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Functionalized Graphene Nanocomposites

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1. Introduction

Graphene is one of the most exciting materials being investigated today, not only out of academic curiosity but also for its potential applications. Graphene, a single layer of carbon packed in a hexagonal lattice, with a carbon-carbon distance of 0.142 nm is the first truly two-dimensional crystalline material, which is stable at room conditions. Graphene has displayed a variety of intriguing properties including high electron mobility at room temperature ($250{,}000$ cm^2/Vs) exceptional thermal conductivity (5000 W m^{-1} K^{-1}) and superior mechanical properties with Young's modulus of 1TPa (Singh, Joung et al. 2011). Thus, graphene sheets offer extraordinary electronic, thermal and mechanical properties and are expected to find a variety of applications, such as sensors, batteries, supercapacitors, hydrogen storage systems and as reinforcement fillers of nanocomposites (Soldano C., Mahmood et al. 2010).

The joint award of the 2010 Physics Nobel Prize to Andre Geim and Konstantin Novoselov, as stated by the Royal Swedish Academy (2010), "for groundbreaking experiments regarding the two-dimensional material graphene", highlights the importance of this single atomic layer of carbon. This discovery is considered a breakthrough in the nanotechnology era, bringing the concept of single atomic component closer to reality.

Even before the studies of Novoselov and Geim, efforts had been carried out to prepare very thin graphite or graphene layers, since interesting properties were expected (Boehm 2010), but there were experimental difficulties in isolating single layers in such a way that electrical measurements could be performed on them, and there were doubts that this was practically possible. Graphene discovery marked the onset of experimental physics on graphene, which then made it relevant to revisit successfully all other methods to produce graphene which had reputedly failed in the past four decades.

So far, the original top-down approach of mechanical exfoliation using the Scotch-tape method has produced the highest quality samples, but the method is neither high throughput nor high-yield, the probability of finding individual graphene sheets of good quality is often low. In order to exfoliate a single sheet, van der Waals attraction between exactly the first and second layers must be overcome without disturbing any subsequent sheets (Allen, Tung et al. 2010). Many studies emerged over the last years with alternatives to mechanical exfoliation including chemical vapour deposition (Zhao, Rim et al. 2011), epitaxial growth (Ushio S, Arata Yoshii et al. 2011), carbon nanotube cutting (Janowska,

Ersen et al. 2009), chemical exfoliation (Wang, Robinson et al. 2009) and direct sonication (Lotya, Hernandez et al. 2009). Each of these methods presents both advantages and disadvantages, dealing with cost and scalability. At the moment, the reduction of graphene derivatives such as graphene oxide stands out as the primary strategy that can yield bulk amounts of graphene-like sheets that, albeit not defect-free, are highly processable.

Particularly attractive is the availability of bulk quantities of graphene as both colloidal dispersions and powders, which enables the possible fabrication of many carbon-based materials. The fact that such large amounts of graphene are somehow easily produced via the reduction of graphene oxide – oxygenated graphene sheets covered with epoxy, hydroxyl and carboxyl groups – offers tremendous opportunities for access to functionalized graphene-based nanocomposites. From the chemical point of view, the presence of oxygen functionalities at graphene oxide surface is very interesting since they provide reactive sites for chemical modification using known carbon surface chemistry. In this frame graphene oxide, because of its easier production and dispersion as well as simple chemical functionalization if compared to graphene, is emerging as a versatile material for applications in nanoscience and nanotechnology (Melucci, Treossi et al. 2010).

This chapter addresses the preparation, characterization and potential applications of graphene-based nanocomposites prepared using chemical strategies, which have been particularly relevant in our research group at TEMA. Special attention will be dedicated to graphene oxide precursor as a building block for the preparation of these nanocomposites. Interesting and promising applications for these materials are also discussed.

2. Graphene oxide

Graphene oxide (GO) has received the attention of a considerable number of researchers as it retains much of the properties of the highly valued super material pure graphene, but it is much easier, and cheaper, to make in bulk quantities; easier to process; and its significant oxygen content has been demonstrated to be very attractive to grow chemical structures at its surface.

2.1 Preparation methods

Chemical exfoliation is an important technique to produce graphene oxide for multifunctional materials. The most interesting advantages of this method are its low-cost and massive scalability. Graphite is the starting material and the technique can be easily scaled up to produce gram quantities or larger of "chemically derived graphene" dispersed in a liquid.

It all started in 1859, when Brodie (Brodie 1860) made the first attempt to produce graphene (at that time known as graphite oxide) using chemical exfoliation. Through adding potassium chlorate ($KClO_3$) to a mixture of graphite with nitric acid (HNO_3) an increase in the graphite mass was detected. The analysis of the obtained product revealed the presence of mainly hydrogen, oxygen and carbon.

Forty years later Staudenmaier (Staudenmaier 1898) achieved a 2:1 C:O ratio in the graphite oxidation by acidizing further the reaction medium. Hummers e Offeman (Hummers and Offeman 1958) used potassium permanganate ($KMnO_4$) in a sulfuric acid (H_2SO_4) medium and achieved similar oxidation levels of Staudenmaier's method.

The first single sheet of GO obtained by chemical exfoliation was based in the use of graphite oxide, which is easily dispersed in water. The exfoliation is accomplished due to

the strength of interactions between water and the oxygen-containing (epoxide and hydroxyl) functionalities introduced into the basal plane during oxidation. The hydrophilicity leads water to readily intercalate between the sheets and disperse them as individuals. Mechanical stirring or sonication is employed in order to break the bonds between the carbon layers. The later allows for a faster and more effective cleavage, as the cavitation of bubbles generated by ultrasonic fields produces shock waves that break apart the graphite flakes.

However there are limitations, mechanical and chemical exfoliation do not allow an absolute control over the graphene layer number, also the quality of the GO 2D crystal framework tends to be lower than graphene, hindering its performance in several applications mainly in the electronic area. These defects in the crystalline network are mainly noticed in the chemical exfoliations due to ample surface modification. In addition the ultrasonication tends to create bigger structural damages in the GO (Stankovich, Dikin et al. 2006; Gilje, Han et al. 2007; Paredes, Villar-Rodil et al. 2008).

Our research group has mainly used the top-down approach to prepare GO sheets from the referred chemical exfoliation of graphite. We followed the methodology suggested by Hummers and Offeman (Hummers and Offeman 1958) with minor modifications. This method involves the addition of concentrated H_2SO_4 (50 mL) into a 250 mL flask filled with graphite (2 g) at room temperature. The flask is cooled to 0 °C in an ice bath, followed by slow addition of $KMnO_4$ (7 g); the flask is then allowed to warm to room temperature. After the temperature is raised to 35 °C in a water bath, and the mixture is stirred with a Teflon-coated magnetic stirring bar for 2 h. The reaction mixture is then cooled in an ice bath, followed by the addition of distilled water in excess to the mixture. H_2O_2 (30 wt % in water) is next added until the gas evolution ceases. The resultant brown yellowish suspension is intensively washed by filtration. Firstly is washed with a diluted solution of HCl (0.1 mol dm^{-3}) and then with distilled water. The resulting slurry is re-suspended in distilled water and then centrifuged at 3.000 rpm until neutral pH.

The resulting material is dried by lyophilization in order to obtain a non agglomerated powder. The characterization of this nanomaterial, referred as graphene oxide (GO) is presented in the following section.

2.2 Characterization of GO sheets

As already referred, GO contains a variety of reactive oxygen functional groups, which renders it a good candidate for use in a wide variety of applications through well known chemical functionalizations.

The detailed structure of GO is still under discussion - since it depends on the chemical oxidation process used to its preparation. Because of this, models for the GO structure proposed in the literature differ considerably; this particular issue is discussed in considerable detail in a critical review by Daniel R. Dreyer (Dreyer, Park et al. 2010).

Meanwhile, the structure of GO can be simplistically assumed to be a graphene sheet bonded to oxygen in the form of hydroxyl (C-OH), ketonic species (C=O), carboxyl (COOH), epoxide (C-O-C) and various C-O and C=O containing chemical species such as lactol, peroxide, dioxolane, anhydride and ether (Acik, Lee et al. 2010).

The FTIR spectrum of GO nanosheets obtained from the methodology described in section 2.1 show the presence of these groups together with sp^2-hybridized C=C (in-plane vibrations) (Figure 1). This figure also includes the spectra of thermally reduced GO (at 1050 °C during 30 s in Argon atmosphere) identified as GTR and chemically reduced GO with

hydrazine (at 100 °C during 24 h) identified as GHR. In these cases, some residual bands at ~1720, 1227, and 1070 cm^{-1} are still detected, showing that even after the application of reduction processes, some residual oxygen groups are still present. It should be noted that all spectra show a band at 1620 cm^{-1}, which can be attributed to aromatic carbon double bonds.

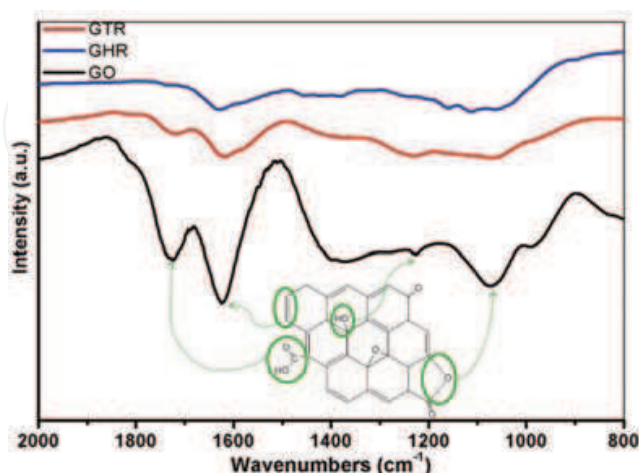Fig. 1. FTIR spectra of as-prepared graphene oxide (GO), thermally reduced (GTR) and chemically reduced (GHR) GO. Reprinted (adapted) with permission from (Goncalves, Marques et al. 2009) Copyright 2011 American Chemical Society.
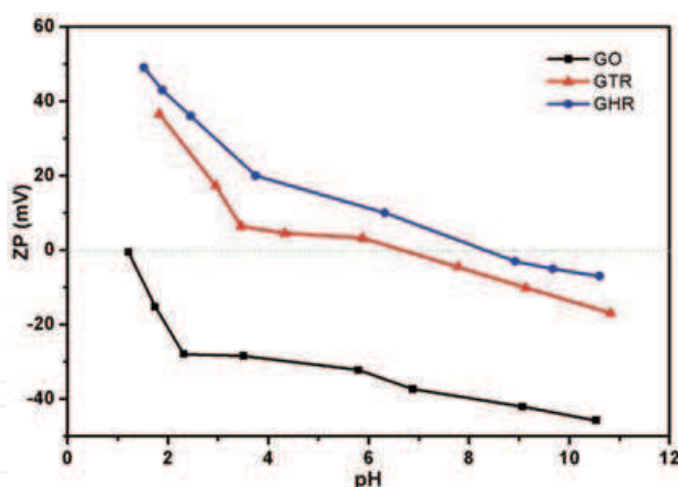

Fig. 2. Zeta potential of aqueous suspensions of as-prepared GO, thermally reduced (GTR) and chemically reduced (GHR) GO in function of pH. Reprinted with permission from (Goncalves, Marques et al. 2009) Copyright 2011 American Chemical Society.

Zeta potential measurements done in aqueous solutions of the previous mentioned samples (GO, GTR and GHR) in function of pH are important to determine the surface charge of the sheets (Figure 2). The results show that GO sheets are highly negatively charged with an average value equal to -35 mV at pH range between 3 and 9. This value is attributed to the presence of the above-described oxygen species at the surface of GO. On the contrary, GTR and GHR show positive zeta potential values near zero for the same pH range, which is indicative of the lower charge density of this type of graphene. The thermal and chemical

treatments of the GO sheets resulted in the reduction and almost complete elimination of the oxygen functionalities at the surfaces of these materials.

The presence of the oxygen functional groups at GO surface is responsible for its hydrophilicity, on contrary to graphene that is hydrophobic. The aqueous solutions of the as-prepared GO are then stable for long periods of time, showing a characteristic brown colour (Figure 3a).

The SEM images of GO reveal translucent sheets with wrinkles and folds as exemplified in Fig.3b. The thickness of these individual GO sheets measured by AFM show an average thickness around 1.8 nm for most GO sheets that is larger than the value of 0.8 nm referred for a single-layer graphene (Novoselov, Geim et al. 2004). Considering that the presence of the oxygen-containing functional groups on both sides of the GO surfaces increases their thickness with respect to nonfunctionalized graphene sheets, we may consider that most of these GO sheets consist of two or three layers of graphene. This result demonstrates the efficiency of the chemical treatment applied to exfoliate graphite into separate graphene sheets.
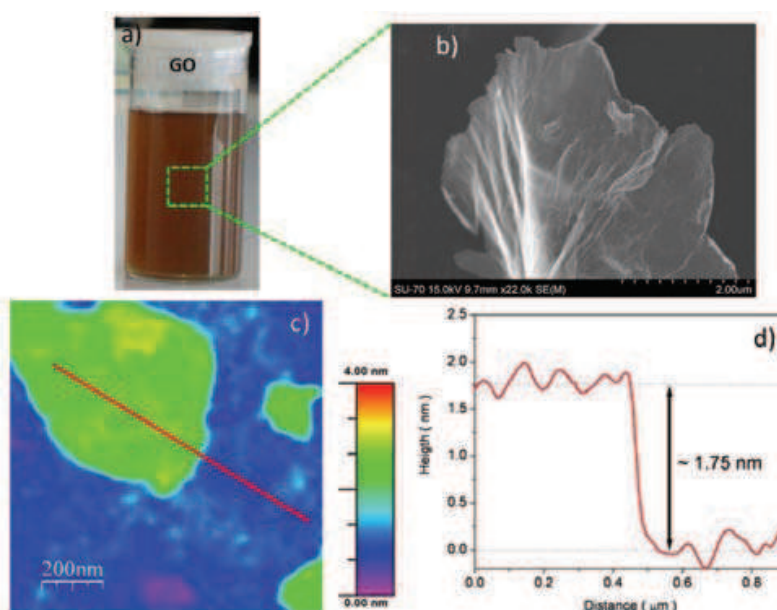

Fig. 3. a) Photographic image of an aqueous colloidal suspension of GO; b) SEM micrograph of graphene oxide sheet; c) Topographic view of contact-mode AFM scan of GO deposited on SiO$_2$ glass; and d) Height profile through the line shown in image (c). Reprinted (adapted) with permission from (Goncalves, Marques et al. 2009) Copyright 2011 American Chemical Society.

A more accurate analysis of the quality and crystallinity of GO sheets can be obtained by HR-TEM analysis. Figure 4a shows a bright-field TEM image of GO sheet attached to a copper grid. The suspended graphene membranes presented here consist of single layer or bilayer sheets with average dimensions of 2 µm. The HR-TEM image (Fig. 4b) clearly shows two-layered graphene (two graphene layers separated by 0.40 ± 0.02 nm) this is marked by green dotted area in Fig. 4b. A 2D fast Fourier transform (FFT) (Fig. 4c) was performed in the region indicated by a red box in Fig. 4b – this figure clearly shows the crystalline nature of bilayer graphene sheet. The corresponding HR-TEM image also reveals the honeycomb structure of graphene sheet (Fig. 4d).

The as-synthesized GO exhibits optical absorption in the visible and near-infrared range (Fig. 4e). The maximum absorbance at ~230 nm could originate from п–п* transition of aromatic sp^2 domains (Novoselov, Geim et al. 2004) whereas a minor peak at ~320 nm was attributable to n–п* transitions of C=O (Luo, Lu et al. 2009).
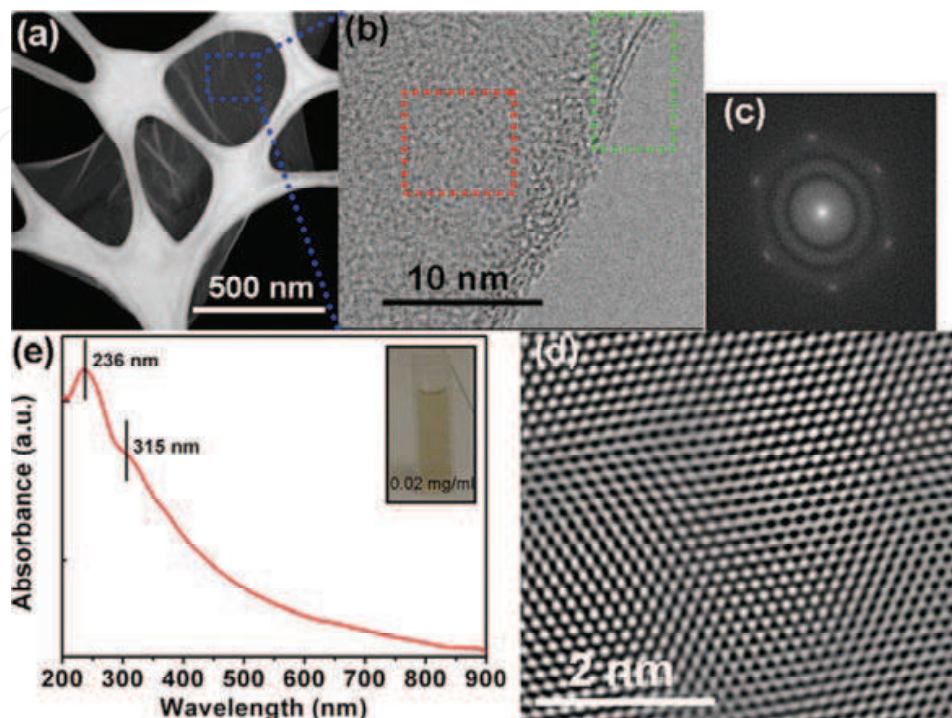

Fig. 4. (a) Bright-field TEM image of suspended GO sheet on carbon grid. (b) HR-TEM image of the blue dotted area denoted in a. (c) 2D FFT performed in the region indicated with red box exhibiting perfect crystallinity of GO sheet. (d) HR-TEM image reveals honeycomb structure of graphene sheet performed at the area denoted by red dotted line. (e) UV–vis absorbance spectra of GO solution in water. Inset shows the colour of the GO solution (0.02 mg/mL). Reprinted with permission from (Singh, Singh et al. 2011) Copyright 2011 American Chemical Society.

Recently, flow cytometry was presented as an alternative tool for analysis of size distribution and intrinsic fluorescence of GO sheets (Singh, Singh et al. 2011). Flow cytometry is a technique that integrates light scattering and fluorescence signals emanated from a group of cells or particles in the path of laser beam, thereby generating extensive statistical data on size, shape and internal characteristics of individual cells within the population. The method has found wide applications in biological research in view of its predilection for multi-parameter analysis at the single-cell level. Flow cytometry usually characterizes cells or particles with typical size range between 0.5 and 70 μm. Scatter signals evoked by submicron nano-sized particles are obligatorily gated along with the background noise, thereby blurring the distinction between noise and signal, which precludes flow cytometric analysis of nanoparticles unless particles are aggregated to larger dimension or have been made fluorescent.

In this work, it is report for the first time, that scatter signals generated by native single or few-layer GO sheets in a flow cytometer are gated distinctly apart from the background sheath fluid noise, thus enabling extensive analysis of size distribution and characterization

of fluorescence properties of individual GO sheets in the population. The results show that GO sheets are asymmetric in size and are endowed with intrinsic fluorescence detectable through the three fluorescence channels (FL1, FL2 and FL3) in the flow cytometer. Flow cytometer may, therefore, prove to be an indispensable tool in graphene research, which can have applications in exploring biomedical potential of this new material in miscellaneous areas like imaging, graphene–cell interaction as well as drug delivery.

3. Functionalization of graphene sheets

Due to the interest of using graphene as reinforcement filler of polymer matrixes to create multifunctional materials, a variety of methods for the graphene surface modification have been developed. Among other factors, the nature of the bonding interaction at the interface between the filler and the matrix has significant implications for the final composite properties, and most dispersion methods produce composites that are non-covalent assemblies where the polymer matrix and the filler interact through relatively weak dispersive forces. However, there is growing research focus on introducing covalent linkages between graphene based filler and the supporting polymer to promote stronger interfacial bonding, as will be presented in the following section entitled organic functionalization of graphene sheets.

On the other hand, graphene-based sheets have been utilized as burgeoning supports to disperse and stabilize nanoparticles, it is expected that such 2D carbon sheets may be appropriated candidates as nanoscale substrates in obtaining nanoparticle films. Metallic nanoparticles play an important role in wide number of applications such as surface-enhanced Raman scattering (SERS), display devices, catalysis, microelectronics, light emitting diodes, photovoltaic cells and also in medical or biological applications. Moreover, nanoparticles show changes in its electronic, optical and catalytic properties depending on the method of synthesis (Hodes 2007). Insertion of the nanoparticles on the graphene based matrix is an important study for the exploration of their properties and applications, examples of these materials will be included on section 3.2 entitled "inorganic functionalization of graphene sheets".

On the account of the importance of using graphene oxide to prepare graphene based materials, we will focus on two main types of functionalization: organic and inorganic.

3.1 Organic functionalization of graphene sheets

Concerning organic functionalization, we will discuss the importance of GO surface modification with organic moieties in order to disperse it in a polymeric matrix. As an example we will discuss in more detail the GO surface functionalization with an atom transfer polymerization initiator (ATRP) and subsequent poly(methylmethacrylate) (PMMA) chains growth via living/controlled polymerization yielding a nanocomposite soluble in organic medium. Polymerizations from surfaces, also known as SIP (surface initiated polymerization), have been widely used in the preparation of nanocomposites. In this context, living/controlled radical polymerization mechanisms, such as ATRP, offer the possibility of preparing multifunctional materials with good control over the polymer molecular weight, polydispersity index, composition and end group functionality. The interest of this organic functionalization of GO sheets lies in their potential to be homogenously dispersed in polymeric dense matrices promoting good interfacial adhesion, of particular relevance in stress transfer to the fillers.

The organic functionalization of GO can be made by two distinct approaches, or by covalent or non-covalent bonds. In addition to other factors, the nature of the interaction at the interface of filler has significant implications on the enhancement of the final properties of the nanocomposites. For example the establishment of covalent bonds between graphene and polymeric matrices allows a more effectively tensions dissipation when the material is under strain which is quite important when talking about mechanical reinforcements. However it should be noted that the covalent functionalization of graphene creates discrete zones of discontinuity on sp^2 hybridized network not allowing the electron conduction, which has significant implications in reducing the conductivity of nanocomposites. In this case the non-covalent functionalization of graphene, through weak interactions minimizes this effect because it does not interfere in any destruction of aromatic structure of graphene.

3.1.1 Covalent functionalization

The covalent functionalization of carbon nanomaterials is usually preceded by an oxidation of the graphitic matrix with strong acids and oxidants in order to obtain oxygen functional groups that serve as precursors for the anchoring of organic molecules desired. As stated above the GO is characterized by being highly functionalized by oxygen groups reaching the C/O ratio of 2:1.

The availability of functional groups allows the use of various approaches already developed in organic chemistry in order to functionalize the GO (Figure 5). In terms of chemical reactions, acetylation is among the most common approaches to promote covalent binding of organic precursor molecules with functional groups at the surface of GO (Loh, Bao et al. 2010).
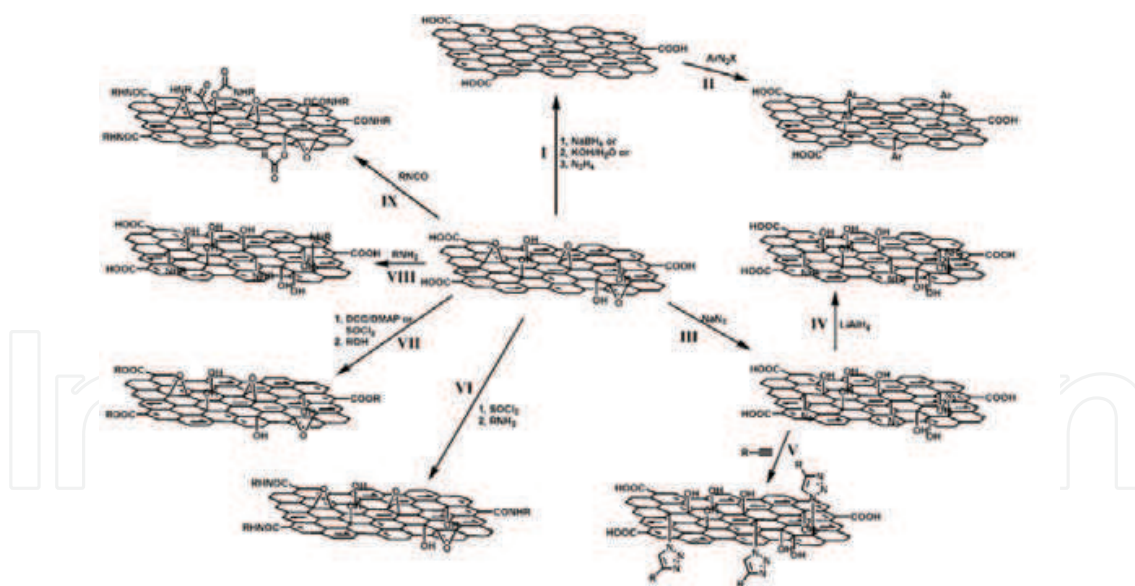

Fig. 5. Schematic representation showing various covalent functionalization chemistry of graphene or GO. I: Reduction of GO into graphene. II: Covalent surface functionalization via diazonium reaction (ArN$_2$X). III: Functionalization of with sodium azide. IV: Reduction of azide functionalized GO with LiAlH$_4$. V: Functionalization of azide functionalized GO through click chemistry (R–ChCH/CuSO$_4$). VI: Modification of GO with long alkyl chains by the acylation reaction. VII: Esterification of GO VIII: Nucleophilic ring-opening reaction of GO. IX: Functionalization of GO with organic isocyanates. (Loh, Bao et al. 2010) Reproduced by permission of The Royal Society of Chemistry (RSC).

The organic functionalization of GO allows the formation of stable colloidal solutions in several different solvents increasing the manipulation and processing of GO (water, acetone, ethanol, 1-propanol, ethylene glycol, dichloromethane, pyridine, DMF (dimethylformamide), THF (tetrahydrofuran), DMSO (dimethylsulfoxide), NMP (N-methyl pyrrolidone), acetonitrile, hexane, diethyl ether and toluene (Park, An et al. 2009; Rao, Biswas et al. 2009; Dreyer, Park et al. 2010), furthermore it also improves the molecular and atomic interfacial interactions between the graphene and solvents.

Stankovich et al demonstrated the surface functionalization of GO with aliphatic and aromatic isocyanates derivatives through formation of amide and carbamate esters with carboxylic groups and hydroxyl, respectively, on the surface of GO (Stankovich, Piner et al. 2006). The results show that these new hybrid materials allow the formation of stable colloidal solutions in various polar aprotic solvents such as dimethylformamide, N-methyl-2-pyrrolidone, dimethylsulfoxide or hexamethylphosphoramide.

Another approach that allows the addition of new functional groups on the surface of GO is silanization (Yang, Li et al. 2009; Hou, Su et al. 2010). Yang et al. described the covalent bond of 3-aminopropiltrietoxisilano (APTS) on the surface of GO, through S_N2 nucleophilic reactions between the epoxy groups of the surface of GO and the amine groups of APTS. This type of modification has a special interest in the dispersion of functionalized GO in different solvents (polar or non-polar), this is due to the fact that the family of silanes provide a wide range of terminal functional groups.

The functionalization of GO via carboxylic acids is one of the most common approaches and is possible by prior activation of these groups through various agents such as thionyl chloride ($SOCl_2$) (Niyogi, Bekyarova et al. 2006; Liu, Xu et al. 2009; Zhang, Huang et al. 2009; Karousis, Economopoulos et al. 2010; Zhuang, Chen et al. 2010), 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide (EDC) (Liu, Robinson et al. 2008), N, N'-dicyclohexylcarbodiimide (DCC) (Veca, Lu et al. 2009) and 2-(7-aza-1H-benzotriazole-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate (Hatu) (Mohanty and Berry 2008). Subsequent addition of nucleophilic species, such as amines and hydroxyl, allow the formation of covalent bonds with functional groups of the graphene oxide through formation of amide or ester groups.

Another strategy for surface functionalization of GO is through the use of epoxide groups on the surface of graphitic planes, which can easily be modified on certain conditions through reactions of ring-opening. The preferred mechanism for this type of reaction involves a nucleophilic attack of amines to α-carbon. The study performed by Wang et al based on this methodology allowed the surface modification of GO with octadecylamine (Wang, Chia et al. 2008). Another author used the same procedure to establish links between an ionic liquid with terminal amine groups and epoxide groups at the surface of graphene oxide. This surface modification is of particular interest when attempting to disperse the GO in polar solvents (Yang, Shan et al. 2009).

A referred one of the main reasons for the surface modification of GO with organic moieties is that it enables a seamless integration with molecular polymeric matrixes. In this sense there is a range of approaches already described by several authors that allow the controlled growth of polymer chains at the surface of GO.

A well-known mechanism for the controlled growth of polymer chains on the surface of GO polymerization is atom transfer radical polymeriztion (ATRP). Usually in such cases the free carboxylic groups of GO are converted to acyl groups, which upon treatment with diols (ethylene glycol), yield graphene sheets rich in hydroxyl groups. These hydroxyl groups at

the surface of GO allows the establishment of covalent bonds with initiator agent of ATRP polymerization, which are usually compounds with terminal bromine groups (2-bromo-2-methylpropionyl bromide or α-bromoisobutyryl-bromide). After the addition of the initiating agent to the surface of GO is possible to perform the controlled growth of polymer chains via ATRP (Figure 6). Another approach is the surface modification of carboxylic groups of GO with diamines through the formation of amide groups, allowing the functionalization of GO with terminal amine groups, that also able to establish chemical bonds with the ATRP initiators (Fang, Wang et al. 2009; Lee, Dreyer et al. 2010).
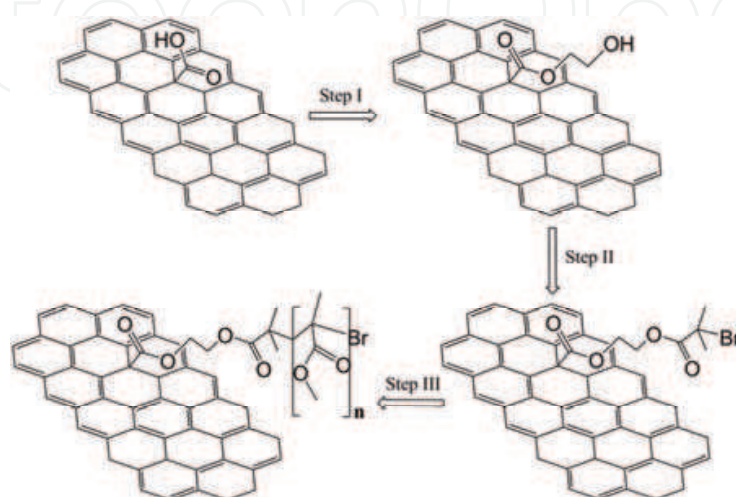

Fig. 6. Schematic representation of the ATRP reaction mechanism for the surface modification of GO with PMMA .

In our work we performed the surface modification of GO with PMMA polymers chains via ATRP in order to test it as a reinforcement of a PMMA matrix (Goncalves, Marques et al. 2010) following the scheme in Fig.6.

After the GO modification with the PMMA chains, hereafter referred as GPMMA, it turned hydrophobic and as a result soluble in chloroform as can be seen in the inset of Figure 7a. It should be also notice that this solution is clearly darker than the original GO in aqueous solution (Fig.3a) indicating the conversion of GO to GPMMA. Figure 7 depicts the TEM image of the GPMMA sample where some dark features can be observed. The high magnification image (Fig. 7b) of the area denoted by the square region in Fig. 7a, clearly shows these dark spots as opposed to what is observed for pristine GO. The presence of such spots can be attributed to polymer brushes and has been observed by other authors with different polymers as described elsewhere (Yang, Wang et al. 2009; Fang, Wang et al. 2010). According to Yang et al. (Yang, Wang et al. 2009), in solution the grafted polymer chains are extended due to their solubility in the solvent, however, after drying the polymer chains collapse onto the surface of the GO sheets forming nanosized domains that may correspond to the dark spots observed.

The characterization of GPMMA by infrared spectroscopy showed an increase of the intensity of the carbonyl band combined with appearance of characteristic bands of –CH_2 at 2850 and 2920 cm^{-1} in the infrared spectrum confirming the presence of PMMA polymer chains at GO surface. In Raman spectrum there was a decrease of intensity of the characteristic D (1330 cm^{-1}) and G (1590 cm^{-1}) bands of graphene in relation to what is normally observed for GO, which is associated with surface defects created during the surface treatments (Fang, Wang et al. 2010).
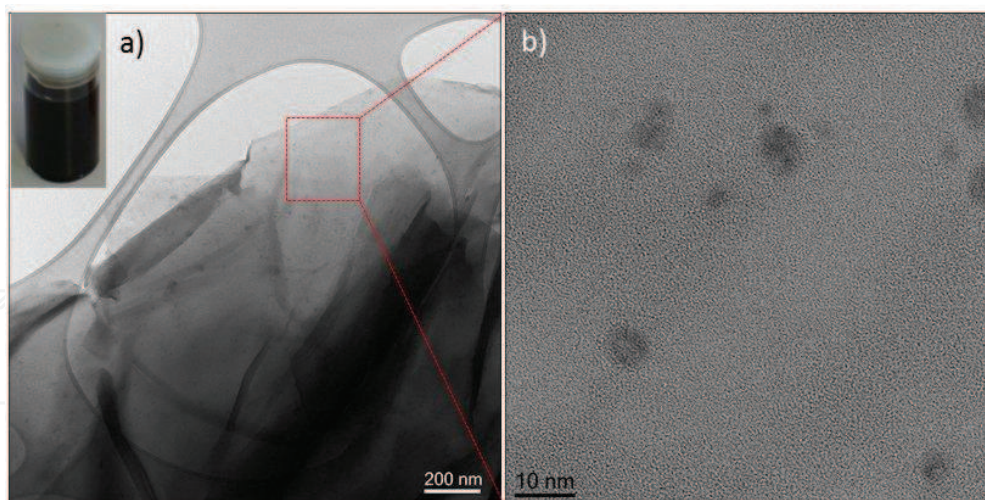
Fig. 7. a) TEM image of the GPMMA sample; b) high magnification image of the area denoted by the square region is shown in a). Inset in Fig. 7a show the photographic image of GPMMA in chloroform. (Goncalves, Marques et al. 2010) Reproduced (adapted) by permission to The Royal Society of Chemistry.

To further understand the surface of GPMMA AFM studies in friction mode were performed on these sheets. It is known that the adhesion force (F_{ad}) and the friction coefficient (μ) of a material depend on its atomic structure and can be calculated by the following equation $F = \mu \, (F_N + F_{ad})$, where F_L is the lateral force, also known as friction force, and F_N the normal force. From the graphics inserted in Fig. 8 it is possible to see the different
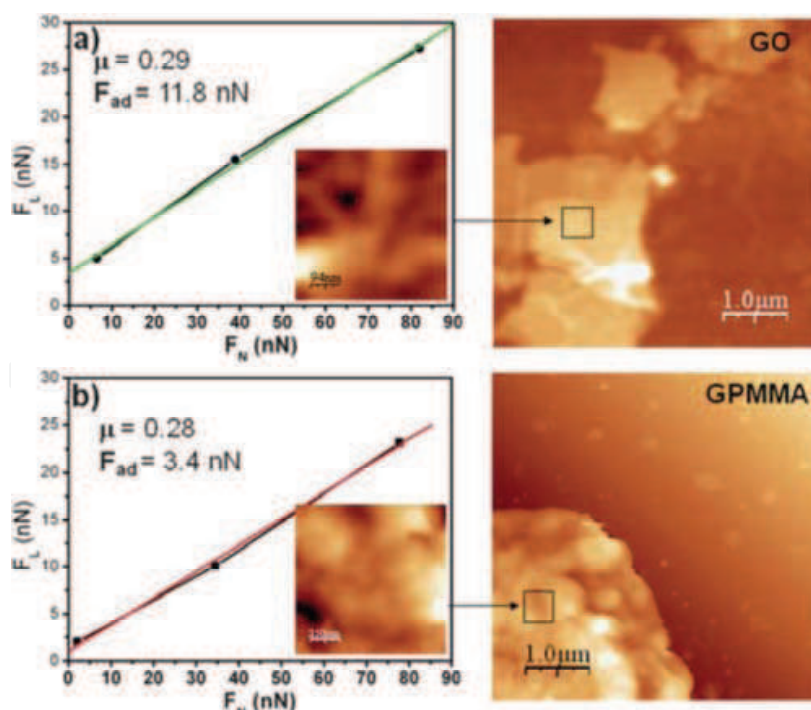

Fig. 8. A graphical representation of lateral versus normal forces determined by the AFM analysis in friction mode and contact-mode AFM topography images of (a) GO and (b) GPMMA (Goncalves, Marques et al. 2010) Reproduced by permission to The Royal Society of Chemistry.

response of the materials (GO and GPMMA) by applying three different normal forces. The results show that the friction coefficients are relatively similar in both samples. However, the adhesion force is three times higher in the case of the GO sheets (F_{ad} GO = 11.8 nN and F_{ad} GPMMA =3.4 nN). These results can be attributed to the different chemical surface of GPMMA which results in different atomic interactions with the AFM cantilever. Careful analysis of the graphs shows a linear relationship between the normal and lateral forces which point to a homogeneous distribution of the polymer chains at the GO surface. These results are in agreement with an effective modification of the GO surface with the ATRP initiator and subsequent uniform polymerization, as previously discussed.

The study of the effect of the incorporation of this GPMMA in a PMMA matrix is discussed in section 4.1.

3.1.2 Non-covalent functionalization

GO can also form various multifunctional materials through non-covalent bonds, either of the Van der Waals or ionic type, this property is mainly due to the fact that its surface is negatively charged due to the presence of oxygen functional groups, in addition to its graphitic structure with delocalized π orbital that allow π-π interaction type.

This type of functionalization has some advantages in certain areas, such as chemical sensors and biomedical materials. In this context, several materials, such as polymers (Hu, Wang et al. 2010; Liu, Tao et al. 2010; Liu, Yang et al. 2010), surfactants (Hao, Qian et al. 2008; Xu, Bai et al. 2008; Liang, Wu et al. 2009), polyelectrolytes (Hasin, Alpuche-Aviles et al. 2010; Qi, Pu et al. 2010; Tian, Meziani et al. 2010) and biomolecules (Lu, Yang et al. 2009; Patil, Vickery et al. 2009; Husale, Sahoo et al. 2010; Laaksonen, Kainlauri et al. 2010; Wu, Shao et al. 2010) can be used to functionalize the surface of GO (Figure 9).
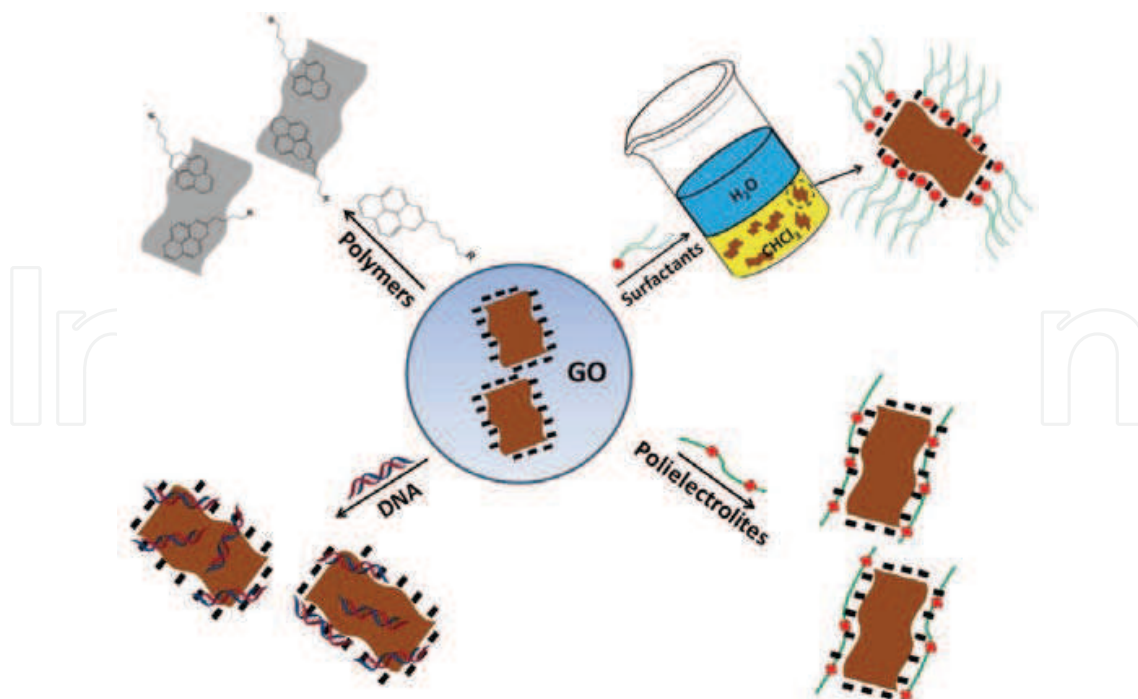

Fig. 9. Schematic representation of non-covalent functionalization of GO through surfactants, polyelectrolytes, polymers and DNA.

Recent studies indicate a growing interest to functionalize graphene with various types of biomolecules such as DNA, proteins and enzymes in order to obtain functional materials with a wide range of applications in nano-electronics and biotechnology.

For example, adsorption of DNA biomolecules on the surface of graphene is enabled due to non-covalent interactions (electrostatic/hydrogen bonding) between the primary amines of the single-stranded DNA and the carboxylic groups of the GO and by the π-π stacking interactions involving both purine and pyrimide bases of DNA. The results demonstrate that these systems are stable in aqueous solutions for several months at concentrations below 2.5 mg/mL (Patil, Vickery et al. 2009). This approach was also developed for chains of double-stranded DNA, yet the results showed that the aqueous suspensions of graphene were less stable, probably due to the pairing of helices limiting interactions with the hydrophilic surface of GO.

3.2 Inorganic functionalization of graphene sheets

Graphene is an interesting substrate for the immobilization of inorganic nanoparticles. The dispersion of metal nanoparticles on graphene sheets potentially provides a new way to develop catalytic, magnetic, and optoelectronic materials. In the last years, the ability of combining well with metallic nanoparticles producing nanocomposites with promising applications such as chemical sensors, energy and hydrogen storage systems and catalysts, among others, has captured the interest of a number of researchers; the advantage, beyond the already mentioned characteristics of graphene, is that we can add specific properties associated to the inorganic nanoparticles like magnetic, optical, electrical, catalytic and others (Hassan, Abdelsayed et al. 2009; Kamat 2009).

The majority of the publications related to the preparation and applications of this new class of graphene based nanocomposites uses noble metals like gold (Goncalves, Marques et al. 2009; Hong, Bai et al. 2010), platinum (Si and Samulski 2008), palladium (Scheuermann, Rumi et al. 2009) and silver (Shen, Shi et al. 2010); however, there is also a growing interest in the use of other metals like, iron, cooper, tin and cobalt.

Some of the published papers about the preparation of graphene/metal nanocomposites makes use of organic spacers, like octadecylamine, to anchor the metallic nanoparticles to the graphene surface or organic solvents such as tetrahydrofuran, methanol, and ethylene glycol (Muszynski, Seger et al. 2008). However, the in situ synthesis of the metal nanoparticles in the presence of GO has received particular attention, since it allows the controlled growth of the nanoparticles on the graphene surface through the use of precursors of the metallic molecules that are then reduced by the addition of reducing agents and reducing GO at the same time. In this context, for the preparation of Au/graphene nanocomposites by in situ synthesis, we have shown that it the presence of oxygen functional groups at GO surface are fundamental for the nucleation and growth of gold nanoparticles (Goncalves, Marques et al. 2009).

3.2.1 Gold/graphene nanocomposites

Gold was selected for its unique optical and surface properties that attract a great deal of attention because of their potential applications in catalysis, optics, and nanobiotecnology.

The synthesis of Au/graphene nanocomposites was based on the reduction of gold(III) complex by sodium citrate. Typically, 2.5 mL of a GO aqueous suspension (1.5 mg/mL) was added to 50 mL of $HAuCl_4$ solution (0.24 mmol dm^{-3}). The resultant suspension was aged

during 30 min to promote the interaction of gold ions with the graphene surface. After that, the solution was heated until 80 °C, after which 940 μL of sodium citrate (0.085 mol dm^{-3}) was added dropwise. The reaction was kept at these conditions during one hour.

The resultant nanocomposite was washed with distilled water using centrifugation (3000 rpm) to remove the free gold nanoparticles that formed in solution. The final nanocomposite was dried by lyophilization.

The SEM and TEM analysis of the resulting material shows a homogeneous distribution of gold nanoparticles at graphene surface with an average particle size of 21.3 ±1.8 nm (Fig. 10a and b). The thin structure of the graphene sheet and smooth surface are confirmed and some corrugation is detected, suggesting a flexible structure of the graphene sheets. The dispersion of the gold nanoparticles on the 2D sheet of carbon can be visualized also in the AFM image in Fig.10c. The AFM analysis further confirms the ability to attain a uniform distribution of ~20 nm diameter gold nanoparticles anchored on the graphene sheets. The corrugated nature of the graphene sheets is also evident by this analysis.

The nucleation of gold nanoparticles at GO surfaces should be mainly governed by the presence of oxygen groups at GO which contribute to an overall negatively charged surface as confirmed by zeta potential measurements (see section 2.2). To study the influence of the presence of the oxygen functionalities at the GO surface we applied the previously described methodology using reduced graphene sheets. In this case almost no gold nanoparticles were detected at graphene surface.
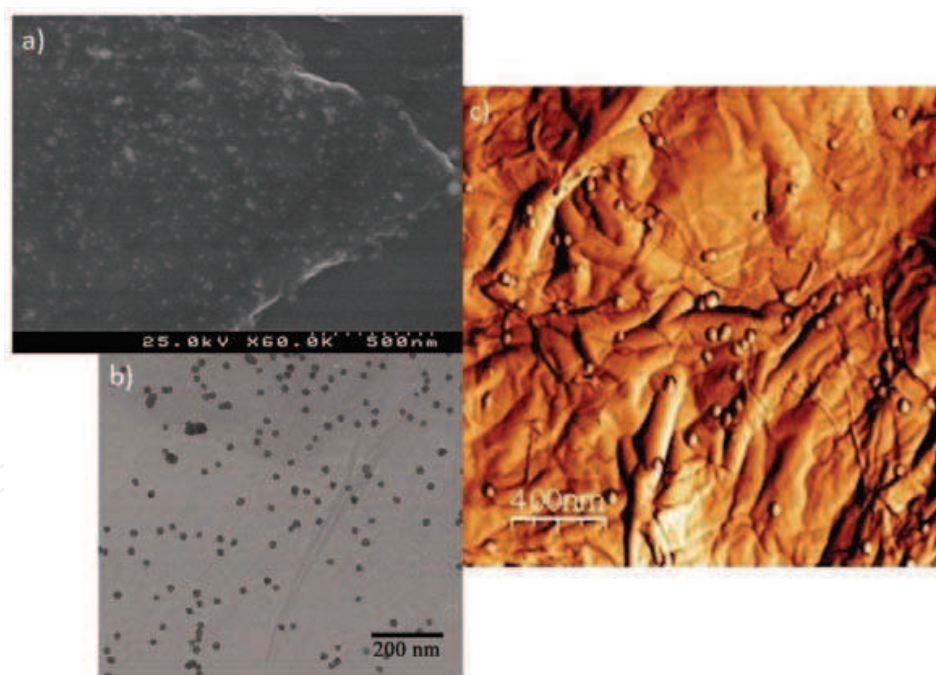

Fig. 10. a) SEM, b) TEM and c) AFM images of gold/graphene nanocomposite prepared from GO.

Although it is not possible to make a distinction between the roles of each oxygen group (carbonyl, carboxylic, or other) present at GO surface on the nucleation of Au nanoparticles, it is supposed that the overall oxygen functional groups are responsible for a previous attachment of the free gold (III) ions in solution because of electrostatic interactions. The initial step of the experimental reaction, which ages the solution containing gold ions in the

presence of graphene, has this main propose. Afterwards, the addition of the reducing agent (citrate ion) to the precursor solution promotes the subsequent reduction of gold (III) ions, enabling the growth of gold nanoparticles at the graphene surface. The scheme presented in Figure 11 illustrates the reaction steps involved in the above described process.
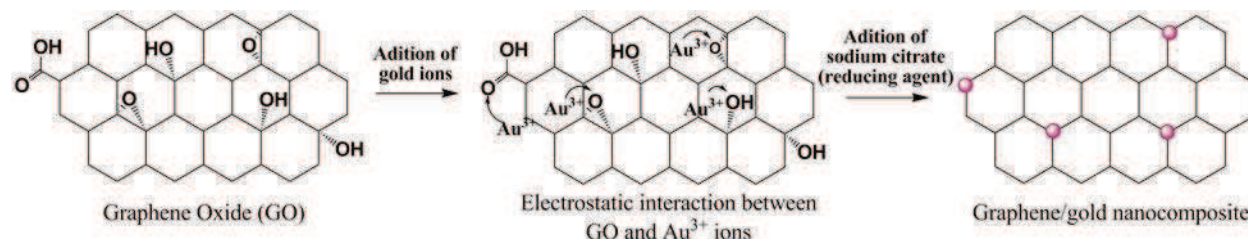

Fig. 11. Schematic representation of the possible mechanism of nucleation of gold nanoparticles at functionalized graphene surface.

3.2.2 Silver/graphene nanocomposites

Like Au nanoparticles, the Ag nanoparticles have excellent optical, electric and biological properties; in addition silver has antibacterial properties which are very important for biomedical applications.

A desire to exploit the unique association of Ag nanoparticles to graphene sheets led us to explore the synthesis of Ag nanoparticles on GO matrix. Silver nanoparticles were synthesized on the surface of GO sheet by the simultaneous reduction of Ag+ and GO in the presence of simple reducing agent, hydrazine hydrate ($N_2H_4.H_2O$). Both the Ag+ and GO were reduced and Ag+ was nucleated onto graphene.

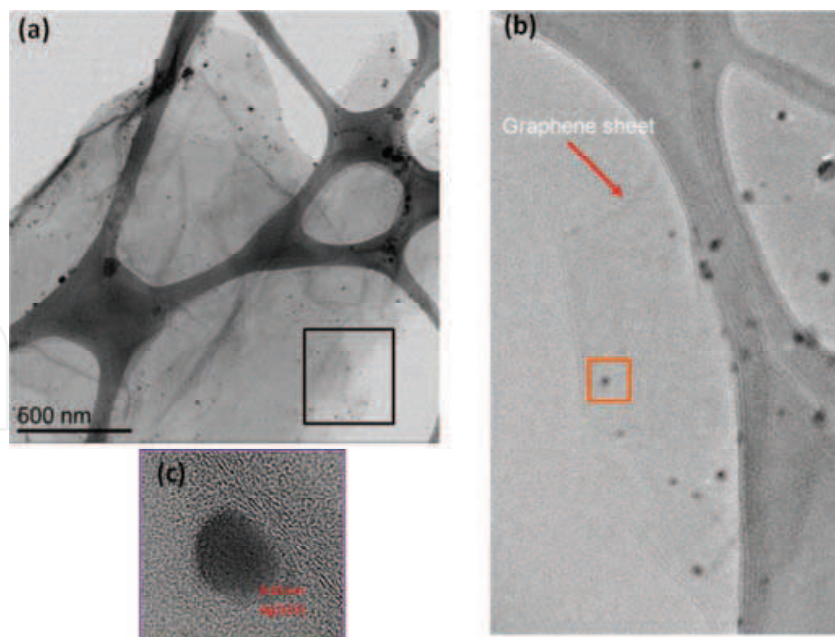Figure 12 shows the TEM image of few layers-thick graphene sheets where the nucleation of

Fig. 12. (a) shows bright field TEM image of Ag/graphene sheet (b) HRTEM image of Ag/graphene sheet performed on the area denoted by black square region (a). (c) HR TEM image of single crystal Ag nanoparticle on graphene sheet which shows the characteristic (111) plane of Ag.

Ag onto graphene is demonstrated. These results clearly exhibited (Fig.12) the ultra-thin nature of reduced graphene sheet with ripples. We have also investigated the oxygen rich sites of GO which behave as a receptor sites for Ag+, and integrate the Ag preventing the aggregation of Ag nanoparticles. Das et al. also demonstrated the synthesis of Ag nanoparticles (of average size 5-25 nm) in an aqueous suspension of GO for antimicrobial activity (Das, Sarma et al. 2011). The incorporation of Ag nanoparticles into the graphene sheets prevents the agglomeration of nanoparticles and privileges the nucleation over growth, this combined effect led to the good particle density and monodispersity observed in the Ag/graphene sample.

4. Applications of graphene nanocomposites

Functionalized graphene has been considered as one of the next-generation nanofillers for polymer nanocomposites due to its outstanding physical properties and low fabrication cost in comparison with that of carbon nanotubes. Improvements of mechanical, electrical and thermal properties of the resulting materials are expected. In this section we show an example of good integration of the previously modified graphene with PMMA chains in a PMMA matrix.

The association of noble metal nanoparticles to graphene sheets is still an unexplored field of research with huge potentialities. Here, we also present one example of the potentialities of Au/graphene nanocomposite as substrate for SERS analysis.

4.1 Graphene modified with PMMA as polymer matrix reinforcement

To assess the compatibility between the previously discussed GPMMA nanosheets with PMMA matrix, nanocomposite films with 0.5, 1 and 3% (w/w) of GPMMA dispersed in PMMA were prepared. PMMA films without fillers and PMMA films with 1% (w/w) of GO were also prepared for comparison. These films were prepared by solvent casting method as discussed by G. Gonçalves et al (Goncalves, Marques et al. 2010)

The mechanical behaviour of the composite films was studied by nanoindentation and uniaxial tensile tests. Figure 13a displays typical loading–unloading curves for pure PMMA
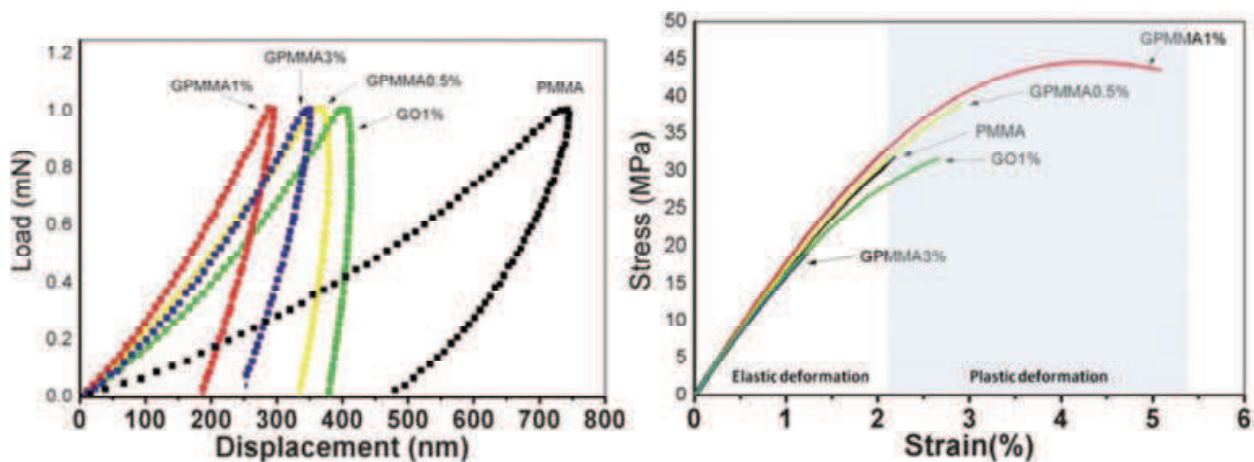

Fig. 13. a) Load-displacement nanoindentation curves of PMMA films with and without graphene fillers; b) Stress–strain dependencies of PMMA films with and without graphene fillers. (Goncalves, Marques et al. 2010) Reproduced by permission to The Royal Society of Chemistry.

films and for the films prepared using 0.5, 1 and 3% (w/w) of GPMMA and 1% of GO which shows that incorporation of fillers into the PMMA matrix increases the resistance to penetration by the nanoindenter.

For the pure PMMA film, the maximum indentation depth at the maximum load of 1.0 mN was 760 nm which was reduced to 420 nm upon addition of 1% (w/w) of GO. This reduction was even more significant for the series of films prepared with GPMMA fillers: 0.5% (w/w), maximum depth 380 nm; 3% (w/w) maximum depth 350 nm; 1% (w/w), maximum depth 290 nm. The results obtained for loads of 1% (w/w) for GO and GPMMA show that the reinforcement effect of GPMMA is significantly more effective due to the surface modification and subsequent increased adhesion with the polymer matrix.

Furthermore, the results obtained for the films prepared with GPMMA show that 1% (w/w) loading yields the stiffest nanocomposite films.

Further confirmation of the tensile properties of the composite films was conducted by performing uniaxial tensile tests. A set of five measurements on five different strips was performed on each sample for statistical accuracy. The stress–strain curves of pure PMMA films as well as for films prepared using 0.5, 1 and 3% (w/w) of GPMMA, and 1% of GO are presented in Fig.13b. At very low stresses and strains, all the samples behave as a linear elastic solid with Young's modulus varying between 18.7 MPa for pure PMMA and 21.8 MPa for films prepared with 1% (w/w) of GPMMA (the highest value obtained). Films prepared with 1% (w/w) of GPMMA also showed plastic regime characterized by average values of uniform and ultimate elongations of 4.0% and 4.8% respectively for a relatively high level of flow stress (42.0 MPa at break). For this condition, the material exhibits elasto–plastic deformation and reasonable ductility. Such mechanical improvements could be attributed to the efficient load transfer between graphene sheet and the PMMA matrix. This kind of polymer matrix could be very interesting for load bearing applications. However, increasing the concentration of GPMMA to about 3% (w/w) deteriorated the mechanical behaviour of the overall composite film. This may be due to the agglomeration of graphene sheets creating defects in the PMMA matrix composite. Concerning the films prepared with 1% GO in the PMMA matrix, the Young's modulus, tensile strength and elongation at break values determined are comparatively lower than the ones obtained for 0.5%, and 1% GPMMA in the PMMA matrix. This indicates that GO sheets do not establish appropriate interfaces with the PMMA matrix. So there might be a lack of load transfer from matrix to GO sheets which directly reflects the mechanical behaviour of the overall composite. Young's modulus and tensile strength values for the film with 1% GO are even smaller than the values obtained for PMMA film prepared without fillers. Moreover, the elongation at break for 1% GO in the PMMA matrix is 2.7%, which is slightly higher than that for pure PMMA (2.3%). This can be explained the presence of graphene sheets which are known for their elasto–plastic behaviour.

From the previous discussion it is obvious that the GO modification with PMMA via ATRP acts as a reinforcement agent of the PMMA matrix. This strategy can be further exploited to grow a large range of polymers from the GO surface only by changing the monomer, for example styrene (Fang, Wang et al. 2009; Fang, Wang et al. 2010; Lee, Dreyer et al. 2010), 2-(dimethylamine) ethyl methacrylate (DMAEMA) (Yang, Wang et al. 2009), butylacrilate (Lee, Dreyer et al. 2010; Li, Liu et al. 2010) are just some of the monomers already used. The versatility of this mechanism also allows the controlled growth of copolymers; if the free radical polymerization remains active, it will allow the growth of another polymer chain just by shifting to the desired monomer.

4.2 Nobel metal/Graphene nanocomposites as SERS substrates

Surface enhanced Raman scattering (SERS) occurs when molecules are adsorbed on nanostructured surfaces, nanoparticles, or rough electrodes of noble metals and it is one of the most powerful microanalytical techniques with single-molecule capabilities and chemical specificity. Different types of SERS substrates have been developed involving either pure or supported nanostructured metals, mostly gold and silver. SERS technique has been implemented widely by a broad scientific research community for chemical and biological sensing and measurements. This technique combines the capability of molecular fingerprinting with ultrahigh sensitivity (Liu, Cao et al. 2010). Increases in the intensity of the Raman signal have been observed by factors up to 10^6, reaching in particular cases the single-molecule detection level. This remarkable enhancement provides high sensitivity and gives an opportunity for the development of ultrasensitive analytical methods for chemical and biochemical detection (Alvarez-Puebla and Liz-Marzan 2010). Numerous applications have demonstrated the potential of SERS for the label-free detection of various analytes. More recently, SERS is increasingly used as a readout method for the selective and sensitive detection of proteins and oligonucleotides. (Schlucker 2009) For SERS it is critical to have a good substrate to obtain a good enhancement. The development and use of highly reproducible substrates is critical in the advancement of SERS as a mainstream spectroscopic technique. This is particularly important in studies of large, complex molecules such as DNA or proteins, because the SERS signal in these molecules already depends significantly on molecular conformation, orientation, and binding specificity to the substrate surface (Barhoumi, Zhang et al. 2008).

Traditionally, the SERS substrate is based on a rough surface of a noble metal such as Ag, Au, Cu, and so on. To make a rough metal surface for SERS, relatively complex methods are used like electrochemical ways by successive oxidation-reduction cycles, depositing a thin film using vacuum evaporation methods, nanosphere lithography with the assistance of micro-nano-fabrication techniques, etc. No matter which method is used, the fabrication process is difficult to control, reproduce, or keep clean, which leads to the low activity of SERS. Also, the enhanced efficiency is often quite different for different metals. Silver is thought to be the best one, but it is expensive and easily oxidized, which will decrease the enhanced efficiency. Besides, metals usually have a bad biological compatibility. Therefore, it is necessary to develop new substrates for Raman enhancement. A material that meets the requirements of being inexpensive and easy to obtain, effective and can be used directly, chemically inert, and biocompatible should be exploited.

Graphene is a very promising material for the use as a SERS substrate. Graphene itself was recently reported by Ling X et al, to induce a clear Raman enhancement effect on adsorbed molecules. (Ling, Xie et al. 2010) From the data presented by these authors, much stronger Raman signals of the molecules on graphene compared with those on the SiO_2/Si substrate were obtained, and the appearance of the Raman signals for molecules on graphene when soaking in solutions with very low concentrations clearly suggests that a Raman enhancement effect exists on the surface of graphene. As a result of the Raman enhancement on the surface of graphene, it is possible to obtain the Raman signals from very few molecules. This enhancement was attributed to the charge transfer between graphene and the molecules, which result in a chemical enhancement.

More recently, Yu X. et al (Yu, Cai et al. 2011) showed that mildly reduced GO (MR-GO) nanosheets can significantly increase the chemical enhancement of the main peaks by up to

1 order of magnitude for adsorbed Rhodamine B (tested molecule), in comparison to mechanical exfoliated graphene. The observed enhancement factors can be as large as $\sim 10^3$ and show clear dependence on the reduction time of GO, indicating that the chemical enhancement can be steadily controlled by specific chemical groups. It was shown that the highly electronegative oxygen species, which can introduce a strong local electric field on the adsorbed molecules, are responsible for the large enhancement. In contrast, the local defects generated by the chemical reduction show no positive correlation with the enhancement. Most importantly, the dramatically enhanced Raman spectra of RhB molecules on MR-GO nanosheets reproduce all important spectral fingerprints of the molecule with a negligible frequency shift. Such a unique noninvasive feature, along with the other intrinsic advantages, such as low cost, light weight, easy availability, and flexibility, makes the MR-GO nanosheets very attractive for a variety of practical applications.

Our research team has shown that graphene/gold nanocomposites prepared by in situ growth of gold nanoparticles in the presence of GO sheets are potential substrates for SERS in particular for single gold nanoparticle SERS studies (Goncalves, Marques et al. 2009). The combination of gold nanoparticles and graphene may confer a unique electron or energy transfer mechanism between both phases that allows the SERS observation. Lately other groups have also referred to the potential of using gold, palladium and silver nanoparticles associated with graphene as SERS substrates. (Wang, Ni et al. 2010) These studies highlight the importance of the development and study of possible applications of these nanocomposites as optical nanosensors.

We have tested the potential application of the gold/graphene nanocomposite as substrate for SERS. SERS was tested for Rhodamine 6G (R6G) using a laser source of 1064 nm. Figure 14 shows the Raman spectrum obtained for R6G adsorbed at the surface of the Au/graphene nanocomposite, together with the one obtained for R6G adsorbed at a single graphene surface, the Raman spectrum of solid R6G is also presented for comparison. The Raman spectrum of R6G adsorbed at a single graphene substrate (GO in Fig. 14) shows only a large broadband in the 1600-1300 cm^{-1} region, composed by the so-called G and D peaks of graphene. A good SERS signal was obtained for R6G adsorbed at gold/graphene nanocomposite (GAu in Fig. 14)

The SERS spectrum (GAu in Fig. 14) shows a selective enhancement of bands when compared to the Raman of solid R6G. The SERS signals observed at 1308, 1360, and 1504 cm^{-1} are assigned to the aromatic C-C stretching vibrations of R6G molecule, according to literature reports on the SERS of R6G. The SERS spectrum obtained for R6G in the graphene/gold nanocomposite (in the range 1300-1550 cm^{-1}) is similar to the R6G SERS spectra found in the literature using different types of gold substrates such as gold nanochains, gold-coated 3D ordered colloidal crystal films, Au-coated ZnO nanorods, or mechanically ruptured nanoporous gold (Goncalves, Marques et al. 2009).

At present, the evaluation of the detection limits is being conducted.

5. Outlook and challenges

Within a short time of being available in bulk quantities, graphene oxide have become highly versatile, inexpensive building blocks for the development of several advanced materials with applications having as the limit only the imagination.
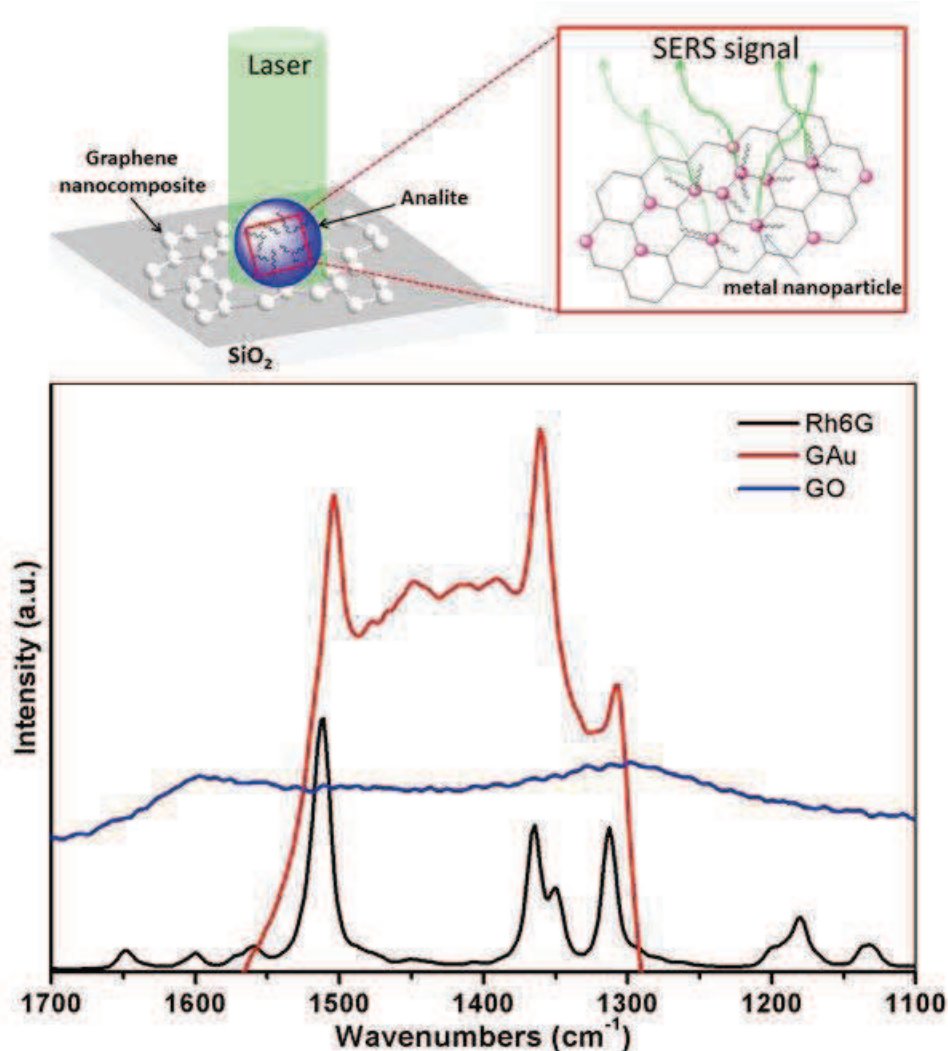
Fig. 14. SERS spectrum of Rh6G adsorbed at the surface of Au/graphene nanocomposite (GAu) and Raman spectra of R6G adsorbed at a single graphene sheet (GO) and of solid Rh6G (Rh6G). The inset shows a schematic representation of the SERS phenomena. Reprinted (adapted) with permission from (Goncalves, Marques et al. 2009) Copyright 2011 American Chemical Society.

Current results have indicated that GO is an interesting platform to build different nanocomposites with very promising properties for different areas of application.
The above mentioned outstanding properties of GO inspired us to explore the potential of multi-functional GO based materials. The future development of GO based nanocomposites that may function as SERS substrates of high activity and investigation of the SERS active nanocomposites as probes for biodetection is one of our goals. It is our aim to increase the knowledge that concerns the chemistry required for graphene/gold and silver nanoparticles applied to the preparation of SERS active substrates. It is predictable to modulate the surface of the nanocomposites in order to make them specific to a given molecule and, in this way, contribute to the development of manageable SERS sensors for the selective detection of biomolecules in targeted research.
We have shown the importance of the previous surface modification of graphene with PMMA chains in order to improve its dispersion in the polymer matrix. The organic

functionalization of GO is special relevant for its interaction with polymers. The suitable modification of the nano-filler by the careful control of the atomic surface chemistry can generate a perfect integration of all components on polymeric matrixes. This allows the combination between the reinforcements and the polymeric matrices to develop multifunctional materials with increased electrical, thermal, mechanical properties or reduction of the penetration of gases. However some challenges remain in order to scale up the synthesis of these modified fillers in order to find real application of the resulting materials. One interesting area of research that we are developing uses graphene fillers as mechanical reinforcement of PMMA based bone cements since GO is also biocompatible.

To achieve these goals it is of fundamental importance to control the synthesis of GO sheets and develop adequate methods to modify their surface in order to tune its properties for the desired applications.

6. Acknowledgments

7. References

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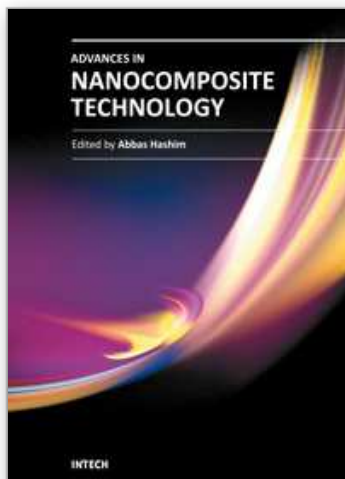
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Advances in Nanocomposite Technology

Edited by Dr. Abbass Hashim

The book â€œAdvances in Nanocomposite Technologyâ€ contains 16 chapters divided in three sections. Section one, â€œElectronic Applicationsâ€, deals with the preparation and characterization of nanocomposite materials for electronic applications and studies. In section two, â€œMaterial Nanocompositesâ€, the advanced research of polymer nanocomposite material and polymer-clay, ceramic, silicate glass-based nanocomposite and the functionality of graphene nanocomposites is presented. The â€œHuman and Bioapplicationsâ€ section is describing how nanostructures are synthesized and draw attention on wide variety of nanostructures available for biological research and treatment applications. We believe that this book offers broad examples of existing developments in nanocomposite technology research and an excellent introduction to nanoelectronics, nanomaterial applications and bionanocomposites.

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