graphIn

Graphene Industry - Challenges & Opportunities

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Index

Foreword

On behalf of the Organising Committee, we take great pleasure in welcoming you to Barcelona (Spain) for the 2nd edition of the **graphIn International Workshop (Graphene Industry – Challenges & Opportunities)**.

This 1 day workshop aims at presenting the current state of the art and the opportunities of graphene-based materials and devices and its industrial challenges and opportunities, focusing on the most recent advances in technology developments and business opportunities in graphene commercialization.

This unique international event will provide a forum for sharing and developing innovations for the functional materials industries. The aim of **graphIn** will be to develop the relationships that will accelerate graphene industrial growth.

This 2nd edition has succeeded to bring together a large number of leading representatives of "graphene companies & labs", sharing their market vision and business opportunities in diverse current market fields of graphene products and applications.

It will be the perfect place to get a complete overview into the state of the art and also to learn about the development of innovative and competitive commercial applications. The discussion in recent advances, difficulties and breakthroughs will be at his higher level.

A specific session will be devoted to "Worlwide Initiatives in Graphene and 2D Materials" where, in particular, the new EUREKA cluster in this area, to be launched under the Spanish Eureka Chairmanship (2016-2017), will be announced. It will aim at facilitating the generation of market-driven pan-European collaborative research and innovation projects for the benefit of the graphene & 2D materials industry. Currently, already 130 institutions (among them 80 companies) in Europe sent an Expression of Interest to join the Cluster.

We are indebted to the following companies and government agencies for their financial support: American Elements, Grafoid Inc. and ICEX Spain Trade and Investment.

We would also like to thank the exhibitors for their participation: Das-Nano, Grafoid Inc., Graphene Square Europe and Institut Catala de Nanociencia i Nanotecnología (ICN2).

In addition, thanks must be given to Parc Científic de Barcelona and the staff of the organising institutions whose hard work has helped planning this workshop.

ORGANISING COMMITTEE

- **Antonio Correia**
  (Phantoms Foundation, Spain)
- **Stephan Roche**
  (ICREA/ICN2, Spain)

IN COLLABORATION WITH

EXHIBITORS

SPONSORS

Contributions list: Alphabetical order

KEYNOTE & INVITED CONTRIBUTIONS

Towards graphene-based biosensing platforms

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Biosensing systems are becoming ever more common in the medical and biomedical fields, spanning a large range of health applications, from prognosis and diagnosis of diseases, to personalized medicine. Increased integration and miniaturization of such devices and systems will enhance performance (specificity, sensitivity and speed of response) while simultaneously allowing for their mass production at economic cost. These are the right ingredients for yet another boost in the use of portable, integrated biosensors in clinical practice and in point-of-care diagnosis and therapy.

Graphene 2D honeycomb lattice, with its unique electronic structure, forms a surface of extreme sensitivity to electric fields and charges, thus suggesting its use for electronic transducing-based molecular detection [1]. However, graphene high sensitivity and chemical stability comes at the cost of a poor analyte selectivity. Therefore, the fabrication of biosensors based on graphene hetero-interfaces requires the functionalization of graphene. In our work, graphene is the transducing element in field-effect transistors (bio-FETs), or part of the transducing electrode, in electrochemical biosensors. Here, probe molecules are immobilized on CVD graphene devices for biorecognition of two important types of analytes: antigens (proteins) and DNA. The devices are fabricated at the wafer scale in the clean-room [2] (Figure 1).

The immuno-FET is developed by immobilization of a linker – a pyrene derivative (PBSE) – via π-π bonding to the graphene. At the other end of the binder molecule, an ester group reacts with a primary amine from the specific antibody, thus immobilizing it on the graphene surface. A blocking agent (ethanolamine) is then used to passivate the unreacted PBSE sites.

The device was able to detect the specific biomarker (MMP-9) in concentrations down to 0.1 ng/mL. Compared with existing MMP-9 immunoassays [3] our immuno-FET has similar sensitivity and, because it is based on a simpler protocol, has a much shorter time to diagnostic. The nucleic acid sensor is developed by immobilization of single-stranded DNA (25 nucleotides long) on the pyrene derivative-functionalized graphene transistor channel. Hybridization with complementary DNA was detected down to 1 aM, with a saturation attained at 100 fM. This limit of detection is observed only in the most sensitive devices found in the literature [4].

Electrochemical microelectrode arrays (Figure 2) covered with graphene functionalized with the same DNA sequence was successful in detection in the range 5 pM to 50 nM, with the ability to detect single nucleotide polymorphism.
These results open the possibility for fabrication of graphene-based biosensors with high sensitivity and low cost that may be used in the health, environment and food industries.

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[4] Abdul Rasheed P., Sandhyarani N., Analyst, 140 (2015) 2713Electroactive Graphene Nanofluids for Fast Energy Storage. Deepak P. Dubal and Pedro Gomez-Romero. 2D-Materials 2016, 3, 031004

Figures

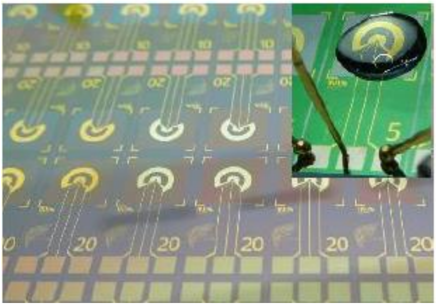

Figure 1: Graphene transistor chips fabricated at the wafer scale (partial view). Inset shows DUT.

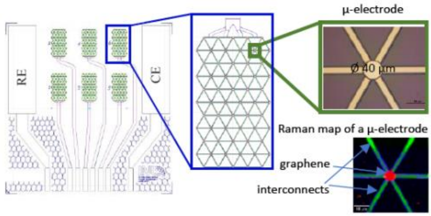

Figure 2: Graphene μ-electrode arrays

Towards the industrialization of 2D crystals-based composite materials

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The full-exploitation of graphene and other two-dimensional (2D) crystals [1] in different fields, ranging from flexible (opto)electronics to energy storage and conversion, relies on the development of industrially scalable, reliable, inexpensive production processes [2]. In this context, a balance between ease of fabrication and material quality with on-demand properties is a must. In particular, liquid-phase exfoliation of bulk layered materials [2-4] is offering a simple and cost-effective pathway to fabricate various 2D crystal-based (opto)electronic [3-5] and energy devices[6], presenting huge integration flexibility compared to conventional methods.

Here, I will show our scaling up approach towards the mass production of 2D crystals based on wet-jet milling of layered materials. Then, I will present an overview of 2D crystals for flexible and printed (opto)electronic [7-9] and energy applications [10-16], from the fabrication of large area electrodes [3,14] to devices integration. Finally, I will present the first commercial prototypes of 2D crystals-based composite materials.

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Grafoid: Collaboration Is the Key to Graphene's Commercializations

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Bilateral co-operation in the low carbon economy offers opportunities for graphene producers. In the coming years, strong bilateral relationships for the commercialization of graphene will flourish. These relationships will bring together mine-to-market industry players to propel application developments that meet market demand.

The natural flake graphite market has changed dramatically in the last five years from a dig-and-sell commodity business to a value-added product business driven by national and international factors. The industry is being shaped by two catalysts - climate change and the graphene revolution.

Globally, national governments are committing to stringent emission targets and are implementing policies that foster innovation and propel new material advancements. Traditional mining industries, weakened by the global commodity downturn, are searching for ways to revive their businesses, while new material enterprises, such as value-added graphite and graphene start-ups seek to leverage these game-changing opportunities.

The introduction of legislation to greenhouse gas emissions is dramatically changing the critical material sectors. As more and more countries ratify the Paris Accord, the faster industry will adopt change.

China's 13th Five Year Plan calls for China to become an innovation power, pushing the boundaries of the technological frontier and moving up the value-added chain in diverse industrial sectors. Six Strategic Emerging Industries are intended to rebalance the economy toward more advanced technologies, and three of those have near-and-medium term implications for graphene's advancement and commercialization - they are: energy storage and distribution, advanced materials and new-energy vehicles.

Grafoid is poised to take advantage of change. As a graphene research, development and investment company, it has positioned itself to expand its base of collaborative commercial alliances for diverse application development. Grafoid's investment in a patented one-step production process has led to an affordable suite of graphene products that are applied to application developments with joint venture partners at Grafoid's Global Technology Centre (GGTC), in Kingston, Ontario, Canada. Further, it has partnered with the Canadian Government to build the world's first automated mass production graphene line. As a founding member of the 2GL Platform (www.2GLPlatform.com) and the GO Foundation, Grafoid integrates mining, science, engineering, application development, manufacturing and marketing into its operations.

No one company can do it alone. Commercialization of graphene will succeed when our industry works together in collaboration, fitting all the necessary pieces together with financial resources, industries' needs, capabilities and ideas. This requires cooperation, education and outreach on our part.

Graphene role in next generation Lithium-sulfur batteries

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Today's Li-ion batteries are under intense pressure to evolve, leading to longer-running electronics, cheaper electric vehicles, and a market for stationary storage. Developers continue to demand even better gravimetric and volumetric energy densities, cycle life, safety, and durability, along with lower costs.

Beyond today's incumbent technology, and among the many next-generation battery options, Lithium-sulfur is leading the way due to initially simpler manufacturing, lower costs, and good performance. Lithium-sulfur (Li-S) batteries use a metallic lithium anode and a sulfur-based cathode with various proposed electrolytes.

Advantages:

- Specific energy is higher than Li-ion batteries
- Sulfur is cheap and abundant

Challenges:

- Cathode volume expansion and cracking is a safety concern
- Capacity fade limits cycle life to about 100 cycles for most developers, due to polysulfide side reactions

Graphene

Graphene offers an opportunity as hosting in Li-S cathode: S/graphene composite.

In GO/sulfur composites, graphene plays a significant role in improving the electronic conductivity of sulfur, inhibiting the shuttle effect of soluble polysulfides and accommodating the large volume change of sulfur during the lithiation/delithiation processes.

Graphene Technology and Applications – from Lab Scale to Production

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One of key the challenges of graphene application in advanced products is the access to mature and reliable technology of high-quality graphene layers. The electronics and sensor industry directs its attention to epitaxial graphene on semi-insulating SiC and the Si-technology compatible Ge wafers. Other markets require large-format graphene sheets deposited on copper foil and reliably transferred onto rigid and flexible substrates.

Here, we present direct graphene epitaxy by *Chemical Vapor Deposition* from hydrocarbon precursor on 4H-SiC(0001), 6H-SiC(0001) [1], Ge epi-layers on Si substrates [2,3] and metal substrates. Certain issues of the quality management and the up-scaling challenges are addressed, including grain size management, reduction of the grain boundaries, film homogeneity improvement and the electrochemical transfer optimization [4].

The samples are characterized with STM, SEM, XPS, AFM, SIMS [5] and Raman spectroscopy. Their room-temperature transport properties are derived from Hall effect characterization in *van der Pauw* geometry.

We focus on graphene implementation in electronics, layered composites, flexible interconnects, heat dissipation, transparent heaters and anticorrosion coatings.

In order to enable graphene-based customer applications we present extensive statistics of the electrical properties of quasi-free-standing monolayer and bilayer graphene on 4H-SiC(0001) and 6H-SiC(0001), being results of hundreds of individual processes, and confront them with the morphological analysis of the average step edge height and terrace width, all related to the place of origin of a specific sample within a 4-in SiC wafer [6].

We pay special attention to the applicability of epitaxial graphene on SiC in magnetic field detection and present a Hall effect sensor that is optimized with respect to charge carrier concentration and mobility, geometry of the active layer, excess noise, magnetic resolution and an encapsulation method that assures stability of the sensor's properties over time and temperature [7].

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Preparation of bulk graphene materials for ultralow percolation threshold and high electrical conductivity graphene composites

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The graphene material market, bulk graphene, graphene nanoplatelets and graphene films, will grow to 350 € million in 2025. Their application in composites is the largest segment, followed by energy storage [1]. Several reviews analysed the applications of the different graphene and related products in in composites.[2, 1b]. Currently, a variety of techniques have been developed to prepare graphene materials. In this presentation, 3 different methods for the production of bulk graphene or reduce graphene oxide: liquid exfoliation, reduced graphene oxides and high expansion were compared with other carbon materials. The complete characterization of pristine graphene and highly reduce graphene oxide, will be presented.

Different types of graphene materials with variation in lateral size, defects and defects concentration, thickness, etc, have been used to obtain graphene-thermoplastic and thermoset composites studying the electrical, thermal conductivity and fire retardant properties of the composites. Related to electrical properties, some of these composites show ultralow percolation threshold limits, lower than the previously reported values, also obtaining very high electrical conductivity, opening a new range of applications and markets. We have also obtained high thermal conductive composites align with the best published result for graphene composites. Other factors as processing technique have been analysed due to their extremely high importance in the final results.

The composites obtained present high thermal conductivity, with enhancement of the thermal conductivity in line with the best results published in literature.

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Energy Storage in Graphene: Batteries or Supercapacitors?

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In the field of energy, and in particular for energy storage, graphene is a unique contender material and it has already been claimed as a champion material for supercapacitors providing large active area for capacitive double-layer storage but also for batteries, both as an additive to improve other electrode materials as well as active material in itself (normally as an anode).

In this presentation we will briefly introduce the emergent and growing field of energy storage and the central role graphene and its hybrid derivatives are playing. Graphene itself promises an extraordinary large potential surface area and correspondingly a large double layer capacitance. In turn, graphene-based hybrid materials offer the opportunity of building synergies thus leading to improved performance over their individual components [1]. In that way, hybrids based on graphene and a variety of molecular species[2.3] or extended phases[4] have been used to design materials with enhanced activity. A wise choice of electroactive species can for instance improve the energy density of graphene-based supercapacitors through hybridization. On the other hand, graphene as anode in batteries has also been tested as a fast alternative to graphite. Furthermore, in our group we have gone beyond the conventional solid state electrode format and have developed graphene electroactive nanofluids as liquid electrodes for flow cells. This novel electrode format is also prone to the development of hybrid materials. In this conference the use of graphene and some hybrid derivatives, with some emphasis on our own group results will be presented in relation to energy storage, discussing supercapacitors, batteries and beyond

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Onyx Graphene and 2D Materials Inspector

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Onyx is a turnkey, non-contact and non-destructive device for the inspection of several properties of graphene and other 2D materials. Onyx generates full-area maps of conductance, resistance, thickness and other parameters from materials such as graphene, GaN, PEDOT, ITO, NbC, ALD, spin coated photo-resins. The maps provide information about the homogeneity and quality. Similar characterization is currently realized by nano-scale methods, such as confocal Raman spectroscopy, Atomic Force Microscopy, or Transmission Electron Microscopy, and/or macro-scale methods [1], such as van der Pauw or optical microscopy. However, nano-scale methods are slow and cannot characterize large surfaces. Macro-scale methods generate characterization that average the magnitudes and, thus, cannot provide localized information.

Onyx provides meso-scale characterization and covers the gap between nano-scale and macro-scale methods. Onyx is a terahertz-based system [2] that works in reflection geometry as opposed to state-of-the-art methods [1-3] and provides conductance and resistance maps in the terahertz range.

Figure 1 shows the conductance maps of 3 CVD monolayer graphene samples, which were characterized using Raman and optical microscopy. Based on this characterization, samples A and B were determined as good and sample C as bad. Onyx shows that sample C is bad and sample B is good indeed. However, sample A is debatable. The average conductance value of A is similar to B but its homogeneity is very different. Onyx acquires data in less than 5 minutes while Raman characterization, which required 3 days to obtain a comparable measurement. The results are in excellent correlation with van-der Pauw method [4].

Onyx can be integrated with reactors and enable monitoring production in real-time. Therefore, Onyx could support the production of graphene at industrial scale. Onyx can implement characterization standardized protocols for accurate and repeatable measurements.

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Figures

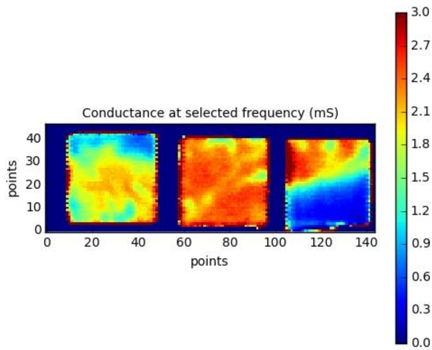

Figure 1: Conductance maps of three samples of CVD monolayer graphene at 0.5 THz.

ORAL

CONTRIBUTIONS

Improved Properties for Graphene Composites

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During this talk I will focus on the synthesis and the application of graphene for the polymer sector, conductive inks, grease and oils mentioning the level of progress achieved in EEA Graphene-Tech. Regarding the characteristics of the graphene material, the addition of single-layer graphene powder to polymeric matrixes at large scale is still far due to its extremely low density that results in important technical difficulties concerning its dosage in extrusion/injection systems and especially, its elevated economical costs. For these reasons, nowadays, graphene nanoplatelets (as our GPx products) represent the most suitable and promising solution. Then, the incorporation of graphene into different matrix is challenged by some parameters as the dispersion. In order to enhance the properties of the composite is strongly required to have a homogeneous material uniformly dispersed. Our R&D department (in collaboration with other companies) develops tailored made dispersions, in polymeric matrix by either in situ polymerization or addition of the GPx products to preexisting polymers.

Era-Net Open Calls on Graphene research and innovation

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Two ERA-NET Programs are being launched that cover research and innovation projects on Graphene and its applications on nanomedicine at European level.

In early December, 2016 FLAG-ERA published the pre-announcement of its second Joint Transnational Call in support of projects in synergy with the Graphene Flagship (www.flagera.eu/flag-era-calls/jtc-2017/). The call aims to add a second wave of transnational partnering projects to support and extend this FET Flagship initiative. The full call announcement will be published in early January 2017. Proposal submissions will have to include information on the potential synergies with the Flagship using a separate template derived from the Flagship Partnering Project application form, which will be published later on.

The FLAG-ERA JTC 2017 comprises two topics, one for each Flagship. The Graphene part of the call is sub-divided into two sub-calls, one for basic research and one for applied research and innovation. The sub-calls cover a specific list of research areas listed below.

Graphene (Basic research): 1) Synthesis and characterization of Layered Materials (LMs) beyond graphene. 2) Large scale production of heterostructures based on LMs. 3) Vertical and lateral epitaxy of Graphene and Related Materials (GRMs) for optoelectronics. 4) Functional ceramics incorporating GRMs. 5) Inks for printing stable, GRM-based, semiconducting thin films. 6) Modelling charge and heat transport in GRM-based composites. 7) Ecotoxicology of GRMs. 8) Nanofluidics using GRMs. 9) Novel device concepts based on GRMs for quantum communication. 10) Beyond CMOS switches and new computing paradigms based on GRMs.

Graphene (Applied research and innovation): 1) In-situ and ex-situ quality control of GRMs. 2) Controlling doping in high quality large-area graphene. 3) GRMs for smart textiles. 4) Functional coatings using GRMs. 5) GRMs for corrosion prevention and as lubricants. 6) GRMs for thermal management and thermoelectrics. 7) Biorecognition of specific disease markers using GRMs. 8) Highly selective gas sensors based on GRMs and 9. GRM-based bioelectronic technologies.

On the other hand, EuroNanoMed III (2016-2020) is the new ERA-Net Cofund Action on Nanomedicine under Horizon 2020 that will build upon the achievements on its predecessors established since 2008 to support the European Nanomedicine research community, with the goal of creating and funding collaborative research and innovation projects that can convert research in nanotechnology into practical gains in medicine. A new call has recently been launched (www.euronanomed.net/joint-calls/8th-joint-call-2017-2/. Applications of Graphene on Nanomedicine are also welcome as far as they cover topics at least of one of the following areas: 1) Regenerative medicine. 2) Diagnostics. 3) Targeted delivery systems. The projects should fall within Technology Readiness Levels (TRL) 3-6.

Tribological behavior of graphene/UHMWPE-coated UHMWPE for arthroplastic applications

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Highly crosslinked ultra-high molecular weight polyethylene (HXLPE) is currently one of the most relevant materials in total hip and knee replacement. The performance of this material is associated to the low wear rates of PE-Co alloy or PE-Al2O3 bearing pairs and also to a good chemical stability against oxidation process in the human body [1]. Since 1970, an alternative of the crosslinking process in UHMWPE was started via the reinforcement of this polymer with carbon fiber (Poly II®) and has been continued with attempts based on different reinforcement materials, including carbon nanotubes and more recently graphene related materials [2].

The goal of this work consists in obtaining a bearing material with tribological behavior, chemical resistance and high mechanical performance. As a consequence that bulk UHMWPE-based composites presents a negative influence in some of the mechanical properties, especially in toughness, we have coated the UHMWPE with a graphene/UHMWPE composite in order to incorporate the outstanding lubrication capability of graphene, to get a good adhesion of this composite layer to the substrate and to avoid the loss of mechanical properties introduced by the post-irradiated thermal process in the HXLPE.

All the composites were prepared by a high energy ball milling process, then incorporated to the surface of a preformed raw UHMWPE, and finally consolidated by a thermal-mechanical process at different temperatures. Graphene platelets (avanPLAT-40 Avanzare) and 1-2 layered graphene (avanGRAPHENE Avanzare) were used for blending with medical grade UHMWPE powder (GUR 1050 Celanese). Besides, graphene was also incorporated to the surface of a UHMWPE disk by means of spray-coating of an ethanol suspension. This painting process was followed by the aforementioned consolidation process.

FTIR and Raman spectroscopy were used for the coating physical-chemical characterization. Hardness and Young modulus of the surface were carried out by a nano-indentation equipment (G200 Agilent Technologies). Friction coefficients were obtained by a pin-of disk tribometer (TRB CSM Instruments) in all the materials.

The results point out that multi-platelet graphene presents better tribological behavior than 1-2 layered graphene. On the other hand, the spray-coated material performed the best friction coefficient, although the stability of the layer was lower than that of the composites.

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The "Graphene & 2D Materials" EUREKA cluster is defined as a complementary enabling and accelerator instrument in the European scene, fully piloted by industries to further take graphene from the mature research developed at academic laboratories into the European society in the space of 5 years, boosting economic growth, jobs creation and international leadership and investment attractiveness. This cluster will help Europe having a more dominant position in graphene patenting, will deploy the proper winning industrial strategies to gain worldwide competitiveness, and will ensure that for all promising industrial sectors of technology innovation, a fully integrated EU-value chain is established, integrating into consortia the relevant actors from low to high Technology Readiness Levels (TRL).

The cluster will clarify the differentiating potential in all sectors where EU-industries is strong and could further gain in competitiveness, and will develop proper incentives towards the achievement of EU-leadership in the fields of graphene commercialization and graphene-driven technology improvement. The cluster will elaborate and foster industrially-driven innovation strategies, that will take advantage of the existing excellent science and transnational platforms in Europe (national networks, Graphene-Flagship, etc.), and will focus on solving current challenges which are limiting the time to market and business growth of graphene-related EU companies.

Centre for the Development of Industrial Technology: Funding opportunities for graphene in Spain

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The Centre for the Development of Industrial Technology (CDTI) is a Public Business Entity, answering to the Ministry of Economy and Competitiveness, which fosters the technological development and innovation of Spanish companies. It is the entity that channels the funding and support applications for national and international R&D&i projects of Spanish companies. The CDTI thus seeks to contribute to improving the technological level of the Spanish companies by means of implementing the following activities:

- Financial and economic-technical assessment of R&D projects implemented by companies.
- Managing and fostering Spanish participation in international technological cooperation programmes.
- Fostering international business technology transfer and support services for technological innovation.
- Supporting the setting up and consolidating technological companies.

CDTI provides companies with its own funding and facilities access to third-party financing (Bank Line for Funding Technological Innovation and Subsidies of the EU R&D Framework Programme) for national and international research and development projects.

In addition, the CDTI is empowered as the competent entity to issue binding motivated reports of the projects funded by any of its lines (Royal Decree 2/2007). These documents will provide greater legal security to Spanish companies with an approved project and funded by the CDTI when seeking tax rebates for costs incurred in the R&D activities of those projects.

It should be noted that in recent years, research and development in nanotechnology can be included within the key funding objectives under CDTI schemes. Thus, different funding instruments have been used to finance this innovative field such as R&D projects, CIEN, FEDER-INNTERCONECTA, NEOTEC at national level as well as international programmes.

Grapholymer®
Extrusion machinery for graphene in polymers

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A worldwide leader in Plastics Extrusion Machinery, Bandera has recently developed a laboratory EA-Extrusion Academy® with the goal of liaising between research and industrial production of the many products obtainable via the extrusion process, also associated to lamination, coating, converting and printing technologies.

Grapholymer is the extrusion process to integrate graphene and 2D materials in many extrudable polymers.

The House of Extrusion® allows the scale up of prototype results to industrial productions of +3,000 kg/h.

Romanian Research Centre for Carbon Based Nanomaterials – Electronics at atomic scale

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This research center having as acronym CENASIC dedicated to graphene and other carbon based materials and was launched 1 year ago. Also wide bandgap semiconductors are developed in this center to be integrated with carbon based materials. The building of this center encompassing a new building, new equipments and a clean room of 250 m^2 class 100 was possible due to an UE financial investment of 6 MEuro via structural founds received by Romania.The main research activities are: graphene monoloyer growth at the wafer level (3 and 4 inches), transfer of graphene on solid and flexible substrates, fabrication of graphene based nanomaterials: aerogel, reduced oxide graphene ,graphene oxide, the integration of graphene with other two dimensional materials such as MoS_2 ,WS_2 , BN and fabrication of van der Waals heterostructures, shielding cables based on graphene based materials, nanoelectronic and nanophotonic devices based on graphene, vapor, temperature and pressure sensors based on graphene , GaN devices such solar cell ,transistors for high temperature operation, biosensors such as DNA hybridization detection, diamond thin films for high power electromagnetic waves and optoelectronics applications. I will present the new research results obtained of this center and its interactions with companies such as Renault and Thales (see some results in Fig.1).

Figures

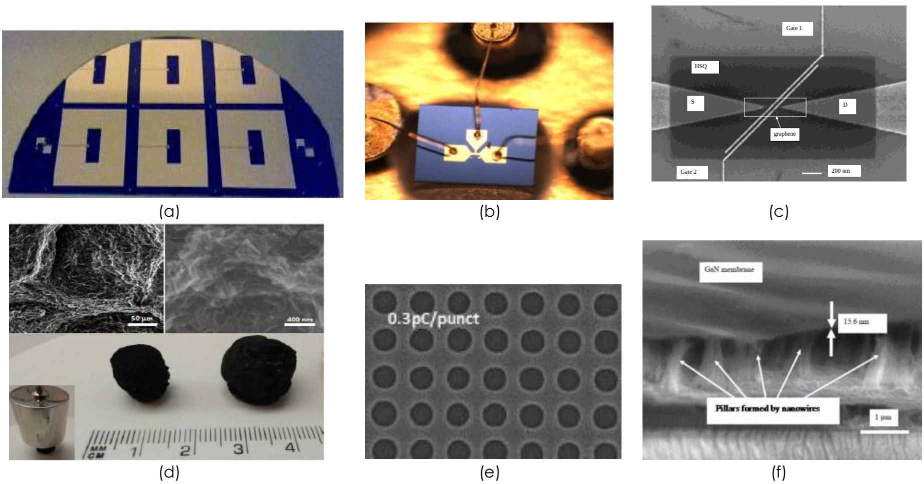

Figure 1: Some results: (a) graphene antennas for microwaves in X band (b) graphene FET with 10^4 on/off ratio (c) graphene ballistic FET at room temperature (d) graphene aerogel for pressure sensors (e) nanopatterned graphene (f) GaN membrane artificial synapse.

Epitaxial graphene on SiC: a route towards high-performance electronic devices

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Graphene exhibits outstanding electronic properties such as high carrier mobility and ballistic transport at room temperature [1]. However, the lack of bandgap and the absence of an affordable method for its mass scale production are still major hurdles for its full exploitation in the field of electronics.

Controlled synthesis of high quality graphene on silicon carbide (SiC) substrates [2] points out that this technique is a competitive approach for producing wafer-scale epitaxial graphene (EG). Remarkably, EG on SiC shows major advantages compared with other methods, e.g. CVD graphene, such as cost efficient compatibility with complementary metal–oxide–semiconductor (CMOS) technology. Beyond EG deposition by SiC graphitization, applying advanced device fabrication, such as novel strategies based on ion implantation [3] and homoepitaxial growth of doped SiC on top of a semi-insulating SiC buffer layer have opened a new avenue to develop e.g. back-gated graphene transistors.

In this talk, we will summarize several of our recent advances in the synthesis and device technology on EG on SiC. For instance (Fig.1.a), our technology development results reflect our capability to create a buried implanted layer in SiC substrates at determined depth compatible with EG. This architecture enables back gate control of graphene electronic devices. The resources of Graphene Nanotech (GPNT), a startup company emerged from the collaboration between the Institute of Microelectronics of Barcelona (IMB-CNM-CSIC), the Institute of Nanoscience of Aragon (INA), and the Aragon Material Science Institute (ICMA), will be fully introduced. GPNT is devoted to fabrication and characterization of EG (see Fig. 1.b) and EG-based devices, and offers its know-how to both academia and industry.

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Figures

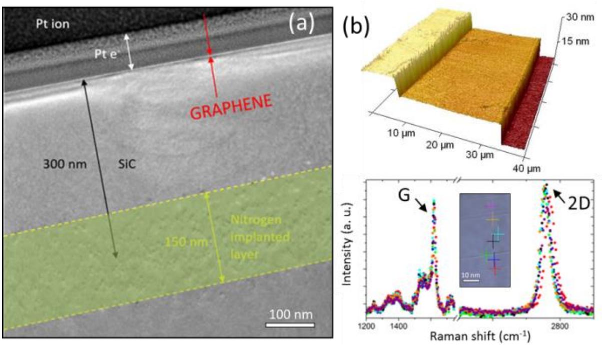

Figure 1: (a) Cross-sectional high-resolution transmission electron microscopy micrograph of an ion implanted (nitrogen) SiC substrate covered with an EG layer. The implanted layer has been highlighted in yellow for the sake of clarity; (b) Atomic force microscopy image (top) and Raman measurements collected at several points located on the surface (bottom) of a selected sample showing the relief and the characteristic peaks of EG grown on SiC, respectively.

Spanish alliance on graphene

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During the last months, the Spanish Alliance on Graphene, has come into light as a result of the activities launched by Excellence network GRAPHENET. The association aims to represent the interests of the industrial group of graphene producers and end users in Spain. We will present the good praxis code, agreed by the main Spanish producers, for the labeling of graphene. Acceptance of the code is associated to the membership of graphene producers to the Alliance and will easy the path to the incorporation of graphene in the formulations and industrial processes. However, the scope of the Alliance is not limited to the industrial partners and academic groups are also welcome, as we aim also to create synergies between both groups and also incorporate the technological centers to the activity in 2D materials. Information on the latest news on strategical calls will be also delivered.

Graphene Based Materials for Ultimate Neuroelectronics

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Neuroelectronic devices are powerful tools to study neural networks activity and to develop neural prostheses. After two decades of investigation and exploitation, the current technologies are about to reach their limit both for fundamental neural investigation and for clinical applications. Thus, important refinements are now needed to fulfill the demanding requirements associated to these applications, such as low invasiveness, long term efficacy as well as large number of recording/stimulating sites. Graphene-based materials belong to the few new material platforms that can be used to reach these ambitious targets. Indeed, graphene and graphene-based materials combine biocompatibility, easy integration in microdevices and CMOS technology, flexibility, and high electronic performance. Further, if integrated together with complementary 2D semiconductor electronic technology, graphene sensors could eventually enable the production of ultimately flat neuroelectronic devices. In this presentation, I will discuss our latest technology developments to record electrical activity in cell cultures as well as in vivo brain activity on rat cortex.

Fabrication of low-doped graphene devices exhibiting small hysteresis. Application to high frequency optoelectronic mixers

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We have performed a statistical study of the electrical performances of more than 500 graphene field effect transistors as a function of the fabrication process1. This leaded us to propose a two-step process including a "protection layer" realized before the lithographic process and a passivation layer deposited once the devices are fabricated. The protection layer is a 1 nm thick evaporated aluminum layer that is subsequently oxidized. The passivation layer corresponds to a 30 nm thick Al_2O_3 film obtained by atomic layer deposition. Implementing the protection layer leads to devices integrating graphene with an average residual doping of 2.5 10^{12} cm^{-2}. With the two-step process, the maximum of the device distribution corresponds to a residual doping smaller than 5.10^{11} cm^{-2}. In other words, the conductance minimum is obtained for a gate field of 0.023 V/nm. The impact of the fabrication process on both residual doping and hysteresis will be presented.

With this methodology, we have fabricated coplanar waveguides (CPWs) integrating low-doped graphene and demonstrated high frequency optoelectronic mixing. The figure below shows the operating principle. An intensity-modulated laser at frequency fopt illuminates the graphene channel and an electrical RF signal at frequency fele is injected in the CPW. This leads to the generation of two electrical signals at the CPW output at frequencies f_{ele} - f_{opt}| and f_{ele} + f_{opt}. In particular, we demonstrated that the optoelectronic mixing operates with optical and electrical signals at frequencies up to 30 GHz. These results open interesting perspectives in graphene optoelectronic mixers for high speed communications.

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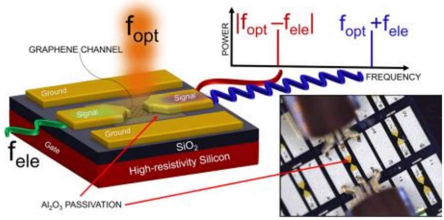

Figure 1: Optoelectronic mixer based on CVD graphene

CFRPs containing reduced graphene oxide for aircraft applications

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The use of carbon fiber reinforced polymers (CFRPs) for structural applications is widespread in the aircraft industry. One of the main research lines for these materials is focused on increasing the multifuncionality, either modifying the polymer matrix or using multifunctional coatings.

The most common polymer matrix for the CFRPs used for aircraft applications are epoxy resins. There are many research activities with the aim of improving their multifunctionality adding different nanofillers. But epoxies are not the only possible matrix. One of the alternatives are benzoxazine reins. They present good mechanical properties, low water absorption, near-zero volumetric change upon curing and low coefficient of thermal expansion, with a cure temperature similar to that of epoxy resins [1-2].

In this communication, some results obtained when adding thermally reduced graphene oxide (rGO) nanoplatelets to a benzoxazine-based thermoset resin will be presented. The effect on the curing reaction has been evaluated, and it was found that the graphene addition has a catalytic effect, reducing the activation energy and the gelation time. As it was expected, the electrical and thermal conductivities increase with the content of graphene oxide in the resin.

After characterizing the main properties of rGO/benzoxazine nanocomposites, they have been used as matrix for CFRPs using the liquid resin infusion (LRI) method. Even though the resin viscosity increase due to the addition of rGO nanoplatelets was not so high, it was not possible to manufacture a composite panel with 2 wt.% rGO in the resin, due to the filtration phenomenon in the carbon fiber fabric. Compared to the reference composite laminate (with graphene nanoplatelets), the mechanical properties evaluated are very similar in the graphene doped CFRP laminate (0.5 wt.% rGO in the resin). The electrical conductivity increases due to the presence of rGO nanoplatelets, mainly in the transverse direction. For the evaluation of the barrier behavior, the water uptake during immersion in hot water has been evaluated, and it was found that it was reduced by 6 % with the addition of graphene nanoplatelets to the thermoset resin.

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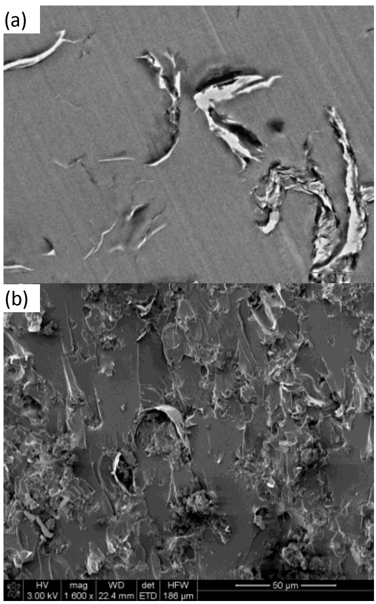

Figure 1: Benzoxazine nanocomposites with 2 wt.% rGO: TEM (a) and FEG-SEM (b) micrographs.

Gas Barrier Performance of Graphene/Polypropylene Nanocomposites

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From a theoretical point of view the improved barrier properties are the result of the presence of impenetrable platelets with high aspect ratio that are homogeneously dispersed in the penetrable polymer matrix leading to an increase of the diffusion path length (tortuosity) and, consequently, a decrease of the gas permeability. Factors that strongly affect the barrier properties of composites are the aspect ratio, dispersion and orientation of the platelets, the platelet/polymer interface and the crystallinity of the polymer matrix [1].

Kalaitzidou et al.1 observed that graphene nanoplatelets (GNP) formed large agglomerates and due to their high aspect ratio tended to strongly orient along the flow direction of polypropylene (PP). The agglomerates were modified during the compression molding used for the fabrication of the film and the platelets slided against each other and aligned parallel to the mold plates, improving the barrier properties of PP. Potts et al. [2] reported a 20% reduction in oxygen permeability for PP with 6.5 wt% GNP.

In the present research, GNP/PP composites were prepared at industrial conditions using blown film extrusion. The incorporation of 0.5 wt% of GNP to PP matrix led to composites with enhanced gas barrier properties. In particular, the normalized oxygen permeability and water vapor permeation of PP foils enhanced with 0.5 wt% GNP, decreased about 60% as it is obvious from the Figure 1. Therefore, their implementation as packaging materials is expected to benefit the food protection, the economy and the society in general.

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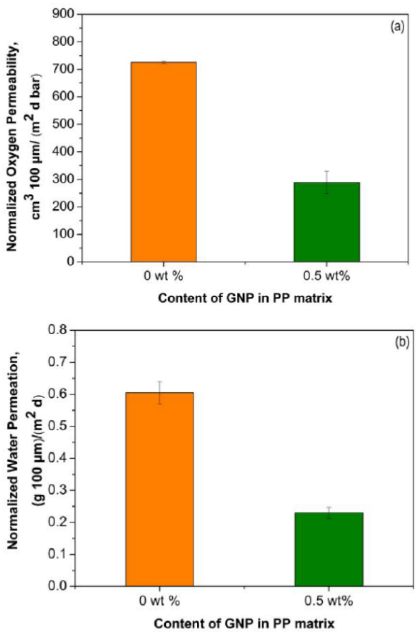

Figure 1: Normalized oxygen permeability (a) and normalized water permeation (b) of PP and GNP/PP foils.

Multifunctional graphene-PA6 composites closer to the industry

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Polyamide 6 (PA6) is a widely used thermoplastic matrix due to properties as mechanical performance, easy processing and chemical resistance. For these attributes, it is present in the market in several formats and many research efforts have been devoted to improve their performance by adding additives (i.e., clays, graphite and derivatives). Automotive industry is one of the sectors which is employing nanocomposites of PA6 (usually reinforced with glass fibers) for replacing metal components and therefore reduce costs, car weight, fuel consumption and CO_2 emissions.

Since decades ago, there were prepared graphite composites (in PA6 and other type of matrixes) to enhance properties as electrical conductivity or thermal management. More recent is the use of CNTs and graphene related materials (GRM), which have shown very positive results in many properties, as described in reviews and papers. [1,2] However, at the moment it does exist a key factor which is limiting the application at industrial level: the price of graphene materials. To address these issues, it is necessary understand that graphene is a new material and now is being scaled up; so it is expected that the price is getting lower; just basing on a pure scale economy factor. Therefore, GRMs will be competitive in few years. Besides, it is of the utmost importance take into account the possibility of obtain multifunctional composites employing graphene. This is a key factor for the introduction of GRM at industrial scale; because there will not be other unique additive which can meet all the requirements.

This work presents GRM-PA6 composites prepared by melt compounding which gather several properties; such as high electrical conductivity and the highest thermal conductivity enhancement reported for PA6-CNTs and PA6-graphene composites prepared by melt compounding [3]; and similar to those prepared by in situ polymerization [2]. Also, we have tested other properties as mechanical behavior and flame retardancy, with positive results.

Regarding the price, it has been analyzed the economic costs, related to the added value that is obtained. Results are very promising for the employment of these GRM composites, achieving multifunctional materials to apply not only in automotive industry, but also in textile areas and other sectors.

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Water decontamination from nuclear sector through graphene derivatives: an alternative and efficient method

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Radioactive isotopes in water generate a great environmental and human health problem. Current decontamination processes are based on chemical precipitation, solvent extraction, ion exchange and adsorption. They are complex, expensive and provide low efficiency.

Within this context graphene and its derivatives (graphene oxide-GO) are shown as the ideal and promising materials for environmental remediation applications [1,2]. Its 2D structure provides high capacity of adsorption, due to the high specific surface and easiness for strong interactions with other molecules. Besides, they have high thermal and radiation resistance and very good chemical stability in severe environment. Specifically, GO has a large quantities of oxygen atoms on the surface as epoxy, hydroxyl, and carboxyl groups. These functional groups promote the formation of hydrogen bonding or electrostatic interaction with radionuclides and heavy metals in water. Therefore makes them excellent candidates for radioisotopes removal from contaminated water.

Graphene is a two-dimensional atomic thickness sheet consisting of a hexagonal flat tessellation (honeycomb shape) formed by carbon atoms in sp2 hybridization, its thickness is the carbon atom diameter, 0.142nm. Currently, there are two kinds of methodologies for graphene production: top-down or bottom-up methods [3]. This work uses a top-down technology by an oxidation-reduction method. This method is based in oxide graphene production from different graphites [4]. The most common way of exfoliating graphite is the use of strong oxidant agents to produce graphene oxide (GO), a hydrophilic carbon material. GO is a functionalized graphene sheet with hydroxyl (-OH), carboxylic acid (-COOH), epoxy (-O-), and/or carbonyl (-C=O) groups.

In this work batch sorption experiments have been carried out at laboratory scale, using Radium (Ra) oxide aqueous solutions as radioisotope and GO aqueous solution as adsorbent. Batch preparation was performed mixing both solutions. Radioactivity measurements were performed before and after of trials using Triathler Liquid Scintillation Counter (LSC). Concentrations of Ra and GO solutions and mixing time were studied in order to optimize the process. Results show high efficient of Ra radioisotopes removal in water, being in some cases up to 94%.

This project has been funded by the company Equipos Nucleares S.A. (ENSA).

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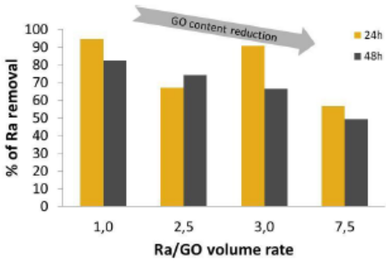

Figure 1: Percentage of Ra removal obtained as a function of Ra/GO volume rate and mixing time.

POSTER
CONTRIBUTIONS

Methodology for the determination of the dispersion index of Graphene derivatives in solvents

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Since the Discovery of graphene [1], more and more applications have emerged, including materials based on it [2]. Of all of them, the most successful are the materials based on top-down graphene, instead of Chemical Vapor Deposition (CVD) based graphene materials [3]. Among top-down graphene products, graphene oxide and its derivatives (GO, rGO…) play an important role as nanofiller in polymer matrices in multifunctional composites, and solvents as conductive inks [3] [4] [5]. More recently, there are great interest in biomedical applications like drug delivery [6], where graphene oxide (GO) dispersed in aqueous phase is required. In all cited cases, a good dispersibility in the solvent is mandatory.

J. I. Paredes et al [7] have shown that GO has good dispersibility in water, ethylene glycol, DMF, NMP and THF, while not so good in acetone, methanol, ethanol… This is because the production process causes that hydroxyl and epoxides groups appear on basal plane. Also appear carbonyls and carboxyl groups on the edge of plane.

In the present work, it has been studied how the GO behaves in different solvents. For that, the dispersion index has been determined, establishing for this, a method and an equation to assign a numerical value for the index. This is an objective way to evaluates de quality of the dispersion.

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Use of lithographic techniques to determine anti-scratch hardness through AFM of samples that exceed the limit index in the Wolf-Wilburn test

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The use of Scanning Probe Microscopy techniques has been growing in recent years, concurrently with advances in nanotechnology. Among the Scanning Probe Microscopes it is worth mentioning the Atomic Force Microscope (AFM). Since its invention in 1986 [1], the AFM technique has been progressively improved, allowing at the present the testing of multitude of characteristics of materials at nanoscale. For that reason is commonly used in surface characterization [2][3][4][5][6].

The main uses of AFM concerns surface imaging. But it also could be employed to measure hardness of the samples [7], determine the adhesion forces between tip and surface, measure electrical conductivity, magnetic forces [8]… Even, changes in surface morphology can be carried out with AFM. An example that illustrates the reliability of the technique is that it is also possible to draw frames or complete pictures at nanoscale like Mona Lisa [9]; this technique is known like nanolithography.

The Wolf-Wilburn Test [10] was traditionally used to determine polymer film hardness in conventional coatings. Nevertheless, the introduction of nanofillers, like Graphene Oxide, in polymeric matrices may causes a material hardness exceeding the Wolf-Wilburn standards. For this reason is necessary to use other alternative methods to determine the reinforced samples hardness. Commercial Nanoindenters could be used to determine hardness [11], but with AFM it could be performed a more complete analysis. The utilization of AFM could also permit the determination of hardness, anti-scratch resistance, adhesions forces and imaging the indentation through the same essay.

This work shows a method to determine the anti-scratch resistance using the nanolithographic mode of the AFM and its previous calibration required to carry out the tests using the mode of nanoindentation.

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Time Domain Spectroscopy of 2D materials: graphene, MoS_2

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In the increasing research field of 2D materials such graphene, Molybdenum disulfide MoS_2 [1] attracted a great interest due to potential applications as thin film transistors, light-emitting diodes or photodetectors. Differently than graphene, the existence of a direct bandgap in monolayer MoS_2, gives the possibility of performing MoS_2 field-effect transistors or optoelectronic devices. Graphene and MoS_2 characterization on the THz and IR bands are a key requirement for its applications and development to high frequency and optoelectronic devices [2-3].

We analyzed by IR and THz-Time Domain Spectroscopy (THz-TDS) graphene as grown and p-doped and MoS_2, deposited on different substrates: quartz, PET, PEN for graphene and sapphire for MoS_2, in the range from 0,1 to 2 THz. Flexible substrates like PET and PEN are interesting for applications as flexible electronic devices, including flexible solar cells. From THz-TDS we obtained the electrical conductivity or impedance, transmittance and attenuation. IR spectroscopy is used in order to check the coherence of both methods. The advantage of THz-TDS method is that we can get significant parameters related to the sample quality like conductivity, transmittance or attenuation, without the need of depositing any electrical contacts or sample preparation.

Our results on graphene show a noticeable dependence with the substrate at high frequencies. We observed that superficial conductivity of p-doped graphene is slightly higher than pristine graphene, moreover p-doped graphene presents an increase of electromagnetic absorption.

By THz-Time Domain Spectroscopy (THz-TDS) on MoS_2 obtained by CVD under different conditions, we found that MoS_2 presents a high sheet conductivity, in the range from 3.4-130 times the value of G0 (G0 is the quantum of conductivity = 77.48 μS while graphene shows a sheet conductivity around 12-25 times the value of G0. We observed a dependence on the growth conditions for MoS_2: we found that CVD monolayer MoS_2 sheet conductivity, is up to 3 times greater for MoS_2 obtained using H_2S as a sulfur gas precursor than the usual CVD MoS_2 obtained with sulfur.

The study of a material transmittance is a key factor to characterize a material over a wide frequency range. We found that at THz frequencies, MoS_2 transmittance is close to 95%, similar to graphene. On the other hand, at IR wavenumbers, MoS_2 transmittance is close to 99.8%. Therefore, the use of MoS_2 is very promising in the development of optoelectronic devices, with similar or even better properties than graphene.

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Low temperature Inductively Coupled Plasma Chemical Vapor Deposition of vertically oriented graphene nanowalls for supercapacitor applications

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Graphene nanowalls (GNWs) are networks of "graphitic" sheets that typically appear vertically oriented on a substrate. Low temperature synthesized and vertically oriented GNWs have some unique characteristics, making them significantly different in many aspects from the conventional horizontal, randomly oriented graphene sheets and great potential for various applications like supercapacitors, lithium-ion batteries, solar cells and sensors. Vertically oriented graphene nanowalls possess a number of unique mechanical, chemical, electronic, electrochemical, and optoelectronic properties that could benefit their potential use in a wide range of applications. For each application, high-quality GNWs should be grown on suitable substrate. For example, GNWs grown on Cu foil becomes an excellent electrode for supercapacitors, meanwhile, GNWs on dielectric (SiO_2) substrate could be used to fabricate gas or bio-sensors, also GNWs on semiconductor substrates could be used rather for potential application of solar cells. However, there are still few systematic studies of this promising material. In this study, we have used Inductively Coupled Plasma Chemical Vapor Deposition (ICPCVD) method for growing the graphene nanowalls on polycrystalline Cu foils, c-Si wafers and amorphous silica substrates in the temperature range of 500-750^{0}C. We have explored the growth parameters: plasma power, gas flow, temperature, pressure or cooling time, and how they affect the morphological and structural properties of the obtained graphene nanowalls. Despite that at present, there is no general agreement on an unified theory to unveil the GNW growing mechanism and to provide guidance for optimum growth condition using different plasma power and temperature, our process and particular technological parameteres can suggest new evidences of the growth mechanisms. The present results of GNWs show new points of view of their morphology (Figure 1).

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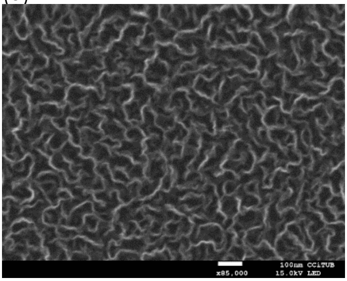
Figures

(a)



(b)

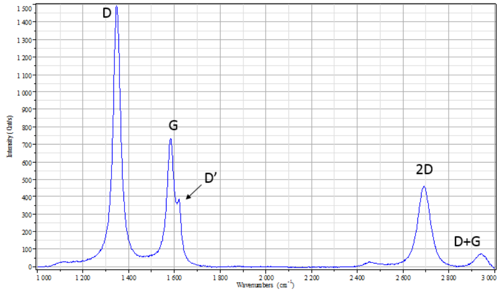


Figure1: (a) SEM image of graphene nanowalls (bar scale of 100nm) (b) Raman spectra of multilayer graphene nanowalls

Improvement of the delamination resistance of carbon fiber composites with taylored Graphene Oxide

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Carbon Fiber Reinforced Polymers are each time growing in applications. Their superior mechanical properties and low weight make them ideal for many structural applications. However, the matrix suffers from poor toughness, and unfortunately, the matrix phase controls the interlaminar properties of the laminate they encompass. Consequently, laminated composites failures are often the result of a delamination failure. In view of this, many researchers have focused their attention on improving the matrix-dominated performance of continuous-fiber composites through use of matrix additives such as silica nanoparticles, copolymers and carbon nanofibers and nanotubes (CNF/CNT).

In this study, the oxidative debris was removed from graphene oxide (GO) sample, through a NH3 basic washing, yielding base-washed graphene oxide (bwGO). Oxidative debris, assimilated to fulvic and humic substances, mainly consist on very small size graphene oxide sheets, below 50 nm, and with high oxygen content due to its higher relative sheet edge. Oxidative debris removal produce an enrichment of higher size sheets, with oxygen contents similar to rGO. The present work deals with the influence of using GO or bwGO in the mechanical properties of the composites obtained. Laminates of various fiber architectures, and with epoxy resin with GO or bwGO content ranging from 0.1 to 1.0 wt.% were fabricated by vacuum assisted infusion. The key point with infusion is to develop very well dispersed GO platelets that allow a valid permeation of the nanocomposite resin through the fiber plies. Results indicated GO and bwGO addition offered increases in tensile stiffness, toughness and flexural strength. Mode I interlaminar fracture toughness test to unidirectional laminate specimens indicated that the fracture energy required for the onset of mode I interlaminar delamination was enhanced by 33% and 65% by adding 0.2wt%. of GO and bw-GO respectively. The effect of adding GO with different surface chemistry is also noticeable, the elimination of the oxidative debris can improve the dispersibility of GO in epoxy matrix, and a better dispersibility may improve the reinforcement efficiency.

Grain size analysis of CVD graphene based on the photocatalytic oxidation of copper

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CVD graphene is a polycrystalline material, with grains typically smaller than a few microns. Although it is known that graphene's grain size affects its properties, not much attention has been paid to developing methods for grain size analysis similar to those existing for other polycrystalline materials (e.g. metals). Reported strategies thus far are incapable of providing real grain size statistics. Methods based on STM [1] and TEM [2] limit the analysis to extremely small areas. Other methods aimed at large area analysis [3,4] succeded in revealing grain boundaries by oxidizing the copper substrate through graphene defects. However, reported oxidation strategies were not selective enough to allow for statistically meaningful grain size analyses.

Here we report a straightforward lab-bench method that uses TiO_2 suspended in water and UV light to selectively and precisely oxidize copper through graphene defects, resulting in well-contrasted darker copper oxide lines on top of the copper background. Graphene grains are then visible via optical microscopy with an unprecedented quality. This allows for the statistical measurement of graphene grain size distributions across large areas applying ASTM standards and automated image analysis.

Measurements on CVD graphene samples directly on copper allow to acurately obtain its mean grain size with the corresponding Gaussian distribution by evaluating large numbers of grains (up 1000 per image). For the first time, it is shown that graphene grain size distributions become wider for larger average grain sizes, as expected for polycrystalline materials. Furthermore, Raman analysis proves that graphene is only slightly damaged during the oxidation process.

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Figures

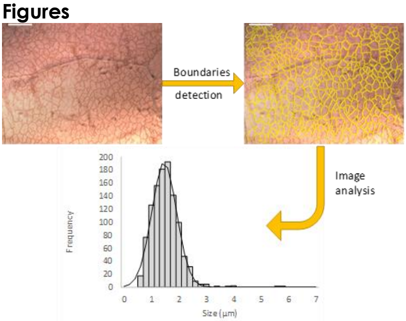

Figure 1: Process for grain size characterization. Sample after photocatalytic oxidation with clearly visible grain boundaries (top left), after

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