graphIn

Graphene Industry - Challenges & Opportunities

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Foreword

On behalf of the Organising Committee, we take great pleasure in welcoming you to Madrid (Spain) for the 4th edition of the **graphIn International Workshop (Graphene Industry – Challenges & Opportunities)**.

This 2 days Conference aims at presenting the current state of the art and the opportunities of graphene and 2DM-based materials and devices and its industrial challenges and opportunities, focusing on the most recent advances in technology developments and business opportunities in graphene and 2DM commercialization. Key representatives of "graphene companies & labs" will share their market vision and business opportunities in diverse current market fields of graphene products and applications, such as energy, bio&health or electronics. This unique international event 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 aim of **graphIn** will be to develop the relationships that will accelerate graphene industrial growth. The discussion in recent advances, difficulties and breakthroughs will be at his higher level.

We would also like to thank the exhibitors for their participation: Hiden Analytical, Graphene Factory, Das-Nano and Abalonyx AS.

In addition, thanks must be given to Real Jardín Botánico (RJB) / CSIC and the staff of the organising institutions whose hard work has helped planning this conference.

ORGANISING COMMITTEE

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GRAPHENE FACTORY

GRAPHENE FACTORY is the CNR web portal born with the aim to show and promote the research on graphene and bi-dimensional materials performed within the CNR network. It also offers contents and information about "graphene" to the scientific community, to the media, to SMEs, Industry and general public.

The National Research Council (CNR) is the largest public Research Institution in Italy. CNR is strongly involved in the research activities on graphene and two-dimensional materials beyond graphene, both on the fundamental research, and on future applications and technological innovation. On a national basis, is the institution with the largest number of researcher involved on these topics and the largest scientific production.

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Abalonyx
Innovative materials

Abalonyx AS is a Norway based company engaged in production and R&D related to graphene oxide and graphene oxide derivatives since 2008. We produce and sell single layer graphene oxide (GO) and thermally reduced graphene oxide (rGO) in Kg-quantities and are presently developing several derivatives for special applications, including protective coatings for autoparts, a process for remediation of water contaminated with heavy metals and radionuclides based on a GO-based scavenger-system. We are also involved in collaborative development of modified GO and rGO for use in composites for construction materials, certain sports equipment and energy storage in several collaborative projects. Our sister company, Graphene Batteries AS uses a special rGO-grade in its battery developments. We actively work with our customers to tune our GO and rGO to their needs.

www.abalonyx.no

das-nano

Das-Nano, founded in 2012, is a company that consists of experienced business and industry entrepreneurs. Our team boasts world-leading scientists with a long track-record in scientific research, technological and international business.

With 40% of our team holding PhDs and being based in Navarre (Spain), we are in a unique position to provide a technology portfolio that is continuously evolving. Our technology provides state-of-the-art solutions for many different industries including but not limited to:

- High Security Printing, working hand in hand with Central Banks and Security Printers.
- Banking and Fintech Industry.
- Automotive Industry.
- Aerospace and Windpower Industry.
- Research & Science equipment.

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ONYX: Full-area non-destructive and non-contact equipment for the fast and accurate characterization of mobility, carrier density, and conductivity of graphene by means of terahertz technology

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 mobility, carrier density, conductance, resistance, thickness and other parameters from materials such as graphene, TiN, GaN, PEDOT, ITO, NbC, ALD, spin coated photo-resins. The maps provide information about the homogeneity and quality of the deposition process. 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 mobility, carrier density, and conductance maps in the terahertz range [4].

Figure 1 shows the conductance maps of a sample of CVD monolayer graphene over quartz substrate. Image (a) shows the conductance measured in reflection configuration while image (b) presents the conductance in transmission configuration. As it is shown in (c), the correlation between the two measurements is strong (98%). The results are in excellent correlation with van-der Pauw method. Figure 2 shows (a) the mobility and (b) carrier density maps extracted without any bias according to model described in [5] of another CVD graphene.

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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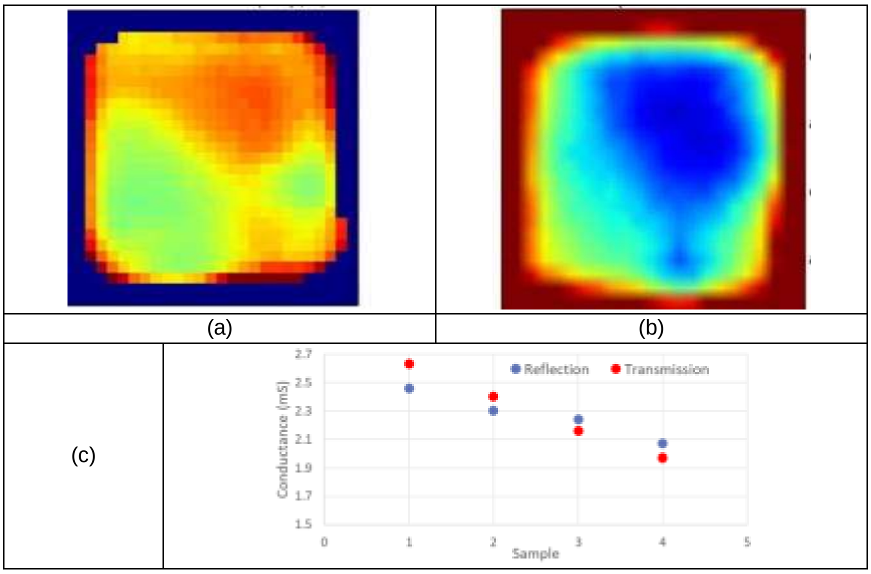
Figures

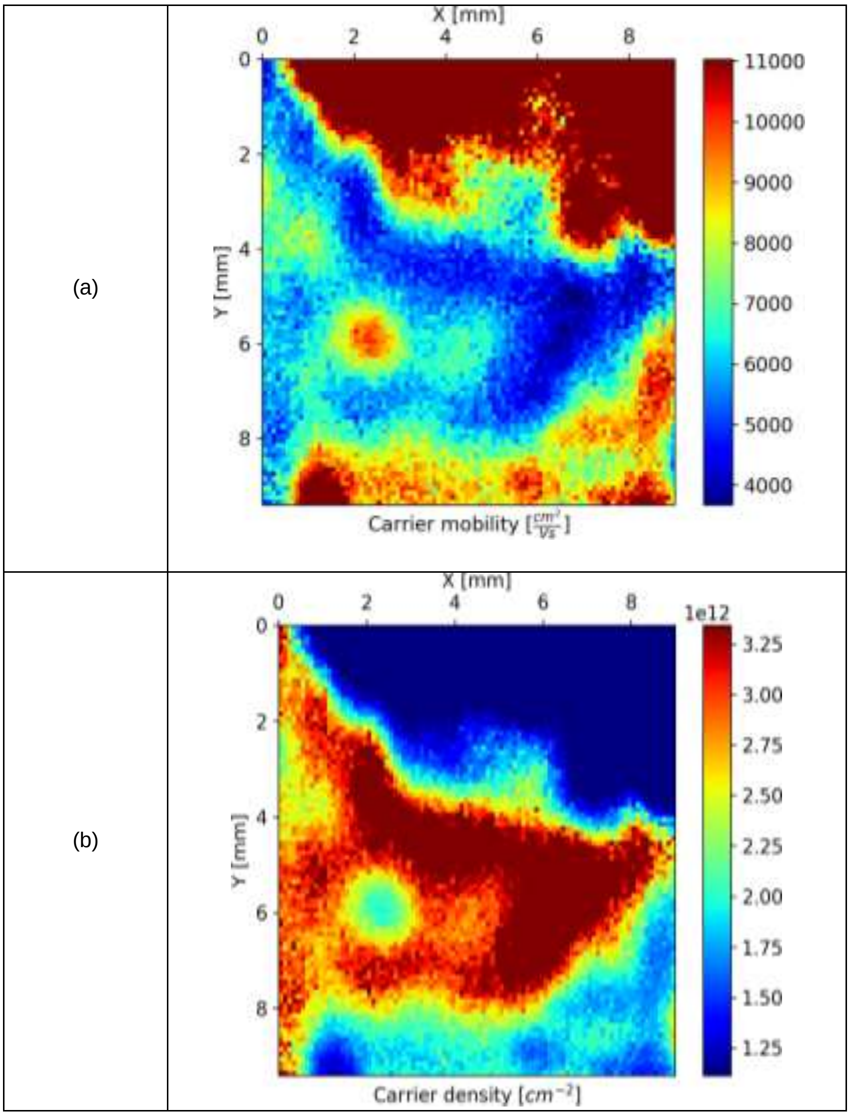


(a)

(b)

(c)

Figure 1: Conductance maps of a CVD monolayer graphene over quartz substrate sample: (a) reflection configuration, (b) transmission configuration, and (c) correlation graph.



(a)

(b)

Figure 2: Mobility (a) and carrier density (b) maps of a CVD monolayer graphene over quartz substrate sample.

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Large scale production of 2D Materials for Energy applications

I will discuss the latest development towards the industrial-scale, reliable, inexpensive production processes[2] for the implementation of 2D materials in energy applications.
I will show how the production of 2D materials by solution processing[2,6] represents a simple and cost-effective path towards the development of 2D materials-based energy devices, presenting huge integration flexibility compared to other production methods. I will first present our strategy to produce 2D materials on large scale by wet-jet milling[7] of their bulk counterpart and then an overview of their applications for energy devices. [3,8,9,10,11,12,13,14]

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Dynamic Spray-Gun Deposition Method for applications in the field of sensors, energy, information storage and EMI.

This contribution deals with the fabrication of devices based on graphene based nanomaterials using dynamic spray-gun deposition method implemented through roll-to-roll. We used this technique to fabricate sensors, supercapacitors [1], flexible memories [1] and conformable Electro-Magnetic Shielding (EMS) layers. In the first case we exploited the nanostructuration of mixtures of graphene and carbon nanotubes (CNTs) to achieve electrodes for supercapacitors. Indeed the CNTs (Multi-Walled Carbon Nanotubes that are metallic and so conductive) are used as sort of spacers to avoid the restacking of graphene. Thanks to that we can exploit the huge surface of graphene to store charges and at the same time we create channels between the layers allowing the rapid charge and discharge of the device. The use of high quality graphene (<5 layers) and MWCNTs, with a diameter of around 20nm, also improve the conductivity for the electrodes and allowed us obtaining an impressive specific power value of around 100kW/Kg using an industrially suitable technique and not only a lab based one [2-3]. To increase the energy storage we have used ionic liquid, which are more viscous, having larger charges. In this case as spacers we have used carbon nanofibers with larger diameters (10nm-100nm). The spray-gun deposition method has been also implemented in the fabrication of Graphene Oxide and Carbon Nanofibers Oxidized based memories. In this case we case spray nanomaterials water based suspensions on a flexible layer previously metallized. The total thickness is around 100nm. After contacting the top with metallic contacts we are able to achieve flexible non volatile memories simply applying a bias (<3V). These memories show bipolar behavior and have been cycled 10000 times. They constitute one of the first examples of information storage devices that can be fabricated using a roll-to-roll implementable method. These devices can open new horizons in the integration of memories for examples in RFID tags or in packages. Finally, we have achieved EMS architectures using nanostructuration of graphene, MWCNTs and carbon nanofibers between polymers layers in order to exploit the Maxwell-Wagner-Sillars effect to absorb X-band frequencies. Thanks to this nanostructuration we are able to trap the charges in sort of micro-capacitors created in the layers. This is a real breakthrough considering that usually heavy metal based layers are used and that in this case mm based conformable layers can be obtained opening the route for new kinds of applications. Also in this case the fabrication will be implemented by roll-to-roll fabrication. During the presentation we will show all the details on the first characterization of devices and we will show also perspectives for other potential field of applications.

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Atomic-scale functionalization of metal-supported graphene: Towards a graphene-based catalyst

Graphitic carbon structures are usually a major obstacle for catalytic processes on transition metals. Due to their chemical inertness, carbon deposits physically block the surface active sites poisoning the catalytic reaction. In principle the effect is more pronounced as the amount of carbon increases, where an extreme scenario would be case of a complete graphene layer. However, as we demonstrated in a recent work, nanostructured graphene on Ru(0001) can be covalently functionalized employing CH2CN• radicals [1], obtaining an extremely high yield and site-selectivity down to the atomic scale [2]. On the other hand, we also know that TCNQ molecules become radicals upon adsorption on gr/Ru(0001) due to a well known charge transfer process [3]. In this work we show that TCNQ molecules can react with the previously attached -CH2CN groups on gr/Ru(0001) forming a new C-C bond, in a chemical reaction promoted by graphene [4]. We study this reaction by means of Scanning Tunnelling Microscopy (STM) and Density Functional Theory (DFT). We also demonstrate that the whole process can be reversed using STM manipulation techniques.

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Figures

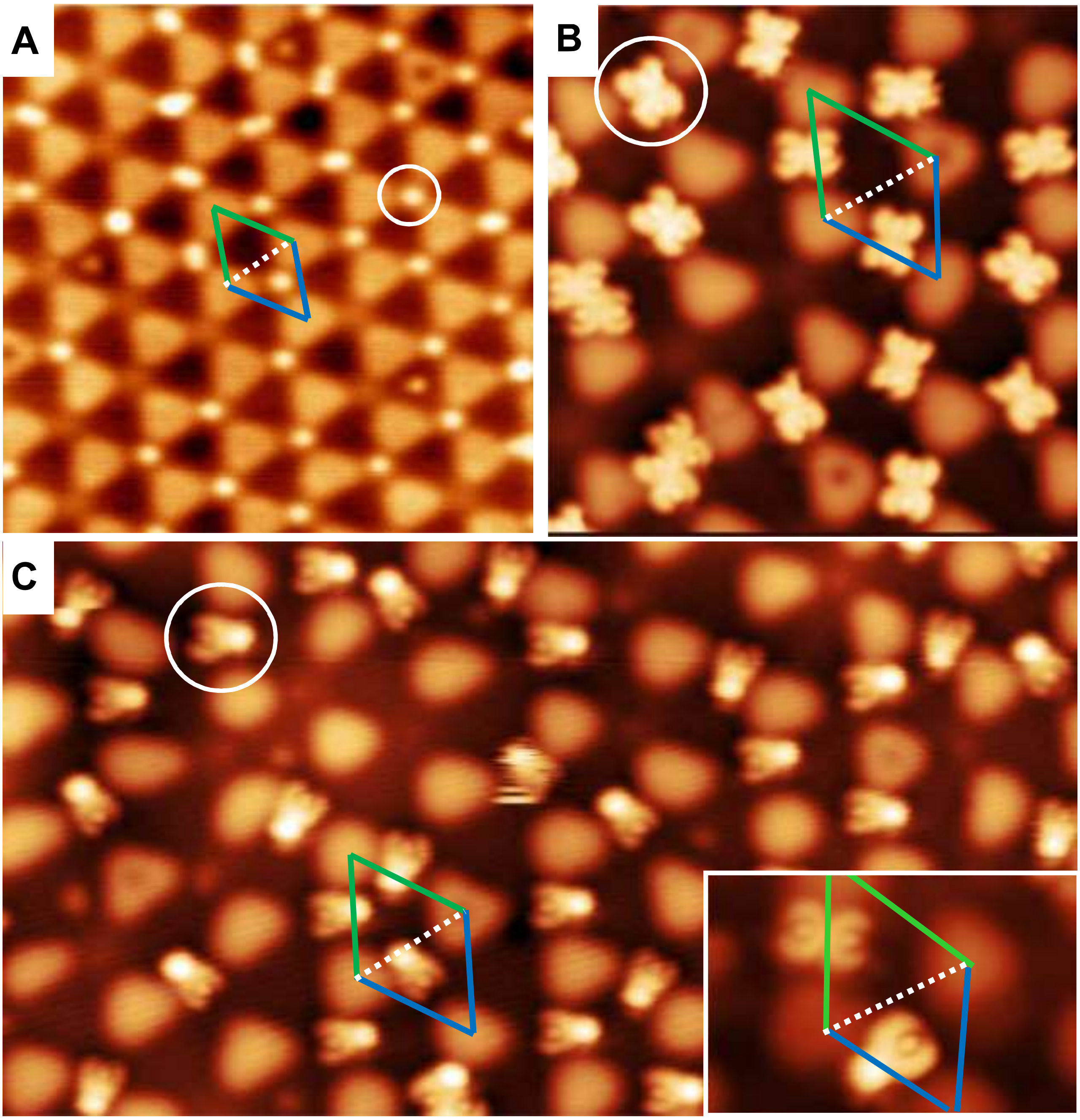

Figure 1: STM images of the gr/Ru(0001) surface functionalized with −CH2CN groups (panel A), covered by TCNQ molecules (panel B) and after the reaction between −CH2CN and TCNQ (panel C). The inset in panel C shows a small area containing a pristine TCNQ and a reacted one. In all cases the moiré cell of gr/Ru(0001) is indicated by the green-blue triangles.

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Strain engineering in 2D materials: towards strain tunable optoelectronic devices

Strain engineering is an interesting strategy to tune a material's electronic properties by subjecting its lattice to a mechanical deformation. Conventional straining approaches, used for 3D materials (including epitaxial growth on a substrate with a lattice parameter mis-match, the use of a dielectric capping layer or heavy ions implantation) are typically limited to strains lower than 2% in most cases due to the low maximum strains sustained by brittle bulk semiconducting materials. Bulk silicon, for example, can be strained only up to 1.5% before breaking. Moreover, these straining approaches induce static deformations of the semiconductor materials and therefore they are not suitable for tunable functional devices.

2D materials can be literally stretched, folded, bent or even pierced.[1] This outstanding stretchability (and the possibility of using dynamically varying strain) of 2D materials promises to revolutionize the field of strain engineering and could lead to "straintronic" devices – devices with electronic and optical properties that are engineered through the introduction of mechanical deformations.

In this talk I will discuss our recent efforts to study strain engineering in 2D materials and to exploit it to fabricate strain tunable functional optoelectronic devices.[2-6]

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Figures

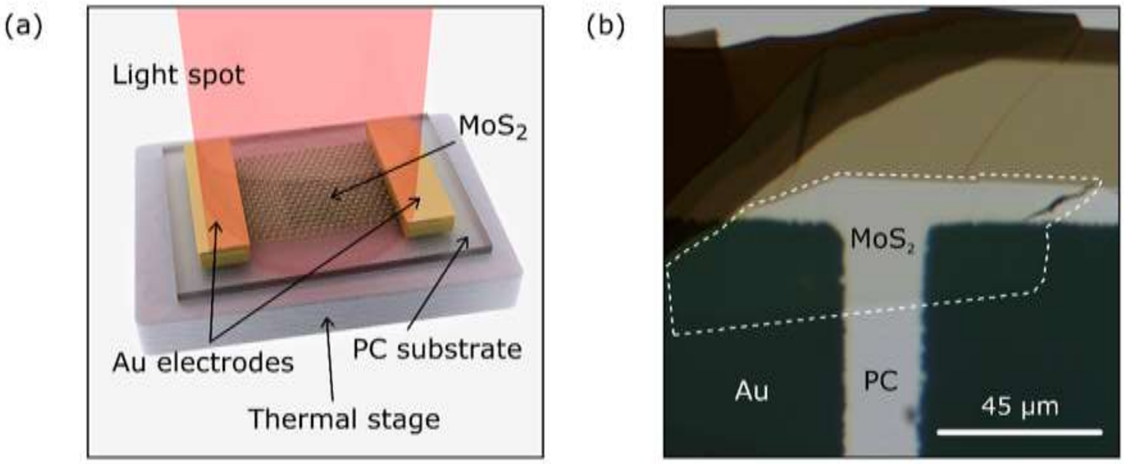

Figure 1: (a) Schematic picture of the setup used to perform all the measurements. The MoS2 photodetectors are placed on a thermal stage and illuminated from the top. (b) Optical transmission photograph of a single-layer MoS2 photodetectors fabricated on polycarbonate.

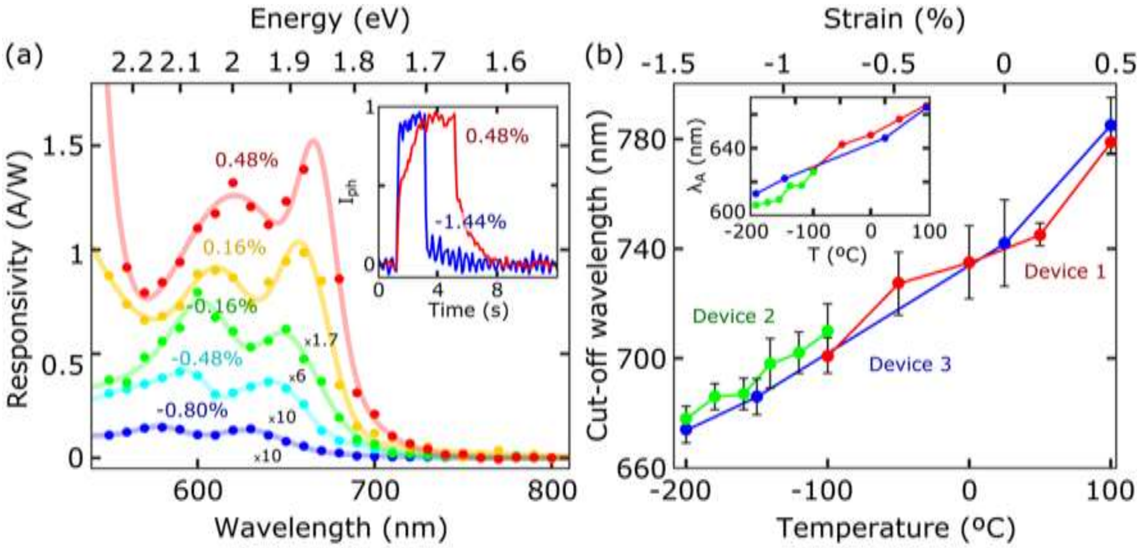

Figure 2: (a) Responsivity spectra of the single-layer MoS2 photodetector #1 obtained by measuring under 5 different strains applied (from -0.80% to 0.48%). Each dot corresponds to the value measured under light power of 8 mW/cm2 and applying a bias voltage of 10 V. Note that the responsivity values for +0.16%, -0.16%, -0.48% and -0.80% have been multiplied by 1.7, 6, 10 and 10 respectively to facilitate the comparison between the spectra. Inset: Response time for different strains applied. (b) Cut-off wavelengths extracted from the responsivity spectra of three single-layer MoS2 photodetectors (#1, #2 and #3) at different strain ranges. Inset: Exciton A wavelengths extracted from the same spectra.

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Two-dimensional materials for efficient halide Perovskite solar cells

Many factors can influence the efficiency and stability characteristics of halide Perovskite Solar Cells (PSCs). In particular, interfaces can influence layers deposition, charge recombinations and compound intermixing/diffusion, representing a critical aspect for scaling up activities aiming to exploit at industrial level perovskite photovoltaics. In this perspective, bidimensional (2D) nanomaterials, such as graphene and related materials can play a primary role owing to their 2D nature and the large variety of 2D crystals, whose complementary opto/electronic properties, can be on-demand tuned by chemical functionalization and edge modification. The so called Graphene Interface Engineering (GIE) has shown to be extremely effective in PSC technology both at lab cells (small area) level and at large area (module) level. We demonstrate the use of graphene and 2D materials as an effective way to control the morphology [1] and to improve stability and efficiency [2,3]. By dispersing graphene flakes into the mesoporous TiO2 layer and by inserting graphene oxide (GO) as interlayer between perovskite and Spiro-OMeTAD layers, we demonstrate a PCE exceeding 18% with a two-step MAPI deposition, carried out in air.[2] Further optimization of the 2D interface layers could promote the efficiency above 20%[4] with a strong improvement of the stability. The proposed approach has been exploited for the fabrication of state-of-the-art large area perovskite modules with a PCE of 13.7% (active area exceeding 100 cm2) paving the way to an industrialization phase compatible with standard fabrication processes [5]. In this respect, the Spear Head project “Solar Farm” of the Graphene Flagship will make use of the GIE for a pilot-line fabrication of Graphene-Perovskite modules to demonstrate the feasibility of the approach in the realization of PV panels..

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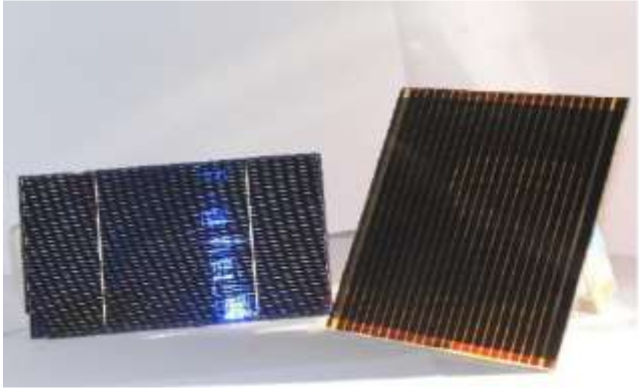

Figure 1: comparison between silicon solar cell (left) and graphene-perovskite solar module (right)

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International standardization: Pre-condition for graphene product conformity assessment

Since its discovery, graphene and other 2D materials have been subject of intense research activities. We saw an extremely high dynamic in peer-reviewed scientific publications on graphene-related technologies increasing from less than 1.000 publications in 2007 to more than 27.000 publications in 2017. In parallel also the number of graphene-related patents increased rapidly. In this talk another type of technical documentation is discussed: International documentary standards.

By its nature standards are not scientific publication as their functionality is not the communication of the latest results of research activities. Standard answers questions regarding characterization, definition and handling of technical items or processes in general which are important for their daily use in a commercial environment. The intension of a standard is to ensure that technical items and services are provided in the same quality from delivery to delivery. As standards are the result of a consensus process performed under involvement of technical experts from industry and academia worldwide, they reflect the state of the art at the time of the publication of the document. Part of the publication process is the setting of a stability date. Latest at the stability date the responsible technical committee reviews the content of the document and update it to include the technical progress achieved. This review process ensures that the standard again represents the new state of the art of the technology or service.

This talk will provide an overview regarding the current status of the international standardization process for graphene and other 2D materials: What are the concepts, who are the key players and what is the role of standards in quality assessment management systems and certification. This includes the technical work in IEC/TC 113 “Nanotechnology for electrotechnical products and systems” and the supporting activities founded by the EU Commission. It will be pointed out that especially the increasing interest on certification indicates that graphene technologies are continuously diffuse into the market.

Acknowledgement: Standardization activities for graphene are part of the project GRACE founded by the EMPIR program and co-financed by the participating states.

Figures

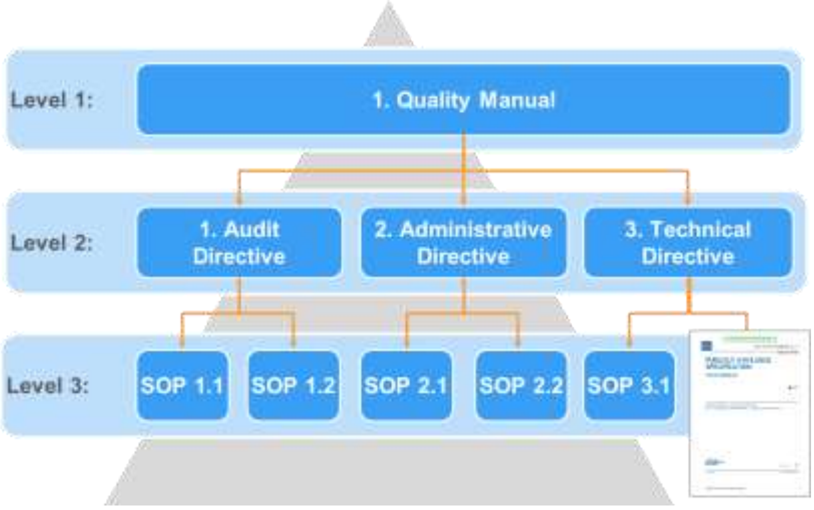

Figure 1: TQM based documentation for validation and certification of products and producers

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2DM@NGI, from research to innovation

National Graphene Institute (NGI) in Manchester is a platform for national and international collaborations on academic research in graphene and 2D materials and for collaborations between academia and businesses on the implementation of 2D materials in innovation. In this presentation, I introduce the facilities available at NGI and, then, overview the highlights of recent blue-sky research in 2D materials and implementation of graphene in innovation carried out by the Institute.

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Multifunctional thermoplastics using Graphene materials

The global market of thermoplastic was 242.7 million tons in 2015 and is expected to reach 296.7 million tons by 2020. This market was traditionally dominated by Europe, however in 2010, the main market is in China.
Compounding market size was estimated at 26.73 million tons in 2016. Growing substitution of metals & alloys with lightweight plastic counterparts. This market is still leader by Europe followed by North America.
Graphene materials can be used for the preparation for thermoplastic composites using 3 different techniques: insitu polymerization, solution blending and melt compounding (Figure 1). The best results for GRM-thermoplastic composites are based on the use of insitu polymerization and solution blending techniques,[1] however clear limitations in their industrial scale up and application.[2]
Melt compounding is the most used technique to produce thermoplastic composites. However, in the case of graphene materials it has some limitations such as the low retention and the discrete shear that can be applied, obtaining poor or discrete dispersion of the filler in the matrix.
Graphene materials (GRM) are a big family of materials with remarkable differences in morphology, dimensions, aspect ratio, surface chemistry, etc. An adequate selection of the GRM and processing technique is a key factor for achieves the desired properties. Also, and adequate nomenclature and standardized or industrial accepted characterization techniques are needed for the application and avoid lost of efforts and resources.
In this presentation we will compare the influence of the various graphene materials prepared by different methodologies, from LPE to oxidation/reduction, with variations in lateral size, dimension and surface chemistry and processing technologies for the preparation of composites in the final properties of the composites. Electrical and thermal conductivity, mechanical performance and fire retardancy results will be presented. Different strategies and results for the production of graphene-thermoplastic composites will be presented.

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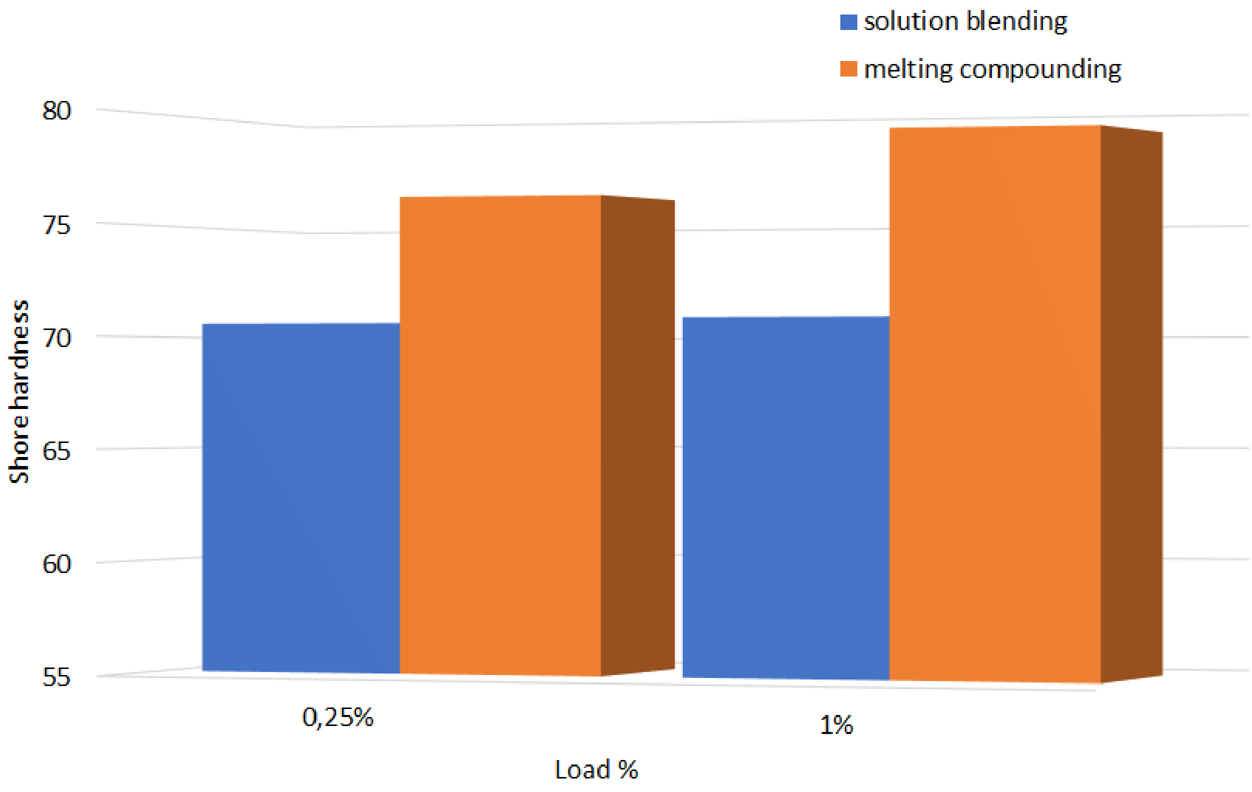

Figure 1: Shore hardness of TPU al different wt% and processing technique

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Graphene for Energy Storage in Supercapacitors

Energy applications of graphene abound. In our laboratory we have explored both electrochemical and thermal properties of graphene in nanofluids and as solid electrodes with emphasis on energy storage applications.
Electrochemical energy storage will be key to our ongoing transition to sustainable energy but is still far from optimal. That is why there is still plenty of room for new and novel types of materials in this trade. Graphene and its hybrids play an increasingly relevant role in this respect. In our laboratory we have researched hybrid materials and devices in order to improve power density of batteries and energy density of supercapacitors [1]
We have explored various approaches for the integration of electroactive species in graphene electrode materials for supercapacitors, both in the electrodes [2] and the electrolyte [3].
In addition to composition and microstructure, we will present also recent efforts to advance in the design of low-cost devices of the class needed for the upcoming low-power energy storage revolution [4] concerning flexible/wearable devices and some of our designs on paper [5].
Finally, we will also present some recent results concerning other novel nanocarbon materials also used as electrodes for energy storage devices, both on their own [6] or in combination with Graphenes[7] (Figure1) and will discuss novel approaches towards flowing electrode materials.

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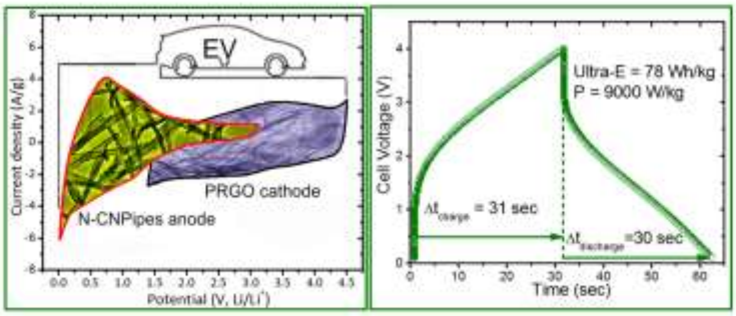

Figure 1: A hybrid device (Li-Ion Capacitor) formed by two different nanocarbon materials leading to high specific energy and power [7]

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Electrochemical Exfoliation of 2D Materials for Composite and Energy Applications

The electrochemical exfoliation of 2D materials can produce flakes with morphologies that are difficult to achieve using other exfoliation techniques [1]. We have exfoliated graphene and TMD flakes using both reductive and oxidative routes, with a range of electrolytes including molten salts, deep eutectic salts, organic and aqueous. Anodic exfoliation of graphite tends to produce material that is more oxidised, but the oxygen content can be reduced using metal salts [2] or by separating the intercalation and oxidation reactions [3]. Whilst cathodic exfoliation produces more "pristine" flakes albeit at slower rates and also gives the opportunity for in-situ functionalisation [4].

Energy storage and composites [5] are both very promising applications for graphene materials and the talk will discussion the design rules these applications, highlighting how the morphology [6] and hence production route of the material [7] is crucial in obtaining the best properties

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Benchmarking of Graphene-based Materials: Real Commercial Products vs. Ideal Graphene

There are tens of industrial producers claiming to sell graphene and related materials (GRM), mostly as solid powders. Recently the quality of commercial GRM has been questioned, and procedures for GRM quality control were suggested using Raman Spectroscopy or Atomic Force Microscopy [1]. Such techniques require dissolving the sample in solvents, possibly introducing artefacts.

A more pragmatic approach is needed, based on fast measurements and not requiring any assumption on GRM solubility. To this aim, we report here an overview of the properties of commercial GRM produced by selected companies in Europe, USA and Asia. We benchmark: A) size, B) exfoliation grade and C) oxidation grade of each GRM vs. the ones of "ideal" graphene and, most importantly, vs. what reported by the producer. In contrast to previous works, we report explicitly the names of the GRM producers and we do not re-dissolve the GRM in solvents, but only use techniques compatible with industrial powder metrology [2]. In previous work we have established an analysis procedure for XPS data that allows an accurate estimation of O/C ratio and of the % C-C sp^2 bonds [3]. A general common trend is observed: products having low defectivity (%sp^2 bonds >95%) feature low surface area (<200 m^2/g), while highly exfoliated GRM show a lower sp^2 content [3], demonstrating that it is still challenging to exfoliate GRM at industrial level without adding defects.

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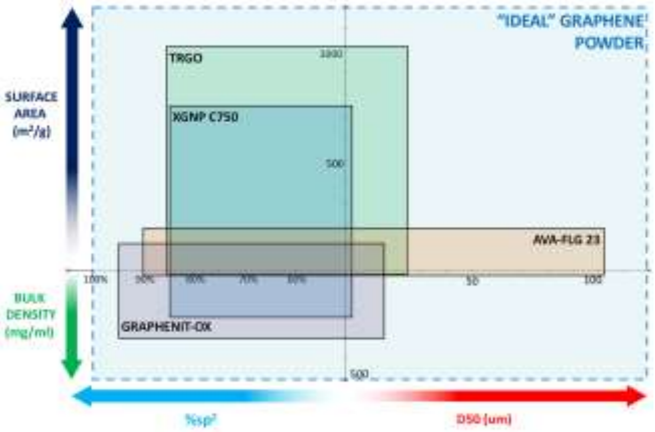

Figure 1: *Composite graph using four axes to represent the different key properties of some of the GRM studied. The positive and negative branches of X and Y axis indicate Lateral size, % of* sp^2*, specific surface area and density. Only selected GRM, with a high value in one or more of the selected properties, are shown for clarity. A large light-blue rectangle indicates the properties of an "ideal" graphene.*

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Integration of graphene into 200 mm CMOS technology

Graphene has attracted a lot of attention for its unique physical properties [1,2]. The high electron mobility together with its two-dimensional structure makes it attractive for high speed electronic devices. Despite the significant progress in the fabrication of various graphene based microelectronic devices, the integration of graphene devices still lack the stability and compatibility with Si-technology processes. In this paper, we present the attempts to integrate graphene into the CMOS line, where several graphene concepts have been realized in 200mm silicon technology platform. We investigated different process module developments such as graphene synthesis on silicon compatible materials like germanium, a non-destructive deposition of dielectric materials on the graphene sheet as well as the combinations of these processes for various concepts of contacting on a full 200 mm wafers (Fig.1.)

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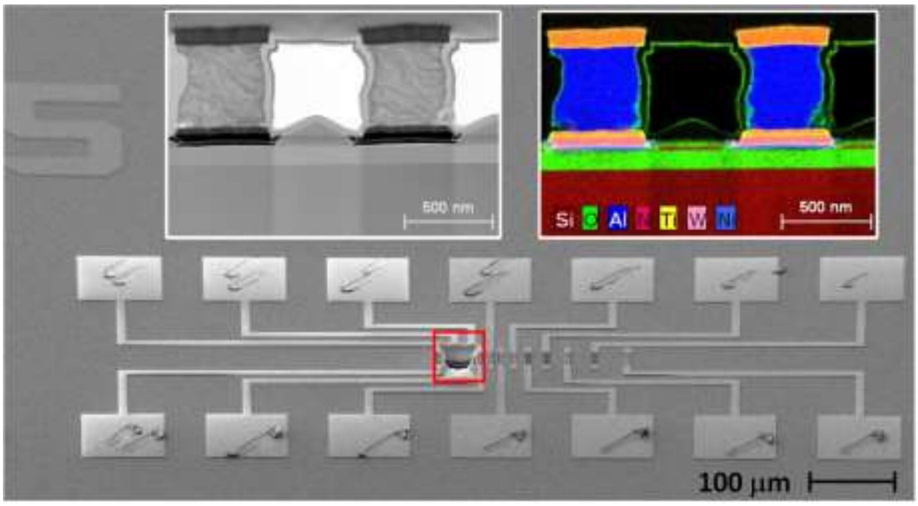

Figure 1: Tilted SEM view of a TLM device with graphene. STEM (inset left) and EDX (inset right) analysis.

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Graphene Related Materials enhancing polymer composites: An application to aerospace structures

Nowadays carbon fibre reinforced epoxy laminates represent the standard material in the designing and manufacturing of aeronautical composite structures. However, advantages related to metals manufacturing could represent an important menace for the role of composite materials in this industry. Therefore, new improvements in composite structures have to be seek in order to improve their competitiveness.

Despite of the high stiffness and strength-to-weight ratio of carbon fibre reinforced epoxy laminates, they are quite vulnerable to impact loading. Hail impacts, bird strike or even tool drops could produce important damages that reduce residual strength of the material. On the other hand, an important disadvantage of this kind of composites is the high cost of manufacturing, related to fiber preimpregnation and autoclave curing. Alternative manufacturing technologies such as Resin Transfer Molding (RTM) could represent a significant advantage due to their lower cost, although some properties of the laminates produced are lower than those of composites obtained by autoclave manufacturing.

Graphene is a nanomaterial that possess the higher stiffness and strength ever measured [1]. Therefore, the use of Graphene Related Material (GRM) for enhancing composite laminate materials could represent an important advance in order to reduce their impact vulnerability and to improve the performance of RTM composites.

In this work epoxy resin doped with GRM were used to manufacture carbon fiber aeronautical composites by RTM. A wide experimental characterization campaign was performed in order to ascertain the impact properties improvement of the laminates produced. Coupons manufactured without carbon fibre reinforcement were tested by quasistatic and high strain rate (Split Hopkinson Pressure Bar) experimental methodologies to evaluate the GRM performance. Concerning laminates, Double Cantilever Beam (DCB), low velocity impacts and Compression After Impact (CAI) tests were performed. Regarding experimental methodology, ASTM and AITM standard were followed, also new measuring techniques were used as 3D High Speed Digital Image Correlations. All tests were performed on GRM enhanced material and reference material to compare their results. One of the most promising results obtained is showed in Figure 1, where it can be seen that GRM enhanced material is able to increase CAI strength in 12%. This challenge entails the possibility to improve current aerostructure performances without significant changes either in their design or manufacturing process.

This research is supported by the H2020 program “Graphene Flagship” Project: Core 1 and Core 2 phases.

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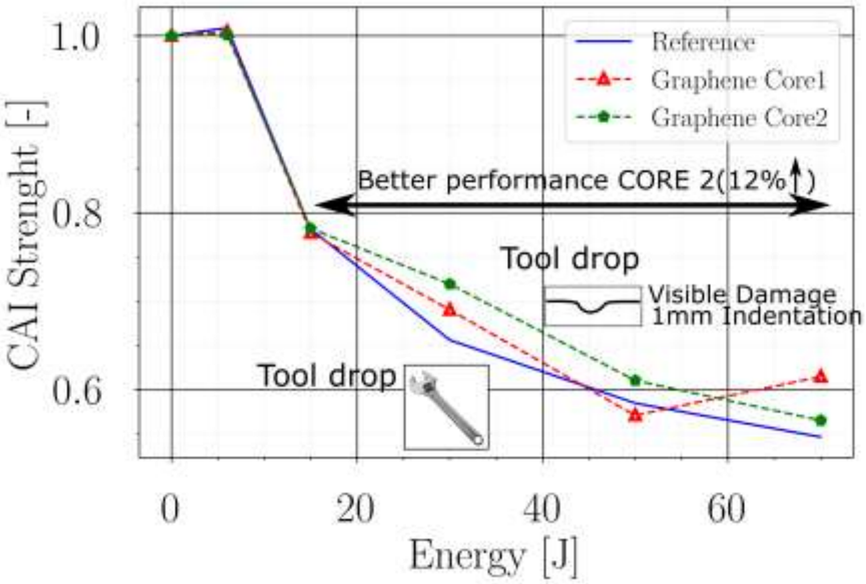

Figure 1: CAI strength of aerostructural composite RTM laminates: GRM-reinforced and reference composite.

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Nanoporous graphene for optoelectronics and molecular sensing and sieving applications

Nanosize pores can turn semimetallic graphene into a semiconductor [1, 2] and from being impermeable into the most efficient molecular sieve membrane [3, 4]. However, scaling the pores down to the nanometer, while fulfilling the tight structural constraints imposed by applications, represents an enormous challenge for present top-down strategies.

Here we report a bottom-up method to synthesize nanoporous graphene comprising an ordered array of pores separated by ribbons, which can be tuned down to the one nanometer range [5]. The size, density, morphology and chemical composition of the pores are defined with atomic precision by the design of the molecular precursors. Interestingly, the hierarchical synthetic method also enables the generation of arrays of decoupled nanoribbons with tunable periodicity [6].

Our study reveals a highly anisotropic electronic structure in the nanoporous structure, where orthogonal one-dimensional electronic bands with an energy gap of ~1 eV coexist with confined pore states that might sense passing ions and molecules. The semiconducting character of the nanomaterial has been further confirmed by fabricating field-effect transistors with state of art on/off ratios. The combined structural and electrical properties makes this nanoporous 2D material a highly versatile semiconductor for simultaneous sieving and electrical sensing of molecular species.

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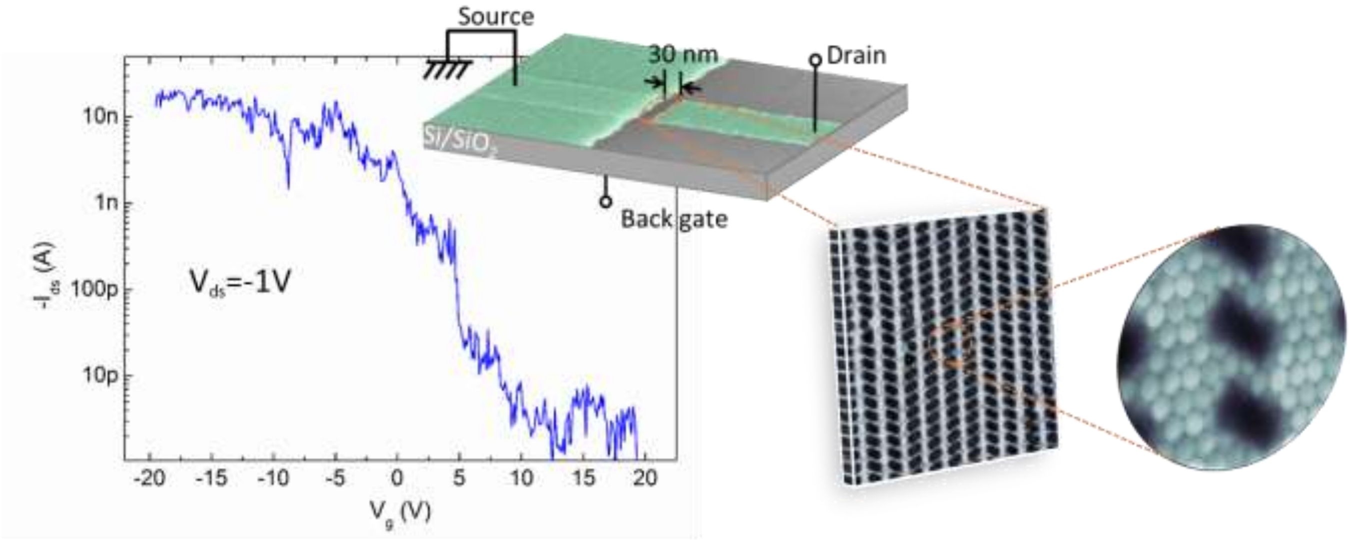

Figure 1: I_{ds}-V_G characteristics of a field-effect transistor fabricated with nanoporous graphene sheets synthesized with our bottom-up method.

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Graphene Technology: synthesis, characterization and reliability-driven technological device integration

Graphene fascinating properties hold promises for a great technological impact [1]. Nevertheless, to allow for a real exploiting of their extraordinary properties, a complete control of the fabrication steps of graphene-based devices is mandatory. In this contribution we will show an integrated approach for the integration of graphene membranes in state-of-the-art technological processes and for the exploitation of their properties in an applicative framework.

Our approach starts from the careful control of the synthesis parameters of the CVD growth of graphene membranes, as well as of their structural and functional properties. It moves then to the definition of tailored transfer processes leading to the integration of graphene membranes in a wide class of functional substrates (technological surfaces, glass, plastic and polymeric flexible substrates), as well as of their surface functionalization, to provide the control of physical and chemical properties over large area, typically mandatory in the device's fabrication processes. [2-5].

Final step is the definition of the complete set of technological processing steps needed to achieve a full integrability of the membranes within the processes of fabrication of micromachined devices. To this aim, since the integration of graphene hybrid devices in silicon CMOS requires high reliability and yield, the full development is supported by the Design for Reliability approach which will address graphene-based electronic devices to really enter the market in the near future, with the maturity level requested by IC technology. More in detail, this is achieved through three main blocks: 1) definition of the requirements for large-scale graphene integration; 2) identification of critical graphene processes for the integration and their optimization; 3) identification of measurement methodologies, standards, data and models for the development of a reliable fabrication process, an accurate process control and the optimization of the processes.

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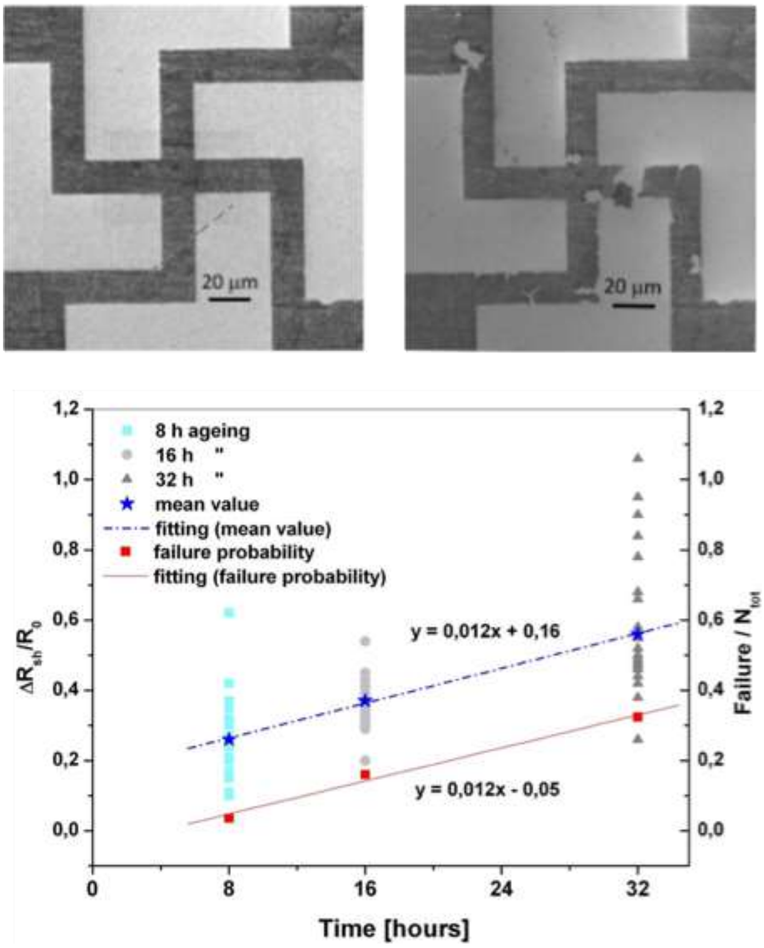

Figure 1: Reliability-driven graphene integration in Si Technology

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Broadband Graphene Photodetectors for Monitoring Personal Wellbeing

Sensors for ubiquitous sensing purposes should be low-cost, invisible and seamlessly integrable with many different surfaces such as bendable plastic, textiles and glass. Graphene based light sensors [1,2] are inherently flexible and transparent and can be integrated with low-cost CMOS technology [3], hence providing a disruptive platform for future wearables and vision devices.

We will show a prototype non-invasive wellness monitor based on graphene-colloidal quantum dot hybrid photo detectors. We leveraged graphene's flexible and transparent properties to create a wearable device that is conformal to the human body so that it can reliably extract vital signs such as heart rate, breathing rate and oxygen saturation. We demonstrated wireless communication between the photodetectors and a smartphone, offering battery-free operation by employing heterogeneous integration of a flexible ultraviolet (UV) sensitive photodetector with a near field communication (NFC) circuit board.

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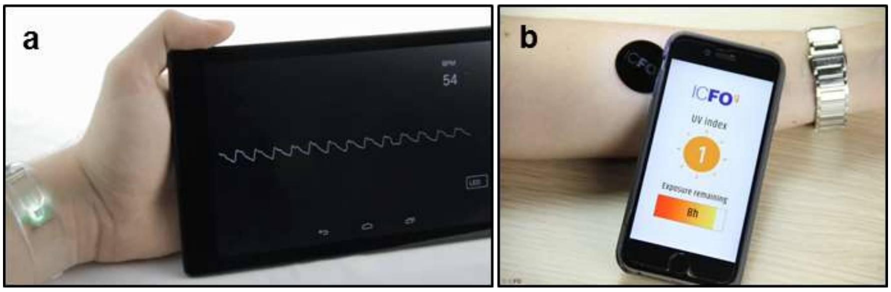

Figure 1: (a) Graphene based flexible and transparent wellness sensing platform.(b) Battery-less UV monitor powered via NFC communication.

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Graphene-enabled terahertz applications

The teraherz (THz) range of the electromagnetic spectrum is technologically relevant for many application fields, such as sensing, security and medicine, as well as for potential future applications such as ultrafast wireless communication. However, currently no THz detectors are available that operate at room temperature, have good sensitivity, are sensitive to a broad range of THz frequencies, and have a short response time. Recently, we have developed a graphene-based THz detector that meets all these requirements simultaneously in a single device [1]. In particular, we find a noise-equivalent power (NEP) below 200 pW/Hz$^{1/2}$, and a response time below 40 ns (setup-limited), which could be as short as 10 ps (RC-time-limited). These device specifications go well beyond the current state of the art.

Our device contains a high-quality, hexagonal BN-encapsulated graphene channel with source and drain contacts, combined with a capacitively coupled dipolar THz antenna with a very narrow gap. In our approach, we exploit the photo-thermoelectric effect, where absorbed light incident on a junction between a p-doped region and an n-doped region of the graphene channel leads to an increase in the temperature of the charge carrier distribution in graphene, subsequently creating a photoresponse [2]. As an essential ingredient for the detector, we note that low-energy THz photons lead to efficient heating, as we have shown earlier [3]. Importantly, our THz photodetector device operates without bias voltage, leading to zero dark current, low noise (governed by Johnson noise), and low power consumption. We expect that this graphene-enabled THz detector will find applications in thickness measurements for industrial quality control (through time-of-flight measurements) and in novel spectroscopic tools.

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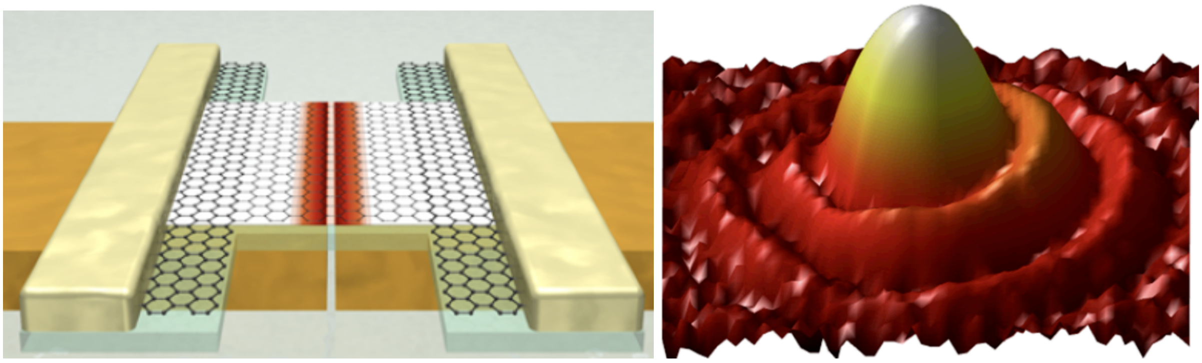

Figure 1: Schematic overview of the ultra-sensitive, ultrafast THz detector based on graphene (left). Typical photocurrent mapping of a THz focus (right) by scanning the device in the THz focus plane. The observation of Airy rings illustrates the high sensitivity of the device.

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Graphene-enhanced elastomers and their applications

Elastomers, particularly natural rubber, are widely used in applications such as tires, gloves, clothing, medical devices, etc. Elastomers, as the name suggests, are characterised by extremely high elasticity, often combined with moderately high strength. However, the composition and chemistry of commercial rubbers has remained more or less unchanged for decades.

We demonstrate that the mechanical properties of elastomers can be improved by the incorporation of graphene fillers. Elastomers are compounded either an aqueous formulation called a latex, or as a solid. In order to maximise the impact on mechanical properties by the addition of a small volume fraction of graphene, it is essential to ensure uniform dispersion of the graphene flakes in the elastomer matrix. Upon optimisation, it is possible to improve an elastomer by making it simultaneously 50% stronger, 50% more elastic and 50% more hard wearing.

A graphene-modified elastomer can then be formed into a number of shapes using, most popularly, dip-moulding of latex or compression moulding of solid rubber. I will discuss the fabrication and testing of dip-moulded elastomer-graphene composite products [1] such as condoms and gloves, as well as compression moulded products such as shoe soles [2].

Lastly, I will present the specific case of athletic footwear, where the rubber-graphene composite gives markedly improved grip on tough terrains while simultaneously improving durability. The graphene-enhanced athletic shoes from Inov-8 Ltd. have been available for purchase, worldwide, since July 2018.

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Figures

Figure 1: (a) Dip-molded graphene-elastomer thin film samples with increasing graphene content ((Left to right). (b) Graphene-rubber composite sole footwear (Inov-8 Ltd.).

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Towards Standardization of Graphene Oxide for Industrial Applications

Abstract

After more than 160 years existence, graphene oxide is now finding use in real industrial processes. First process out is corrosion protection of auto-parts, now being produced by the Swedish company Provexa AB. Other processes in line are production of load-speaker membranes, corrosion protection of PCBs, welding paste for electronic components and additive to polymers. There are also a range of additional promising technologies being developed like stabilizing agent in LiS-batteries, water treatment and sports equipment.

Industry has certain requirements that researchers in R&D-labs do not consider in their everyday lab-scale research. To start up an industrial process, large investments are required, and reliable supply of all the ingredients or components must be in place. Also, reproducible quality is fundamentally essential, as well as predictable and affordable costs. Up to now, graphene oxide has not been readily available in the market other than in small amounts from a range of suppliers each with their own version of GO. In Abalonyx, we have in the last 7 years focused on scale-up of GO and we now have a scalable, safe and cheap process established and verified, so we are in a position that we can sign supply-agreements with industry. It is our hope that this will encourage more industries to dare to invest in the use of this unique material.

Finally, graphene oxide is not only "graphene oxide". It can be modified in a number of ways, by functionalization, doping, partly and fully reduction to graphene-like rGO. Furthermore it can be prepared with larger and smaller sheet-size and it can be more or less oxidized and it can be de-acidified to different degrees and all these varieties can be pillared. All these possibilities should be considered in order to optimize GO for any final application. At Abalonyx we work with all these modifications in different R&D-projects which will be reviewed.

Figures

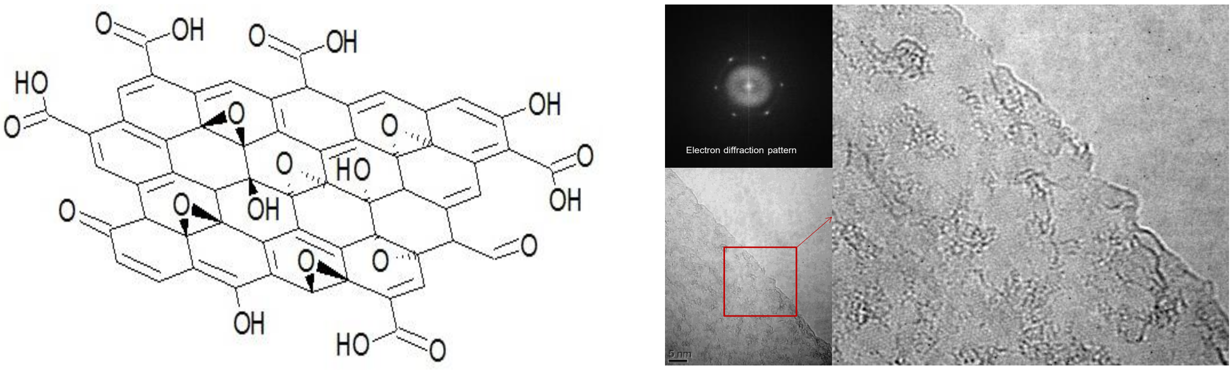

Figure 1: a) schematic illustration of the graphene oxide, and b) TEM-image with electron diffraction insert showing a single layer og GO, and TEM image clearly showing the peculiar structures with oxidized and no-oxidized regions.

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Improved control in elimination of white impurities on graphene by chemical vapor deposition(CVD)

Abstract (Arial Narrow 12)
Chemical vapor deposition (CVD) is one of the most preferred technique of graphene fabrication. However, it still faces some challenges, such as contamination with white particulate impurities which occurs commonly when furnaces with quartz tubes are used in the process. In this work, the source of contamination on copper substrates was traced and tackled in three stages of the graphene fabrication process. The cleaning, annealing, and finally the fabrication stage was studied. No evidence was found to support that copper foil or cleaning tools were sources of the contamination. XPS, EDS and XRD results reveal that the white impurities are silicates, formed due to the phase transition of quartz at elevated temperatures in presence of copper vapor and oxygen gas. It was evident that due to the appearance of this contamination, quartz tubes are not ideal for use in graphene synthesis. However, if unavoidable this study proposes a special substrate configuration which has been found to suppress the contamination during fabrication.

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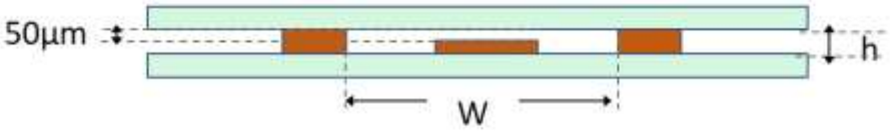

Figure 1: Configuration of copper substrates in RTP furnace. (a) Totally uncovered. (b) sandwiched with 25 μm free space over.

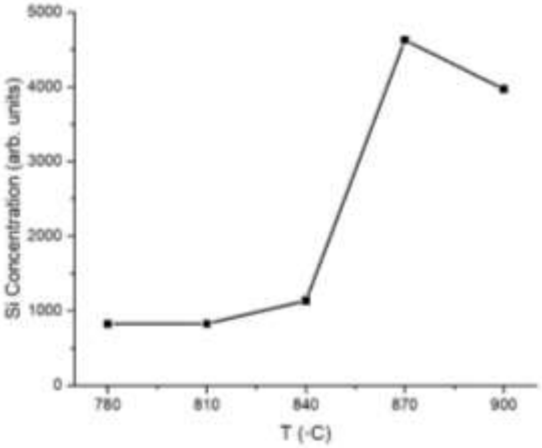

Figure 2: XPS Silicon concentration at different temperatures and in absence of hydrogen gas flow, and constant argon flow.

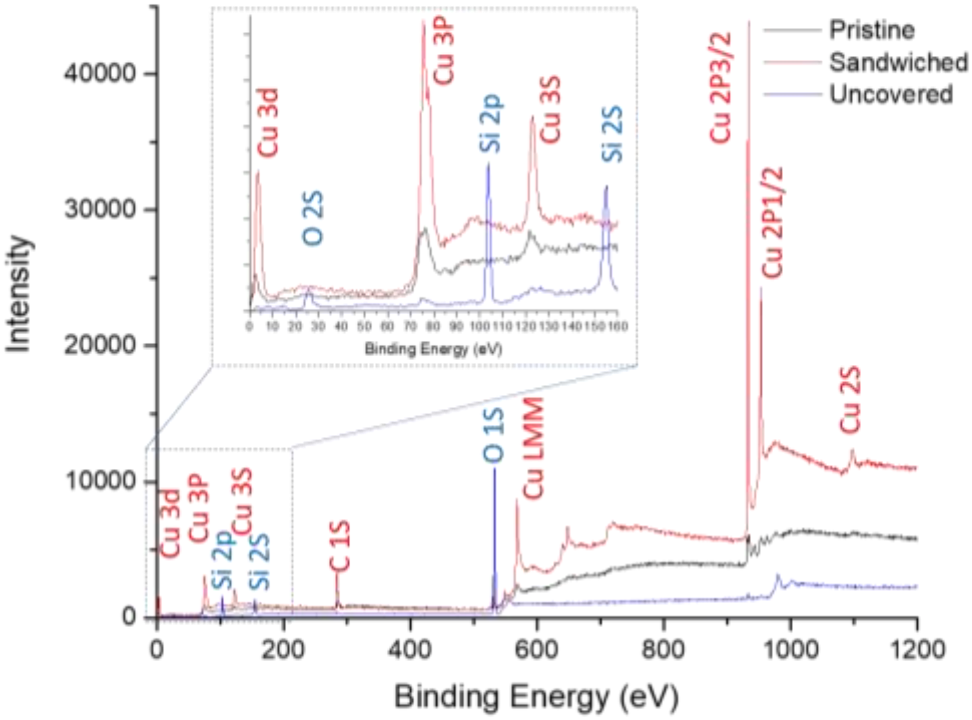

Figure 3: XPS spectra (a) XPS survey spectra for the pristine, sandwiched and un-sheltered sample.

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Interaction and reactivity of cisplatin physisorbed on graphene oxide prototypes

The physical adsorption of cisplatin (CP)[1] on graphene oxide (GO) and reduced graphene oxide (rGO) is investigated at the DFT level of theory by exploiting suitable molecular prototypes[2] representing the most probable adsorbing regions of GO and rGO platelets. The obtained results show that CP is preferentially adsorbed in correspondance of the epoxy and hydroxy groups (see Figure 1) and an energy decomposition analysis of the related binding energy reveals that the most attractive contribution comes from the electrostatic attraction between the -NH_3 ends of CP and the oxygen groups on the (r)GO basal plane. Moreover, it is found that the reactivity of the physically adsorbed CP is practically unaltered being the free energy variation related to the first hydration reaction almost matching that of its free (unadsorbed drug) counterpart[3]. The reported results suggest that overall the CP physical adsorption on GO and rGO carriers is feasible being an exergonic process in an aqueous medium. The CP adsorption could facilitate its solubility and transport in water solutions, exploiting the high hydrophilicity of the peripheral carboxylic acid groups located on the edge of the GO and rGO platelets.

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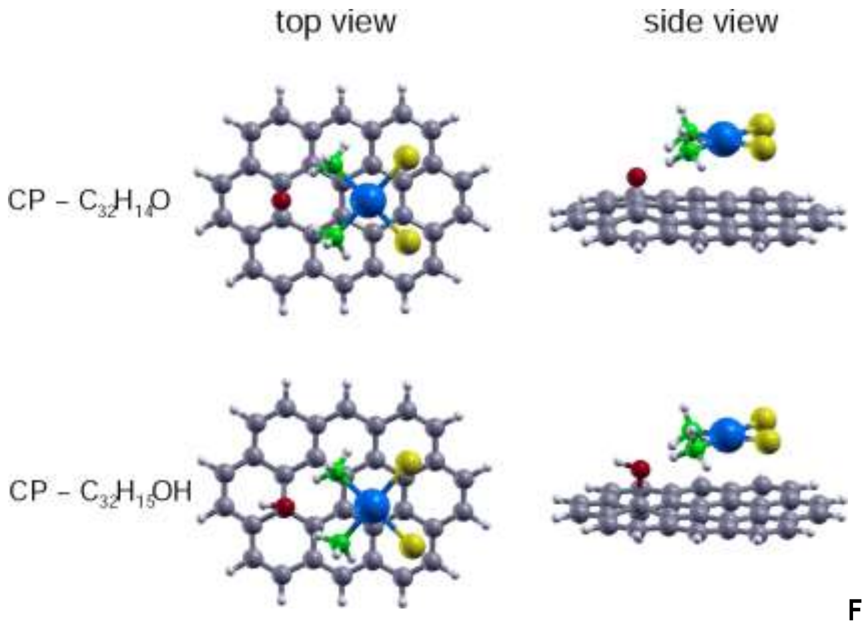

Figure 1: Top and side views of optimal molecular structures for CP physically adsorbed on (r)GO platelet prototypes.

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A cooperative multi-proton mechanism for proton permeation in graphene

It has been recently experimentally shown that the rule of impermeability of pristine graphene and some other 2D materials, to any kind of atom or molecule at room temperature is not fulfilled in the case of protons and their isotope deuterium[1,2]. These charged species permeate through the 2D material following a low barrier (~0.8 eV) activated process. Most of the theoretical attempts to provide with a reasonable explanation have found that permeation of the H^+ (D^+) involves large energy barriers (around 3.5 eV) and are therefore too high to explain the experimental findings[3]. In most previous models it was assumed an isolated proton permeating the 2D membrane. In this work however, we consider protonated graphene at high local coverage and explore the role played by nearby chemisorbed protons in the permeation process. By using density functional theory calculations applied to large molecular prototypes for graphene we have found[4] that when various protons are adsorbed on carbons belonging to the same hexagonal ring, permeation barrier can be lowered down to 1.0 eV, thus making feasible the permeation of protons through pristine graphene. The proposed insertion mechanism necessarily need to count with the nearby protons and it could be of relevance not only to help in the understanding of experiments from ref.[1,2], but also in many other scenarios.

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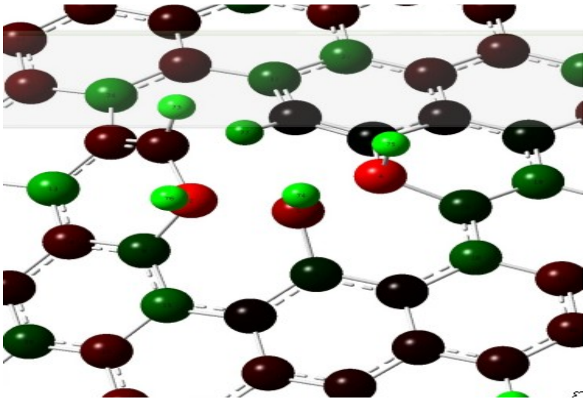

Figure 1: Transition state (TS) for proton fliping in the cooperative multiproton mechanism.

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"Graphene and 2D Materials" EUREKA Cluster: Fostering European Competitiveness

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.

Graphene has a huge potential to impact established industrial sectors, building new emerging industries and niche segments and creating economic value. The "Graphene and 2D Materials" Strategic Research Agenda currently targets 7 interlinked priority R&D areas for Europe. These areas are (1) Standardization, (2) Production and Scalability, (3) Composites, (4) Energy, (5) Biosensors and Health, (6) Optoelectronics and Electronic Devices; (7) Functional coatings. Currently, 248 Institutions from 27 countries (among them 158 companies) expressed interest in joining the Cluster.

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Tuning properties of thermally reduced graphene oxide for CO_2 capture technology

Thermal exfoliation is believed to be a promising approach for the mass production of graphene that minimizes processing time. Another advantage is that the exfoliation and reduction can be achieved simultaneously without the introduction of impurities in thermal exfoliation.

CO_2 capture process represents typically about 70% of the total cost of the carbon capture and storage (CCS) chain. One of the most promising technologies for CO2 capture is based on the adsorption process using solid sorbents. As a member of this family, the metal–organic frameworks (MOFs) are well recognized for their extraordinary surface area, ultrahigh porosity, and most importantly the flexibility to tune the porous structure as well as the surface functionality. For more efficient utilization of MOFs sorbents, several hybrid systems based on MOFs with other solid sorbents have been investigated in order to utilize the synergism between the two sorbents and therefore ultimately improve the overall performance in CO_2 separation. Moreover, sorbents such as activated carbons, reduced graphene oxide (rGO) and Carbon nanotubes (CNTs) provide the added feature of high surface area and easily functionalized sites, which contribute to the tuning of the final properties of the composite material. The rGO is an important carbonaceous functional materials that has attracted considerable attention owing to its high aspect ratio, high mechanical strength, unique electrical properties, and chemical stability.

Abalonyx is a partner of a Horizon 2020 project entitled “CARMOF” in which aims to combine the advantage of physical and chemical adsorbents in a hybrid structures composed by functionalized MOFs, and rGO for CO_2 capture[1].

In this work, we present some parts of the results obtained for synthesis of rGO through thermal heat treatment. The thermal heat treatment in this work has been performed with two different strategies: in the first one, the GO samples were heated at different temperature for different soaking times. In the second approach, as reduced GO (rGO) was annealed at 800 °C and 1000 °C for 1hr under the vacuum. Indeed, the second approach combines an initial flash pyrolysis of GO at lower temperatures and a subsequent ramp-heating treatment (annealing) up to the selected final temperature (800 °C and 1000 °C). The results of characterizations obtained for annealed rGO and heat treated GO, have been compared and discussed.

References

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Figures

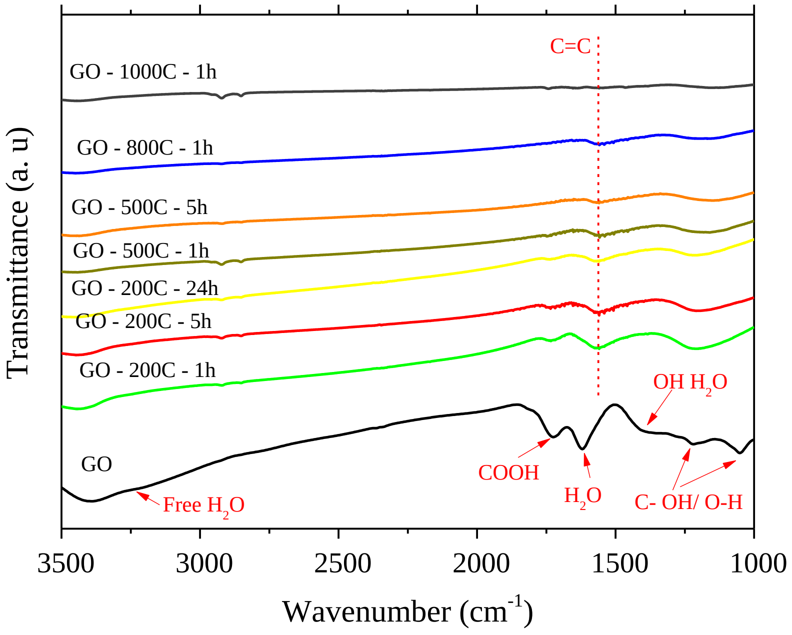

Figure 1: FTIR spectra for as received GO and heat treated GO at different conditions.

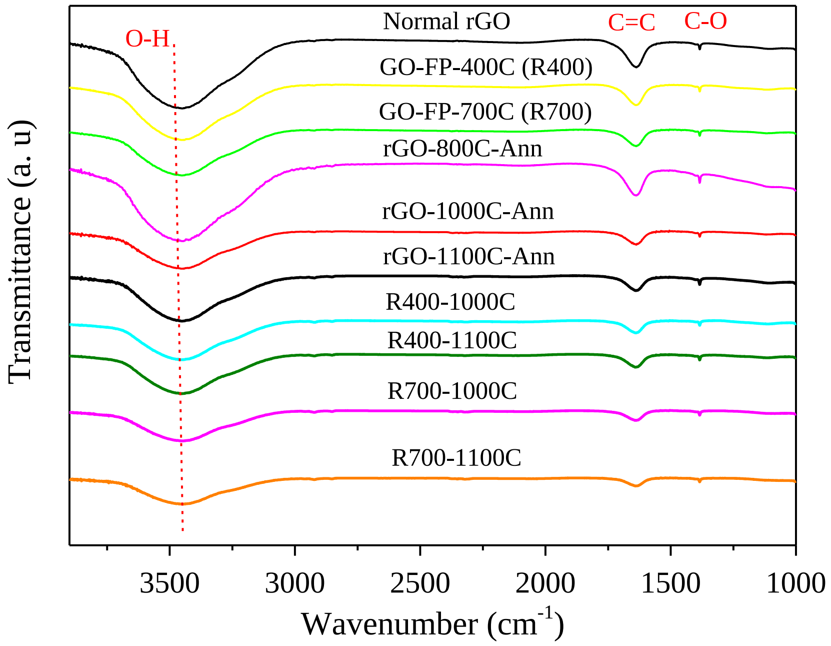

Figure 2: FTIR spectra for Normal rGO, annealed rGO at 800°C and 1000°C and Flash Pyrolysis (FP) GO at 400°C and 700°C .

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3D rGO CATHODES COMBINED WITH BUCKYPAPER INTERLAYER FOR MORE EFFICIENT Li-S BATTERIES

Lithium–sulfur batteries have become an attractive candidate for the new generation of high-performance batteries due to their high theoretical capacity (1675 mA h g−1) and specific energy (~2600 Wh kg−1) overcompensating its low operation potential around 2V [1],[2], . Although the theoretical specific energy values of the Li-S, outperform Li-ion batteries, in practice there are many drawbacks that mean that, nowadays, the energy densities obtained are lower than expected. These issues are due to i) the insulating nature of sulphur, ii) the shuttle effect caused by the solubility of the intermediate polysulfides, iii) the volumetric change taking part in the cathode during cycling and iv) the need to protect the Li anode due to safety considerations [3].

In the present work, we present the development of cathodes for Li-S batteries based on 3D rGO structures to increase the S loading and incorporating a MWCNT buckypaper interlayer to suppress the polysulfide shuttle. The MWCNT interlayer is a low weight sheet consisting of entangled carbon nanotubes that has been manufactured in a continuous mode on a pilot plant designed and developed by Tecnalia.

The buckypaper pilot plant can produce continuous filtered films (MWCNTs only or with selected carrier membranes) with current processing capacities up to 1000 m^2 per year. This plant is part of the e-Platform joint venture that provides industrial access to nano-enabled advanced composites services and products. The facilities are unique in Europe as they enable the scaling of the manufacture of buckypapers from the laboratory scale to a semi-industrial production.

The results of the batteries when the BP interlayer is employed combined with the 3D rGO cathode show specific discharge capacities up to 671 $mAhg^{-1}$ and areal capacities of 2 $mAhcm^{-2}$ at 1C after 200 charge/discharge cycles.

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The Future of Graphene Commercialization

The evolution of graphene, from its original isolation in 2004, through the establishment of major government programs to advance research (such as the EU's one billion Euro and ten year Graphene Flagship initiative), to the most recent creation of the Graphene Engineering and Innovation Centre (GEIC) at the University of Manchester in the UK has reached a critical pivot point.

Today there are more than 150 identifiable graphene producing companies worldwide with many times that amount declared in mainland China. More importantly, major industrial companies have begun to incorporate graphene-enhanced materials in their products. One of the most visible and high profile of these is the inclusion of graphene enhanced polyurethane parts in the Ford automobile company's Mustang and Ford 150 production cars and trucks. The addition of small amounts of graphene in the material matrix resulted in greatly improved thermal transfer as well as a reduction in vibration and noise.

This presentation will provide an overview of the main forms of graphene commercially available today (CVD single layer graphene, multilayer GNP's, graphene oxides, etc.) and the more than 40 major vertical application markets that have been identified to date (plastics, electronics, composites, structural materials, etc.)

The content presented is based on the day to day interaction of The Graphene Council with its more than 20,000 individual material science and Corporate members, as well as original research, specifically a survey of more than 350 graphene producers, application developers and end users regarding the types of graphene they are using for specific applications and to obtain well defined performance improvement.

The Graphene Council is the leading community in the world for graphene professionals and is an Affiliate member of the Graphene Engineering and Innovation Centre (GEIC) at the University of Manchester in the UK. The mission of The Graphene Council is to advance th commercial adoption of graphene materials globally.

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Toward Controllable Growth of Millimeter-Size CVD Graphene Single Crystals and Its Application in 2D van der Waals Heterostructure Based Photodetector

In conventional chemical vapor deposition process, as-grown large-area graphene films on catalytic metal foils are regarded as coalescence of many small graphene grains with lateral size of less than 50 μm. The dense graphene grain boundaries would introduce severe electron/hole scattering, which degrades physical properties of graphene, such as carrier mobility, therefore retarding graphene-related applications. Through nucleation density control in height-confined graphite reaction cavity, the high-quality millimeter-scale graphene single crystals can be synthesized using commercial chemical vapor deposition equipment.

The graphite reaction cavity is able to mimic the Cu enclosed configuration [1], which can suppress Cu sublimation, therefore reducing roughness of Cu substrates. In addition, the sublimated Cu is trapped in graphite reaction cavity, where the Cu vapor-rich surroundings can appropriately boost the growth rate. Inside the graphite reaction cavity, a height-confined sapphire slit is designed for the insertion of the growth substrate, which can consecutively provide trace amount of oxygen to oxidized the Cu substrate. The formation of copper oxide can block the pathway of graphene growth [2], i.e. the graphene nucleation is restrained. Therefore, through adjusting the height of the sapphire slit as well as ex situ pre-oxidation of Cu substrates, the oxygen concentration near the Cu surface can be controlled, implying the control of graphene nucleation density. Figure 1(c) and (d) shows the size of graphene single crystals is up to millimeter scale before coalescence.

The as-grown millimeter-size graphene single crystals is then transferred by low average molecular weight (AMW) PMMA, which is an optimized supporting layer developed for the low-residue transfer of CVD graphene. Compared with the long-chained PMMA, the graphene sample transferred by low AMW PMMA suffers less p-type doping and contamination. Through X-ray photoelectron spectroscopic analysis in Figure 2, the binding energy intensities of C–C, O–CH3, and O–C=O components confirm the extensive reduction of the residue using low AMW PMMA, which can serve as a promising supporting layer for the transfer of graphene and other two-dimensional (2D) layered materials.

The high-quality large graphene single crystals and well-developed low residue transfer method can be applied in 2D van der Waals heterostructure based photodetectors. In Figure 3, $ReSe_2$ based photodetector is presented. $ReSe_2$ is a promising transition-metal dichalcogenide (TMDC), which has a weakly layer-dependent bandgap (it increases from 1.29 eV to 1.31 eV when passing from bulk to atomically thick layers) but a high photo-responsivity when in few-layer form [4]. Here, the as-fabricated 2D few-layer $ReSe_2$-based photodetector with high photosensitivity (~106 photo-to-dark conductivity ratio, see Figure 3(c)) and fast switching time is reposted. The device has a planar architecture based on high-quality CVD-grown 2D materials that are van der Waals stacked.

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Figures

Figure 1: (a) Graphene grown by conventional CVD method. (b) Cu surface pre-treatment in $FeCl_3$/HCl solution. About 600 nuclei/cm2 can be achieved. (c) Large graphene single crystals through a height-confined graphite reaction cavity (d) As-transferred millimeter size graphene single crystal.

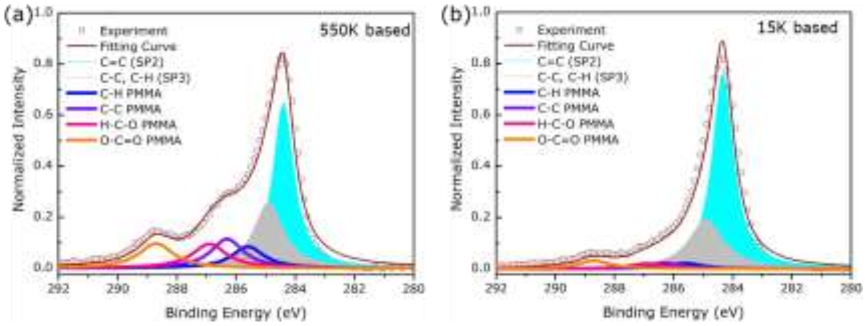

Figure 2: The XPS results of graphene samples transferred by (a) 550K and (b)15K-based PMMA.

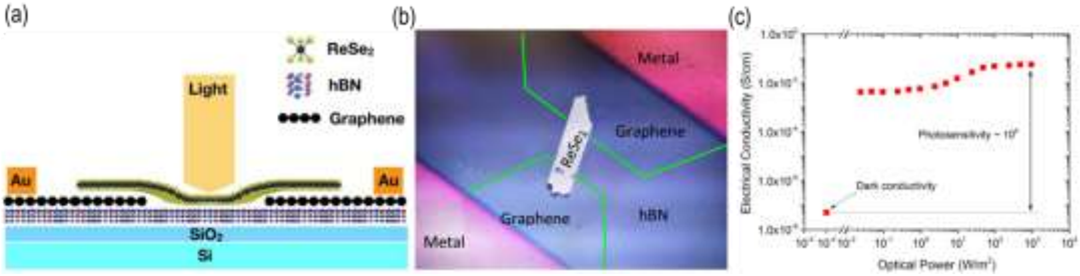

Figure 3: (a) 2D material hetrostructure. (b) Top view of van der Waal stack device. (c) Electrical conductivity as a function of irradiance under white light illumination.

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Graphene Structures for Applications in Fuel Cells and Supercapacitors

Abstract

The proposed paper is synthesizing the results obtained in the implementation of the MULTISCALE Project (Scientific Research Activities on the Development of Advanced Materials by Integrating Nano-structured Materials and Multiscale and Multiphysics Optimization Dedicated to Advanced Energy Systems, ID P_40_279, code MySMIS 105531), by a research group from the Institute for Nanotechnologies and Alternative Energy Sources at “Ovidius” University of Constanta.

The aim of the research activities is to analyze the possibilities to develop robust solutions of advanced materials for energy systems based on the integration of nanostructures and appropriate multiscale and multiphysics optimization [1].

The graphene flakes there were obtained by aqueous arc discharge process. The selected graphene production process has the following features: (1) Low energy power consumption process to exfoliate graphene from graphite rather than to evaporate carbon molecules. (2) Water used as a dielectric medium uses a coolant to maintain the temperature during the process. (3) Controllable graphene layers and the number of oxygen-related functional groups. (4) A seamless process for morphological transition of graphene from 2D to three-dimensional (3D) construction [2].

Figure 1: Testing facility for the electrochemical performances of the obtained samples.

There were carried out several tests with various compositions of electrodes and solutions. The synthesized carbon materials have been investigated using electronic microscopy and spectrometric analyses. The results were evaluated in respect to the composition of the electrodes, solution composition and the arc discharge parameters that have been used in the experiments.

Using the testing facilities presented in figure 1, selected samples of graphene flakes have been tested for the possibility of being used as catalyst supports in electrochemical applications and porous electrodes for supercapacitors.

The fuel cells are complex systems with an elaborated architecture as system of systems, emerging behavior in the sense that lower hierarchy structures are determining the behavior at higher hierarchies and in some cases might be considered as adaptive by adjusting the response function according to the values of some output parameters. The complexity is also at the level of coupled processes as electrochemical reactions, mass, heat and charge transport phenomena, irreversible physical and chemical degradation processes and control and automation processes.

Supercapacitors, also called supercapacitors, store electro- chemical energy by accumulating the charge from electric double layer, which is caused by electrostatic attraction. The capacity of supercapacitor is proportional to the electrode surface, i.e., the electrochemically active surface.

There were prepared catalyst layers that have been integrated in Membrane Electrode Assemblies – MEAs and layers for porous nanostructured carbon materials that have been tested for their performances.

In the presentation there will be included results obtained on the testing of sample MEAs and porous films.

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Direct growth of graphene on insulators and semiconductors by plasma assisted chemical vapor deposition: a route towards industrial applications

Direct growth of graphene films on insulating or semiconducting substrates of technological interest has been an ambition for the past years, as transfer methodologies usually degrade the outstanding graphene properties or contaminate the interfacial contact between both materials. Among all the explored methods, plasma assisted chemical vapor deposition (PA-CVD) has been recently proposed as a valuable technology to direct and catalyst-free growth of graphene thin films on relevant substrates of industrial use [1]. In tune with this trend, recently we have devised new protocols to growth graphene films on top of diverse oxide substrates (silicon oxides, titanium oxide) at low temperature by using PA-CVD and now, we are extending its application to transition metal dichalcogenides (MoS_2) [2,3]. These materials have important applications in several fields, improving their performance and operation range in combination with graphene related materials [4,5].

In this contribution, we present our synthesis approach and recent experimental results. The fabricated graphene films are characterized in terms of morphology, chemical structure and composition, conductivity and light absorption properties in combination with the substrates. The observed properties of the films present interdependence with the substrate used. We also point out many examples of novel applications of this graphene coated substrates. The methodologies shown are intrinsically pure, easily scalable and avoid the transfer of the films. The results presented here represent a step forward in graphene integration for a variety of applications.

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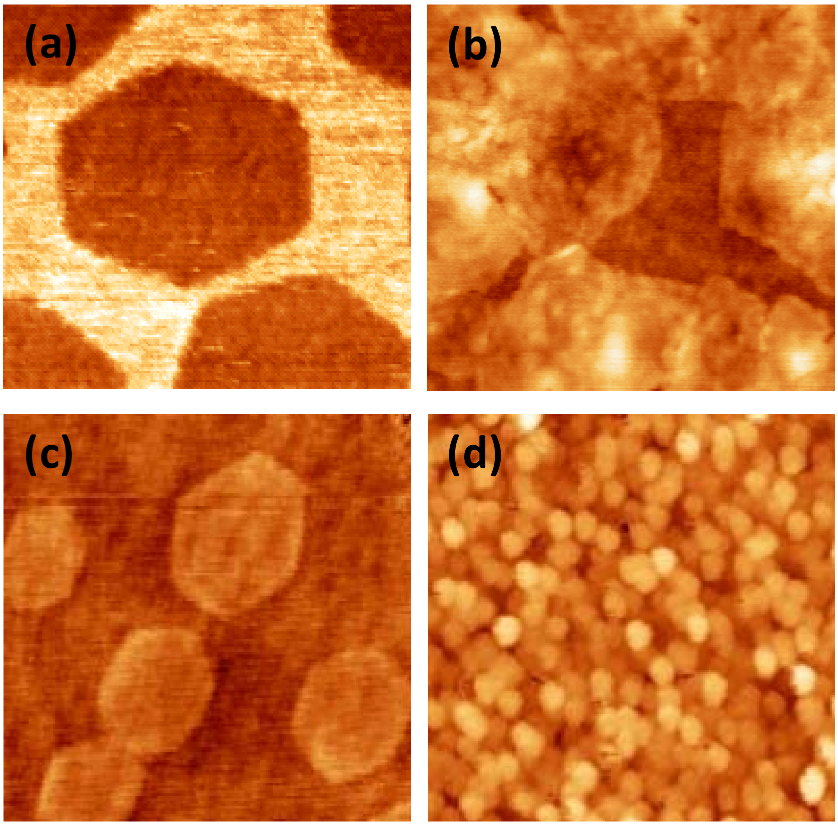

Figure 1: AFM images of graphene crystals (submonolayer coverage) and continuous films structures grown on a variety of substrates. (a) Quartz (b) Silicon wafer. (c) Fused silica. (d) TiO_2.

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Cooperation Opportunities with China in Advanced Materials

The Center for Industrial Technological Development (CDTI) is a Public Business Entity, answering to the Ministry of Science, Innovation and Universities, which fosters the technological development and innovation of Spanish companies. 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 RTDI projects implemented by companies.
-Managing and fostering Spanish participation in international technological cooperation programmes (H2020, Eureka, Iberoeka, Bilaterals currently Japan, China, India, plus Unilateral Programme).
-Fostering international business technology transfer and support services for technological innovation.
-Supporting the setting up and consolidating technological companies.

Functions
CDTI provides companies with its own funding and facilities access to third-party financing (Subsidies of the EU R&D Framework Programme) for national and international research and development projects.
It offers companies user-friendly and flexible support services for the implementation of R&D business projects and for the tenders´ submission for industrial-technological supplies to scientific and technological organizations. CDTI likewise provides funding for technological promotion, innovation projects and technology transfer.

RTDI internationalization -What do we offer?
-R&D International Cooperation Projects: promoted by international consortia related to Spanish participation in international technological cooperation programs managed by CDTI (multilateral and bilateral programmes, programme for international projects with certification unilateral tracking by CDTI. The project funding method will be a Partially Reimbursable Loan, up to a maximum of 85% of the approved total budget, with a stretch of non-refundable up to 33%.
-Global Innovation Line: support for investing in innovation incorporating innovative technology projects. These projects must involve the incorporation and adaptation of technologies to meet the requirements of new markets and improve the competitive position of the company. CDTI aid will be in the form of a loan.
-Aids for internationalization: support for submitting proposals to H2020 Program (APC), support for the submission of tenders in large scientific and technological facilities (APO), support for technological missions (AIPT).

External Network
The mission of the External CDTI Network is to help innovative Spanish entities come to have a good technological position the international Therefore, it offers support to those Spanish entities which are interested in developing technological cooperation projects with companies in other countries, facilitates the identification of technological opportunities outside the EU and promotes technology transfer.
The External CDTI Network is present all over the world, promoting the establishment of institutional partnerships between CDTI and other counterpart agencies from different countries with similar competences in the field of RTD.

In the session there will be a brief introduction about China's R&D policies. Subsequently, the role of CDTI and its support for R&D international cooperation, in particular with China and especially in the area of advanced materials, will be exposed.

The goal of this small session is to expose the new scene that is being forming for R&D cooperation with Chinese entities in the field of advanced materials.

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Graphene/Cobalt interface for spin-orbitronics

A major challenge for future spintronics is to develop suitable spin transport channels with superior properties such as long spin lifetime and propagation length. Graphene can meet these requirements, even at room temperature [1]. However, the development of all-graphene spintronic devices requires that, in addition to its passive capability to transmit spins over long distances, other active properties are incorporated to graphene. The generation of long range magnetic order and spin filtering in graphene have been recently achieved by molecular functionalization [2,3] as well as by the introduction of giant spin-orbit coupling (SOC) in the electronic bands of graphene [4]. On the other side, taking advantage of the fast motion of perpendicular magnetic anisotropy (PMA) chiral spin textures, i.e., Néel-type domain walls (DWs) and magnetic skyrmions, can satisfy the demands for high-density data storage, low power consumption and high processing speed [5].

Here, we report on high quality, epitaxial Graphene/Co(111)/Pt(111) stacks grown on (111)-oriented oxide crystals, characterized by STM, LEED, STEM, Kerr Magnetometry, XMCD and Kerr Microscopy, that exhibit enhanced PMA for Co layers up to 4 nm thick and left-handed Néel-type chiral DWs stabilized by interfacial Dzyaloshinskii-Moriya interaction (DMI) localized at both graphene/Co and Co/Pt interfaces with opposite sign [6]. While the DMI at Co/Pt side is due to the intrinsic SOC [7], the sizeable DMI experimentally found at the gr/Co interface has Rashba origin (Figure 1) [6]. The active magnetic texture is protected by the graphene monolayer and stable at 300 K in air, and, since it is grown on an insulating substrate, amenable to transport measurements [8].

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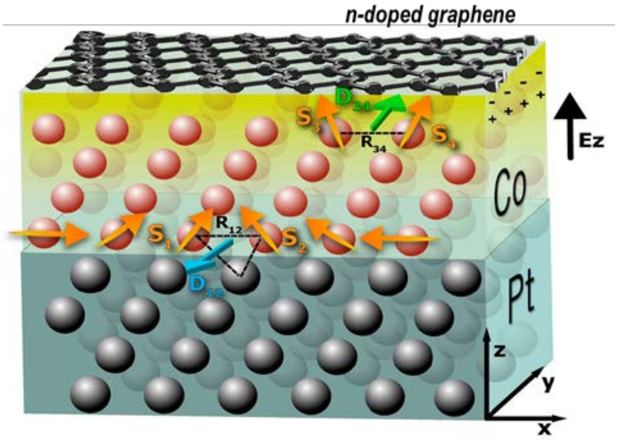

Figure 1: Sketch of the interplay between Spin-Orbit Coupling-induced Dzyaloshinskii Moriya Interaction (DMI) at the Co/Pt and opposite Rashba-type DMI at the gr/Co interfaces [6].

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Synthesis of pure graphene and graphene/carbon nanotubes hybrid by atmospheric pressure plasma

Since the discovery of carbon nanotubes (CNTs) in 1991 [1] and, more extensively, after the isolation of graphene in 2004 [2], the development of new procedures for the synthesis of these one- and two- dimensional nanostructures has been in the spotlight due to their suitability to be utilized in many applications in different fields as electronics or biomedical [3,4] as well as in the development of new improved materials [5]. In addition, it has been demonstrated that graphene-CNTs hybrid nanomaterials exhibit the virtues of both graphene and CNTs which make them to be of special interest in energy storage [6] or the fabrication of supercapacitors [7].

Among other techniques, Chemical Vapour Depositon (CVD) or Liquid Phase Exfoliation (LPE) are presented as suitable technologies for these carbon-based nanomaterials synthesis. However, both procedures present several limitations such as (i) the need of complementary treatment to extract graphene from the substrate or the solvent or (ii) the use of harmful catalyzers which increase the number of defects of the synthetized material. Therefore, CVD and LPE can be hardly considered as potential techniques for the synthesis of high-quality graphene and graphene-CNTs hybrids at large scale.

To overcome these major drawbacks, the use of non-thermal microwave plasmas working at atmospheric pressure for the synthesis of graphene or graphene-CNTs hybrids using aliphatic alcohols as precursors has been successfully proven [8-10]. Microwave atmospheric-pressure plasmas are extraordinarily energetic media which allow some reactions to take place. For instance, organic compounds such as alcohols are decomposed into their fundamental entities, *e.g.* carbon atoms, which are the departure point for the synthesis of graphene and graphene-CNTs hybrids. Finally, the use of atmospheric-pressure plasmas enables the development of online high-throughput processes, which is crucial for industrial applications.

Concerning the formation of high quality few-layers graphene by ethanol decomposition, an argon microwave plasma torch: Torche à Injection Axiale sur Guide d'Ondes (TIAGO) was used with an ethanol flow rate of 2 g/h [11], whereas graphene-CNTs hybrid was successfully obtained from the decomposition of the aforementioned alcohol (0.22 g/h) by means of a surface wave discharge sustained by a surfatron device [12]. Among others, X-ray photoelectron spectroscopy and energy dispersive X-ray analysis were performed in the material synthetized by the TIAGO torch plasma and SWD, respectively. In both cases, the results showed the presence of carbon atoms as unique element of graphene flakes and graphene-CNTs hybrids.

Concerning the study of high-resolution transmission electron microscopy (HRTEM) images (Figure 1), less than 7 layers-graphene sheets without CNTs or graphitic particles are observed in the images from the powder created by the TIAGO torch (Figure 1 a, b) whereas the material synthetized by a SWD contains both multilayer graphene sheets (Fig 1c) and short carbon nanotubes (Fig 1d). The analysis of Raman spectra (Figure 2) confirms the presence of sp^2 hybridized carbon atoms by the so-called G and 2D band in the solid synthetized by both microwave plasmas. Moreover, the location of G band in both spectra at ≈ 1580 cm^{-1} discard the formation of graphene oxide. The intensity ratio of D and G band is, in both cases, lower than the unity, which points out the existence of small defects in the material synthetized ($I_D/I_{G\ (TIAGO)} = 0.24$ and $I_D/I_{G\ (surfatron)} = 0.60$).

As far as the production rate is concerned, plasmas sustained with the TIAGO torch can generate 1.33 mg/min of few-layers graphene, whereas 0.07 mg/min of graphene-CNTs hybrid is synthetized by a SWD. These two catalyst-free methods are carried out in a single step and offer the possibility of scaling it to industrial level.

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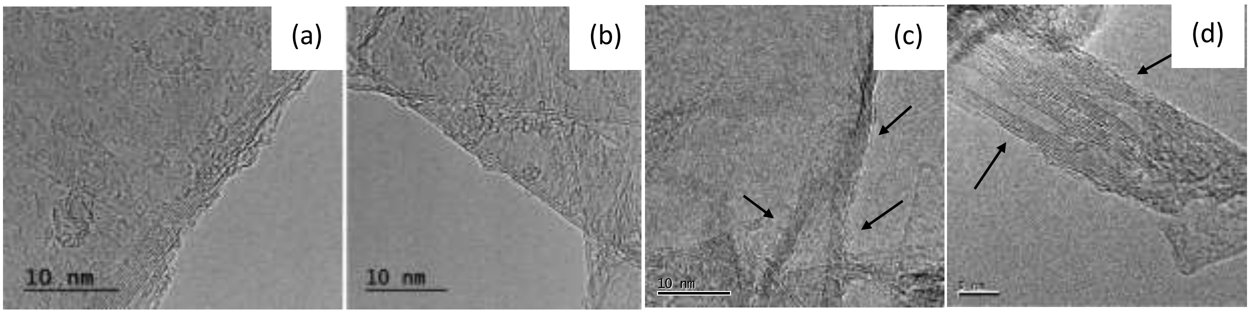

Figure 1: High-resolutionTEM images of solid matter synthetized by TIAGO torch (a,b) and SWD (c,d)

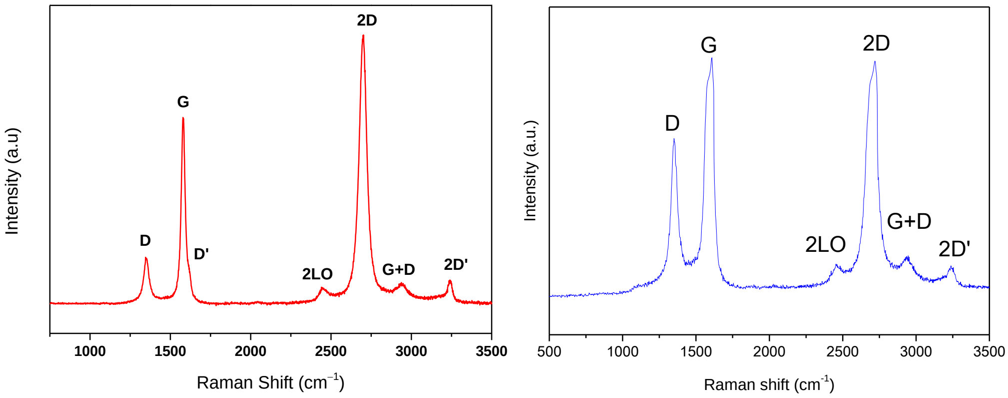

Figure 2: Raman spectra of solid matter synthetized by TIAGO torch (a) and SWD (b)

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Graphene based nanofluids as Heat transfer Fluid

Abstract

European Energy set plan states that "The development and uptake of innovations which substantially reduce the energy cost of industry must be prioritized, for energy intensive industries and Small and Medium Enterprises (SME). European energy intensity industries are those that have a high dependence on resources (energy, utilities and raw materials.) Main representative processes of this type of industries are: steel makers, foundries, ceramic, chemical, cement, food & beverages and paper industries).

Taking into account the needs to reduce energy consumption, the aim of this research is the synthesis of graphene based nanofluids to apply in an industrial manufacturing company. The goal is to reuse in other applications the energy that is waste during different plant processes.

Heat transfers fluids (HTFs) are compounds specifically manufactured for the purpose of transmitting heat from one system to another, to store heat, and to prevent excess heating of any thermal device. These fluids are used to transport energy in the form of heat from the point of generation of heat (burners, nuclear reactors, solar fields, etc.) The most commonly used thermal fluids are water, ethylene glycol, thermal oils, and molten salts. A Common feature to all of them is its low thermal conductivity, which limits the efficiency of heat exchange systems. With the aim to enhance the thermal conductivity of HTF the scientific community is researching on a new concept. Nanofluids. Nanofluids are a new class of fluids engineered by dispersing nanometer-sized material smaller than 100nm (nanoparticles, nanofibers, nanotubes, nanowires, nanorods, nanosheet, or droplets) in base fluids [1]. Considerable researches have been carries out on this topic and it has been noticed that most authors agreed that nanofluids provide higher thermal conductivity compared to base fluids [2]. Its value increases with particles concentration. Temperature, particle size, dispersion and stability do play an important role in determining thermal conductivity of nanofluids.

There are several techniques to disperse nanoparticles o other nanomaterials in a host fluid. These techniques are divided in two groups: One step technique and two step technique. In this case two step technique is applied, the graphene was added into the host fluid. There are different techniques to improve the dispersion of nanoparticles in a host fluid such as nanoparticles modification, pH modification or dispersant addition. In this work the third option has been applied, dispersant addition. Dispersants are employed to increase the contact of two materials, sometimes known as wet ability [3]. In a two-phase system, a dispersant tends to locate at the interface of the two phases, where it introduces a degree of continuity between the nanoparticles and fluids. A repulsion force between suspended particles is caused by the zeta potential which will rise due to the surface charge of the particles suspended in the base fluid. The figure 1 illustrate effect of stable dispersion and aggregation.

Heat transfer fluids can be divided according to their working temperature range; low temperature range (glycol/water mixtures) and medium temperature range (mineral oils) and high temperature range (synthetic organic fluids, silicones, molten salt, liquid metal). The figure 2 shows some examples of these different heat transfer fluids. In this research silicone-based heat transfer fluids have been selected. These fluids are very stable at high temperature.

Synthesized nanofluids were characterized measuring different thermo-physical parameters, such as thermal conductivity, viscosity, density, etc. The results have shown that at 0.5% of Graphene has increased the thermal conductivity in 9%. These results indicate that graphene it could be very useful material to increase the properties of the heat transfer fluids.

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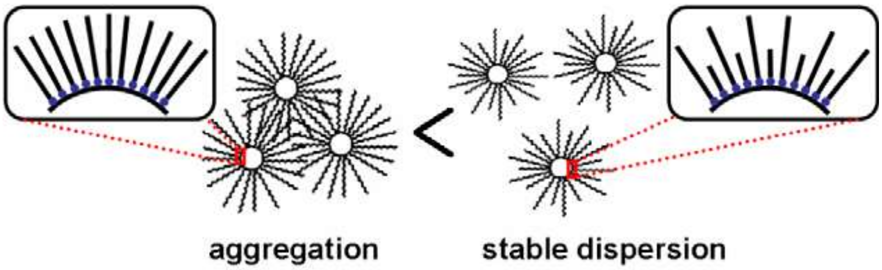
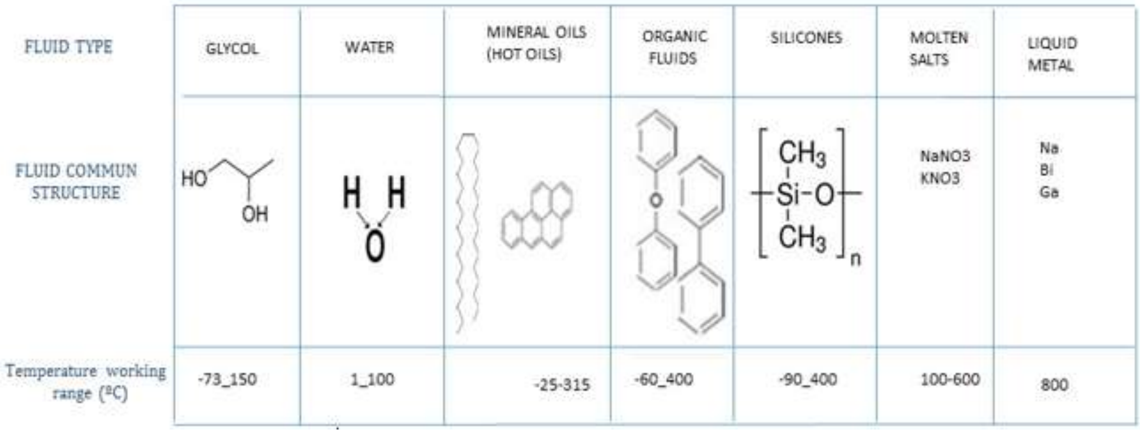


Figure 1: Effect of stable dispersion and aggregation.



FLUID TYPE	GLYCOL	WATER	MINERAL OILS (HOT OILS)	ORGANIC FLUIDS	SILICONES	MOLTEN SALTS	LIQUID METAL
FLUID COMMUN STRUCTURE	HO OH	H H O		O	CH_3 Si-O CH_3 n	NaNO3 KNO3	Na Bi Ga
Temperature working range (ºC)	-73_150	1_100	-25-315	-60_400	-90_400	100-600	800

Figure 2: HTF classification according working temperature

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Tuball ™ Single wall Carbon Nanotubes: Health, Safety & Environmental issues

The company OCSiAl is been founded in 2009 and is also the first SWCNT manufacturer who has completed his EU-REACH registration for a tonnage band of up to 10T/a and is planning to receive approval for a tonnage band up to 100T/y by the end of Q3/2019. At the end of the 2017 we achieved our signed consent order with the EPA that allows us to import up to 25T/y. Because Tuball™ is used and also tested in various applications on an ongoing basis, also receiving a lot of interests worldwide. That is why it is obvious that the company OCSiAl is establishing the necessary regulatory and quality standards worldwide. The first part of this presentation will aim at providing a short introduction of our Tuball™ substance and his product line, a second part of the presentation will be about the morphology vs Health & Safety status, the third part is an overview about the status and plans of the ongoing registrations an compliance. The fourth and last part of the presentation will focus on the health, safety and environmental aspects of our Tuball™ substance and the different applications. As SWCNT manufacturer, OCSiAl is doing continues investments in improving our understanding of our different (new) Tuball products themselves and potential hazards through their (entire) life cycle. We are involved in generating additional test data and collaborating with industry associations and networks.

This presentation will describe the steps being taken by the company's H&S Lead manager, Van Kerckhove Gunther to successfully introduce our carbon nanotubes (SWCNT's) regulatory status and outline our (future) plans for numerous of studies and qualifying our Tuball™ substance including the different kind of compositions.

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STM study of single-layer graphene nanoribbons adsorbed on fcc(111) noble metals by using drop cast and vacuum spray

Single-layer graphene nanoribbons (sGNR) (width ~45 nm) were unzipped from double-walled carbon nanotubes (diameter ~15 nm) with a use of ultrasonic waves in a liquid solution [1,2]. The obtained GNR solution was drop casted on a Au(111) film substrate in air. Subsequently, the sample was introduced into our home-built ultrahigh vacuum (UHV) scanning tunneling microscopy (STM) setup. In UHV, the sample was further annealed and STM measurements were performed at 78 and 300 K [1].

In contrast to the atomically-flat GNRs via the bottom-up process, the drop casted sGNRs were bucked on Au(111) (see Figure 1). Most of local areas of the sGNR floated from the substrate (GNR-substrate distance: 1-3 nm). Only some points of the sGNR contact with the substrate (GNR-substrate distance: 0.5 nm). However, STM spectroscopy maps directly showed that the buckled sGNR have very uniform local density of states (LDOS) and metallic property (our DFT calculation confirmed that GNRs with a width larger than 19 atoms has no gap). The conductance through the buckled sGNR was ~3.5 Go measured by contacting the STM tip to the edge of the sGNR [1].

Because we prepared the sGNRs on Au(111) by drop casting, sGNRs frequently formed stacked structures. When we placed the GNR droplet on Au(111) in air, sGNR were sunk and deposited on Au(111) one by one. By a chance, one sGNR sit on another sGNR, forming a stacked crossing structure. STM spectroscopy mapping found that the crossing areas have an energy gap (250 meV gap between -50 meV and +200 meV around the Fermi energy, p-type semiconductor). We found that this is not due to the bending of the sGNR, but the electronic interactions between the up and down sGNRs are driving force [1], i.e., only the upper sGNR changes the electronic property from metal to semiconductor.

Using the drop cast method, we succeeded to fabricate the unique backed sGNRs on Au(111). However, this process required to perform in air. Therefore, the sample surface contaminations cannot be excluded.
We developed a home-built vacuum spray setup combined with our UHV-STM. The vacuum spray setup consists of three room. The first room was pumped by a rotary pump, second room was pumped by a small turbo molecular pump, and the third room is an introduction chamber of our UHV-STM setup. Each room was separated by a 5 mm hole. A 0.05 mm hole was set at the entrance of the first room. The sGNR solution was placed on a 0.05 mm hole, and immediately sucked into the vacuum of the first room. The sucked solution was sprayed and pass through the second room. In the third room, the cleaned Au(111) or Cu(111) was set and the sGNRs were adsorbed. We show sGNRs on Au(111) or Cu(111) using this new vacuum spray method.

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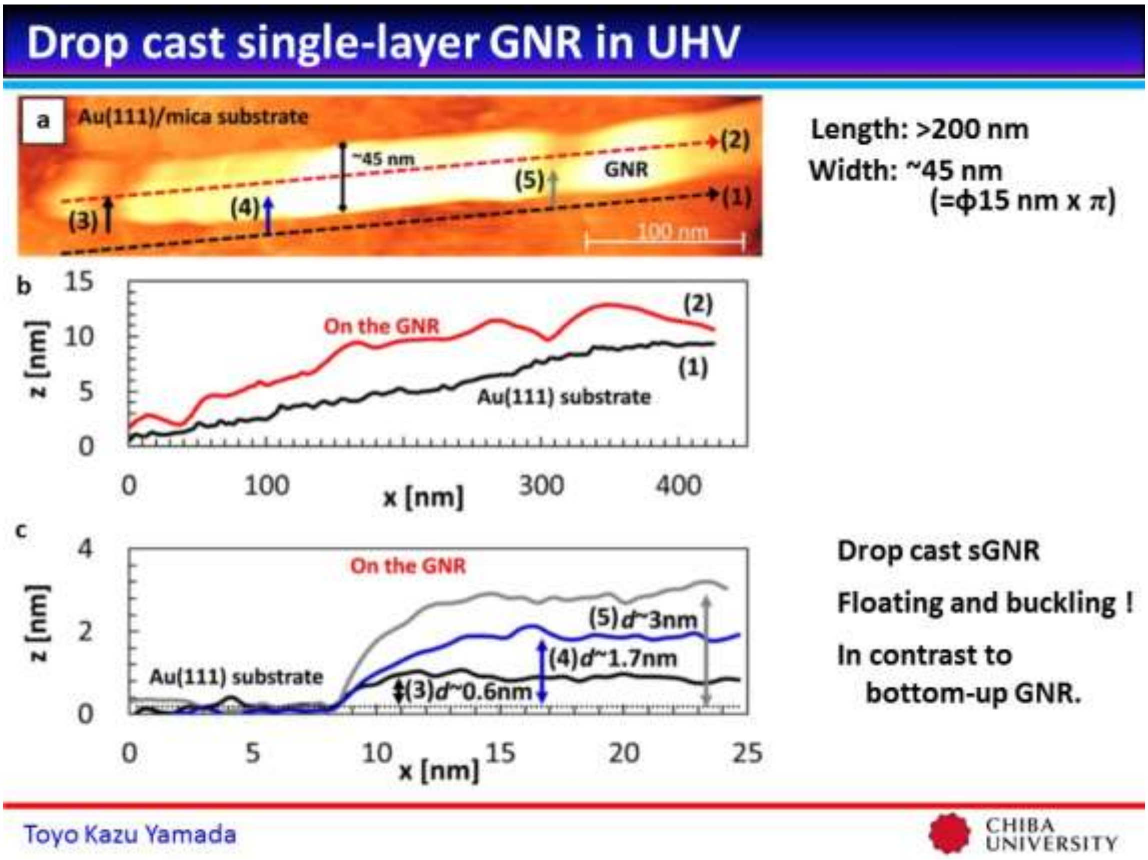
Figures



Drop cast single-layer GNR in UHV

Length: >200 nm
Width: ~45 nm
(=ϕ15 nm x π)

Drop cast sGNR

Floating and buckling !

In contrast to
bottom-up GNR.

Toyo Kazu Yamada

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Figure 1: (a) STM image obtained on a single-layer graphene nanoribbon (sGNR) adsorbed on an atomically-flat Au(111) substrate by using drop cast in air [1]. (b) Line profiles along the substrate and the sGNR (arrows No. 1 and 2 in (a), respectively). (c) Line profiles along the arrows No. 3, 4, and 5 in (a), showing heights of sGNR from the substrate.

POSTER CONTRIBUTIONS

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Transfer of 2D Materials Using Smart Cut™

Graphene is a promising candidate for the next-generation electronics and optoelectronics as it offers charge carrier mobility over 10,000 cm^2/Vs, high saturation velocity and high thermal conductivity. Apart from graphene, there is a variety of other two-dimensional (2D) materials, such as transition metal dichalcogenides, that offer unique electronic and optoelectronic properties in combination with ultimately thin, two-dimentional nature. Recent progress in the synthesis techniques has made the cost-effective wafer-scale production of 2D materials possible. However, the direct growth of these materials on a dielectric substrate remains challenging. That is why a reliable and scalable technique for transfer of 2D materials from the growth substrate becomes a key technological step. The existing methods of transfer are unreliable or have severe disadvantages. Direct mechanical delamination leads to rupture of the 2D layer. Polymer-based methods of transfer, as well as chemical etching of the growth substrate, lead to deterioration of 2D material properties due to contamination and uncontrolled doping. Besides, implementation of such methods on the large industrial scale is improbable due to their low reliability.

Wafer-scale transfer of thin layers of materials is commonly used on the semiconductor-on-insulator (SOI) industry. Smart Cut™ is one of the most advanced technologies for such transfer and it was developed at CEA. It is based on the implantation of gas ions inside a target substrate with a well-defined implantation depth. As a result, a nm-thick layer of crystalline material can delaminate from the rest of the wafer and get transferred to another wafer (typically SiO_2/Si) via direct wafer bonding. Numerous studies have optimized each step of this process for a wide range of materials, such as Si, SiC, Ge, etc.

The objective of this project was to develop a novel method of wafer-scale transfer of 2D materials - such as graphene and TMDCs - to a target dielectric substrate (SiO_2/Si wafer). The proposed technique is based on the Smart Cut™ technique conventionally used for the transfer of ultrathin layers of silicon, and paves the way for monolithic integration of graphene and other 2D materials with Si-based electronics. Successful implementation of this technique required a thorough investigation of surface interaction of the transferred layer with the donor and target substrates using Raman spectroscopy, AFM, SEM and TEM studies presented in this report.

Figures

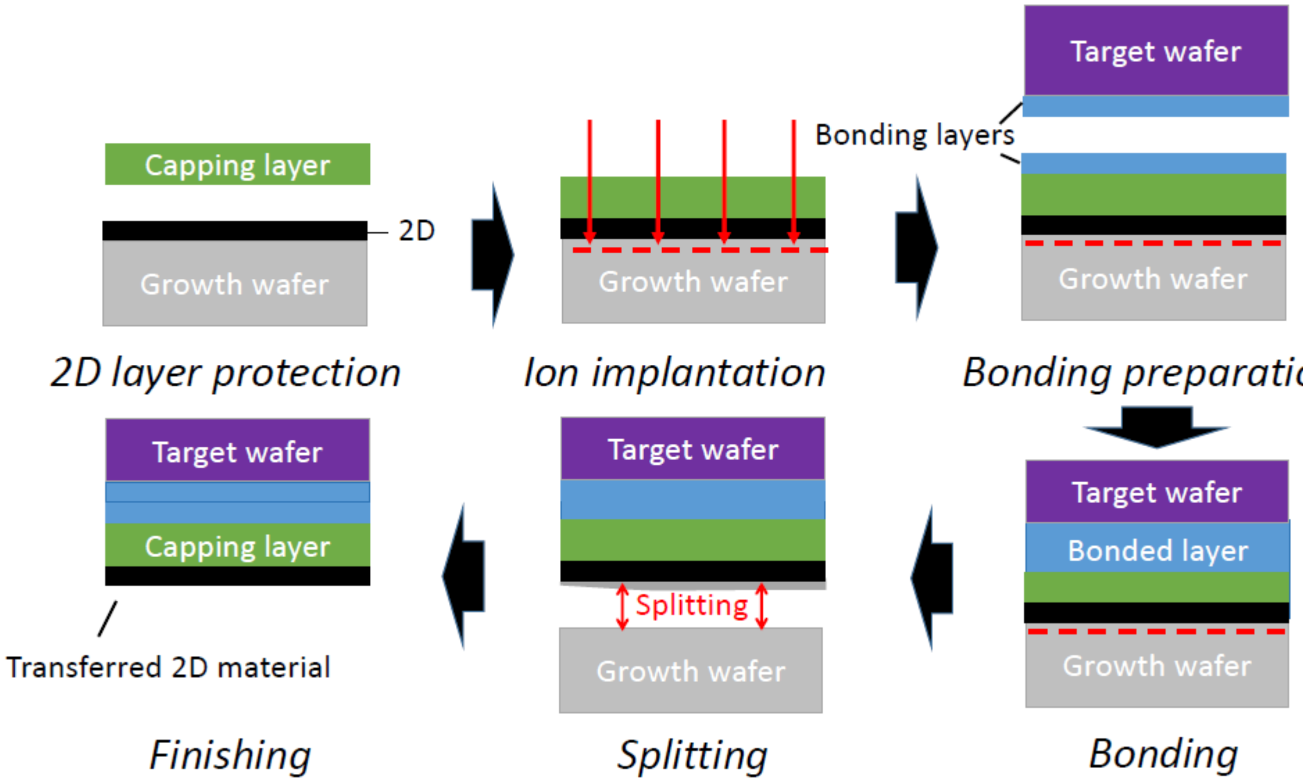

Figure 1: Graphic representation of wafer-scale 2D material transfer using Smart Cut ™

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Highly-controlled thiol-functionalization as a route to versatile graphene-based platforms for robust nano-bio-hybrid devices

Although pristine graphene is one of the most relevant materials this decade, several important shortcomings must be overcome before it can step from fundamental physics to applied technology.[1] In particular, its extreme chemical inertness and the absence of an electronic band-gap present important limitations to its use as an active element in electronic devices and hybrid structures. Thus, technologically useful and robust graphene-based interfaces for nano-bio-hybrid devices require highly selective, stable and covalently bonded functionalities on the graphene surface, but in order to be effective and competitive they must essentially retain the electronic properties of the pristine graphene surface. There have been many attempts to modify graphene via non-destructive methodologies that aim to preserve its extraordinary properties and incorporate added value.[2] The most common covalent functionalization methods are via chemical routes, mainly by reacting free radicals or dienophiles with the C=C bonds of pristine graphene,[3] and although well-developed wet chemistry may succeed in linking diverse groups to the surface, the resulting graphene platforms are usually poor performers either due to low functionalization yield or to the nature of the reaction conditions that disrupt the graphene layer with an unacceptable amount of defects.

In this work [4], we describe a relatively straightforward route to the covalent chemical functionalization of graphene sheets with a robust thiol-terminated moiety. We employ a recently reported and patented strategy [5] for the selective functionalization of graphene through the controlled formation of atomic vacancies (Fig. 1a), obtaining a graphene surface uniformly covered with a covalently bound spacer molecule that is formed from the spontaneous bonding of *p*-aminothiophenol (pATP) molecules at the vacancies. The result is a controlled decoration of the graphene surface with active thiol moieties, which can subsequently be directly used to bind diverse nanoarchitectures to graphene. We have used this strategy to covalently couple two systems of broad interest: gold nanoparticles (Au-NPs) and thiol-modified nucleic acid aptamers (Fig. 1b).

The highly-controlled covalent functionalization protocol is undertaken under UHV conditions and the properties of pristine graphene are largely preserved, as shown by a large number of experimental techniques including XPS, Raman microspectroscopy, UV-vis spectroscopy, AFM and TEM, and confirmed by theoretical methods.

Two types of Au nanoparticles of different origin were used; citrate capped Au-NPs produced in a salt solution and NPs made using a multiple ion cluster source in UHV conditions.[6] A nucleic acid aptamer, in this case a single-stranded DNA (ssDNA) oligonucleotide that binds with high affinity and specificity to a target protein molecule that mediates relevant biological processes, PCBP-2, was used. Both systems studied, which were also characterized using multiple techniques, remain firmly anchored to the graphene surface even after several washing and annealing cycles, thus demonstrating the highly robust nature of the nanostructures. Further, atomic force microscopy images show that, when coupled to the graphene surface, the conjugated aptamer retains the functionality required to recognize its target protein.

We believe that this functionalization mechanism paves the way to the integration of high-quality graphene layers into technological platforms for plasmonics, biosensing or advanced field-effect transistor devices. As an example we assess its applicability for graphene solution gated field-effect transistors (gSFET).

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Figures

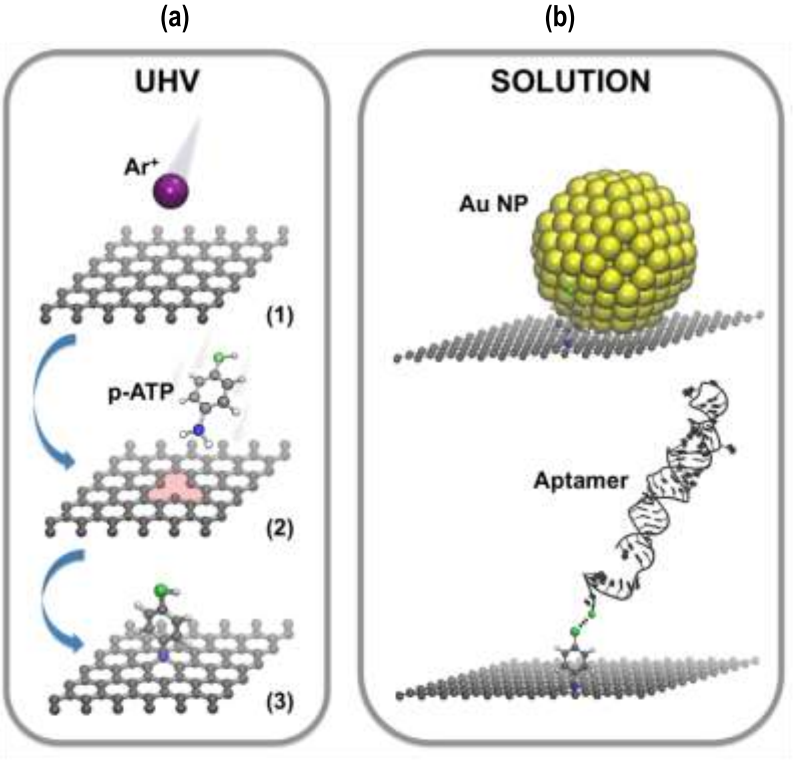

Figure 1: (a) Schematic illustration of the functionalization process: (1) 140 Ar+ irradiation of the graphene surface; (2) exposure of the graphene surface with ion-beam induced vacancies to pATP molecules; (3) covalent bonding of the N terminal of pATP to the carbon network at the induced vacancy in the carbon network, leaving the thiol group exposed to the medium. (b) *top:* scheme of the thiol linkage to gold nanoparticles; *bottom:* conjugation of a thiol-modified DNA aptamer to the graphene-anchored thiol group through the formation of a disulfide bond.

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Challenges of CVD graphene integration into transparent electrodes for green energy solutions

Graphene materials have been regarded as promising candidates for the new emerging generation of transparent electrodes in several applications such as displays, touch screens and/or solar cells [1,2]. Those materials are generating enormous expectations, and there is no doubt that they have outstanding properties that could fit in well with many research areas, among which energy-generation devices highlight [3,4]. Graphene shares many of necessary desired properties to be used as transparent electrode: high optical transmittance, exceptional electronic transport, outstanding mechanical strength and environmental stability [5]. Recent advances in the synthesis, characterization and transfer of graphene material show its strong potential. As example, the figure of merit of a wet-chemically doped monolayer of graphene grown by chemical vapor deposition (CVD) onto copper substrate reveals a material with a sheet resistance of 125 ohms/sq and transparency of 97.4% [6].

In the renewable-energy sector, it is expected that photovoltaic (PV) industry plays a major role due to the fight against the climate change. Currently, PV market is being dominated by silicon-wafer technology that requires exhaustive technological solutions to achieve thinner and cheaper products. In this sense, silicon-heterojunction technology is emerging as low-temperature reliable solution, where new architectures of transparent conductive electrodes to generate and extract the current in a more efficient way are being required [7]. Taking into account the prominent and unique properties of graphene, several approaches incorporating it are proved to be especially interesting. In particular, hybrids concepts as high-quality electrode solutions have been already demonstrated [8,9].

In the present work, new architectures of hybrid transparent conductive oxides (TCOs) and graphene electrodes incorporating one, two and three atomic graphene layers, respectively in different configurations (see Fig. 1) are fabricated to evaluate the optoelectronic properties of whole structure. Graphene material is grown by CVD onto 4-inch copper foil, and transferred using an automatic transfer system (see Fig. 2) that is suitable for most type of substrates and also adapted for industrial applications [10]. In addition, the TCO materials are deposited in large areas at low temperature using a commercial UNIVEX 450B magnetron sputtering. The challenges of introducing graphene in the transparent electrode structure are evaluated. In particular, the compatibility between process temperatures required in each step, the dependence of the place where the atomic graphene is located as function of the TCO material used or the effect of sputtering deposition parameters on the electrical electrode performance are checked carefully. In this sense, the key parameters for choosing the most appropriated and reliable combination of electrode are determined, as function of its figure of merit. The work undergone so far clearly suggests the possibility to noticeably improve transparent electrodes with this approach and therefore to further enhance silicon-heterojunction technology performance.

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Figures

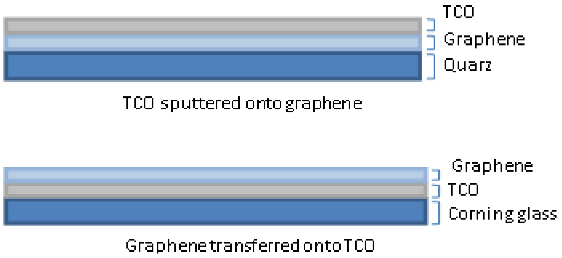

Figure 1: Electrode configurations used in the samples in study

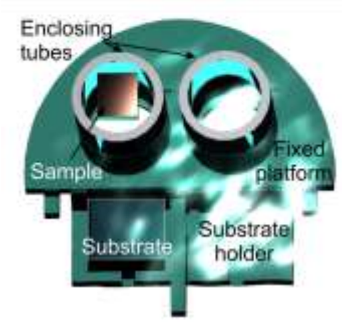

Figure 2: Graphene automated transfer system

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Preparation of reduced graphene oxide-nickel oxide-zinc oxide nanocomposites with potential capacity for desulfurization of organic sulfur from gasification gases. Preliminary studies

The removal of sulfur species from the biomass-derived producer gas after gasification represents an operational and economic challenge in order to protect catalysts. Sulfur containing compounds is usually present in biomass gasification gas, since sulfur is typically found in the feedstock. The presence of organic sulfur compounds present in the gas streams is undesirable, because of its contaminating behavior. Even at concentrations as low as a few ppm they can poison catalysts causing significant technical difficulties to the production process.

Graphene, one of the most promising carbon-based materials, has gained immense attention in the field of nanomaterials research because of its excellent properties regarding electrical and thermal conductivity, mechanical strength and large specific area. Its large π-conjugated planar structure makes graphene as an attractive material to support catalysts. In addition, chemical functionalization of graphene by a solvothermal route is a facile approach to obtain large quantities of nanocomposites. Hence, graphene-metal oxide nanocomposites are being extensively investigated for a variety of heterogeneous catalytic reactions.

In this work, we study the synthesis of reduced graphene oxide rGO-NiO-ZnO nanocomposites in order to explore its possibilities as efficient catalysts for removing organic sulfur compound from gasification gases. The proposed procedure is based on a simple solvothermal process starting from graphene oxide (GO) prepared by the classical Hummers method and the improved Tour method. The morphology, microstructure and composition of the as obtained GOs and its corresponding rGO-NiO-ZnO nanocomposites have been systematically characterized by X-ray diffraction (XRD), scanning electron microscopy with EDS detector (SEM / EDS), Fourier transform infrared spectroscopy (FT-IR) and N_2 adsorption at -196°C. Results show that GO from Hummers method is slightly more oxidized than GO from Tour method, probably due to the relatively mild temperatures used in the last one. The formation of metal oxides particles, mainly ZnO, associated to rGO sheets, was observed for both nanocomposites. Obtained surface area of rGO-NiO-ZnO NiO by the Hummers method was 78.57 m^2/g, giving rise, a priori, to be the composite with the highest potential of catalytic activity.

This work is in the framework of the ECOSGAS project “Removal of Sulfur Organic Compounds from gasification gases by reactive adsorption”. The objective of this project is to make contribution to R&D in deep desulfurization technologies of biomass and waste gasification gases, at high temperature (300-500ºC), for integration in renewable fuels production (SNG, biofuels, DME) and thus reduce the use and dependence on fossil fuels. Specifically, the proposal focuses on the assessment of a commercial sorbent, based on zinc and nickel oxide, for the removal of organic sulphur species from gasification gases (thiophene, benzothiophene and dibenzothiophene) in a single stage, by means of reactive adsorption. The technology has been successfully proven for gasoline sulphur removal and for H_2S removal from syngas. Both facts mean a sound assumption for evaluating its feasibility for removal of organic sulphur compounds present in gasification gases. In order to improve the performance of sorbent for desulfurization process, an exploratory activity in preparation of novel Zn-Ni sorbents supported on graphene, is included as part of this initiative.

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Optimization of amorphous silicon deposition for fabrication of high-quality inverted graphene/silicon heterostructures

Introduction

Graphene is known as a material with exceptional electrical, mechanical as well as optical properties. It can be transferred to semiconducting materials, such as silicon, to form Schottky heterojunctions with the potential for producing low cost but very effective electronic devices, for example solar cells [1, 2] or photodetectors [3]. Graphene/silicon heterostructures are usually made of chemical vapour deposited (CVD) graphene transferred from metal catalyst (e. g., copper or nickel foil) to target substrate (e. g., silicon) by dry or wet transfer technique (stamping or fishing). Both transfer techniques use graphene-support polymers and are suitable for a high precision transfer of CVD graphene. However, they introduce substantial quantity of defects (graphene wrinkles, cracks) and impurities (from etchant or polymer residues) [4]. Therefore, these commonly used approaches are not suitable for fabrication of high-quality graphene/silicon heterostructures, especially not for large scale applications.

Here, we present an inverted approach to fabricate graphene/silicon heterostructures where hydrogenated amorphous silicon (a-Si:H) is grown on the top of 2D material by well-established plasma-enhanced chemical vapour deposition (PECVD). The first deposition of silicon film on the CVD graphene transferred to SiO_2/Si substrate has already been done by Arezki et al. [5]. In our study, to avoid the ill-defined interface and transfer-induced contamination, the a-Si:H films were deposited directly on top of CVD graphene covered copper foils. We aim to investigate a wide range of PECVD deposition temperatures (from room temperature to 350 °C) to find a compromise between minimizing the damage in graphene and maintaining, in the same time, electrical conductivity of a-Si.

Methods

Intrinsic a-Si:H films with a thickness of roughly 20 nm were deposited in a capacitively coupled PECVD setup operated at 40 MHz. The substrates (CVD graphene on copper foil) were heated up to various temperatures (the range between 150 °C and 350 °C is discussed in this abstract) and exposed to a glow discharge in a mixture of SiH_4 and H_2 with an RF power of 0.05 W cm^{-2} under a pressure of 70 Pa. Gas mixture ratios were set by gas flows: 8 sccm of SiH_4 and 40 sccm of H_2. To eliminate oxide contamination during the a-Si:H deposition, high purity silane (99.999%) and hydrogen (99.99999%) gases were used in a PECVD chamber with the base pressure of 10^{-5} Pa. The thickness of the silicon films was confirmed with Tencor Alpha–step 100 profilometer measurement of a step-edge made at a same time on a glass substrate.

Raman spectra were measured in a Renishaw Reflex setup using a 442 nm excitation He-Cd laser on a silicon/graphene/copper stack from the top side of a-Si:H. The wavelength of 442 nm is strongly absorbed in the silicon film; however, the film thickness of only 20 nm still allows measuring a graphene layer beneath it.

Experimental results and discussion

At first, the quality of graphene layer after the a-Si:H PECVD deposition was assessed by non-destructive Raman spectroscopy. Fig. 1(a) presents a Raman spectra series of CVD graphene capped by a-Si:H under PECVD temperatures ranging from 150°C to 250 °C. Interestingly, all samples show the G and 2D peaks characteristic for graphene monolayer indicating that the PECVD silicon deposition is not destructive for graphene in general. However, from the absence of a D-band in spectra it is evident that the high structural quality of graphene monolayer was preserved only for the a-Si deposition up to 200 °C. Above this temperature, PECVD deposition causes graphene damage, as the D band starts to grow up.

Indeed, the electrical conductivity of intrinsic a-Si:H layers prepared by PECVD under selected temperatures on glass substrate was measured. As can be seen from Fig. 1(b), the measurement of a-Si:H prepared at 150 °C is very similar to 250 °C and has one order of magnitude lower conductivity than materials prepared at 300 °C and 350 °C. The slope of lines was used to calculate activation energy. Its values are gradually decreasing with the temperature increasing from 150 °C to 350 °C (0.67 eV, 0.64 eV, 0.60 eV, 0.58 eV, respectively) which proves that the electrical quality of silicon is getting worse. To sum up, we observed the electrical conductivity optimum for a-Si:H PECVD deposition at 150 °C.

Conclusion

Since the ‘standard’ configuration of graphene/silicon heterostructure with graphene transferred on top of silicon suffers from transfer-induced defects and contamination, the inverted structure with silicon deposited on graphene still on the copper foil has a great potential to avoid these pitfalls. We found compromise temperature of a-Si:H PECVD deposition on graphene at 150 °C, enabling us to produce high quality inverted graphene/silicon heterostructure with minimized graphene damage. At the same time, the a-Si layer has the best electrical conductivity. Next, we will try to solve another issue which is the removal of copper without damaging the graphene and not breaking the stack due to stress release. To conclude, we demonstrated that a-Si:H deposition by PECVD is a viable method for fabrication of inverted graphene/silicon heterostructure and would be valuable not only for potential solar cells but in the ‘silicon’ industry in general.

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Figures

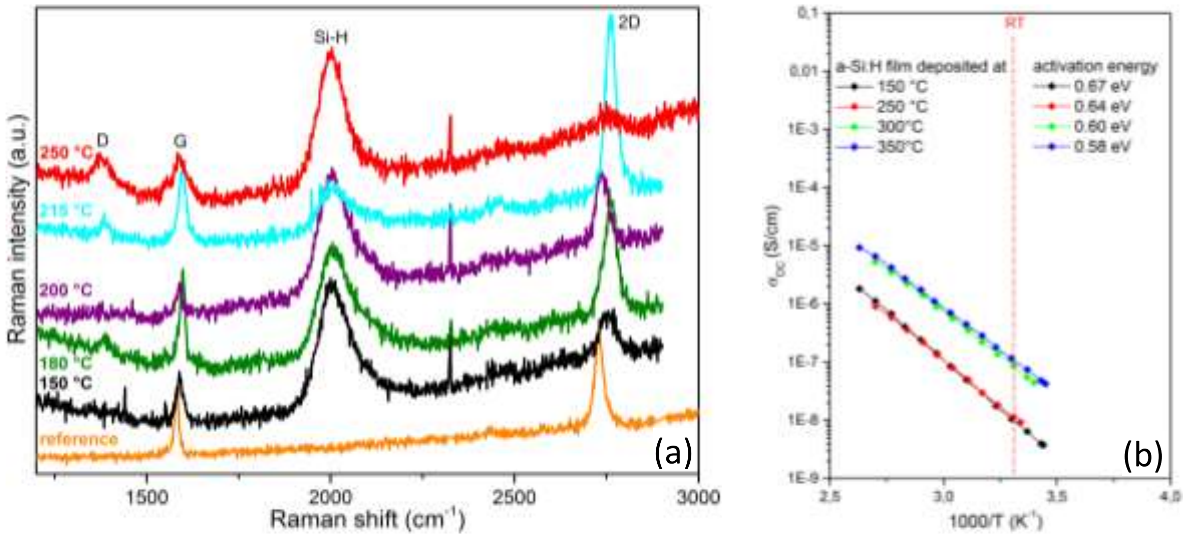

Figure 1: Characterization of a-Si:H/graphene inverted heterostructures prepared by PECVD under various temperatures. (a) Raman spectroscopy of CVD graphene covered by 20 nm of a-Si:H. (b) Results of a-Si:H electrical conductivity measurements.

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Tin dioxide-graphene based chemiresistive device for NO_2 detection in the sub-ppm range

In this work chemical devices based on films of nanofibers of tin dioxide (SnO_2) - pure and doped with pristine graphene (Gr) - are developed and characterized for the detection of nitrogen dioxide (NO_2) at sub-ppm level, and their performance compared to state-of-the art sensors of complementary metal oxide semiconductors (CMOS) available in the market.

The devices are fabricated by depositing nanofibers on the surface of micromachined silicon substrates with interdigitated electrodes and heating resistance (microhotplates). Nanofibers of SnO_2 and SnO_2-Gr are prepared by electrospinnig of an aqueous solution of polyvinyl alcohol (PVA), tin(IV) chloride pentahydrate ($SnCl_4{\cdot}5H_2O$) and eventually Gr, and collected onto microhotplates [1]. An optimal trade-off between electrospinn-ability and significance in regard to gas sensing is attained for a content of 1000 ppm of Gr to Sn in the solution. The as-prepared films are subjected to thermal annealing at 500 ºC in air for four hours and then analyzed by SEM (Figure 1). SEM images show highly porous layers of randomly oriented nanofibers of different morphology. Whereas nanofibers of SnO_2 are continuous, show a uniform diameter (30-50 nm) throughout their length, and have a granular surface with grains smaller than 10 nm [2,3]; discontinuous beaded nanofibers and nanoribbons are obtained when Gr is added to the solution.

The performance of the nanostructured sensors to detect NO_2 on the sub-ppm level was assessed in the laboratory with controlled air-NO_2 mixtures as a function of temperature, from room temperature up to 300 ºC, and compared to the performance of sensors CCS 801 and CCS 803 (ams AG, Austria) [4,5] operating at higher temperature (300-400 ºC). An improvement in sensing performance in terms of sensitivity and response time, together with higher response at room temperature, is obtained when composite nanofibers of SnO_2-Gr are used. The response of nanofibers-based sensors and CMOS sensors to NO_2 is displayed in Figure 2. As it can be seen, the performance of the nanostructured sensors largely exceeds the performance of the commercial sensors.

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Figures

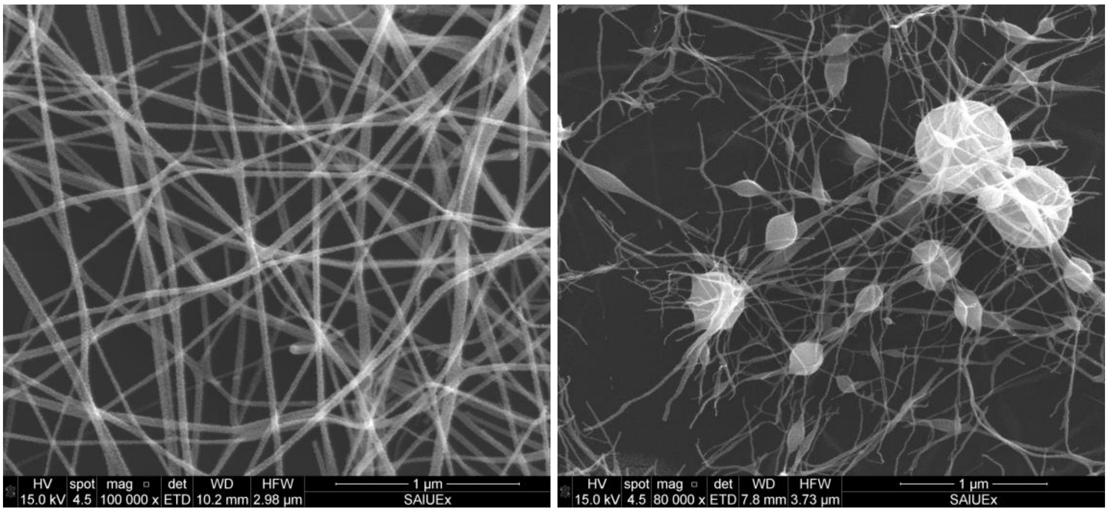

Figure 1: SEM images of nanofibers of pure tin dioxide (left) and tin dioxide doped with pristine graphene (right).

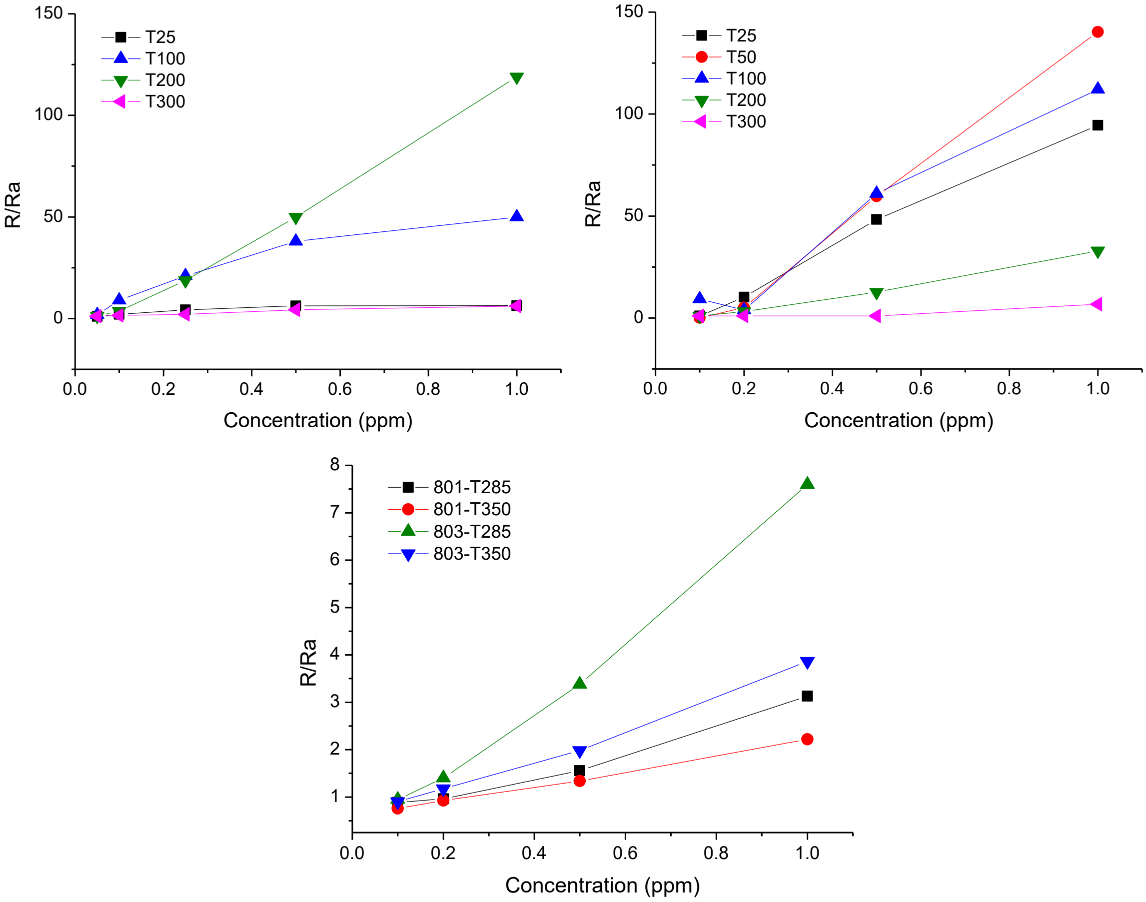

Figure 2: Response to NO_2 of resistive sensors based on SnO_2 nanofibers (top-left), SnO_2-Gr composite nanofibers (top-right) and commercial CMOS sensors (bottom) at various temperatures.

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Chemiresistive devices based on graphene decorated with metal oxide nanoparticles for NO_2 detection

Graphene is seen as a promising material for gas detection at room temperature, as to open the door to a new generation of low cost and low energy consumption sensors. However, a number of limitations have been identified when applying graphene to gas sensing, like low selectivity, slow response and long recovery times [1]. The present work is aimed at decorating graphene with metal oxide nanoparticles (MO-NP) to overcome these drawbacks. In particular, it has been found that the addition of MO-NP to graphene is able to modulate the selectivity of the material, and they improve the overall detection performance [2].

We present the sensing performance of chemiresistors based on graphene functionalized with MO-NP upon exposure to nitrogen oxide (NO_2). Four types of sensitive materials were investigated: pristine graphene (G), SnO_2-NP doped graphene ($GSnO_2$), ZnO-NP doped graphene (GZnO), and TiO_2-NP doped graphene ($GTiO_2$). The preparation of MO-NP doped graphene was performed by first freeze drying of graphene suspension previously prepared by a method described elsewhere [3]. The obtained graphene powders were mixed with MO-NP (3:1 mol/mol) and finally microwave irradiated for 5 minutes at 1000 W. The materials were characterized by SEM, TEM [Figure 1] and Raman spectroscopy.

Dispersions of these powders in ethanol and isopropyl alcohol/water were deposited by drop casting onto two types of substrates: alumina substrates for room temperature measurements and silicon microhotplates for measurements up to 300 ºC.

The sensors were characterized in an automated gas line. As results of this investigation, an improvement in the response, especially in case of ZnO- and TiO_2-NP doping, was obtained; the latter device showing a remarkable sensitivity gain. Therefore, an improvement in sensor performance is demonstrated in terms of sensitivity and response time [

Figure 2].

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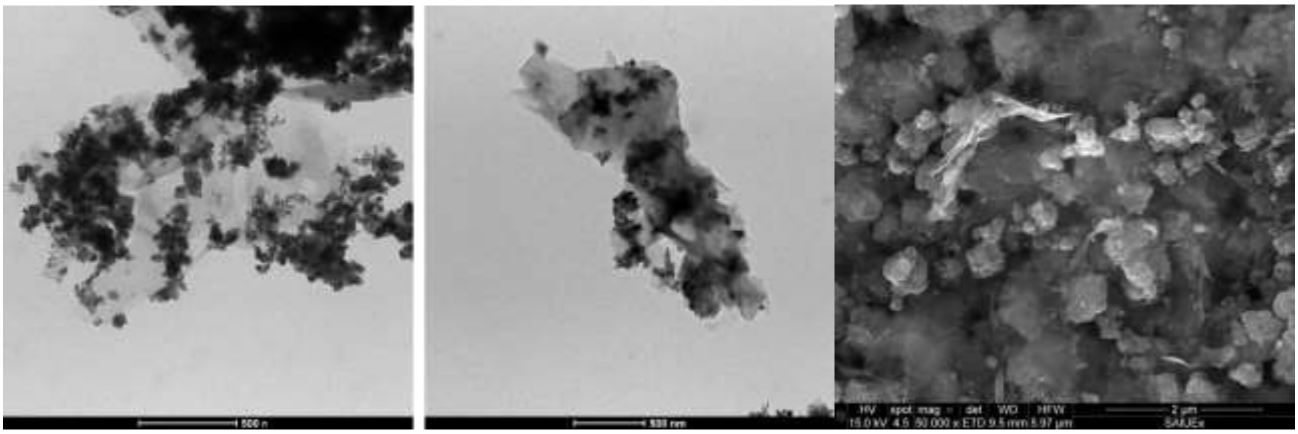
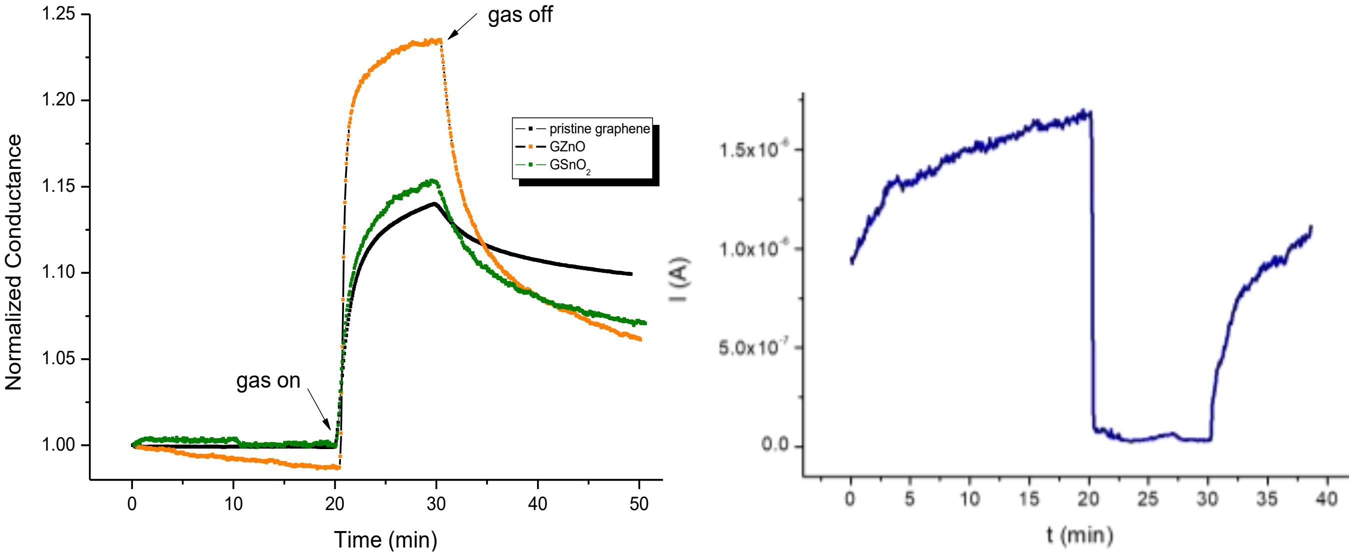
Figures



(a) (b) (c)

Figure 1: TEM images of (a) $GSnO_2$ and (b) GZnO; (c) SEM image of $GTiO_2$.



(a) (b)

Figure 2 (a) Dynamic response of pristine graphene, GZnO and $GSnO_2$ sensors to 1 ppm NO_2 at room temperature; (b) dynamic response of $GTiO_2$ sensor to 1 ppm NO_2 at room temperature.

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Optimizing the methodology for the production of reduced graphene oxides (rGO) by laser irradiation, chemical, thermal, and combined routes

Graphene has multiple potential applications [1], due to its unique structure, with extraordinary electrical, optical, mechanical or thermal properties. Some of these applications include energy generation and storage, electronic devices, nanocomposites, supercapacitors and so on [1].

Several approaches have been developed for producing graphene [2] and graphene based materials. These graphene based materials have paid a lot of attention because of their versatility, lightweight, abundance and their large surface-to-volume ratio in some cases. One of the most promising graphene-like materials in terms of high yield, low cost and easily up-scalable is the reduced graphene oxide (rGO) produced by chemical routes. The strategy for rGO chemical production is based on the oxidation of graphite to graphite oxide (GO) followed by exfoliation to obtain graphene oxide. Subsequent reduction processes afford a variety of rGOs with tunable Carbon-to-Oxygen (C/O) ratios depending on the reducing agent and reaction conditions although never results in complete removal of oxygen-containing groups [3]. Since the presence of residual functional groups and defects can alter the structure and properties of reduced graphene oxide (rGO), the application of feasible reduction strategies to obtain high quality rGO with low number of defects is crucial [4]. In this work, some routes have been proposed and optimized for reduction of GO for comparison and optimization purposes. These approaches include laser irradiation [5], ascorbic acid addition [6], thermal expansion [7,8] and combined chemical and solvothermal reduction [9]. rGOs from each approach were characterized chemical, structural and morphologically in order to obtain precise information to apply these rGOs to the appropriate application.

GO was prepared following the Hummer's method [10] with slight modifications. Laser irradiation was made using an infrared laser that reduces the graphene oxide [5], converting the initial graphene oxide compact layer into a three dimensional open network of exfoliated graphene flakes. Synthesis of rGO by ascorbic acid as green reducing agent (rGO-AA) was carried out by dispersing of GO in ultrapure water and reduction at room temperature. Thermal reduction and exfoliation was simultaneously performed inserting graphite oxide in an electric furnace For the solvothermal assisted reduction, a GO aqueous solution was treated with L-ascorbic acid, transferred to PTFE-lined autoclaves and heated at 120 ºC for 24h.

The obtained rGO samples were characterized by XRD, SEM, BET and other techniques. These characterizations were performed in order to obtain adequate information to select the best application: high conductivity for electronical applications and high surface area to volume ratio for pollutant removal or energy storage (hydrogen, batteries and supercapacitors). One of the promising applications is the hydrogen storage, in which high surface area is highly recommended. Wherefore, BET analysis provides surface areas information, important parameter in the sorption capacities of these rGO samples (table 1). Laser irradiation treatment has provided the high surface area.

Table 1. BET analysis of rGOs samples reduced by different methods.

Sample	Specific surface area ($m^2 g^{-1}$)
rGO-AA	37
rGO-AA-T	27
rGO-thermal	338
rGO-Laser	742

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Preparation of graphene-based conducting coatings on multicomponent textiles

Conductive fabrics have attracted increased interest due to their potential use in areas such as energy, health and security, amongst others. In recent years there has been growing interest in the development of functional fibres and fabrics containing graphene, due to them being lightweight, and having excellent mechanical, electrical and thermal properties that graphene can impart to the materials.[1,2] The main objective of our ongoing project is the development of conductive fabrics through the incorporation of graphene into commercial polymeric fabrics. One of the approaches consists in the preparation of graphene-based coatings on textiles, more specifically coating the fabrics with graphene oxide (GO) and its subsequent reduction to obtain conductive fabrics. Both chemical and thermal reduction methods are evaluated in order to determine the best conditions to in which to achieve conductive properties, whilst preserving the textiles integrity. In addition, the effect of bending and washing cycles on the conductivity of the fabrics is evaluated.

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Influence of carbon nanotubes and graphene nanoplatelets on the surface free energy and zeta potential of high density polyethylene

Abstract

In the recent years, graphene as multifunctional 2D-atomic nanomaterial, was found of interest in different research fields such as biomedical, tissue engineering, material sciences etc. Graphene becomes one of the most studied nanomaterials in the world, due to its properties. In the frame of this experimental investigation Graphene nanoplatelets (GNPs) were chosen as one of the nanofillers for preparation of binary and ternary nanocomposites, due to the unique properties of graphene. As second filler in this experimental investigation multi-walled carbon nanotubes (MWCNTs) were used. In order to obtain innovative composites focused on the applications in fused deposition modelling (FDM) technique, thermoplastic polymer was chosen as basic polymer matrix. The most widely used thermoplastic materials are polyolefins, due to their excellent thermomechanical properties and good environmental compatibility, including easy recycling [1].

High density polyethylene (HDPE) is one of the most commonly used polyolefin polymers, due to its low cost, good processability, nontoxicity, light weight, high mechanical flexibility, high specific strength and high chemical resistance. However, the preparation of nanocomposites based on HDPE is challenging due to its strong non-polar behavior. This is especially true for CNT- and graphene-based composites, as their high surface area make the agglomeration phenomenon most likely during the processing, especially for melt-mixing techniques. This happens despite the fact that both graphene and MWCNT, in their pristine forms, are hydrophobic, with reported water contact angles of ~92˚ [2] and ~139˚ [3], respectively. However, recently advances have been done to understand the peculiarities of these systems, especially when using two-dimensional (2D) fillers into high-shear processes (e.g. twin-screw extruder).

In this study two-step method for developing HDPE/MWCNT, HDPE/graphene and HDPE/MWCNT/graphene nanocomposites were proposed. This methodology was applied in order to obtain exfoliation of the graphene and wrapping of both fillers onto polymer particles. As first step for mixing of polymer powders with the carbon fillers was chosen ball milling technique [4-6].

In frame of this experimental study, contact angle measurements were provided, firstly in order to evaluate the influence of the fillers (graphene and CNT) on the surface properties of the polymer matrix. By the results of contact angle of mono-filler and bi-filler composites, we can evaluate the influence of fillers on the wettability and surface free energy (SFE). On other hand, streaming potential measurements were carried out to evaluate the charge changing on the surface of the thin films by the presence of the fillers. Both techniques allowed a more complete understanding of the surface properties of the composites and correlate these results with the morphology of these materials.

Experimental results show quite homogeneous hybrid materials with increased wettability, of all investigated nanocomposites. Figure 1 present water contact angle results of composites containing graphene nanoplatelets (GNP). On the graph can be seen water contact angle versus weight content of GNP filler.

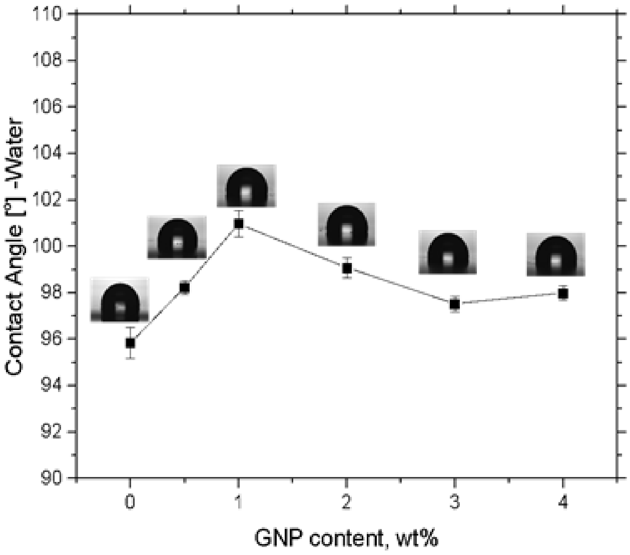

Figure 1. Water contact angle of HDPE/GNP composites

The contact angle results show negligible changes in surface free energy of mono-filler and bi-filler systems. On other hand, dispersive components for all samples are increased, which is due to better Van der Waals interactions. Due to non-polar behavior, of HDPE and both fillers, all composites have increased contact angles and decreased polar components, which is related to dipole-dipole forces in the investigated materials.

Zeta potential results show that composites with added MWCNT (mono-filler and bi-filler) have better stability and quite well dispersed fillers. In the case of GNPs composites, only HDPE/1wt% GNP have good filler distribution and stable system, which was also observed by optical microscopy analysis.

Acknowledgements

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