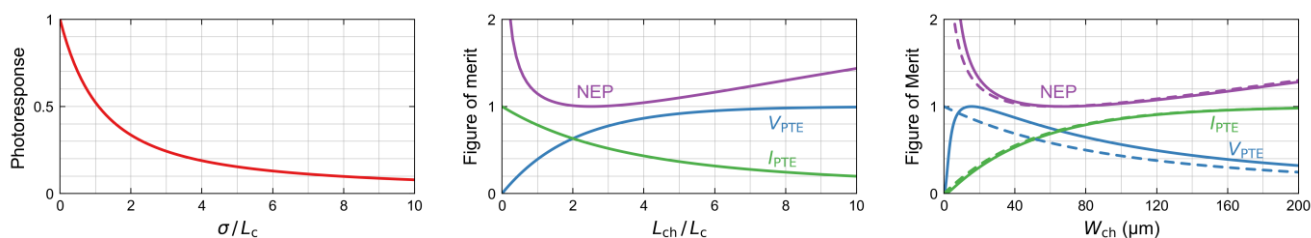


Figure 1: Graphene photodetector performance as a function of light profile size (left), channel length (middle), and channel width (right). NEP is the noise-equivalent power, I_{PTE} is the photocurrent, and V_{PTE} is the photovoltage. I_{PTE} and V_{PTE} are normalized to their maximum values, and NEP to its minimal value.

Phototransistors from Liquid-Phase Exfoliated Transition Metal Monochalcogenide Flakes

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Abstract

LAYERED semiconductors of IIIA–VIA group, have attracted considerable attention in (opto)electronic applications thanks to their atomically thin structures and their (opto)electronic properties. Currently, two-dimensional (2D) indium selenide (InSe) and gallium selenide (GaSe) are emerging as promising candidates for the realization of thin-field effect transistors (FETs) and photodetectors due to their high intrinsic mobility ($10^2 - 10^3 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) [1] and their direct bandgap in an energy range (1.3 – 3.2 eV) suitable for UV, visible and NIR light detection [2,3]. A requirement for large-scale electronic applications is the development of low-cost, reliable industrial production processes. In this context, it has been recognized that liquid-phase exfoliation (LPE) of InSe and GaSe is a cost-effective and environmentally friendly way to formulate inks for FETs, presenting a significant advantage over conventional methods [4]. In this study, we present printed InSe and GaSe phototransistors that exhibit high responsivity ($13 - 274 \text{ AW}^{-1}$) and fast response velocity ($15 - 32 \text{ ms}$) [2,3]. Moreover, the GaSe phototransistors show an on-off current ratio of $\sim 10^3$ in the dark, which can be readily achieved without the need for complex design of drain/source contacts or gating techniques [2,3]. The gate-dependent photoresponse shows that the phototransistors can be modulated by the gate voltage. These results demonstrate that liquid-phase exfoliated InSe and GaSe are valid candidates for low-cost high-performance (opto)electronic devices.

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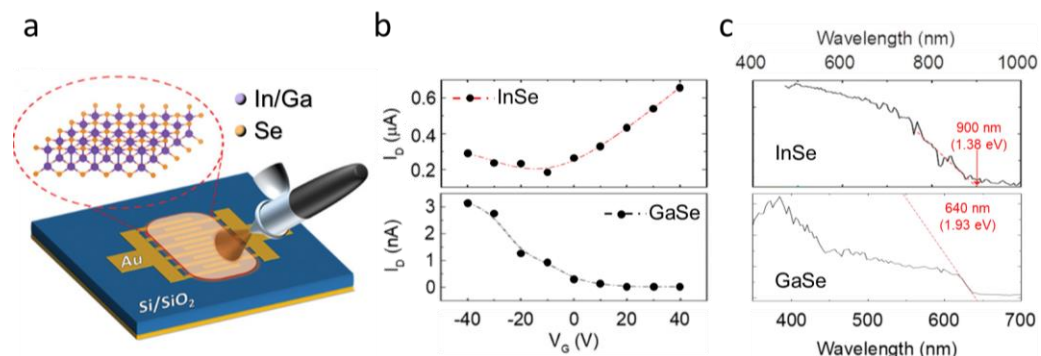


Figure 1: a) Schematic illustration of the InSe and GaSe phototransistors. b) Source–drain current (I_D) versus gate voltage (V_G) curve for InSe (top) and GaSe (bottom). c) Spectral responsivity of InSe (top) and GaSe (bottom) phototransistors

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

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

SIO Grafen is now in the end of its sixth year out of a maximum of twelve. SIO Grafen has funded 119 projects with a total funding of about 21 million euros where graphene has been the key factor in solving industrial challenges. 140 organisations, including 60 SMEs, have participated in these projects. Most of these organisations are based in Sweden, but not all. We would now like to encourage even more international collaboration.

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

Harnessing the Charge Transport in Covalently Interconnected TMD Networks

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Solution-processed semiconducting transition metal dichalcogenides (TMDs) are at the centre of an ever-increasing research effort in printed (opto)electronics^[1]. However, device performance is limited by structural defects resulting from the exfoliation process and poor inter-flake electronic connectivity.

We developed a new molecular strategy to simultaneously heal sulfur vacancies (V_S) in solution-processed MS_2 ($M = Mo, W, \text{ and } Re$) and increase the inter-flake electronic connectivity by means of dithiolated molecular systems. By taking advantage of π -conjugated dithiolated molecules (HS-R-SH), we proved *via* diverse multiscale analysis the simultaneous: i) healing of V_S to restore the MS_2 crystal structure and decrease the related stoichiometric deficiencies acting as charge scattering centres, ii) the covalent bridging of adjacent flakes, resulting in an enhanced charge carrier transport through an interconnected network.

Our approach represents an innovative and universal functionalization method capable of improving the performance of devices based on solution-processed MS_2 for large-area electronic applications. In particular, we implemented this strategy in liquid-gated thin-film transistors (LG-TFTs), boosting their characteristics by one order-of-magnitude and reaching state-of-the-art electrical performance characterized by competing field-effect mobilities (μ_{FE}) and I_{ON} / I_{OFF} , along with the fastest switching speed reported to date for devices of this kind^[2]. Moreover, covalently interconnected MS_2 networks show additional unique features, such as improved water stability and mechanical robustness.

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FIGURES

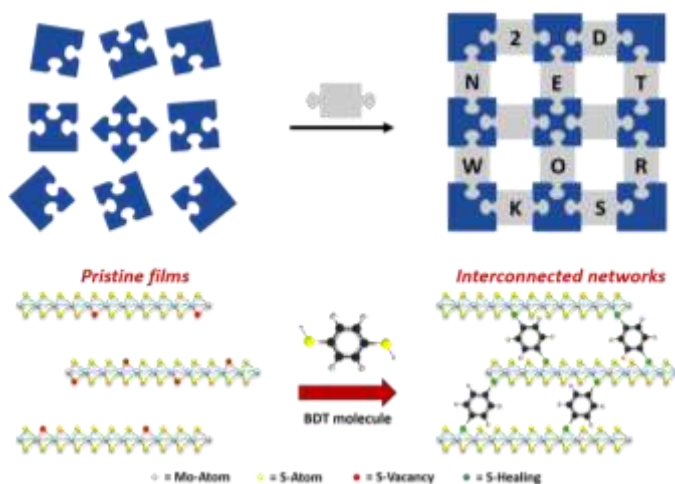


Figure 1: Sketch of V_S healing mechanism in MS_2 films by means of dithiolated molecules to form networks.

High yield nanographene oxide production for biomedical applications

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Abstract

Graphene is increasingly attracting interest from the scientific and business community, due to its great potential for the development of new high-value technologies in the scientific and industrial environment. Current methods for graphene oxide (GO) production, like mechanical exfoliation, chemical exfoliation, chemical vapor deposition, and others, are not capable of producing nanosized GO with high yield and concentrations, having water stability, and being biocompatible. Therefore, improvement of the methods is necessary to achieve higher yield and higher concentrations of materials that meet the quality specifications demanded for different industrial applications, especially in areas related to biomedicine. Among the limitations in the production of graphene from current production methods are high cost, low efficiency and low reproducibility on a high scale. [1,2,3]

Herein, single layer nano-sized graphene oxide (GOn) was produced through the modified Hummers method, followed by ultrasonication using a custom-built industrial grade system with technical specifications that allowed to achieve materials with the desired characteristics, for biomedical applications, in very high concentrations with a simple process. Particle size was determined by transmission electron microscopy (TEM) and dynamic light scattering (DLS). Surface charge was measured using a zeta potential analyser. Oxidation degree was characterized by X-ray photoelectron spectroscopy (XPS) and Fourier-transform infrared spectroscopy (FTIR). Thermal stability of the samples was determined by thermogravimetric analysis (TGA; 30-1000 °C, 10 °C min⁻¹, under N₂ flow). Biocompatibility was evaluated using human foreskin fibroblasts (HFF-1) and by assessing cell viability through resazurin assay.

Single layer GOn was obtained with mean lateral dimensions of 99 ±43 nm (52 % <100 nm, 99 % <200 nm). Original GO size was of 1178 nm ± 479 nm. GOn dispersion showed colloidal stability with zeta potential values around -39.4 ± 1.8 mV, at neutral pH and a concentration of 8 mg mL⁻¹. After 6 months no decrease in particle stability was observed. XPS analysis revealed that GOn oxygen atomic percentage (at.%) was of 30% and that its carbon at.% was of 70%, also a typical FTIR spectra was obtained, confirming that a material with the desired chemical functionalities was produced. TGA analysis revealed that a first step of 25% weight loss occurred between 141 °C and 200 °C, due to the degradation of thermolabile oxygen-containing functional groups. Also, a second step of 5% weight loss occurred between 200 °C and 548 °C, corresponding to the combustion of the carbon skeleton. The material revealed to be biocompatible at concentrations (100 – 250 µg mL⁻¹) above the usual amount used for biomedical applications or that can be release *in vivo* by implants containing those.

In sum, a biocompatible single layer nanosized material was obtained with high yield and at high concentrations, which presented stability for at least 6 months kept at room conditions. Currently, materials with such characteristics are not available commercially. Therefore, we are seeking translation to industry and exploring their applications in the biomedical field and other areas.

Acknowledgements

This work was financed by FEDER funds through the COMPETE 2020 - Operacional Programme for Competitiveness and Internationalisation (POCI), Portugal 2020, and by national funds (PIDDAC) through FCT/MCTES in the framework of the project POCI-01-0145-FEDER-031143, and Base Funding - UIDB/00511/2020 of the Laboratory for Process Engineering, Environment, Biotechnology and Energy – LEPABE.

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Solution processed nickel-iron layered double hydroxides for energy storage applications and glucose sensing

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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 recently drawn attention because of their electrocatalytic and photocatalytic properties[2][3]. Contrarily to other layered materials[4], LDH layers are held together by electrostatic forces and a dense network of hydrogen bonds[1]. For these reasons, a careful choice of solvent capable to break hydrogen bonds is pivotal for an efficient exfoliation of the LDHs. One of the most effective solvent for LDHs exfoliation is formamide[5]. However, due to formamide toxicity and its high boiling temperature (210°C), other solvents are recommended for the processing of LDHs[6]. In our work, we report that stable dispersions of nickel-iron layered double hydroxide (NiFe-LDH), in water or ethanol, can be obtained by carefully tuning the pH during the NiFe-LDH synthesis and treating the final product with sodium acetate. The formation of single-layer nanosheets is confirmed by X-ray diffraction and atomic force microscopy data. Lastly, the investigation of NiFe-LDH as electrocatalyst for the OER and glucose oxidation is showing promising performances for practical applications.

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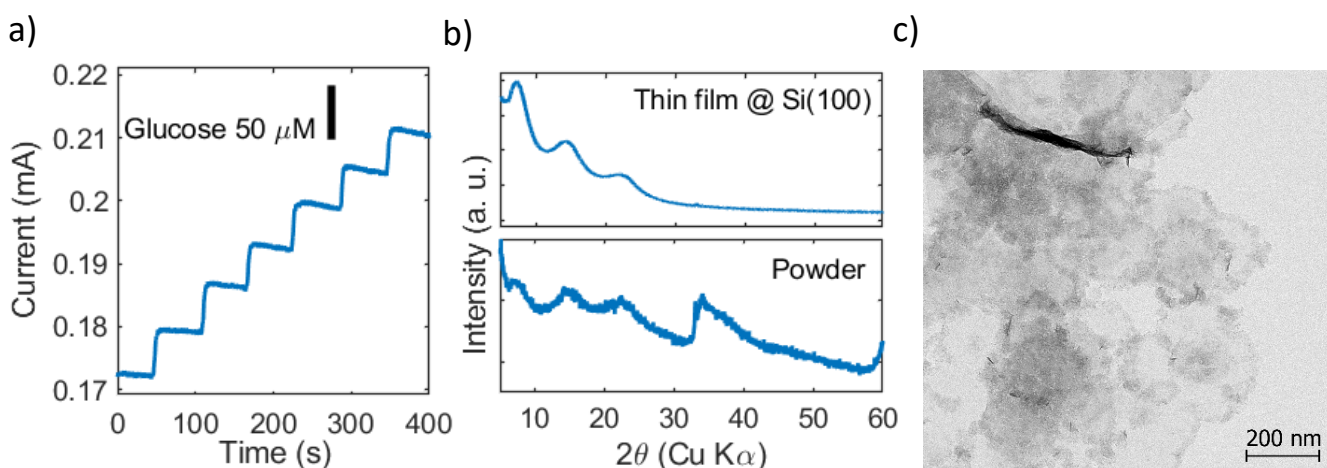


Figure 1: a) Glucose response of a NiFe-LDH electrode, b) XRD profiles of NiFe-LDH, c) TEM image of NiFe-LDH nanosheets.

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

Near-infrared light emitting diode based photothermal therapy with graphene: skin permeation studies

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Abstract

Basal cell carcinoma (BCC) is the most common form of human cancer, and treatment usually involves surgery. However, several non-invasive strategies such as photothermal therapy (PTT) have been explored. Graphene-based materials (GBM) are good candidates to act as photothermal agents since they can absorb near-infrared (NIR) light energy that can induce hyperthermia (39-47°C), leading to tumour cells apoptosis. We have demonstrated that low power (150 mW cm⁻²) NIR irradiation using light emitting diodes (LED) resulted in reduced nanographene oxide modified with polyethylene glycol (rGOn-PEG) heating up to 47 °C, which is within the mild PTT temperature range. PEGylation strongly enhanced the dispersibility of rGOn in physiological media (phosphate buffered saline, fetal bovine serum, and cell culture medium) and also improved the biocompatibility of rGOn-PEG, in comparison to GOn (25–250 µg mL⁻¹). After a single NIR LED irradiation treatment of 30 min, a decrease of ≈38% in A-431 cells viability was observed for rGOn-PEG (250 µg mL⁻¹). [1,2]

In this study, we propose the use of nano graphene oxide (GOn) and rGOn, non-PEGylated, as platforms for PTT treatment of BCC. To perform this, GO was produced through the modified Hummer's method, [1,2] and further sonicated and centrifuged to obtain GOn. GOn was photo-reduced to obtain rGOn. Materials obtained were characterized in terms of physical-chemical and optical properties. Particle size and morphology were determined by transmission electron microscopy (TEM) and by using a zetasizer equipment, zeta potential was also measured. GBM absorbance spectra (200-850 nm) were obtained using a UV-Vis spectrophotometer. GOn and rGOn were irradiated with a LED source of 810 nm (150 mW cm⁻²) and temperature increase recorded using a thermocouple. Biocompatibility of the materials with primary human fibroblasts (HFF-1) was tested using the Alamar Blue method. The permeability of GOn and rGOn water suspensions through human skin was determined using a Franz cell system. Skin samples were analysed by TEM and stained with haematoxylin and eosin for histological analysis.

Single layer GBM were obtained with average lateral dimensions below 200 nm. GOn and rGOn dispersions showed colloidal stability with zeta potential values of -39.4 ± 1.8 and -37.8 ± 1.2 mV (neutral pH), respectively. The increment of rGOn temperature triggered by NIR irradiation revealed to be time-dependent. rGOn temperature reached 59.4 °C after 30 min irradiation, around 1.3 fold higher than GOn heating. GOn and rGOn (100-250 µg mL⁻¹) didn't affect HFF-1 cell viability after 24h of incubation. Both materials were able to cross epidermis and dermis in a time-dependent manner. Skin permeability of rGOn revealed to be lower and slower than GOn permeability, during the 1st hour of contact with the skin. After 6 h, the amount of rGOn that permeated to the receptor compartment was 1.2-fold lower than for GOn.

Together, our results demonstrate the potential of irradiating GBM using lower energy, cheaper, smaller, and safer LED, as alternative to high power lasers, for NIR mild hyperthermia therapy of cancer, namely BCC. The potential use of GBM for BCC treatment as biocompatible photothermal agents able to penetrate deep into skin is also demonstrated, a step towards translation to clinics.

Acknowledgements

This work was financed by FEDER funds through the COMPETE 2020 - Operacional Programme for Competitiveness and Internationalisation (POCI), Portugal 2020, and by national funds (PIDDAC) through FCT/MCTES in the framework of the project POCI-01-0145-FEDER-031143, and Base Funding - UIDB/00511/2020 of the Laboratory for Process Engineering, Environment, Biotechnology and Energy – LEPABE.

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Nebulization of nanomaterials suspensions for woven non-woven fabrics coating

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Nanomaterials such as nanoparticles and 2D-materials can be prepared as stable suspensions or colloids in different solvents and/or solvent mixtures [1, 2]. These suspensions are frequently used to prepare composites in which the nanomaterials act as the filler of different organic matrix providing new physical and/or chemical properties [3]. However, in these composites, the area of the nanomaterials at the surface level of the matrix is low. In order to optimize the surface area of the nanomaterial exposed on the surface of the organic polymer, an alternative strategy is the use of the coating [4]. In particular, this approach can be useful for the decoration of woven non-woven fabrics, which are widely used in clothing, home textiles, medical and health, electronics industry, air purification, sewage treatment, among others, because of their excellent performance. This work focuses on the preparation of graphene and graphene oxide suspensions using liquid phase exfoliation and the use of these suspensions for coating polypropylene and polyamide woven non-woven fabrics. The developed nebulization method used in this work is adjustable to different nanomaterials suspensions giving rise to a homogeneous coating of the fibers. Finally, due to the strong interaction between graphene and their derivatives with different viruses [5], the modified textiles are being tested for potential medical health uses and, more specifically, for facial mask modification.

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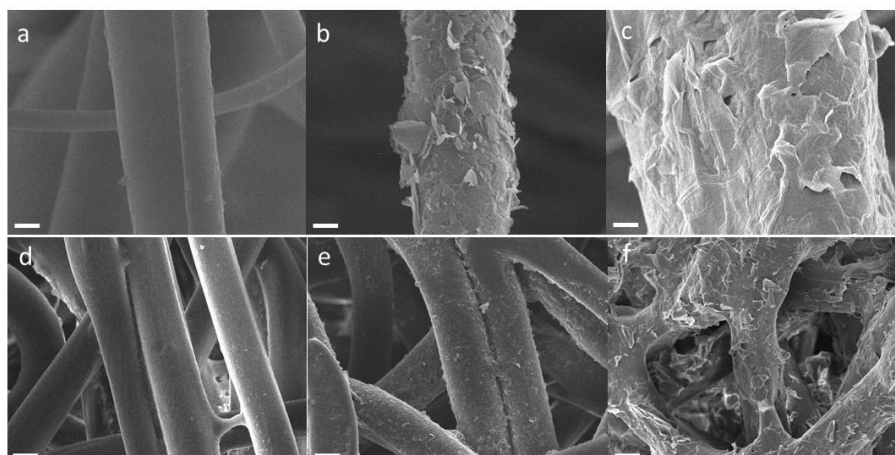


Figure 1: SEM images of (a) Fibres of non-woven Polypropilene (NW-PP). (b) NW-PP fibres modified with graphene. (c) NW-PP fibres modified with GO. Scale bar in (a-c) 1 μm . (d) Fibres of non-woven Polyamide NW-PA before been modified. (e) NW-PA fibres modified with graphene. (f) NW-PA fibres modified with GO. Scale bar in (d-f) 10 μm .

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

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Hall sensors are a type of magnetic field sensors widely used in application fields like consumer electronics and automotive, mainly 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 appears to be an ideal material for Hall sensors because of its unique high mobility μ and low charge carrier concentration n ($S_v \approx \mu$ and $S_i \approx 1/n$) due to the zero band gap nature as well as its mechanical flexibility. Graphene based Hall sensors outperforming all other technologies on flexible substrate were demonstrated in the literature. 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 with a scalable approach 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 nT/ $\sqrt{\text{Hz}}$ at 2 kHz gate frequency were found for Hall sensors fabricated on flexible foil.[3] 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..

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Acknowledgements

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FIGURES

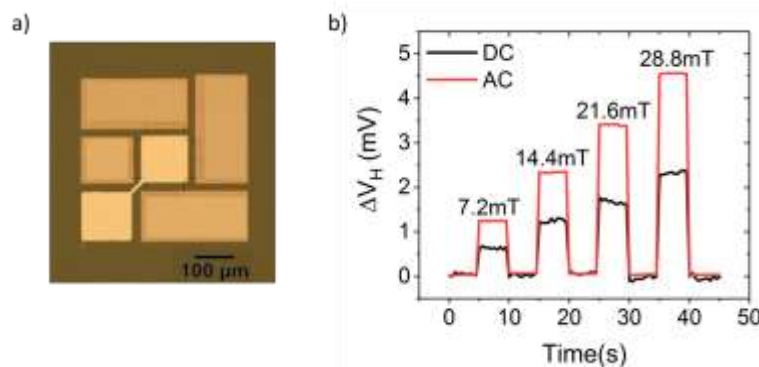


Figure 1: a) Microscope image of the top gated graphene Hall sensor on flexible substrate. b) Hall voltage under DC (black) and AC (red) operation

FLASHPOSTER

New Composite Material Based on Graphite Microparticles in Glassy Matrices for Applications in Piezoresistive Sensor

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Results of development of a new low cost piezoresistive composite material for use in pressure sensors are presented. Usually, piezoresistive sensors are fabricated using high sintering temperature glassy matrixes (frits) and conductive metal oxides like ruthenium oxide [1].

Here, the piezoresistive material is composed by porous glassy matrix with graphitic particles (~ 3 μm lateral dimension) as a conductive filler. Several different frit compositions (consisting of oxide mixtures $\text{PbO/ZnO/SiO}_2/\text{Al}_2\text{O}_3$, $\text{Bi}_2\text{O}_3/\text{B}_2\text{O}_3/\text{ZnO}$ and $\text{Bi}_2\text{O}_3/\text{B}_2\text{O}_3/\text{SiO}_2/\text{Al}_2\text{O}_3/\text{ZnO}$) were developed and tested to provide low sintering temperatures (down to 600°C) in order to prevent burning of micrographite during final composite preparation [2].

A new methodology for producing piezoresistive films from pastes prepared using a frit powder, micrographite particles and an aqueous phase of sodium carboxymethyl cellulose (CMC) was developed. The resistances of films (with lateral dimensions of 50 x 5 mm) were measured to vary between ~ 1.2 and 142 k Ω , depending on composition.

The preliminary results showed that low-cost micrographite particles can replace expensive metal oxides like RuO_2 in piezoresistive sensors with comparable performance.

An important role of CMC in providing the paste homogeneity and good adherence of graphitic layers to glassy matrix was confirmed. The paste based on $\text{Bi}_2\text{O}_3/\text{B}_2\text{O}_3/\text{SiO}_2/\text{Al}_2\text{O}_3/\text{ZnO}$ was proved to be the most stable under multiple flexure tests and it was successfully tested in piezoresistive sensors.

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Highly Conductive Nanostructured Composites Based on Multi-Layer Graphene and Polymers for Flexible Heaters

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ABSTRACT

Flexible heaters, such as body heating devices for thermal comfort and improvement of poor blood circulation are increasingly necessary and desired devices. Relatively high cost of these devices nowadays prevents their high scale use. This work presents the results obtained with low cost multi-layer graphene sheets with excellent electrical and thermal conductivity produced from natural graphite and used as fillers in flexible composite materials. Flexible highly conductive films were prepared by mixing multi-layer graphene platelets with various polymers (~10% m/m) and water until formation of a viscous paste. The material was stirred continuously for 10 minutes at room temperature and then spread on a PTFE substrate film using a doctor blade technique. Samples were dried for 4 hours at 90°C and finally were calendered to provide better uniformity, alignment of graphene flakes and reduced porosity of the film material. Figure 1 shows an example of a sheet obtained (A4 size) and the micrograph image of a film cross-section.

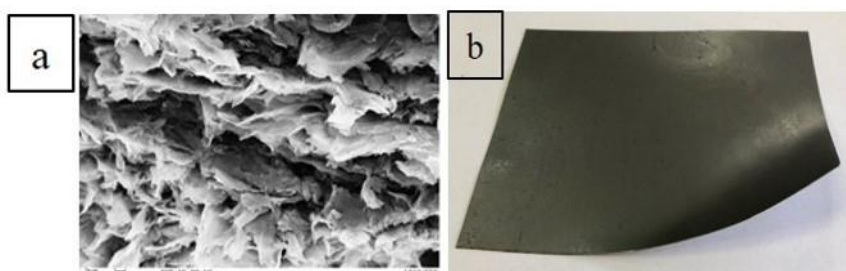


Figure 1: Multi-layer graphene based composite (A) cross-section SEM micrograph, 6000x magnification, and (B) sheet sample, 300 μm thick, A4 size.

Preliminary results obtained with development of nanocomposites based on graphene nanoplatelets, show good results with the film thermal conductivity of 40,6 W/m.K and electrical resistivity of $1,2 \cdot 10^{-2} \Omega \cdot \text{cm}$. The results obtained for resistivity, are superior compared with those reported in literature for various polymeric composites with carbon nanomaterials: carbon nanotubes with best results in the range of $7 \cdot 10^{-2} \Omega \cdot \text{cm}$ [1], for buckypaper of multi-walled carbon nanotubes with values close to $1.4 \Omega \cdot \text{cm}$ [2] and with exfoliated graphite in cellulose solutions of $4 \cdot 10^{-2} \Omega \cdot \text{cm}$ [3]. The reports in literature show comparable thermal conductivity results: 11,2 W/m.K for graphene/epoxy polymer composites in the cross-plane direction [4]. Preliminary results obtained here in development of nanocomposites based on multi-layer graphene with polymers, show good performance compared with the results in literature.

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ePOSTER

Au/Pd Nanoparticles Immobilized on TiO₂/Graphene as a Functionally Catalyzed membranes

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Abstract: A novel catalytic membrane was fabricated with Au/Pd nanoparticles produced by a novel blast method (Figure 1) following the supported by TiO₂ graphene, where the TiO₂ graphene were then synthesized on the ceramic membrane. The obtained activation energy was much lower than the values before, implying that the p-nitrophenol reduction could take place more easily on our system compared to others. A flow-through catalytic membrane reactor was developed for testing the catalytic properties. The effect was investigated in detail and to meet the need of the optimal conditions. The characterization results highlighted that the as-prepared bouquet-like TiO₂ nanotubes could significantly improve the loading amount and also for the degree of Au/Pd nanoparticle dispersity as well as the size of particles. In addition, this catalytic membrane exhibited much more improved activity and stability, with a full conversion of p-nitrophenol and no loss in catalytic activity with several times running.

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FIGURES

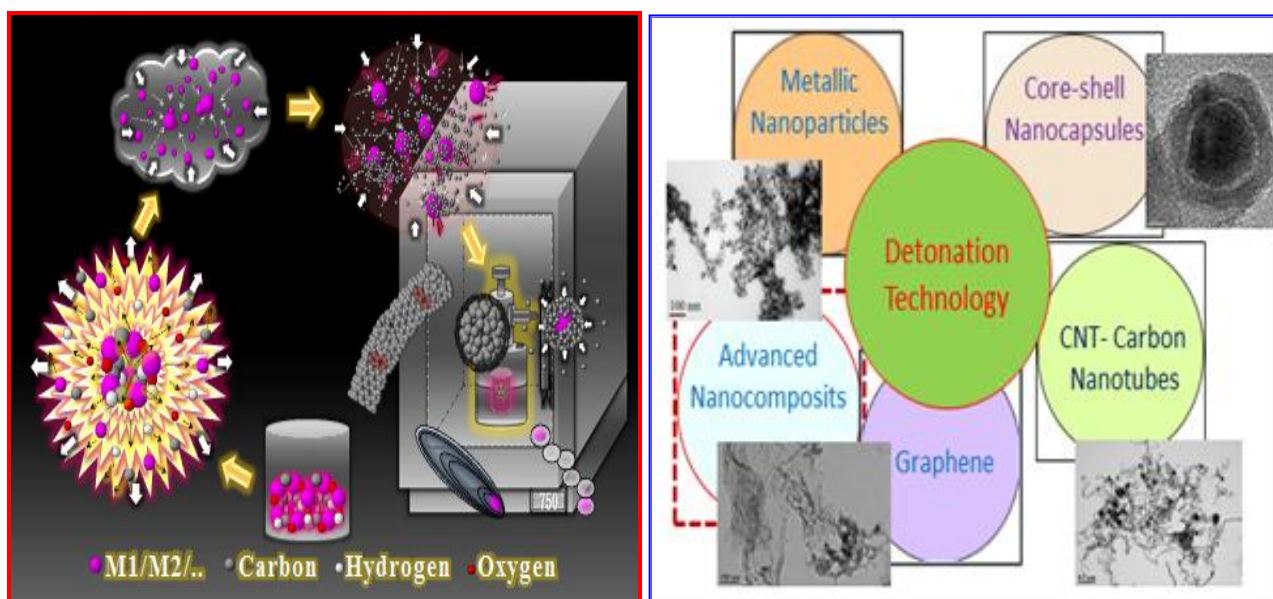


Figure 1: Reaction schematic diagram (left) and these nanostructured applications (right) through the blast of CHNO energetic materials over different metal-catalysts.

Micromechanical Characterization of Oxidized Carbon Nanotube and Graphene Oxide Papers

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In the present work the endurance of graphene oxide and oxidized MWCNT papers on tensile stress is tested. Graphite oxidation and exfoliation [1] and KMnO_4 reaction [2] of MWCNTs are employed to produce GO and oxidized carbon nanotubes respectively. Hybrid GO/OMWCNT papers that exhibit GO weight percentage that ranges from 0 wt% to 100 wt% are fabricated by vacuum filtration and are subjected to tensile testing. Results across the whole sample range show a general increase in stress at failure for higher GO contents. The increasing stiffness of the samples tested is indicative of the formation of hydrogen bonds between the hydroxyl and carboxylic acid functionalities [3] of the decorated nanoparticles brought on by the more ordered stacking of GO nanoparticles.

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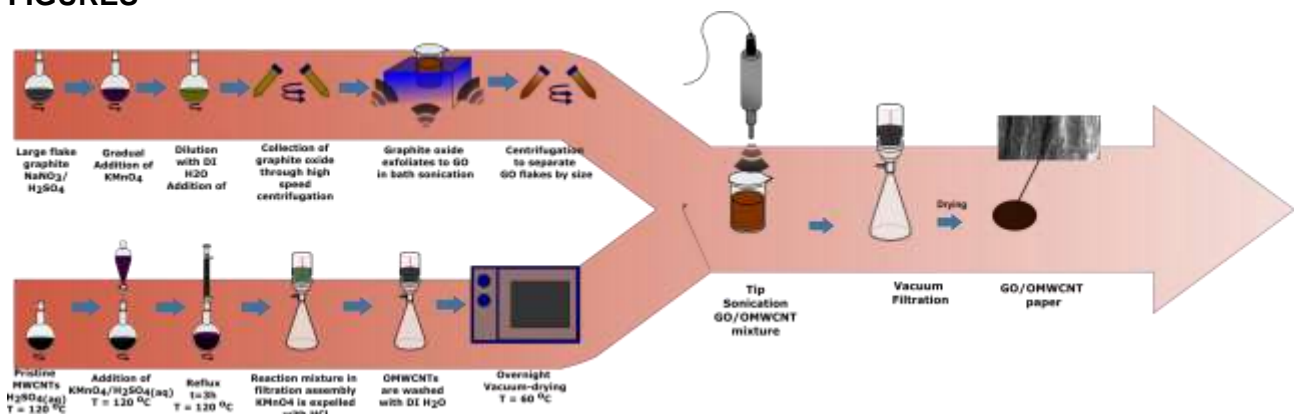


Figure 1: Insert caption to place caption below figure (Arial 10)

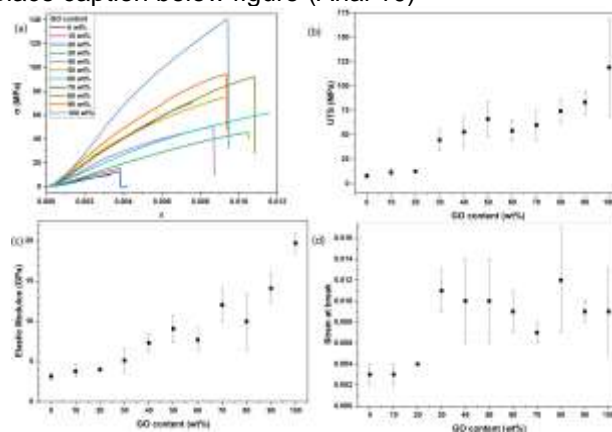


Figure 2: Insert caption to place caption below figure (Arial 10)

Graphene Nanoporus Membranes with ZrO₂-based Nanoparticles for Gas Separation

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Abstract: Graphene coated nanopores membranes with zirconium dioxide based nanoparticles were prepared by carbonization of the nano-technical ones. Gas permeation performance of the above membranes was evaluated and compared to performance after doping the membranes with these nanoparticles introduced into the membranes as fillers and acting as functionally active materials. The addition of n-ZrO₂ nanoparticle fillers to porous-based to form mixed matrix membranes can affect gas mixture separation owing to variation of magnetic susceptibility. The nano-composites coped with the different gas molecules and variable interaction with the dispersed magnetic fillers can also show higher molecular sieved capacity and well dispersion ability to alter the separation selectivity. The properties of the resulting materials were evaluated and the permeation effect using a series of gas molecules as well as being conducted. The results indicated that the introduced the nanoparticles performed the gas permeance and separation properties of the composite nano-membranes.

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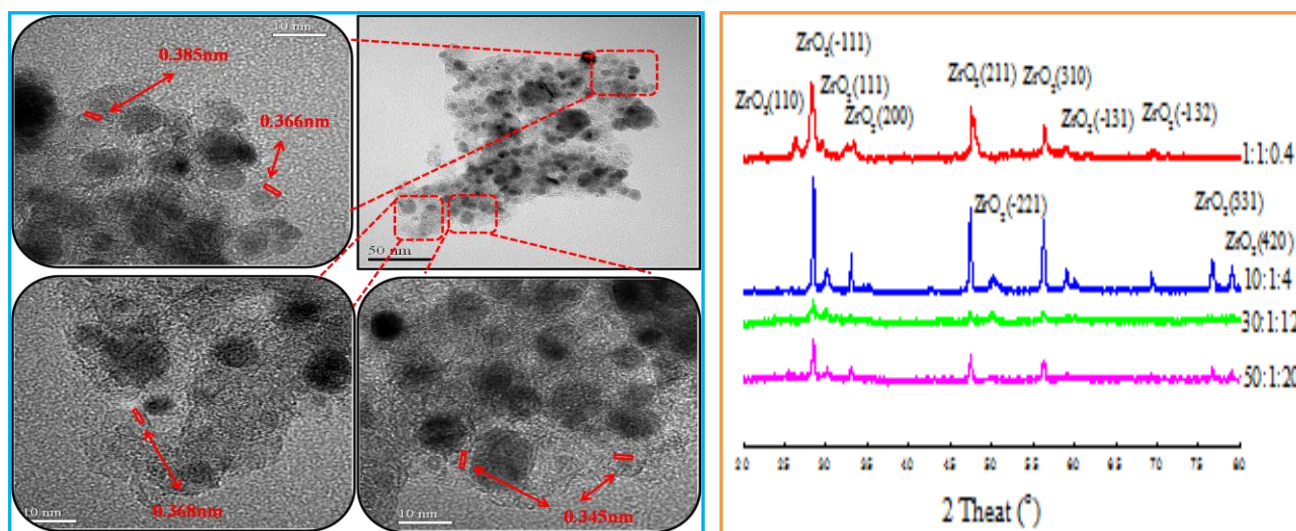


Figure 1: As-synthesized TEM images of graphene nanoporous nanocomposite (left) and XRD results (right) for the applying on the functional gas membranes.

Graphene-Biopolymer Based RFID Tag: A Low-cost, Flexible and Environmentally Friendly Alternative

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A conductive and flexible film based on a mixture of graphene and biopolymers have been used to fabricate a passive Ultra High Frequency (UHF) Radio Frequency Identification (RFID) tag consisting of a dipole antenna and a microchip on paper substrate. The preparation of the composite material, as well as the design, manufacturing and characterization of the tag are presented. The results of the fabricated tag are presented, focusing on the most relevant parameters for real applications: read range, dimensions and mechanical robustness. Read range of 9.3 m was reached with a conductivity of 2.3×10^4 S/m. It demonstrated that this material can be used for long-range applications, constituting a low-cost and environmentally friendly alternative unlike commercial metal-based tags.

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Graphitic materials decorated with bio-based silver nanoparticles as antiviral filters for face masks

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Silver nanoparticles (AgNPs) have well known antimicrobial properties against various types of human, animal, and plant pathogens, such as virus, bacteria, and fungi [1]. In parallel, graphitic materials are acknowledged for their excellent mechanical and thermal properties [2]. The present research focused on the fabrication of antiviral filters for face masks based on graphitic materials (graphene oxide – GO or expanded graphite – EG), cellulose nanofibers (CNF), and bio-based silver nanoparticles (BB-AgNPs). The deposition method is efficient and low-cost, with the fabricated materials being sustainable since they employ biodegradable components prepared through a clean and energy-efficient process. Hesperetin (HST) was dissolved in sodium hydroxide solution (0.005 mol L⁻¹) to a final HST concentration of 1 mmol L⁻¹. AgNO₃ was dissolved in deionized water in a concentration of 1 mmol L⁻¹. The solutions were mixed in a ratio of 1 to 1 (v/v) by drop wise addition of reduction reagent into Ag(I) solution. The formation of bio-based silver nanoparticles (BB-AgNPs - Fig. 1a), having mean diameter size of ~22 nm and Zeta potential of -40 mV, was monitored using UV/Vis measurements and Plasmon band at 404 nm. GO and EG suspensions were obtained by submitting the materials to ultrasound for 10 to 15 minutes. Subsequently, the 10%-CNF suspension in 7% of NaOH (Fig. 1b) was added into the GO or EG suspensions and then the CNF-GO or CNF-EG co-suspensions were filtered, leading to the fabrication of freestanding composite sheets. The BB-AgNPs were added to the suspensions and submitted to ultrasound before filtering (Fig. 1c) or sprayed/drop casted onto the recently obtained layers. The fabricated freestanding films as well as their individual components were characterized using SEM, TEM, XPS and challenged in antiviral tests. The obtained filters (GO-CNF@BB-AgNP and EG-CNF@BB-AgNP) showed excellent physical appearance, mechanical properties (hardness and elasticity) and were efficient in fighting viruses, such as SARS-CoV-2. Cellular toxicity was low or absent in the developed filters. Altogether, the filters might be used for fabrication of face mask due to their highly water absorbable materials (CNF), antimicrobial properties, and low resistance to breathing and sneezing, thus protecting the users from infections.

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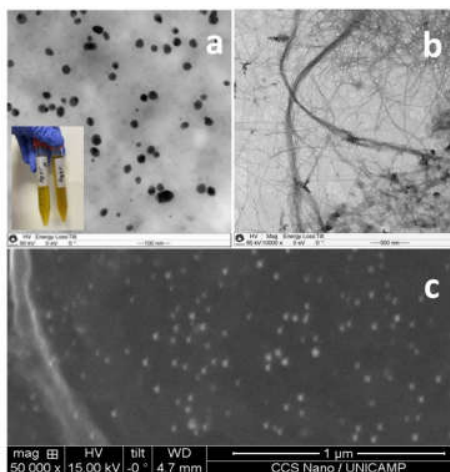


Figure 1: TEM images of BB-AgNPs (a) and cellulose nanofibers (b); SEM images of a GO sheet decorated with bio-based silver nanoparticles (c). The inset in (a) show the picture of BB-AgNP suspensions.

Piezoresistive sensing performance of ex-situ transferred nanocrystalline graphite on a flexible substrate

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Piezoresistive-based strain sensors can be used in a multitude of applications, from tracking industrial structural integrity, to health monitoring and man-machine interactions. Commercial-grade strain foil gauges usually employ – as a sensing element - either a patterned metallic film or a semiconductor bar; their gauge factor (GF) could be either ~ 2 , or ~ 100 , respectively. From this perspective, the carbonic materials, with a graphene-like structure, have proven to be a feasible alternative, exhibiting GFs with one order of magnitude higher [1]. In particular, the large area scalability of nanocrystalline graphene/graphite (NCG) [2] and its intrinsic and inter-molecular structure (Figure 1a) makes this type of material one of the top candidates for high-sensitivity (GF ~ 300 , 600), low-strain ($<1\%$), piezoresistive sensing [3, 4]. Our contribution presents the performance of NCG as a piezoresistive element in strain sensors. The NCG film is grown by plasma enhanced chemical vapour deposition (PECVD) on a metallic substrate; the structure and the morphology of the film is investigated by Raman spectroscopy and scanning electron microscopy (SEM). After the ex-situ transfer on a flexible substrate, the piezoresistive performance is investigated by measuring the electrical resistance of the sensitive layer during controlled mechanical stretching of the device (Figure 1b). Experimental results confirm NCG is a fitting material for low-strain piezoresistive sensing, GFs of up to 236 being recorded.

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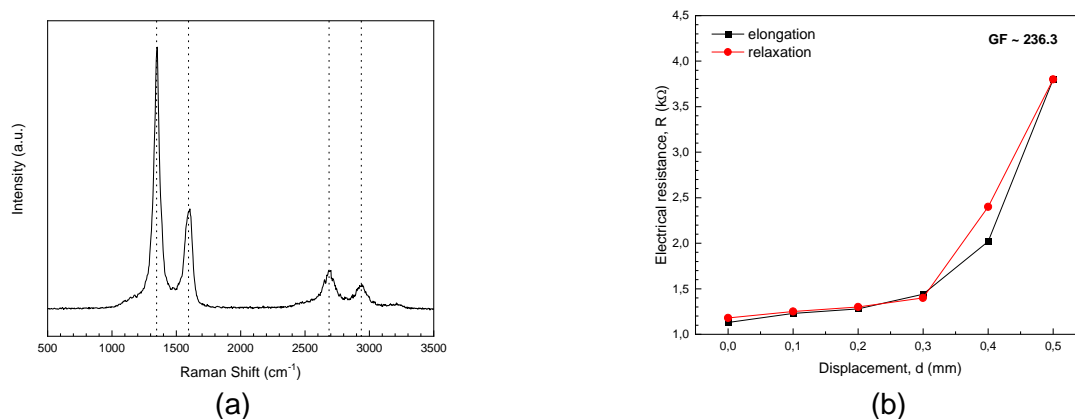


Figure 1: (a) Raman spectrum of a NCG film grown on a metallic substrate. The dotted lines at ~ 1347 cm^{-1} , 1595 cm^{-1} , 2687 cm^{-1} , 2937 cm^{-1} represent the specific D, G, 2D and D+D' peaks, respectively. (b) Electrical resistance variation with respect to the mechanical displacement for a 1.25 μm thick NCG film.

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