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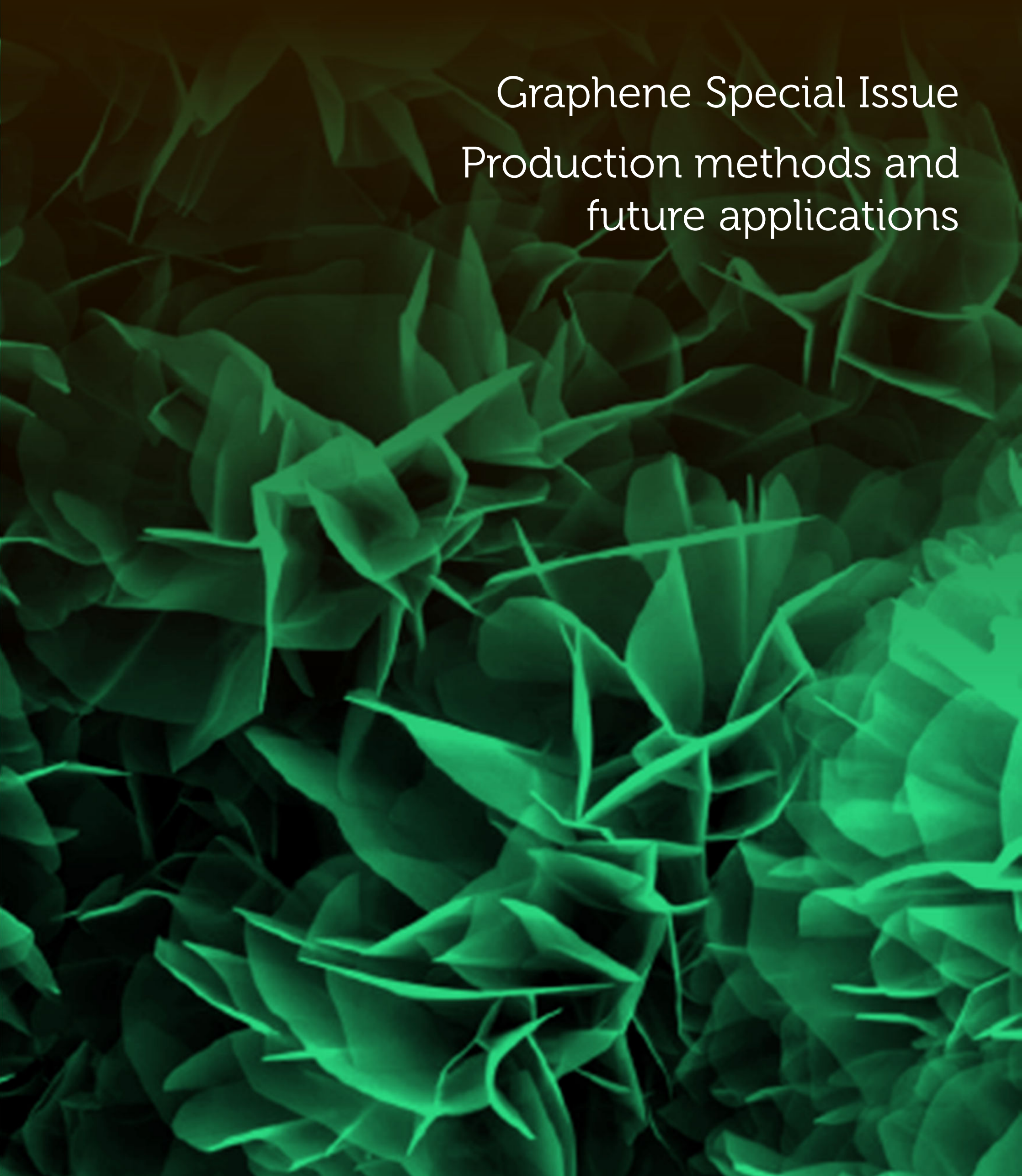
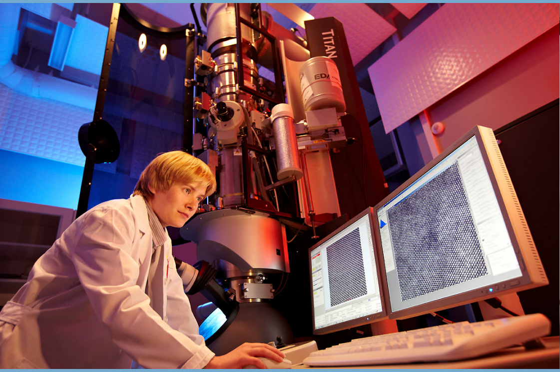


## Graphene Special Issue

## Production methods and future applications


TITAN

# dear readers,

Considering the huge number of future applications in almost all markets (aerospace, photovoltaics, optical communications, displays, data storage, etc.), graphene-based emerging technologies are certainly going to revolutionize the 21st century.

This E-nano Newsletter special issue contains articles providing new insights on “Production methods and future applications” of Graphene (one-atom-thick sheet of carbon / in 2010, A.K. Geim and K. Novoselov, were awarded the Nobel Prize in physics for “groundbreaking experiments regarding the two-dimensional material graphene”) - five leading companies in the field (Aixtron, Graphenea, Haydale, Incubation Alliance and Grupo Antolin/GRAnPH) contributed.

We would like to thank all the authors for the time and effort they invested in writing these manuscripts.

**> Dr. Antonio Correia** Editor - Phantoms Foundation

**Cover Image**
Courtesy: Incubation Alliance, Inc.

# contents

# editorial information

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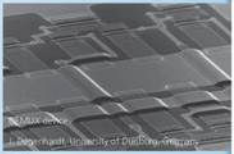

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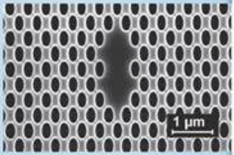

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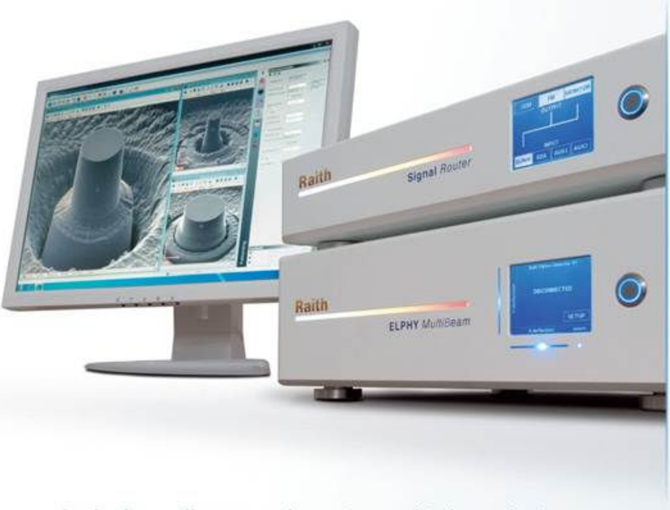

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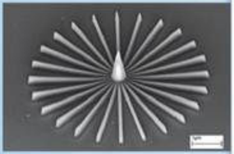

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# Advances in Graphene Chemical Vapour Deposition

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Due to its wide ranging and distinctive mechanical, optical and mechanical properties [1-3] graphene research is advancing rapidly and is undergoing a shift in focus from fundamental research to more pragmatic, industrially viable applications. Within the last decade significant commerce and entire industries have spawned from this one material, including companies developing growth, isolation and integration techniques. Indeed, there is little sign of the field slowing down. It is this fast-pace which necessitates regular brief reviews. Here we report on some recent advances in graphene chemical vapour deposition. We focus on the growth on metallic catalysts and dielectric substrates, the use of plasma enhancement, as well as the the underlying kinetics. We conclude by detailing the push of the research community for large-grained materials and what progress has been made toward large area deposition.

In the past decade some of the highest quality graphene devices have been fabricated through mechanical exfoliation techniques from natural sources such as highly oriented pyrolytic or Kish graphite. Though the graphene produced in this manner is very high quality, and as such ideally suited for fundamental studies, it is unfortunately not scalable to the dimensions required by integrated circuit foundries with crystals of irreproducible size, thickness and shape, often forming in uncontrollable positions. Chemical vapour deposition (CVD) is perhaps the most promising deposition technique available to date. CVD is scalable, comparatively inexpensive, and a familiar and already adopted process in Si foundries. CVD is also capable of producing high quality graphene conformally over very large areas. Grain size, morphology, layer number, and graphitic quality are all sensitive to the growth conditions, and small variations manifest readily in the material's electrical and optical properties and though the field of graphene CVD is still in its infancy, high quality materials have already been produced with room temperature field effect mobilities nearing 10,000 $cm^2V^{-1}s^{-1}$ [5, 6].

CVD of pyrolytic graphite on transition metals by the catalytic deposition of carbon precursors was proposed over a century ago [7, 8], however, it was not experimentally demonstrated until the 1950s [10, 11]. Since then the field of graphite production has developed sporadically [13-15], and it was not until 1984 when Kholin *et al*. [17] undertook what is considered to be by many as the seminal growth of graphene by CVD. Only in 2004 did graphene growth become a main stream research theme after gaining significant traction due to the isolation of graphene monolayers [18].

Early work on graphite growth revealed that metals with low carbon solubility were inefficient catalytic materials. Nevertheless, Cu, perhaps the most widely used graphene catalyst to date [19, 5, 20], due to its low cost and established compatibility with integrated circuit manufacturing processes, was unintentionally used to grown graphite in 1991 [21, 22]. Since then various other low carbon solubility (approximately $10^{-3}$ - $10^{-2}$ at.% for Cu at 1000°C [23, 24]) metals have proven viable catalysts, such as Ir [25], Pd [26], Ru [27], Rh [28] and Pt [29], with solid and liquid Cu showing potential also [30, 31]. Other catalyst materials have been identified though in the case of precipitation mediated catalysts, such as Ni [32-34] and Co [35], the significantly higher carbon solubility (approximately 1.3 at.% at 1000°C [36]) makes it increasingly challenging to controllably deposit monolayer graphene rather than multi-layer graphite-like materials which often form in a spatially chaotic, patch-work fashion. Formed from multiple grains, these films are polycrystalline and are, macroscopically at least, dominated by electron transport at the grain boundaries. Portions of CVD films often contain more than a single layer, where each of these layers may possess a distinct stacking character and orientation relative to the other layers. Thus, there remains significant scope for the detailed study of the mechanisms associated with, and the subsequent control of, the underlying catalysis as this has yet to be fully understood.

To exemplify the current state-of-the art in large-area reproducible graphene growth, using 500 nm physical vapour deposited Cu thin films on 1 µm thermally oxidised Si under a 25 mbar $H_2$/ Ar / $CH_4$ atmosphere at 1000°C, we have deposited 100 mm diameter, wafer-scale, low-defect density, monolayer graphene films by cold-walled thermal CVD (Aixtron Black Magic Pro., Figure 1a), as confirmed by Raman spectroscopy before and after polymer-mediated transfer to $Si/SiO_2$ ($I_D/I_G$ = 0.01 - 0.05, Figure 1d,e). By monitoring the time-dependent evolution of the graphene crystals (Figure 1b), grains approximately 2-5 µm in diameter, immediately prior to coalescence, were observed where both the nucleation density and growth rate showed an evident dependence on carbon precursor partial pressure. Raman mapping showed a polycrystalline material with a high degree of connectivity (Figure 2a). Transport studies supported these findings with capped graphene transistors showing high mobilities in the range of 3000-6000 $cm^2/Vs$ with symmetric hole/electron transport (Figure 2b). Spatial correspondence between low-energy electron micrographs of the graphene grains and optical micrographs of the catalyst grains showed not statistically significant correlation suggesting incommensurate registration. Nonetheless, these films are predominately monolayer (> 95%) with millimetre scale coverage with a variation in 550 nm optical transparency of approximately ± one monolayer and a spatially resolved sheet resistance of 3.2±2.1 kΩ/sq. (Figure 2c). Using these materials we have demonstrated artificial graphene multi-layer stacks allowing us to systematically control both the sheet resistance and optical transmission (Figure 2d) and though this is certainly one approach toward the fabrication of artificial stacked media further work is required to achieve this by direct CVD.

Self-limiting growth, where only single monolayers form with no new layers being deposited irrespective of the precursor exposure time or growth conditions, is hotly debated [19]. Bhaviripudi *et al.* [37], showed a pressure dependence with self-limiting deposition between 0.1 and 1 mbar, whilst they noted multi-layer deposition at atmospheric pressures. Indeed, we have evidenced bilayer and trilayer growth on Cu [38], where the degree of hexagonality suggested that the growth proceeds from beneath the primary layer.

In the case of high carbon solubility catalysts growth nominally precedes from beneath the already deposited graphene films by means of precipitation from a supersaturated carbon reservoir. The underlying mechanisms are, however, less clear in the case of Cu, as are the nucleation sources.

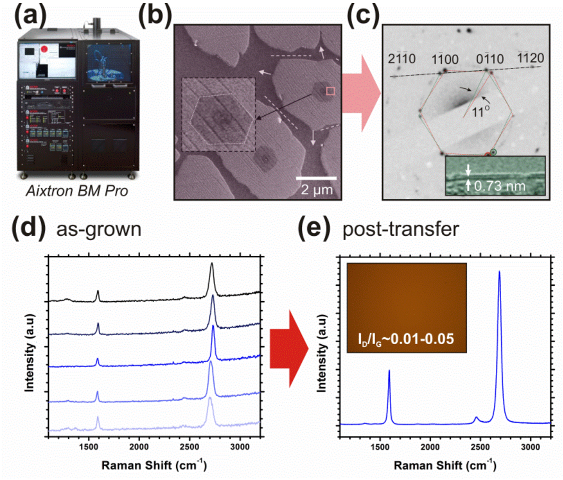

**Fig. 1 >** *As-synthesised Aixtron Ltd. / Cambridge University thermal CVD graphene.* (a) An Aixtron Black Magic Pro carbon nanotube and graphene deposition system. (b) A scanning electron micrograph of trilayer graphene growth on Cu at 920°C after 4 min precursor exposure grown on Cu (Copyright 2013 American Chemical Society) [38]. (c) A select area diffraction pattern substantiating turbostratic alignment in our bilayer materials with an inter-plane rotation of 11°. *Inset:* High resolution transmission electron micrograph showing an as-synthesised 0.73 nm thick graphene bilayer. (d) 457 nm Raman spectra directly on the as-grown graphene at the control points, as shown in Figure 3b. (e) 512 nm Raman spectra following PMMA-transfer to a 200 nm thermally oxidised Si substrate. Inset: Optical micrograph of a transferred film showing extremely uniform coverage with few pin holes./

Using nano auger spectroscopy, Celebi *et al.* [38] evidenced spatially coincident Cl agglomerates at the graphene grain centres. The commercial foils used here were electropolished with HCl - an industry standard cleaning process - which likely produced the observed nucleation centres. Nevertheless, several alternative sources of nucleation centres have been proposed, including crystal facets and metal step-edges [39] as well as carbon centres themselves [40]. Thermally stimulated specific crystallographic surfaces have also been implicated in effecting the graphene quality and growth rate. Wood *et al.* [41] determined that faceted Cu(111) produced pristine monolayer graphene with higher growth rates than faceted Cu(100) [41]. Though there is some evidence to suggest that careful control over the lateral dimensions of the Cu grain boundaries themselves, which vary with the catalyst thickness, the annealing pre-treatment time and annealing environment, this is still somewhat controversial as individual graphene grains can span multiple catalyst grains and have shown no definite epitaxial relationship with the substrate [6]. The formation of nucleation centres only occurs during initial precursor exposure, with inhibited nuclei formation thereafter, as revealed by Kim *et al.* [42]. Here they also showed that higher growth temperatures lead to lower nuclei densities. Catalyst pre-treatment, precursor partial pressure and total growth pressure have also been proposed as ways in controlling the nucleation density.

Interfaces between adjacent graphene grains degrade the graphenes electronic properties. These scatter centres disrupt intrinsic transport reducing the range of viable technological applications. As such, much research has been directed toward the growth of films formed from large grains. Typical graphene domains are around 10 µm in diameter, however, using LP-CVD with a methane precursor and a Cu catalyst at 1035°C, Li *et al.* demonstrated monolayer dendritic crystals of a single crystallographic orientation up to 0.5 mm in diameter [43, 44]. By patterning and etching a primary graphene layer, Yu *et al.* [6] reported on a regrowth approach from regular arrays of etched graphene as one viable alternative to increase grain size, facilitating inter-domain referencing and controlled nucleation density.

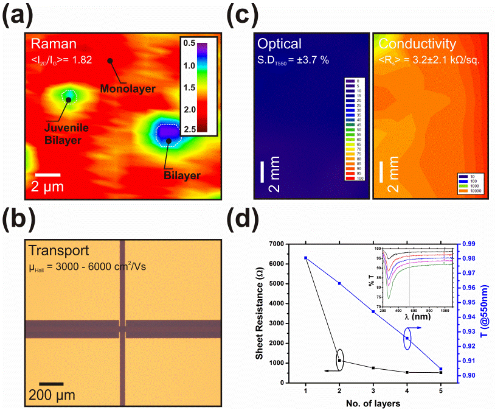

Fig. 2 > (a) Raman map showing high inter-grain connectivity and the presence of sub-micron juvenile bilayer regions surrounded by a predominantly monolayer material ($<I_{2D}/I_G>=1.82$) (Scale bar: 2 µm). Adapted from [38] (Copyright 2013 American Chemical Society). (b) Optical micrograph of a four-terminal, back gated field effect transistor with measured mobilities of 3000-6000 cm$^2$V$^{-1}$s$^{-1}$ (Scale bar: 200 µm). (c) Spatially resolved 550 nm optical transmission showing a minor variation of approximately a monolayer over millimetre length scales (left), and four-probe DC conductivity map (right) showing $<R_s>= 3.2 \pm 2.1$ kΩ/sq. for the as-synthesised graphene (Scale bar: 2 mm). (d) Variation in sheet resistance and 550 nm optical transparency of our as-grown CVD graphene following multiple graphene transfers by PMMA./

The interesting optoelectronic properties of graphene also depend critically on the number of layers, as well as inter-grain registration (defined as the orientation of individual grains relative to the adjacent grain). Grains can be dendritic [45], lobed [44], rectangular [46], to near-perfect hexagonal [19, 47, 6], as well as a range of intermediary forms [30]. The composition of the inert gas / $H_2$ ratio [30], total growth pressure and precursor partial pressure [48] are all possible mediators of these morphological variations. LP-CVD typically produces nominally hexagonal grains whilst our mid-pressure CVD (1-20 mbar) experiments tend towards increasingly dendritic growth, as similarly reported elsewhere [44]. Particular grain morphologies favour low-defect interfaces between grains, whilst others, such as dendritic crystals, can be extremely defective thereby degrading, and perhaps even masking the intrinsic transport properties of the graphene, which too can be augmented by grain stacking. Whilst the detailed stacking order of CVD-synthesised graphene has yet to be explicated in any great detail, our Raman findings and select area diffraction studies suggest turbostratic layers, as have others [49]. Nevertheless, recently Bernal AB - the most energetically favourable stacking configuration - has been reported [50-55]. Bernal AA and AC, though theoretically predicted to be rich sources of interesting electronic properties, have yet to be synthesised. Despite the evident advances in the growth of these prototypical layered materials, at present, there is no conclusive experimental evidence to explain the fundamental mechanisms involved in registered growth. Nevertheless, though recipes to achieve novel stacked materials have been developed, full device integration will only be achieved when the fundamental challenges of reduced growth temperature and direct growth on dielectrics are resolved.

At present, the narrow thermal budget of conventional CMOS processing, typically limited to temperatures lower than 300°C, requires, by necessity, that graphene can only be integrated by integrated by mechanical transfer approaches. This is costly, time-consuming, requires trained individuals, and is not scalable. Moreover, even if suitable dielectric catalysts are found in the near future, the graphene itself would still be limited to the base level due to the low thermal budget. Thus, to afford true CMOS compatibility growth temperature reduction is imperative. At present, the most time consuming, and therefore costly feature of most CVD growths is the heat-up and cool-down cycles, particularly in the case of hot-walled reactors such as tube furnaces. Any reduction in temperature immediately increases throughput, with consequent financial savings. Significant mismatch between the negative thermal expansion coefficient of the graphene and the positive thermal expansion coefficient of almost all catalyst materials thus far available necessitates reductions in growth temperature also. This will likely minimise catalyst-graphene interfacial strain, and hence the cumulative degradation of the graphenes electronic properties, such as augmenting the local work function due to wrinkle and corrugation formation. Addou *et al*. [56] reported the growth of SLG on Ni(111) at 500-600°C under ultra-high vacuum conditions using an ethylene precursor, whilst Li *et al.* [57] demonstrated growth on Cu using benzene at 300-500°C. The use of increasingly reactive hydrocarbon precursors, which readily thermally dissociate at lower temperatures, such as acetylene (ca. 400°C), is favourable, though increased lattice disorder and reduced uniformity, partly attributed to accelerated deposition rates, is to be expected. Nevertheless, alternative and increasingly exotic catalyst materials may also enable a reduction in growth temperature.

Studies on graphite precipitation highlighted the catalytic potential of various transition metal carbides, including TaC [58], WC [58], TiC [58], HfC [58] and $LaB_3$(100) [59]. However, few of these materials have been investigated. Rather, increasingly exotic metallic catalysts, often based on binary alloys of metals of disparate carbon solubility, have been developed. Weatherup *et al.* [60] employed Au-Ni, whereas Liu *et al*. [61] investigated a Cu-Ni solid solution, and Lin *et al.* employed a Co-Cu system [53]. In a similar vein, significant research efforts have been toward the development of dielectric catalysts.

Most electronics applications require graphene on dielectric substrates. Though various mechanical transfer processes have been developed to this end, these approaches ultimately inhibit full-scale industrial adoption. Direct growth of graphene on dielectrics is currently limited to epitaxial techniques where Si sublimation from expensive and size-limited SiC substrates occurs under ultra-high vacuum or near atmospheric Ar atmospheres. CVD is significantly cheaper and more flexible with respect to the variety of substrates. Many attempts at CVD on various dielectrics ($SiO_2$ [62], sapphire [63], $Si_3N_4$ [64], ZrO [65], MgO [65, 66], h-BN [67], and SiC [68]) have been reported. However, to date, high quality graphene, at industrially viable growth temperatures, has only been achieved using metal catalysts and though regions of graphitic materials have indeed been evidenced, yields and areal coverage remain low with most reporting

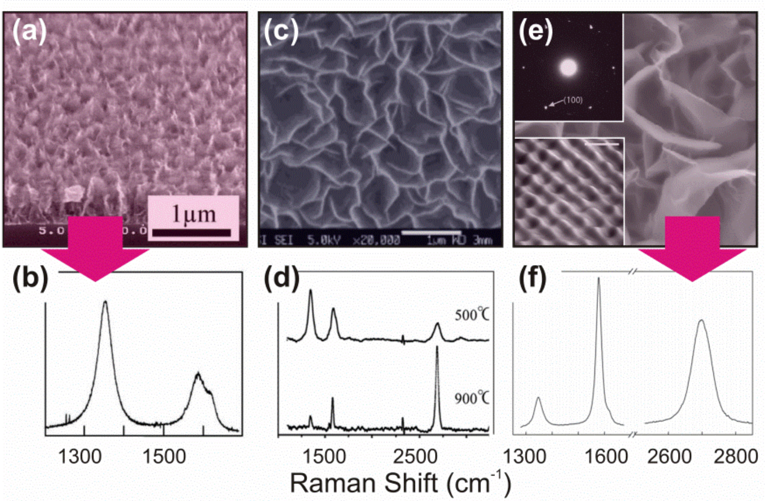

**Fig. 3 >** *Graphene growth by PE-CVD.* (a) A cross-section scanning electron micrograph of carbon nanowalls grown by capacitively coupled plasma [4] and (b) the corresponding Raman spectrum highlighting the high degree of defectiveness [4] (Copyright 2004 American Institute of Physics). (c) An areal scanning electron micrograph of a defective graphene-like folded material by microwave PE-CVD [9] (Copyright 2002 Wiley). (d) Raman spectra of graphene grown by radio frequency PE-CVD at 500°C and 900°C [12]. (Copyright 2012 Elsevier). (e) A scanning electron micrograph of micro-wave PE-CVD graphene corrugations, select area diffraction pattern (*inset*), scanning tunnelling microscope image (*inset*) [16] and (f) the corresponding Raman spectrum highlighting the potential growth of higher quality materials via plasma processing [16] (Copyright 2010 The Institute of Physics)./

the formation of defective few layer nano-graphitic flakes and amorphous carbon. Nevertheless, plasma processes are considered to be one possible route to the direct deposition on dielectrics.

Introducing plasma during thermal CVD of carbon nanotubes and amorphous carbon facilitated significant reductions in growth temperature. Plasma stimulates the formation of highly reactive gas species [69-71] and has been used to grow graphene-like materials at temperatures as low as 317°C [72]. However, these films, as per the growth on dielectrics, were highly defective and are only suitable for flexible transparent electrodes due to the relaxed technological requirements on material quality. Few have managed to grow low-defect density graphene of quality equivalent to high temperature thermal CVD as aggressive plasma, which readily etch, makes it particularly challenging. Residual oxygen partial pressures exacerbate this and may induce further deleterious etching during deposition. Nevertheless, several plasma enhanced CVD (PE-CVD) strategies are presently being pursued. These include rapid heating [73], capacitively coupled (Figure 3a,b) [4], radio frequency [74, 35] (Figure 3d), microwave (Figure 3c,e,f) [75], direct-current [76], and inductively coupled [74]. Using Cu foil at 500°C, Terasawa *et al.* [12] measured the composition of the plasma-dissociated growth atmosphere during the formation of highly corrugated graphene-like films. Using *in-situ* UV-Vis spectroscopy the dominance of CH, $C_2$, H, and $H_2$ was noted, whilst Wu *et al.* reported the growth of carbon nanowalls by PE-CVD [9]. Though some progress has certainly been made toward the PEC-CVD of graphene no studies to date have successfully demonstrated truly planar monolayer graphene to a quality comparable to thermal CVD.

At present there is an on-going debate as to the underlying growth kinetics dictating graphene growth during CVD [38, 42]. The fundamental kinetic pathways and atomistic mechanisms are clearly disparate for different catalysts. However, in general, growth proceeds via the decomposition of a carbon feedstock (albeit solid [57, 48], liquid [57, 77] or gas [78, 38, 79]), followed by an incubation and nucleation period, and finally larger domains grow and coalesce. During growth physicochemical phenomena compete - such as precursor dehydrogenation, adatom surface and bulk diffusion, thermally mediated desorption, and lattice integration. Each kinetic pathway presents a distinct temperature dependent activation energy which are empirically accessible through temporally monitoring the crystal morphology. Cu-catalysed graphene growth is thought to occur by surface limited processes from the crystallization of a supersaturated catalyst surface and sub-surface. Indeed, isotope labelling of precursor gases revealed that growth on Cu is surface mediated, rather than bulk diffusion as in the case of Ni-catalysed growth which proceeds by a segregation-precipitation process from a solid solution reservoir [80]. By studying the time-dependent activation energy, Celebi *et al.* [38] rationalised their findings using a Gompertzian sigmoidal growth model which was rate determined by adsorption−desorption and the dispersive kinetic processes of catalytic dissociation and dehydrogenation of the carbon precursor. Using a Robinson and Robins growth model and a conventional Johnson-Mehl-Avrami-Kolmogorov approach of phase transformation, a bimodal activation energy, indicative of two dominant nucleation regimes associated with adatom capture, surface diffusion, and re-evaporation was reported by Kim *et al.* [42]. It was suggested that growth-limiting was due to carbon adatom attachment to the grain edge. Distinct differences in the underlying kinetics are certainly evident for atmospheric- and low-pressure CVD [37]. For ambient pressure-CVD, Bhaviripudi *et al.* [37] suggested that mass transport of the carbon species - which itself is yet to be experimentally identified - to the catalyst surface presents the dominate activation pathway, supporting previous claims of diffusion-limited growth.

Large-area deposition, broadly defined as areas > 100 mm x 100 mm, has thus far been primarily demonstrated through the use of wet-chemistry processing based on chemical-mechanical exfoliation techniques coupled with established transfer processes such as Langmuir-Blodgett [81], screen printing [82], spray coating, spin coating, inkjet printing [83], dip pen nanolithography, Mayer bar, flexographic printing, and gravure printing. Though the number of *chemi douche* techniques is unquestionably wide, as is the type of destination substrates that these approaches can be used with, such films are ultimately ensembles of graphene flakes and as such lose the intrinsic electronic and optical properties of truly monolayer and few-layer graphene. Though an exceptionally flexible technique that allows transfer of mono layer graphene to a wide range of arbitrary substrates, polymethlymethacrylate-mediated transfer [84] becomes challenging for CVD films greater than a few centimetres square. Folding and corrugations become particularly problematic. Dry-transfer techniques, like hot press lamination [5] and anodic bonding [85, 86] afford large area transfer though such approaches limit the variety of destination substrates. Nevertheless, regardless of the exact transfer technique employed, to facilitate large area transfer it is first necessary to be able to grow large area uniform films.

Using our current understanding of graphene catalysis here we demonstrate uniform, centimetre area graphene growth by CVD, as similarly demonstrated elsewhere in 2009 [19, 77]. In 2010, 30 inch graphene films were deposited by hot-wall thermal CVD and transferred via hot press lamination [5] in a pseudo roll-to-roll process. Truly roll-to-roll processing has yet to be demonstrated due to the challenging catalyst transfer and vacuum conditions required. Nevertheless, large-area cold-wall CVD reactors are emerging on the market place (Aixtron BM 300MT, Figure 4a). Four inch wafer growth by thermal CVD is now a standard procedure (Figure 4b) and we have reproducibly deposited graphene monolayers ($\langle I_{2D}/I_G \rangle = 2.65$) on > 200 four inch wafers with consistently low defects ($\langle I_D/I_G \rangle = 0.089$) (Figure 4c) and near 100% area coverage (Figure 4d). We have also realised the deposition on 65 mm x 65 cm Cu foils to grow similarly high quality graphene.

On-going research into the parametric growth window will undoubtedly yield detailed correlations between controllable growth processes and material quality and if a link can be established therein this may well accelerate wider scale graphene adoption.

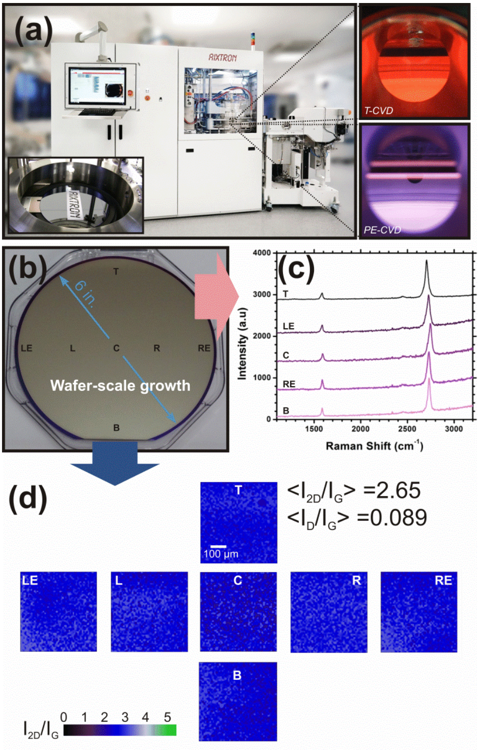

**Fig. 4 >** *Large-area graphene CVD.* (a) Aixtron Ltd. BM300T 300 mm nanocarbon deposition system operated in thermal (top inset) and plasma enhanced mode (bottom inset). (b) Image of a 6 in. Si/$SiO_2$ supported Cu growth wafer following graphene CVD. (c) Typical Raman (457 nm) spectra at positions denoted T (top, 37.5 mm from centre), LE (6 mm from left edge), C (centre), RE (6 mm from right edge), and B (bottom, 37.5 mm from centre), as per (b). (d) 500 x 500 µm Raman maps at positions denoted in (b), showing the high degree of uniformity with $\langle I_{2D}/I_G \rangle = 2.65$ and $\langle I_D/I_G \rangle = 0.089$ (Scale bar: 100 µm). (Courtesy of L. Tao and D. Akinwande, University of Texas at Austin)./

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nanoresearch

# The Great Potential of Graphene

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## Abstract

Graphene has emerged as a new material with a very bright future. Even if it has come a long way since it was first isolated in 2004, there is still a long road ahead until it becomes a commercial success story. It is predicted that graphene will have different time to market depending on the application complexity and required graphene properties. At present, there are graphene manufacturing methods that could be suitable for the large scale production of this material. However, this is not the only requirement that has to be fulfilled in order to have a successful market uptake of graphene. In this article graphene production methods and potential applications will be discussed as well as trying to shed some light into its bright future.

## Introduction

Since its early days, graphene has attracted a great deal of attention due to its extraordinary properties. Never before did one same material comprise so many incredible properties such as very high electronic mobility, high thermal conductivity, good mechanical properties, high transparency, flexibility, etc. In addition, graphene has also opened a new dimensionality for other materials. Some of graphene's properties are a consequence of the 2D nature of this material (transparency, flexibility) while other properties are due to the chemical structure (electronic mobility, thermal conductivity). These properties render graphene with a great potential to be applied in many different fields from electronics, optoelectronics, energy storage, photonics, lighting and up to aerospace. However, in order for academic interest to be translated into commercial success there are a number of requirements that have to be fulfilled such as the availability of suitable production methods (cost effective, scalable, reliable), an effective technological progress, market readiness/ awareness, industrial readiness of value chains, public sector support and socio-political considerations.

Charge carriers in graphene can travel thousands of interatomic distances without scattering, as a consequence graphene presents very high charge carrier mobility values (> $10^5$ $cm^2/Vs$) even at room temperature [1]. It can stand current densities up to $10^8$ $A/cm^2$, a few orders of magnitude higher than copper [2]. It is the best heat conductor known to date with thermal conductivity values > 4,000 W/mK at room temperature [3]. Graphene absorbs 2.3% of light over a broad range of the visible spectrum [4]. It has also been found to be impermeable to gases including helium [5].

These unique properties provide graphene with one of the requirements that has to be fulfilled in order to become industrially successful. Depending on the application the required graphene properties and in turn the format will vary. As a consequence there are two main graphene grades that are determined by the format: graphene films and platelets. The graphene films are continuous and uniform that can cover the whole surface of the substrate. While the graphene platelets are smaller flakes (< 100 μm lateral dimensions) in the form of powder. There have identified two main graphene manufacturing techniques that could supply graphene in relatively large scales. On one hand, chemical vapour deposition (CVD) has been identified as the technique to produce graphene films in large scale while liquid phase exfoliation techniques are suitable to manufacture graphene platelets in an industrial scale.

In addition, technological progress, market awareness and industrial readiness are also requirements that would have to be fulfilled [6]. However, taking into consideration that a new material could take up to 20 years to be taken up and incorporated in final market applications; there is still a time margin in the case of graphene. Furthermore, the term graphene includes different types and grades of graphene. Therefore it is expected that depending on the complexity of application and graphene grade the time to market will vary.

## Graphene Synthesis

Graphene was first isolated in 2004 using the micro-mechanical exfoliation or “Scotch tape” method [7]. The obtained flakes had very high quality, however, this method was not an industrially scalable technique due to the extremely low yields and limited size of the obtained flakes.

Then, the liquid phase exfoliation methods were developed to fabricate graphene platelets. These methods could in principle be suitable to produce large quantities of graphene platelets. Among them, the chemical exfoliation of graphite to produce graphene oxide (GO) in a first step was found to be a high yield and efficient method to produce monolayer platelets of GO. In a second step these GO platelets are reduced chemically, thermally or via irradiation with ultraviolet (UV) or infrared (IR) light in order to restore up to some extent the electronic properties of the starting material.

Graphene films were initially produced using the sublimation of silicon atoms from silicon carbide (SiC) wafers. However, the main drawback of this method is the high cost and limited size of the starting SiC wafers.

Subsequently, CVD techniques started to be developed in order to produce graphene on metal substrates. The real breakthrough occurred when graphene could be grown on top of polycrystalline metal foils thus leading the way to a relatively economically viable production of graphene films. In the beginning graphene was grown on top of polycrystalline nickel foils however monolayer graphene could not be obtained homogeneously distributed across the foil surface [8]. Almost in parallel graphene was grown on polycrystalline copper foils over 1 x 1 cm areas [9]. This time due to the low carbon solubility within the copper foil the growth of graphene could be limited to only one layer over the entire metal surface. The graphene formation mechanism on copper was found to be different to the one on nickel where graphene is mainly formed via the precipitation of the dissolved carbon within the metal during the cool down stage. More recently, a 100 m long graphene film grown on copper foil was reported [10].

Graphene grown on copper has to be transferred onto insulating or arbitrary substrates for subsequent device fabrication or final application investigations. Therefore, the copper catalyst is typically etched away using wet chemicals and the graphene films placed on the final substrate. This transfer process could be turned into an advantage since it provides quite a versatile way of obtaining graphene on top of almost any substrate. In Figure 1 a graphene film that has been grown using copper foil via CVD and transferred onto a silicon wafer (with a 300 nm silicon dioxide layer) can be observed.

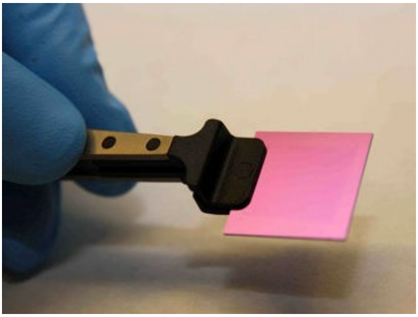

**Fig. 1 >** Image of a 1 x 1 cm graphene film on a Si/$SiO_2$ wafer./

## Applications

As a consequence of the broad range of properties, graphene has the potential to be applied in many very diverse fields such as energy, electronics, optoelectronics, touch screen and display technology, lighting, sensors, aerospace and biotechnology to mention a few. Graphene films are typically used in electronic and optoelectronic applications, touch screen and display technology, lighting, batteries, sensors and solar cells. While the graphene platelets have been applied in composites, coatings, printed electronics, batteries, supercapacitors and sensors.

It must be said that currently graphene is at a research stage and therefore the demand for this material is fairly low. However, it has shown very promising results in many applications, a few of these examples will be described thereafter.

The application of graphene in energy and more specifically in solar cells has been reported. Most publications deal with the use of graphene as the transparent electrode in inorganic [11, 12] and organic photovoltaic cells [13-15]. However, the application of graphene as the active material is not so obvious due to the low light absorption of this material. Nevertheless, graphene was found to be a very promising material for highly efficient broadband extraction of light energy into electronic degrees of freedom [16]. A single absorbed photon could create multiple hot carriers providing an essential ingredient for light harvesting with very low energy loss. The carrier-carrier scattering was found to be the dominant process, over the optical phonon emission, that dominated the ultrafast energy relaxation of the photoexcited carriers. In the carrier-carrier scattering process the energy of photoexcited carriers remains in the electron system being transferred to secondary electrons (originated from the conduction band) that gain energy, whereas in the phonon emission process the energy is lost to the lattice as heat. The energy relaxation process of the primary photoexcited electron hole pair in doped single layer graphene was investigated and the extent of the competing relaxation mechanisms determined. Due to the speed at which these relaxation processes occur an ultrafast optical pump-terahertz probe measurement technique was employed (Figure 2).

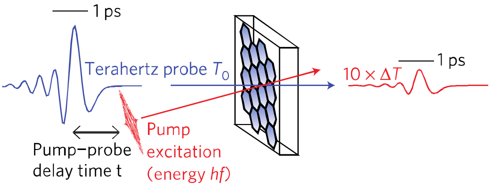

**Fig. 2 >** Experimental set-up used to study carrier dynamics [16]. Reprinted with permission from Nature Physics./

The ultrafast optical pump pulse was used to excite the carriers while the terahertz pulses provide the time resolved probe of the high frequency photoconductive response of the photoexcited carriers. The terahertz probe pulse passed through the sample after a variable delay time. The sample was prepared by transferring CVD grown monolayer graphene onto a quartz substrate.

This technique has been used before with a fixed pump wavelength to study charge dynamics in multilayer graphene [17-20] and with a variable pump wavelength to study the effects of carrier-carrier scattering in semiconductor materials [21-23]. In ref. 16 this technique was applied with a variable pump wavelength to study the energy relaxation cascade of photoexcited carriers in graphene. It was found that increasing the photon energy led to an increased number of electron-electron scattering events during the relaxation cascade and in turn a hotter carrier distribution, see Figure 3.

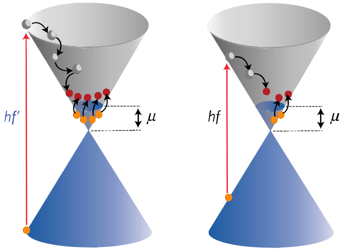

**Fig. 3 >** The effect of varying photon energy on the relaxation cascade shown for two photon energies hf′ > hf [16]. Reprinted with permission from Nature Physics./

The photoexcited density of carriers was found to scale linearly with photon energy for energies above the Fermi energy and at constant absorbed photon density. This linear relationship was found to apply over a wide range of photon wavelengths from the IR (0.16 eV) up to the UV (4.65 eV).

The experimental results were found to be in good agreement with a theoretical model that considered both electron-electron and electron-optical phonon scattering processes.

The fraction of the photon energy that remained in the electronic system after the cascade (integrated electron-electron efficiency) was found to be greater than 50% for photoexcitation energies as high as 3 eV. This further strengthened that the carrier-carrier interaction in graphene was highly efficient. In addition it was found that 9 additional hot electrons were created from a single photon energy of 3 eV at an extracted efficiency of 80% [24].

In conclusion, the transfer of energy from photoexcited carriers to electronic degrees of freedom was found to be efficient over a wide range of frequencies (from the UV to the IR) unlike in conventional semiconductor materials where the frequency range is limited by the bandgap. Future challenges to be addressed include finding ways of extracting the created electrical current and enhancing the absorption of graphene. This light harvesting efficiency could also be applied in the field of photodetection.

In another application, graphene showed great potential to be used in future optical transistors [25]. The electrical control of light was achieved by means of plasmon polaritons (coupled excitations of photons and charge carriers) in graphene. By electrically varying the graphene charge carrier density the plasmon modes could be switched on and off. The visualisation in real space of propagating and localised graphene plasmons was achieved using near field scattering microscopy with IR excitation light. The metallised tip of an atomic force microscope was illuminated with a focused IR laser beam using a scattering type scanning near field optical microscope (SNOM). The backscattered radiation was recorded simultaneously with the topography providing nanoscale resolved IR near field images. The extracted plasmon wavelength was 40 times smaller than the wavelength of illumination. CVD grown monolayer graphene was transferred onto wafers that had a 300 nm $SiO_2$ layer on them. The graphene was etched to create a triangular shaped ribbon and the voltage was applied perpendicular to the graphene through the Si backgate. By increasing the backgate voltage ($V_B$) and in turn vary the carrier density, the resonances (signal maxima) shifted towards larger ribbon width, see Figure 4. This was attributed to an increase in plasmon wavelength when the carrier density and thus the Fermi energy increased.

In Figure 4 the plasmonic switching and active control of the plasmon wavelength by electrical gating can be observed. The effect of plasmon damping (Fig 4 left panel corresponding to $E_F \leq E_p$ where no signal is observed) allowed the possibility to actively switch the graphene plasmons on and off by means of an electric field.

Electrical control of confined and propagating plasmons was demonstrated paving the way towards the miniaturisation of active nanoscale photonic devices [25].

In yet another application, flexible all solid state batteries were fabricated using monolayer graphene [26]. Graphene was found to behave like a hybrid between a thin film lithium battery and a graphene supercapacitor. This could provide graphene with a great potential to be used in portable electronic devices as the energy storage material. In order to build the thin battery (50 µm total thickness) monolayer graphene grown on copper foil was used as the cathode material and lithium foil as the anode. While a thin solid polymer electrolyte was sandwiched in between to form the cell. An energy density of 10 Wh/L was obtained at a power density of 50 W/L. This energy density is much higher than the highest energy density of graphene supercapacitors (≈ 1 Wh/L) and similar to Li thin film batteries. However, Li thin film batteries can only reach a power density of 5 W/L.

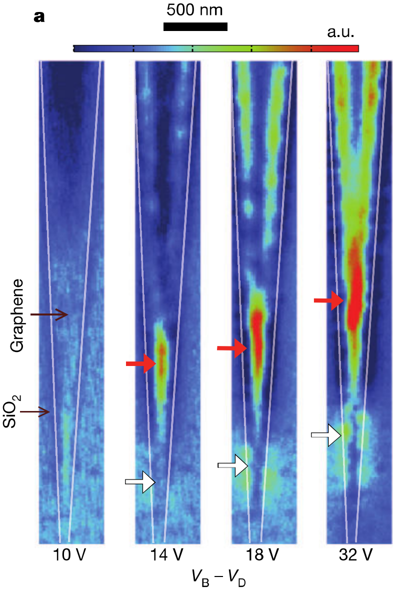

**Fig. 4 >** Near-field amplitude images for tapered graphene acquired while applying backgate voltages ranging from -15 V to +11 V [25]. Reprinted with permission from Nature./

Since monolayer graphene does not rely on $Li^+$ intercalation and conversion reactions (as in conventional bulk electrode materials), very fast surface $Li^+$ absorption and ultrafast $Li^+$ diffusion and electron transport can be achieved. Therefore, graphene could lead to very fast and high performance flexible batteries.

The time to market for the three examples shown above will be quite different. The graphene based batteries could probably be the closest to the market while the other two application examples will require a much longer time to market due to the complexity of the application.

## Future

The future is very difficult or impossible to predict, however there are some indicators in order to assess the market potential of a new advanced material [6].

To begin with a new material should have advantages and strengths over existing or incumbent materials. In the case of graphene as a transparent conductor the added flexibility could be a clear advantage over existing materials that are brittle such as indium tin oxide (ITO). In purely cost driven applications it might be very complicated to replace an incumbent material.

In addition, graphene could enable the development of entirely new products and unlock new markets that would not be possible without this material.

Based on the above we could say that the market uptake of graphene is very real. How broad and fast this happens will depend on a number of factors:

- technological progress (time needed to move up the technological readiness ladder)
- consumer awareness
- overcoming existing value chains
- socio-political considerations
- public sector support

Among the indicators to take into consideration in order to assess the industrial uptake of graphene patenting activity and incubation time should be highlighted. The incubation time required for advanced materials is at least 20 years (e.g. silicon, carbon fibre, poly vinyl chloride, etc.). In the case of graphene the time required for its uptake may vary since we are not dealing with only one material but a family of carbon based structures with different forms and grades. It is expected that the time to market will vary depending on the complexity of the application and the required graphene form [6]. The patenting activity curve in graphene is steeper than in other materials [6], therefore the market uptake could may well occur sooner than the average time to market (20 years).

## Conclusions

Graphene's unique properties provide it with a high potential for future industrial applications. However, excellent properties are not the only requirement in order to have a successful market uptake. There are other conditions that have to be fulfilled such as technological progress, market awareness and industrial readiness. However, considering the money invested by many governments across the world (EU, US, South Korea, etc.) as well as some private initiatives, and the steep patenting activity, graphene could turn out to be a game changing material.

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# Plasma modification of graphene and graphene like materials for component performance enhancement

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C. Spacie

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## Introduction

Graphene is an allotrope of carbon consisting of single sheets of densely packed sp2 hybridised carbon atoms. Its discovery in 2004, by a group led by Professor Andre Geim at the University of Manchester, led to Geim and Novoselov being awarded the 2010 Nobel Prize “for ground breaking experiments regarding the two dimensional material graphene” [1]. Subsequent interest in graphene’s extraordinary properties [2, 3, 4, 5] has led to an enormous amount of research into its application in fields as diverse as high frequency electronics [6], heat dissipation [7], nanocomposites [8], oil spill cleanup [9], desalination [10], transparent conductive films [11], antifouling membranes [12], supercapacitors [13], biomedical [14], anti-static materials [15], and biosensors [16]. Transferring the unique properties of these materials from the single-particle, nanoscale, into macroscale devices has been one of the biggest challenges in nanotechnology. Haydale has developed its processes for application improvements, successfully demonstrating enhancements in stable dispersions without the requirement for additional surfactants or other similar additives. This provides the ability to create molecular bonding and interactions between the particles and the matrix; the results are ideal for manufacturing system improvements, such as electrical and mechanical properties, without using often detrimental dispersing technologies.

Fig. 1 > Haydale production site in Carmarthenshire./

While numerous applications have been identified, the techniques currently used to produce graphene nanoplatelets (GNPs) are often detrimental to the material’s physical and chemical properties [17]. Haydale has developed a plasma process, used for discrete parts and complex components to enable large volumes of nano materials, such as carbon nanotubes (CNTs) and GNPs to be processed. The method uses a graphite feedstock to produce GNPs by a patented plasma modification process. The Haydale Split Plasma process is a high yield, robust and dry alternative to the wet and harsh chemical functionalisation methods more commonly employed. The Split Plasma method does not damage nanostructures, unlike the more widely used acid treatments.

Haydale's plasma functionalisation method is a low pressure, low temperature process. This type of plasma discharge is often referred to as a glow discharge, and can be characterised by its fluorescence as shown in Figure 2.

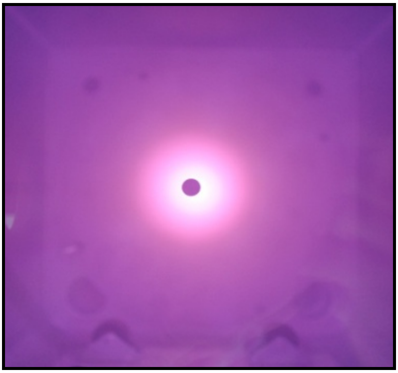


Fig. 2 > Haydale's plasma process uses a patented reactor design, which allows exfoliation and uniform surface chemical modification of graphene nanoplatelets./

The Haydale Split Plasma method has been designed to enable the take up of nanocarbon materials and powders as functional fillers. The plasma process performs four fundamental actions:

- **De-contamination**: preferentially etches-out non-crystalline contaminants such as amorphous carbon and catalytic residues.
- **Surface Engineering**: ability to tailor virtually any surface with desired chemical groups, therefore giving greater dispersion and compatibility between different matrices and nano materials; this has been shown to enhance product properties.
- **De-agglomeration**: uniquely encourages disentanglement and exfoliation of the nanostructure without compromising or damaging its structure. This is seen as bulk density loss - confirmed using electron microscopy, surface area and particle size analysis.
- **Deposition**: possibility to sputter molecular layers of many liquid and solid chemicals directly onto the surface of the nanomaterial. This technique could be employed to coat nanoparticles with metal layers or polymerized dispersant or other coupling agents.

There is no standard definition of product offerings such as a GNP. Typically a GNP is a nanoparticle consisting of stacks of multiple layers of graphene, which often vary in purity, manufacturing methods and critically, thickness. A typical TEM micrograph of the Haydale HDPlas™ GNP materials is shown in Figure 3. Plasma modification alters the surface chemistry, purity and levels of agglomeration of the graphene nanoplatelets, which are important factors in optimising the properties of a component containing nano materials.

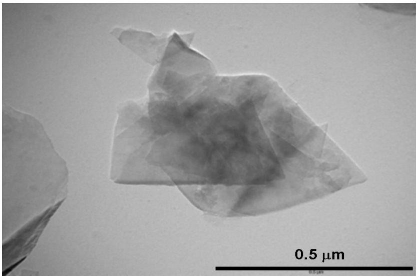
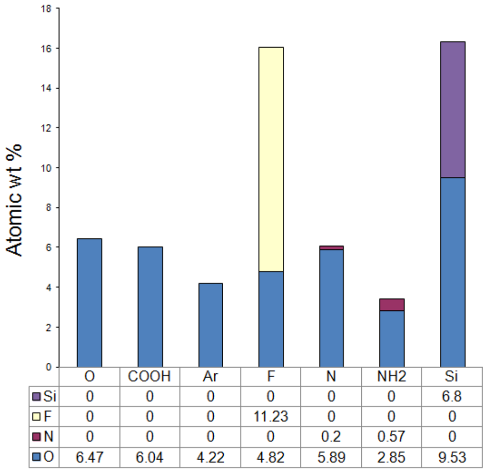


Fig. 3 > Tunnelling Electron Micrograph of a HDPlas™ Graphene Nanoplatelet./

As materials approach the nano-scale, their surfaces become more and more important; a single layer of graphene is effectively just an atomically flat and chemically inert surface, with reactive edges [18]. Although these properties make them strong and chemically resistant, it also makes them very difficult to utilise in a component or application. Graphene voids in the carbon lattice are important for improving compatibility with the target matrix; however, too many voids can degrade the material's physical properties. This can be seen in the extreme of graphene oxide, where each carbon atoms is bonded to an oxygen atom, rending the material electrically



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| 🟦 O | 6.47 | 6.04 | 4.22 | 4.82 | 5.89 | 2.85 | 9.53 |

Fig. 4 > XPS Analysis of Haydale's range of HDPlas™ GNP materials - Plasma Functionalised Graphene Platelets./

insulating. The key, therefore, is to deliver a material with just the right amount, and right sort of surface "imperfections", in the form of functionalisation.

The plasma process has a number of benefits when compared with competing functionalisation techniques, such as amidation or esterification acid treatment, which is known to cause defects in the crystalline structure of graphene type material [19]. It also generates a corrosive effluent stream and residual impurities in the product, or non-covalent functionalisation methods such as surfactant wrapping [20] which acts as a physical barrier between particles and between the particle and matrix material. Plasma by comparison results in minimal changes to the structure of a material and can be used to create a wide variety of chemical species [21, 22, 23]. Almost any gas and most liquids, including monomers, acids and other solvents, can be used in the plasma process to create surface functional groups, while many metals can be applied through *in-situ* Physical Vapour Deposition (PVD). The plasma process is low energy, low temperature and readily controlled to deliver the specific quantity of functionalisation required.

## Surface Modification

Selection of process gas(es), processing time, power transferred from the plasma generator to the chamber, and chamber pressure are all important parameters when determining the types of functional groups that are to be imparted on the GNP. The most important processing parameter for plasma treatment is the process gas, as this determines the chemical groups, whereas the remaining processing parameters determine the types and concentration of chemical species produced in the plasma.

Plasma processed surface chemical modifications can be characterised using a number of analytical techniques including: Fourier Transform Infrared spectroscopy; Time-of-flight Secondary Ion Mass Spectroscopy and X-ray Photoelectron Spectroscopy (XPS). XPS analysis shows how various plasma treatments alter the surface chemistry of GNPs. This is shown in Figure 4.

Plasma processing can be used to impart surface functionalisation; however, only Haydale's patented process can deliver large volumes of functionalised nanoparticles. Haydale's split plasma process can also remove contaminations such as amorphous carbon, effectively increasing the crystallinity of the material; this can be shown by XRD analysis, Figure 5.

Crystallinity of a graphene-like material is important for mechanical and electrical properties.

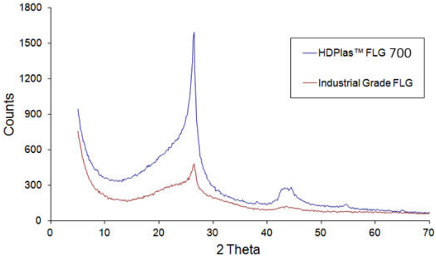

**Fig. 5 >** XRD graph of industrial few layered graphene and HDPlas™ few layered graphene./

## Dispersions and Applications

One of the key challenges to overcome in achieving the utilisation of nanoparticles is dispersing them in a matrix. The quality of dispersions can be measured by how long a particulate remains suspended in a liquid medium, and this is a function of the differences in density between the particulate and the liquid, the frequency of particle-particle interactions, and the respective surface energies of the particles and the liquid. Through Haydale's unique plasma process the surface energy of the particles can be tailored to improve wetting behaviour, and therefore compatibility of a liquid, including solvents and polymers [24]. This can be demonstrated in Haydale's recently launched HDPlas™ Graphene Inks, which produces excellent dispersability and compatibility with the binder and solvent systems. Haydale's Graphene Ink Sc213, a screen printable carbon ink, can achieve surface resistivity of <15 ohm/sq and a surface covering of 550 sq cm per gram. These inks have been designed for a variety of applications, print methods and substrates. Custom formulations can also be offered to enable these materials in your application.

HDPlas™ Graphene Inks are cured at low temperatures and can be formulated for various printing techniques allowing easy application to a variety of substrates, including PVC, polyester and ceramics. HDPlas™ Graphene Inks are:

- Supplied in ready to print format
- Available in both high quantities and trial quantities
- Available with formulation and customisation support

In addition to being able to control the surface free energy of nanoparticles, Haydale controls the reactive species present on the surface of the nano materials. Surface functionalisation of nano materials leads to improvements in solubility and processability of nano materials when compared with non-functionalised versions [19]. This means that HDPlas™ materials are capable of covalently bonding with the matrix material in which they are dispersed [25, 26].

GNPs have also been shown to improve functional properties of composite materials. These functional properties range from electrical enhancements to barrier properties [27] and functionalisation can be shown to have a significant impact on these properties. Research has shown that HDPlas™ GNPs can successfully improve the barrier properties of common polymers, this is important for packaging polymers, which are often enhanced with metalized surfaces. Including HDPlas™ graphene materials in packaging materials could result in fully organic and biodegradable packaging systems.

## Conclusions

Dispersion capability is the key to unlocking the potential of the carbon based nano materials such as GNPs and CNTs. Haydale can now deliver commercial quantities of graphene type materials which are surface engineered through plasma process enhanced compatibility between the nanomaterial and matrix materials. The Haydale branded HDPlas™ GNP materials are manufactured in high volumes and can be used for a variety of applications. This is enhanced through functionalisation which includes standard products but also the ability for custom functionalisation to enable optimal compatibility and homogeneous dispersion for enhanced material properties in almost any matrix material.

Haydale has developed a number of nano-enhanced products including HDPlas™ Graphene Inks, thermoplastics and resin systems. Also available are solvent dispersions to remove barriers to the development of nano-enhanced products.

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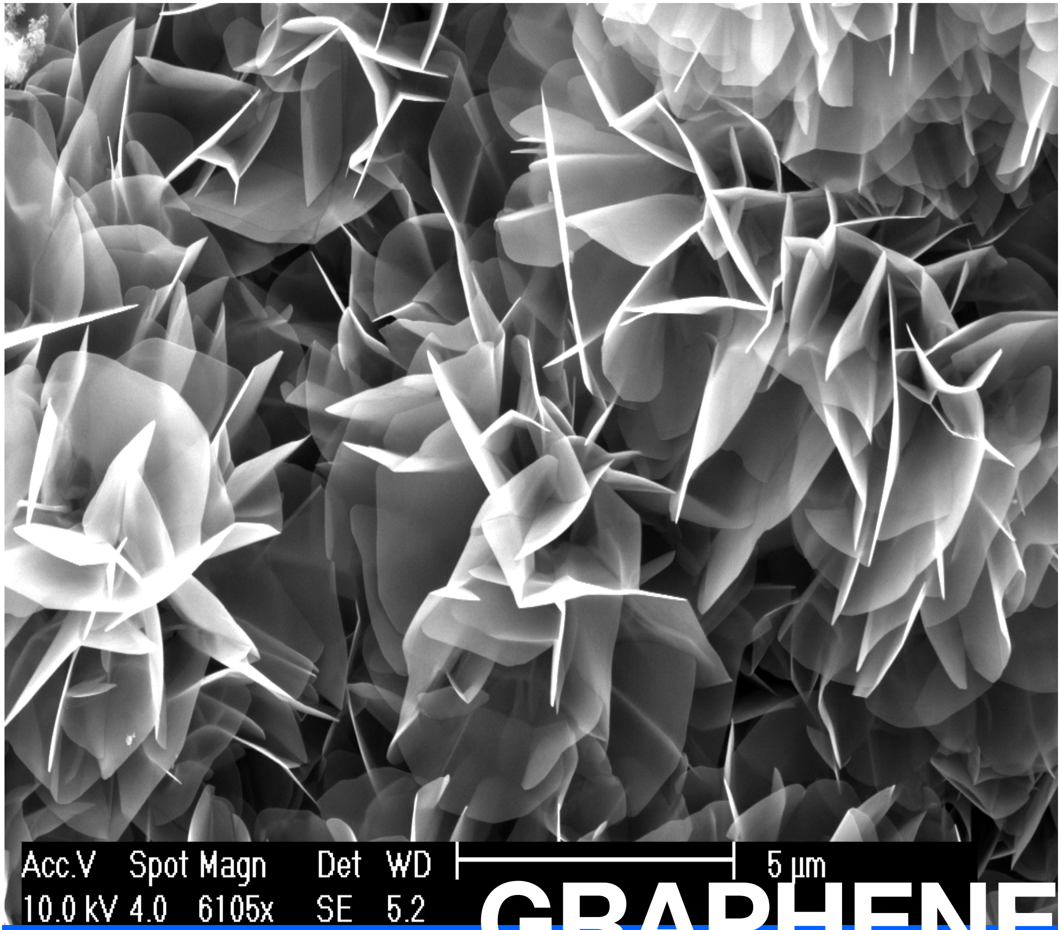
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# Synthesis of few layer graphene from organic raw materials without a substrate and catalyst under hydrostatic pressure

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## Introduction

Graphene has unique properties that include a high electrical mobility, a high thermal conductivity, transparency over a very wide wavelength range, and excellent mechanical properties [1]. Much research is currently being done to investigate the potential use of graphene in practical applications such as transparent conductive electrodes for touch panels of mobile phones, tablet PCs, flat panel displays, and thin-film solar cells. Graphene has a very high tensile strength because of its strong carbon–carbon $sp^2$ hybridized orbitals. It thus has the potential to improve the mechanical properties of resins and rubber-based composite materials. Current research and development of graphene is performed on laboratorie's scale with small quantities of the material. Graphene is typically fabricated by top-down approaches such as peeling off graphite layers using scotch tape, ultrasonication in an organic solvent, and exfoliation of graphite intercalation compounds [2-8]. However, these synthesis methods produce small quantities of graphene with very low yields.

We have synthesized few-layer graphene (including monolayer graphene) by using a unique synthesis method [9]. The raw materials heated to obtain suitable residual hydrogen contents are placed in a reactor made from heat-resistant materials and then heated under a high hydrostatic pressure to a higher temperature than the pre-heat treatment temperature [10].

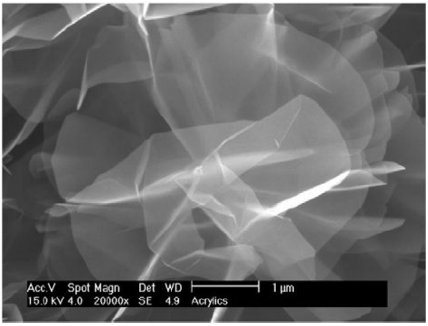

Fig. 1 > FE-SEM of Graphene as grown../

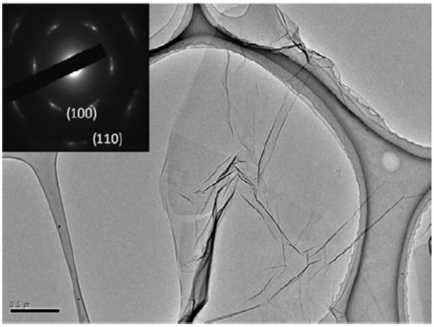

Fig. 2 > TEM for Graphene dispersed in 2-metoxethanol./

## Synthesis method

Solid resin was heated in a furnace to various setting temperatures to control residual hydrogen content in carbonized resin. These carbonized resins were placed in a porous reactor that had a

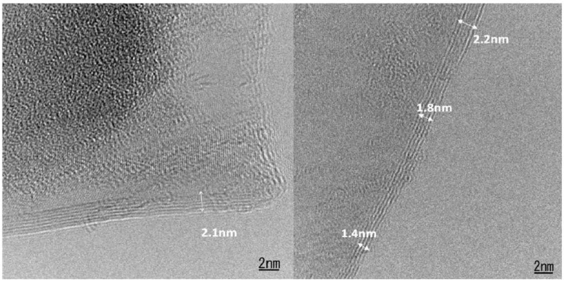

Fig. 3 > Lattice images of the *c*-axes in Fig.2./

high heat resistance and the reactor was loaded in the heating equipment to perform hydrostatic pressing at a high temperature under Ar gas. The solid raw materials generate gases such as $H_2$, $CH_4$, CO, and $H_2O$ when they are heated under a high hydrostatic pressure. These gases cause graphene growth through chemical vapor deposition on the solid raw materials. After a few hours of reaction, very thin graphene sheets that resemble flower petals simultaneously grow on all the surfaces of the raw materials, converting them to bulk porous graphene mass.

## Characteristics

After hydrostatic pressing and heating, a very thin graphene that resembled flower petals grew remarkably on the surfaces of carbonized resin as shown in Fig.1. TEM images of the graphene products dispersed in 2-methoxyethanol reveal that they have dimensions in the range 1–10 μm and that they are square in shape (Fig. 2). There is an area that is orientated perpendicular to the plane with thin carbon at the edge of it (Fig.3). These lattice images of the *c*-axis indicate that the thin carbon products consist of few-layer graphene that is 1 to 2 nm thick and has three to seven stacking layers. It is difficult to obtain lattice images of the *c*-axes of monolayers, bilayers, and trilayers because the graphene points are perpendicular to the plane and have very low aspect ratios. The graphene layers will be flat in an organic solvent because the solvent polarity relaxes the Van der Waals force, whereas in a dry atmosphere such as air they will readily adhere to each other due to Van der Waals forces and they shrink and roll up like carbon nanotube bundles. The crystalline structures of the products were also characterized by Raman spectroscopy. Fig. 4 shows Raman spectrum obtained at the specimen, just as for the TEM observations. The peak ratio of the 2D band to the G band was around 1.0, which implies that the specimens consist of a few layers of graphene. Dimension and stacking number of graphene is controllable, because this synthesis method mentioned above is the bottom-up type of synthesis method. Fig.5 shows the correlation between the dimension and thickness in this synthesis method.

## Extrusion of graphene

The stacking number of graphene obtained in this method is only 3-7 layers

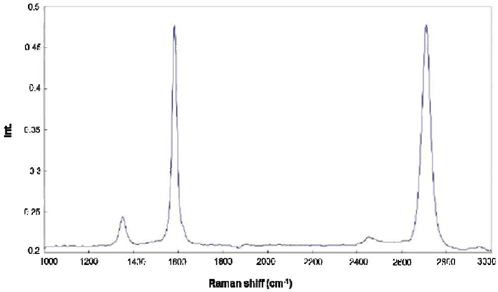

Fig. 4 > Raman Spectrum obtained at the specimen in Fig.3./

thick, so compared to conventional graphite, it has a strong Van der Waals force, causing the graphene to adhere easily and integrate. As such, if mass of graphene is pulverized into powder through milling or crushing in a dry atmosphere, the graphene will adhere together and agglomerate, so will take on a form and structure similar to that of thin flakes of graphite. Dispersions are composed of graphene that has been finely powdered while suppressing the adhesion of the graphene by placing masses of graphene in an organic solvent and storing the powder in the solvent. Dispersions can also be composed of recovered supernatant produced by ultrasonic wave treatment separation and centrifugation [11].

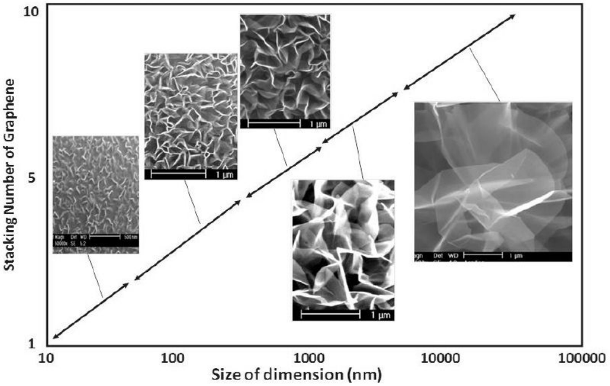

Fig. 5 > Correlation between the dimension and the thickness./

## Graphene products

Incubation Alliance Inc. has used this unique process to successfully mass-synthesize graphene without the use of substrates, catalysts, or stripping. “GRAPHENE FLOWER” (registered trademark) is a mass of graphene that has been grown into individual flower petal shapes, which together form a unified quantity of graphene. GRAPHENE FLOWER and dispersions already form several layers of graphene without needing the conventional approaches of stripping graphite, reducing graphite oxide, and using metal catalysts to extract the graphene. By applying GRAPHENE FLOWER and dispersions as starting materials for applied research and development, we hope to develop many new applications early on.

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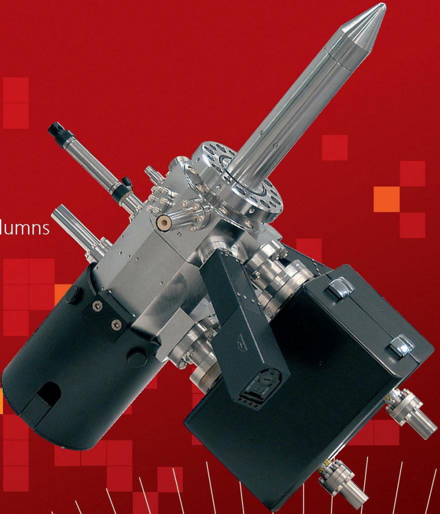

nanoresearch

# GRAnPH®: High quality graphene oxide obtained from GANF® carbon nanofibres

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Graphene, an individual sheet of $sp^2$-hybridized carbon atoms, has attracted increasing interest due to its unique electronic, mechanical and thermal properties [1-3]. Therefore, graphene is a promising candidate to be applied in a wide variety of technologies, such as transparent conducting electrodes [4], field effect transistors [5], hydrogen storage [6] and gas sensors [7].

There are two widely used procedures to obtain graphene: based on (i) physical and (ii) chemical methods. Physical methods such us chemical vapor deposition (CVD) [8] or micromechanical exfoliation [1], render high quality graphene sheets. However, they are difficult to use in industrial applications due to their elevated production cost and complexity (CVD) or to the low efficiency in the case of micromechanical exfoliation. Chemical methods [9] are based on the chemical oxidation of graphite to obtain graphene oxide (GO) followed by a reduction process and they are considered one of the most attractive routes to obtain graphene in large-scale production due to their low cost and versatility. However, chemical oxidation introduces O-containing groups in the lattice, which cannot be completely removed by chemical or thermal reduction producing chemically modified graphene sheets or reduced graphene oxide (rGO). Defects in the basal structure of graphene are related with the material quality and thus influence its future applications. Accordingly, the synthesis of good quality graphene oxide is crucial to the success in chemical graphene preparation.

Graphene oxide is mainly produced from graphite although other graphitic materials have also been employed. The major disadvantage of graphite, as starting material, is the low efficiency of the oxidation process due to the high number of stacked layers present in its structure. As an alternative route, we present an industrial process to obtain few layer sheets of graphene oxide (GRAnPH®) by using GANF® carbon nanofibers as starting material and the Hummers' method as oxidation procedure. GANF® presents a singular helical ribbon graphitic structure, composed by a graphitic ribbon of approximately five graphene layers rolled along the fiber axis. This structure makes them very attractive as starting material for graphene production. See ref. [10] for more details.

The low number of stacked graphene layer in GANF® allows the achievement of a highly effective oxidation. Thus, whereas GRAnPH® can be used without further purification, several centrifugation steps are absolutely necessary to remove none oxidized graphite when the oxidation was carried out from graphite as starting material.

In order to analyze the quality of GRAnPH® graphene oxide the following techniques were used X-Ray Diffraction, UV-Vis, XPS and Raman spectroscopy. The most representative results are collected in table 1. For comparative purposes, results corresponding to graphite oxide (GO) have also been included.

| Technique | Results | | Ref |
|---|---|---|---|
| | GRAnPH® | GO (Graphite) | |
| UV-Vis | $\lambda_{max}$=235 nm | $\lambda_{max}$=230 nm | [11] |
| XPS | O/C=0.61<br>60% C-C<br>26% C-O<br>14% C=O | O/C=0.62<br>49% C-C<br>45% C-O<br>6% C=O | [11] |
| XRD | $d_{(002)}$=0.77 nm | $d_{(002)}$=1.02 nm | [12] |
| Raman | $I_D/I_G$ = 1.03 | $I_D/I_G$ = 1.4 | [12] |

**Table 1 >** GRAnPH® and GO characterization./

As it can be observed in table 1, the position of the maximum of GRAnPH® UV-Vis spectrum is five nanometers red-shifted respect to the maximum corresponding to GO. The red-shift of this band can be related to the higher amount of sp$^2$ carbons in the graphene network. This result is consistent with the information obtained from the XPS measurements. On the other hand, XPS spectra show different chemical composition for the two samples. Alcohol or epoxy groups are in higher percentage for the case of GO than for GRAnPH®, whereas GRAnPH® presents higher percentage of carboxylic acid groups than GO. This difference could be due to differences in the structure of the starting materials, GANF® and graphite respectively.

Taking into account that C-O groups are mainly localized at the nanoplatelet core, we expect that the interlayer distance between nanoplatelets could be higher for GO samples. To confirm this issue the XRD spectra were recorded and results are summarized in table 1. As expected, the interlayer distance between the nanoplatelets is higher for GO than for GRAnPH®. Finally, the size of the sp$^2$ domains was evaluated by means of the $I_D/I_G$ ratio obtained from the Raman spectra. The results, table 1, show lower ratio for GRAnPH® than for GO. This fact means that the size of the Csp$^2$ domains is larger for GRAnPH® than for graphite oxide [13].

The chemical composition of GRAnPH® graphene oxide allows the preparation of stable suspensions in different polar solvents without any additional stabilizers. Moreover, it can be deposited over a wide variety of substrates by different methods and be used for diverse applications.

Spin coating and spray coating, are two of the most applied methods in industry to deposit suspensions due to their versatility and low production costs.

Concerning spin coating, it is a film deposition technique already introduced in a variety of industries such as microelectronics and coating technologies, also applied to graphene, G, and GO deposition [8]. Its benefits include accurate thickness control, high deposition uniformity, fast process time and low equipment cost. However, substrates size and shape are the principal drawbacks to implement the technique at industrial scale. Spray coating has been also applied to G and GO deposition [9]. It is a deposition technique widely used in industry for multiple applications due to its fast process time, low equipment cost and versatility. As a drawback, the technique provides lower thickness control compared to spin-coating. The deposition of GO films by means of these techniques would represent a plausible alternative for the industrial application of graphene with low production costs.

GRAnPH® suspensions have been deposited by spin and spray coating with two main objectives: to completely characterize the material, and to develop a process capable to provide a continuous and homogeneous film onto different material surfaces.

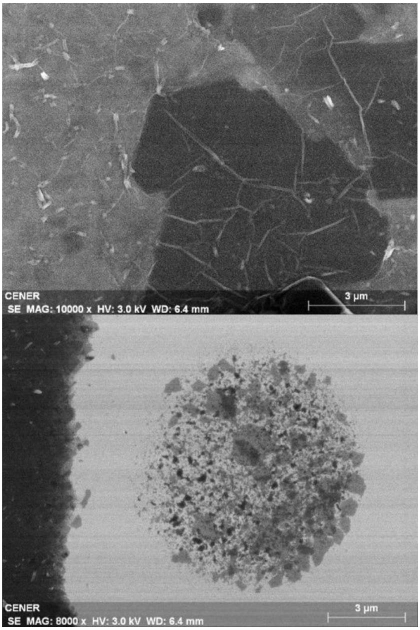

**Fig. 1 >** SEM image of a continuous GRAnPH® thin film deposited by spin-coating on a silicon dioxide/silicon substrate (top). SEM image of a GRAnPH® droplet deposited by spray-coating on a silicon dioxide/silicon substrate (bottom)./

GRAnPH® suspensions have been deposited onto opaque substrates, such us silicon dioxide and silicon nitride deposited onto a silicon wafer; transparent materials like glass and different plastic materials. While the spray coating process can be easily applied to any kind of surface (regardless of the material properties and shape), spin coating process requires an individual optimization depending upon the material surface nature. Continuous GRAnPH® films have been obtained by means of these two deposition techniques, exhibiting different morphologies as well as electrical and optical properties.

GRAnPH® deposits have been morphologically characterized by means of a wide variety of techniques, such as optical microscopy, atomic force microscopy (AFM) and scanning electron microscopy (SEM). Additionally, GRAnPH® deposits on opaque substrates have been optically characterized by means of reflectivity measurements, and deposits on transparent substrates by means of transmittance measurements. Finally, the GRAnPH® thin film electrical characterization has been performed by means of a four point probe technique.

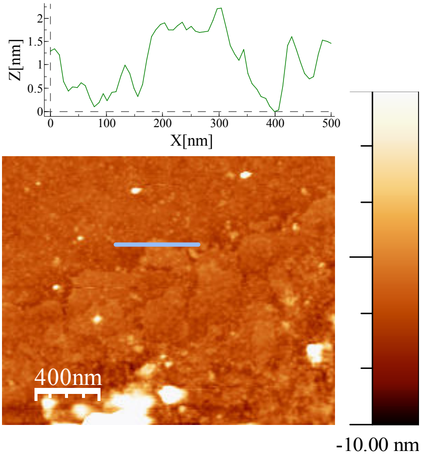

**Fig. 2 >** AFM image (bottom) and profile (up) of a GRAnPH® droplet edge deposited by spray-coating on a silicon dioxide/silicon substrate./

SEM images of GRAnPH® thin films deposited by spin-coating on silicon dioxide/silicon substrates showed the high substrate surface coverage obtained by means of this deposition technique (Figure 1). GRAnPH® flake frontiers could be observed due to the color scale, exhibiting darker grey levels those regions with higher thickness. G and GO typical wrinkles could be identified as white lines in the SEM images (Figure 1).

As it was expected, GRAnPH® thin films present poor conductivity, exhibiting values higher than $10^9$ Ω/sq. On the other hand, transmittance values measured on the transparent substrates were in the range of 83%.

Most of the graphene applications require high conductivity, and in some specific cases high transmittance too. Therefore, in order to decrease the sheet resistance of the GRAnPH® thin films obtained by spray or spin coating techniques, different reduction procedures to obtain reduced graphene oxide, GRAnPH® rGO, have been used.

GRAnPH® rGO thin films were characterized using the same techniques, transmittance and sheet resistance values were used as control parameters in the process development.

Sheet resistance values as low as ~$10^4$ Ω/sq have been obtained combined with a transmittance value of 86%, in agreement with some of the most promising results reported in literature (Figure 3).

In addition, depending upon the specific application, both sheet resistance and transmittance can be tuned separately by varying the applied reduction processes.

As a conclusion, GRAnPH® sheets obtained from GANF® carbon nanofibres are suitable for the preparation of highly exfoliated and stable suspensions in different polar solvents avoiding the use of additional stabilizers. These suspensions have been deposited over a wide variety of substrates by means of spin and spray coating, and reduced by different methods. Continuous GRAnPH® rGO layers with tunable optical transmittance and sheet resistance have been obtained, demonstrating the high potential of GRAnPH® sheets obtained from GANF® carbon nanofibres for their industrial application.

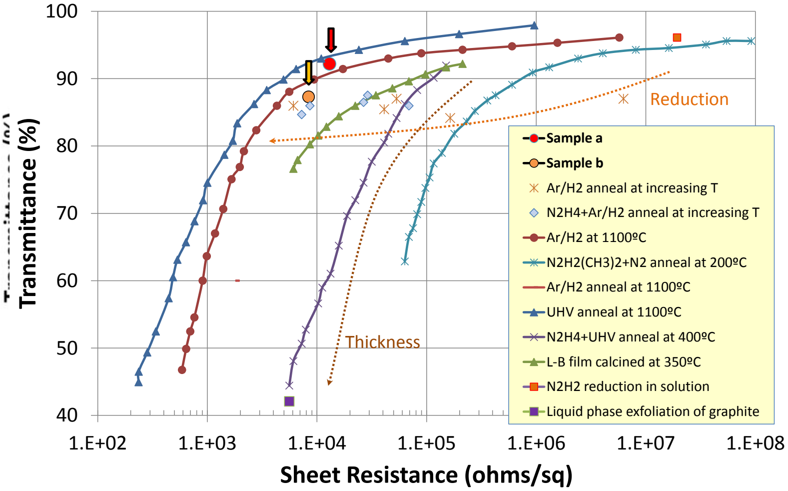

Fig. 3 > Optical transmittance and sheet resistance obtained for reduced GRAnPH® films on glass substrates compared with results reported in the literature (adapted from [8])./

This work has been developed within the research project "Investigación sobre la obtención de nanoplaquetas de óxido de grafeno a partir de nanofibras de carbono y la purificación, reducción y depósito controlado de las mismas (GRAnPHTEC)", ref. IDI-20111312, supported by the Centre for Industrial Technological Development (CDTI), from the Spanish Ministry of Economy and Competitiveness.

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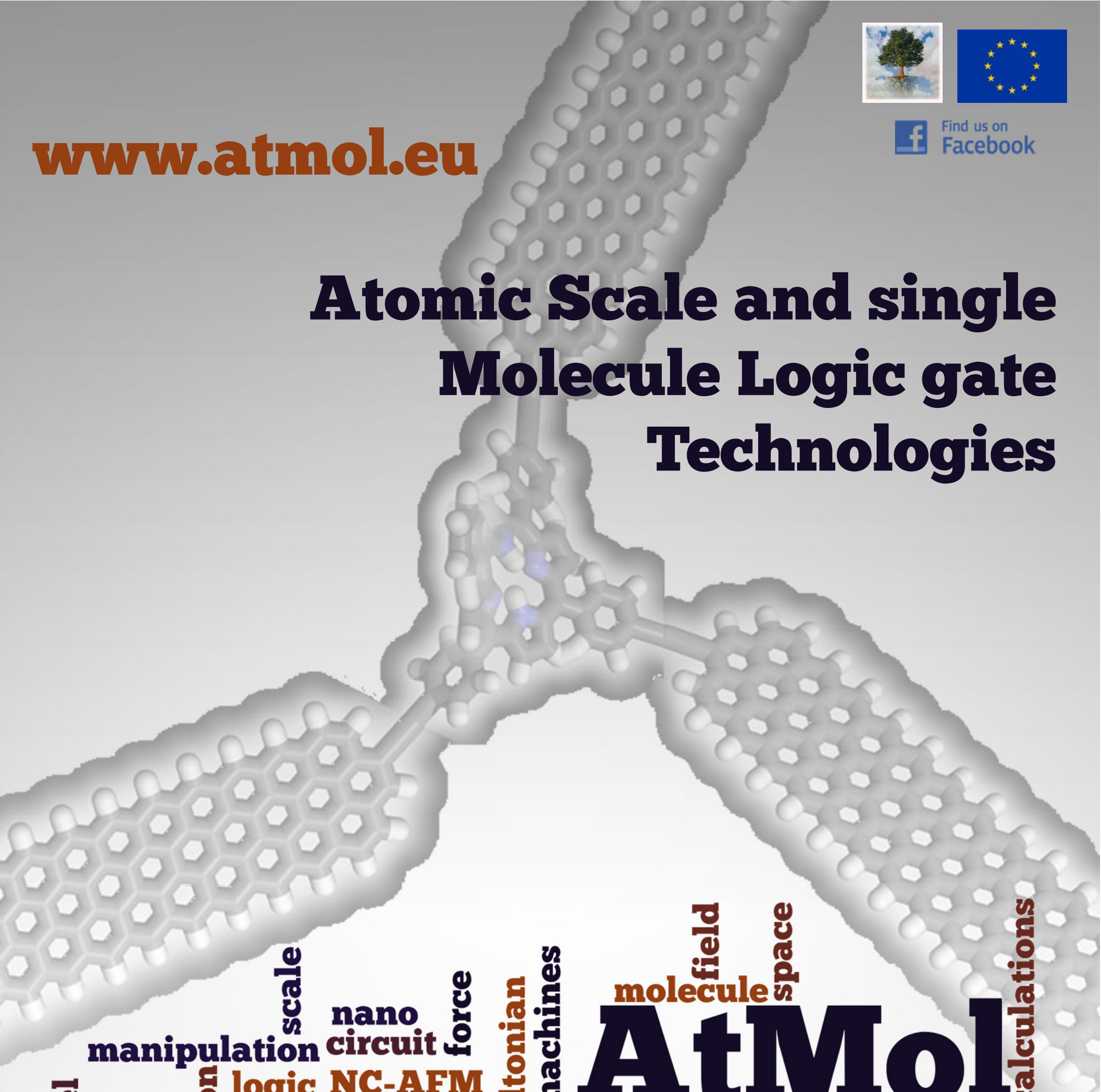
# Atomic Scale and single Molecule Logic gate Technologies



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- **PostDoctoral Positions (4):**

*"Physics and technology of graphene"*
Contact person: RRHH
**hrservices@manchester.ac.uk**
(University of Manchester, UK)
**Deadline:** September 15, 2013

- **Job Position:**

*" Business Development Manager"*
Contact person: Anaïs Normand
**a.marketing@nanoimmunotech.es**
(nanoimmunotech, Spain)
**Deadline:** September 16, 2013

- **PhD Position:**

*"PhD at the Phononic and Photonic Nanostructures group"*
Contact person: Rosa Juan
**hr@icn.cat**
(ICN2, Spain)
**Deadline:** September 17, 2013

- **PostDoctoral Position:**

*"Synthesis and characterization of functionalized/metalized DNA fragments"*
Contact person: Didier Gasparutto
**didier.gasparutto@cea.fr**
(CEA-Grenoble, France)
**Deadline:** September 17, 2013

- **PostDoctoral Position:**

*"Conception and preparation of 2D/3D DNA and proteins assemblies "*
Contact Person: Raluca Tiron
**raluca.tiron@cea.fr**
(CEA- Grenoble, France)
**Deadline:** September 17, 2013

- **PostDoctoral Position:**

*"3D interconnections development"*
Contact Person: Xavier Baillin
**xavier.baillin@cea.fr**
CEA- Grenoble, France)
**Deadline:** September 17, 2013

- **PostDoctoral Position (2):**

*"Characterization and simulation of RF Electronic Devices"*
Contact Person: Javier Mateos
**javierm@usal.es**
(Universidad de Salamanca, Spain)
**Deadline:** September 18, 2013

- **Job Position:**

*"Crystal Plasticity Finite Element modeling of the static and fatigue behavior of polycrystalline Ni-based superalloys"*
Contact Person: RRHH
**jobs.materials@imdea.org**
(IMDEA Materials Institute, Spain)
**Deadline:** September 18, 2013

- **PostDoctoral Position:**

*"Synthesis and characterisation of graphene films suitable for spintronic applications"*
Contact Person: RRHH
**jobs@graphenea.com**
(Graphenea, Spain)
**Deadline:** September 30, 2013

- **Job Position:**

*"Bioconjugation Project Manager"*
Contact Person: Anaïs Normand
**a.marketing@nanoimmunotech.es**
(nanoimmunotech, Spain)
**Deadline:** October 01, 2013

* More info and other jobs available at: **www.phantomsnet.net/jobs**

# nanoconferences

### • EMRS 2013 Fall Meeting.
**September 16, 2013. Warsaw (Poland)**

This symposium, as third Symposium on “Bioinspired and Biointegrated Materials as New Frontiers Nanomaterials”( previously organized symposia 2009, 2011), is aimed to give overview of bioinspired and biointegrated materials multifunctional applications in all human activities using biological and mimetic molecules, materials for desgn biointegrated and bioinspired ones.

**www.emrs-strasbourg.com**
NanoMaterials, NanoBiotechnology

### • 39th International Conference on Micro and Nano Engineering (MNE2013).
**September 16-19, 2013. London (UK)**

The Conference brings together engineers and scientists from across the world to discuss recent progress and future trends in the fabrication, manufacturing, operation and application of micro and nano-structures and devices. Applications in electronics, photonics, electromechanics, environment and life sciences are also discussed.

**www.mne2013.org**
NanoFabrication, NanoLithography, NanoPatterning

### • IEEE NMDC 2013.
**October 6-9, 2013. Tainan (Taiwan)**

This conference aims to foster communication between the diverse groups interested in nanodevices and nanostructured materials. Interdisciplinary exchange between scientists and contributions from industrial researchers will help inspire a new perspective on this exciting area.

**http://conf.ncku.edu.tw/nmdc2013/**
NanoMaterials, Nanotechnologies

### • EC COST Thematic Workshop.
**October 8-9, 2013. Leipzig (Germany)**

The workshop (Nano-scaled arrangements of proteins, aptamers, and other nucleic acid structures – and their potential applications) is part of the COST action “Bio-inspired nanotechnologies: from concepts to applications” organized by the members of the management committee Beate Strehlitz (UFZ) and Fred Lisdat (TH Wildau).

**www.bioinspired-nano.eu**
NanoBiotechnology

### • ICT 2013.
**November 6-8, 2013. Vilnius (Lithuania)**

More than 4000 researchers, innovators, entrepreneurs, industry representatives, young people and politicians are expected in Vilnius. The event will focus on Horizon 2020 - the EU's Framework Programme for Research and Innovation for 2014-2020.

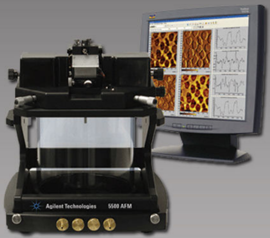
**http://ec.europa.eu/digital-agenda/en/ict-2013**
Nanotechnologies

### • NanotechItaly 2013.
**November 27-29, 2013. Venice (Italy)**

NanotechItaly, now at its 5th edition, is an International Conference on nanotechnologies. The Convention aims at illustrating the latest developments at world level and the nanotech trends in the key industrial sectors and the speakers that confirmed their attendance to the Conference are the best in the field of nanotechnologies.

**www.nanotechitaly.it**
Nanotechnologies

✱ More info and other conferences available at: **www.phantomsnet.net/conferences**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