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# Promising alternative routes for graphene production and functionalization

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A decade after scientists from Manchester University isolated a single graphene sheet the development of a method for mass-scale production of graphene with similar quality to that obtained, and the implementation of a modular chemical route to incorporate graphene into multicomponent/multifunctional materials are still fundamental challenges. The methods for graphene production and the synthetic procedures for its modification are limited to a handful of established methodologies, each with important limitations. In this manuscript a non-conventional electrochemical method for preparation of high-quality graphene, and a recently reported general chemical approach for graphene functionalization through thiol-ene click reactions are highlighted.

## Introduction

Although graphene as a material that can be manipulated is almost 10 years old,<sup>1</sup> contrary to the initial optimistic predictions, graphene-based technologies are still to make direct impact in aspects of our daily life. In other words, despite the large interest stimulated by this 2D carbon monolayer, and subsequent predictions for an important market position in a short period of time, we can observe that the evolution of graphene from the laboratory to real applications follows similar timescales those of other breakthrough materials.<sup>2</sup> The main reason is the marked worsening of the properties that occurs when the material is scaled-up, when isolated graphene monolayers are transferred to any substrate, or when it is modified to improve its interaction with other materials, for instance in the case of polymer nanocomposites. Thus,

despite its potentiality, for example, as a candidate for strong, lightweight nanocomposites for transportation (decreasing fuel consumption and emission of gasses) or energy conversion (wind turbine blades), electrodes in super-capacitors or batteries for energy storage, the transition from exceptional material to market value requires mass-production whilst essentially preserving the outstanding properties of mechanically exfoliated graphene. This is the principal challenge that needs to be addressed. The development of methods to prepare large quantities of high-quality graphene is still somewhat utopic, and it is clear that researchers must choose the preparation method and source of graphene as a function of the application in which the material will be used. Thus, a series of basic questions need to be considered: Are we employing adequate methods for graphene preparation? Should we explore new, less common methods? Indeed it is possible that the ideal method has not yet been discovered. Thus, the first part of this Highlight will enumerate the principal methods of preparation of graphene and will emphasize the role of electrochemical tools, often ignored, for the preparation of reasonable amounts of high quality- graphene.

With respect to the compatibilization of graphene with materials very different in nature, like polymers, metals, semiconducting or magnetic nanoparticles, biomolecules or biological agents, etc., the key lies in the chemistry of graphene. However, despite significant recent advances on the functionalization of graphene, much effort is necessary in order to combine it with these materials to prepare advanced materials or devices. For this purpose, the main tools for researchers are chemical strategies mostly inherited from the wealth of work and developments based on “older” carbon nanoforms such as fullerenes and carbon nanotubes (CNTs) that have paved the way for the modification of graphene, despite its lower reactivity.<sup>3</sup> Recently, several authors have reviewed the chemical routes to modify graphene,<sup>4-11</sup> and generally it can be found that the methods employing diazotisation of graphene and

esterification of graphite oxide (GO) encompass the major volume of research. In the second part of this Highlight the chemical routes employed thus far will be briefly outlined, with strong emphasis on a recently reported modular chemical strategy based on the attack on the graphene lattice using thiol radicals, known as the thiol-ene click reaction.

### **Beyond typical methods for the production of graphene.**

The first, and most famous method to obtain graphene consisted in peeling off of graphene sheets from highly ordered pyrolytic graphite (HOPG) specimens using sticky tape,<sup>1</sup> and was denominated mechanical exfoliation. Methods such as this and epitaxial growth of graphene films generally produce high quality graphene and have been very useful for the investigation of graphene properties, but are clearly unsuitable for large-scale production. One method that has unquestionably evolved over the last five years in terms of quality and quantity is the chemical vapour deposition (CVD) on metallic surfaces.<sup>12, 13,14</sup> However, CVD is still a slow process, it doesn't produce as much graphene as required and, depending on the application, it requires further steps such as metal etching and transfer to other substrates.<sup>15,16,17</sup> Top-down methods based on graphite oxidation/reduction of graphite provides a route that allows higher amounts of graphene, or more appropriately reduced graphene oxide (rGO), to be obtained. However this approach involves the preparation of highly defective GO that, after reduction, renders a relatively low quality material. Despite chemical treatment of graphite, the solution-phase physical exfoliation from graphite in organic solvents having a determined surface tension permits the preparation of low amounts of single layer graphene.<sup>18</sup> However, to increase the quantity, long ultrasonic treatment is necessary that is detrimental to the quality of the graphene obtained.<sup>19</sup>

An interesting comparison on the scope of these general methods for graphene production can be found in a recent review by Novoselov et al.<sup>2</sup> However, when revising the different approaches for graphene preparation,<sup>20,21</sup> less common methods like microwave irradiation<sup>22,23,24,25,26,27,28</sup>, including the magnesiothermic reaction<sup>29</sup> and electrochemical exfoliation of graphite<sup>30,31,32,33, 34</sup> are strategies that are usually not considered.

Microwave irradiation offers an interesting alternative to produce graphene, but normally it is used to reduce the highly defective GO.<sup>22, 23,24,25,26,27,29</sup> However, the combination of microwave plasma with CVD can be useful for the preparation of centimetre-scale high quality graphene films at much lower temperatures than those employed in CVD.<sup>35,36-38,39,40</sup> In addition, this technique has been used to prepare vertically standing graphene films, which are very promising as supercapacitors, biosensors and high-efficiency field emitters.<sup>36</sup> Nevertheless, this method displays the same principal limitation of typical CVD; the need to transfer the graphene to substrates of technological interest.

Regarding the electrochemical strategy, the polarization of graphite electrodes by applying positive (or negative) potentials leads to electrochemical intercalation of anions (or cations) between the graphene laminates that increases the interlaminar distance, generating what is known as graphite intercalation compounds (GICs). These GICs can serve to address the two main issues of graphene, i.e. preparation of high quality laminates and chemical functionalization. In the first case the induced increase in the interlaminar distance leads to a reduction in interlayer interactions facilitating exfoliation under more gentle conditions. With respect to graphene modification the greater interlaminar distance allows the easy intercalation of specific chemicals that can be designed to react with the graphene laminates. In fact, the intercalation of metallic potassium first reported by Kaner and col.<sup>41</sup> for the

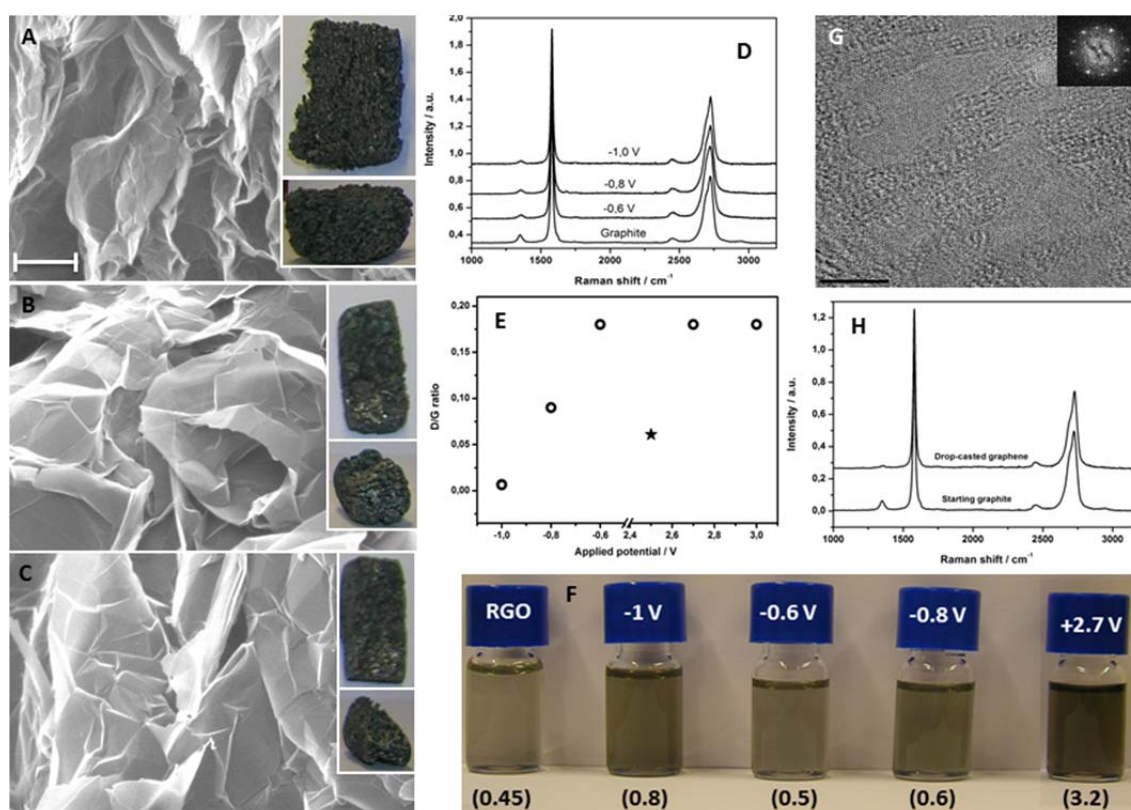
preparation of graphene nanoscrolls has been subsequently used by others for graphene functionalization.<sup>8,42</sup>

The use of electrochemistry for graphene preparation represents an interesting alternative to other procedures as it does not need sophisticated equipment (simply a laboratory potentiostat), it proceeds at room temperature and ambient pressure for short time periods, “green” electrolytes can be employed (ionic liquids or aqueous solutions), and both the quality of the graphene and the surface groups introduced can be controlled by tuning the applied potential and reaction time. Despite the importance of GICs over the last decades,<sup>43,44,45</sup> the interest in their use as precursors for graphene dates from 2008. Initially, graphite electrodes were polarized to very positive potentials that caused delamination and the subsequent formation of solid deposits on the bottom of the electrochemical cell.<sup>31, 33,46,47,48,49</sup> However, whilst this methodology allows large-scale production, the quality of this material is poor, showing a very high density of oxygen-containing groups. Decreasing the anodic potential leads to materials with slightly better structure but also decreases the amount of material obtained,<sup>50,51</sup> establishing a quality/quantity trade-off.

The use of cathodic reduction potentials has a fundamental advantage, since the conditions to intercalate cations are non-oxidising and thus the  $sp^2$  network can be preserved. Despite the fact that, in some cases, further steps after GIC preparation are needed to achieve effective exfoliation, the overall time for these procedures is relatively short. In our laboratory we succeeded in the preparation of few-layer graphene dispersions by reductive electrochemical intercalation of graphite in aqueous perchloric acid, followed by short microwave-assisted thermal expansion and gentle sonication.<sup>52</sup> During electrochemical intercalation hydrogen evolution plays an important function in the expansion mechanism since the large amount of molecular hydrogen produced in a short time induces mechanical stress in the interface of the

carbon/electrolyte solution helping to overcome the van der Waals forces between graphene layers. Hydrogen evolution is more pronounced as the cathodic potential becomes larger leading to more effective intercalation of hydronium (Figure 1). An electrode polarization equal to or less than 0.8 V is insufficient for effective cation intercalation (hydrogen evolution) and the final material shows a structure that is quite unlike the typical worm-like morphology generally observed for expanded graphite (Figure 1A-C). In addition, exceeding a certain potential threshold, in this case ca. -1.7 V leads to exfoliation of graphite particles that are deposited on the bottom of the cell.

Normally, higher polarization potentials assure higher concentrations of dispersed graphene. However, in this case the application of these potentials for long periods of time was avoided since it leads to delamination of the electrode with a drastic reduction in the dimensions of the flakes. Regarding quality, the  $I_D/I_G$  Raman ratio is a useful marker of defects in the carbon network.<sup>53</sup> The Raman spectra in Figure 1D compare the initial graphite and a graphene prepared using several reductive perturbation potentials, and are quite similar. The first-order G mode at  $1581\text{ cm}^{-1}$  is clear in both samples, whereas the D-mode (around  $1350\text{ cm}^{-1}$ ) observed for the starting electrode is almost imperceptible in the case of expanded graphite (EG). Therefore the quality of the expanded graphite obtained under different reductive polarizations can be regarded as similar to the starting graphite electrode. In fact, the quality of the sample treated at -1 V appears to be of higher quality than the graphite electrode, and this is represented in Figure 1E, where oxidative potentials for shorter times (15 s) are also shown for comparison. Therefore, this pre-treatment does not have a negative influence on material integrity, and it seems that the procedure leads to some purification/selection of the best quality graphene laminates.



**Figure 1.** SEM images of EG obtained after polarizing the graphite electrode at -1 (A), -0.8 (B) and -0.6 V (C) for five minutes and microwave assisted expansion. Scale bar in A applies to all and corresponds to 2 μm. The insets show top and side views of the graphite electrodes after treatments. Raman spectra of expanded graphite prepared under different applied reductive potentials (D) and variation of the  $I_D/I_G$  Raman ratio as a function of the applied potential (E). The asterisk in (E) corresponds to the  $I_D/I_G$  ratio of the untreated graphite electrode. (F) Photo of graphene dispersions in NMP after intercalation at different potentials, microwave expansion and ultrasonic exfoliation. The numbers in brackets below the vials correspond to the concentration of dispersed graphene in mg mL<sup>-1</sup>. (G) HRTEM micrographs of final graphene deposited from the NMP solutions. The inset corresponds to FFT electron diffraction pattern simulation, where the superposition of two hexagonal structures rotated 30° is observed. (H) Comparison of the Raman spectra of starting graphite electrode and final drop-casted graphene obtained after intercalation at -1.0 V. Some parts of this figure are adapted from Carbon, 49, 2809, Copyright 2011, with permission from Elsevier.

The expanded graphite sponges in Figure 1 are easily dispersed in NMP by ultrasonication for less than five minutes. The resulting solutions contain different graphene concentrations and qualities depending on the applied potential (Figure 1F). In addition, the dispersions are

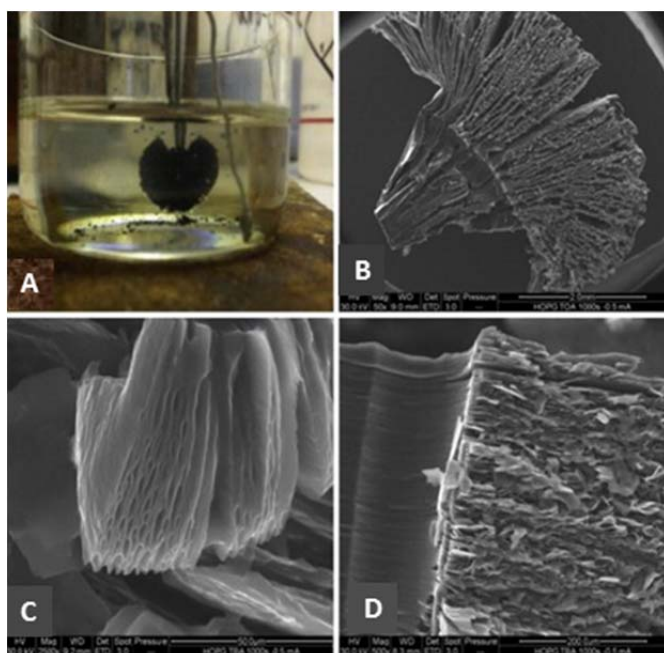


composed of three, four, few and multilayer graphene. Figure 1H shows a HRTEM image of a bilayer graphene, where the fast Fourier transform (FFT) pattern simulation (inset) indicates the superposition of two hexagonal structures rotated by 30°. Regarding the quality, the material integrity remains unaltered during the entire process of intercalation/expansion/exfoliation (Figure 1H).

In a similar manner, the reductive procedure was extended to other electrolytes in organic media, where higher negative potentials can be applied. Wang et al. expanded a HOPG electrode by applying higher reductive potentials ( $-15 \pm 5$  V) in a solution of  $\text{LiClO}_4$  in propylene carbonate (PC),<sup>54</sup> taking advantage of an unwanted feature in lithium ion batteries, i.e. the destruction of the graphite electrode by intercalation of  $\text{Li}^+/\text{PC}$ . After sonication they obtained FLG dispersions in dichlorobenzene and diphenyl ether. The authors demonstrated that the capacitive current of the expanded graphite electrode increases with the charging voltage applied during the electrochemical expansion as a consequence of the separation between laminates increasing the specific surface. With this approach they obtained expanded graphite on the scale of several grammes (15 g) leading to dispersions composed of more than 70 % of few layer graphene (<5 layers) of good quality.

Very recently, Cooper et al. intercalated different tetraalkylammonium cations into HOPG and graphite rods to produce few-layer graphene.<sup>34</sup> They applied potentials intermediate to those used in the previous two examples ( $-5$  V for HOPG and 2.4-2.6 V for graphite rod) in organic solutions and observed differences between both systems. In the case of HOPG, the electrochemical treatment led to the expansion of the electrode (Figure 2), but exfoliation was also achieved after long ultrasonic treatments. However, flakes of high lateral dimensions were obtained. In the case of graphite rods, no post-treatment is required as the exfoliation occurred during the electrochemical steps leading to deposits of material in the bottom of the cell. But in

this case, smaller flakes with 2-5 layers were produced. The differences are attributed to the varying anisotropy of the materials. While HOPG is highly anisotropic with crystallographic orientation very uniform, in the commercial graphite rods the flakes are randomly oriented. One interesting point that the authors did not address in this manuscript is the quality of the graphene obtained from both systems.



**Figure 2.** Characterization of HOPG electrode after applying a reductive potential (-5 V) in tetrabutylammonium perchlorate: (A) Photo showing the HOPG expansion after by 10,000 s. SEM images showing the HOPG expansion (B), micron sized pores in HOPG after TBA intercalation (C), and selective exfoliation of only the submerged part of the HOPG electrode (D), after 6000 s of tetrabutylammonium intercalation. This figure is reproduced from Carbon, 66, 340, Copyright 2014, with permission from Elsevier.

### **Towards a comprehensive strategy for the preparation of graphene-based materials.**

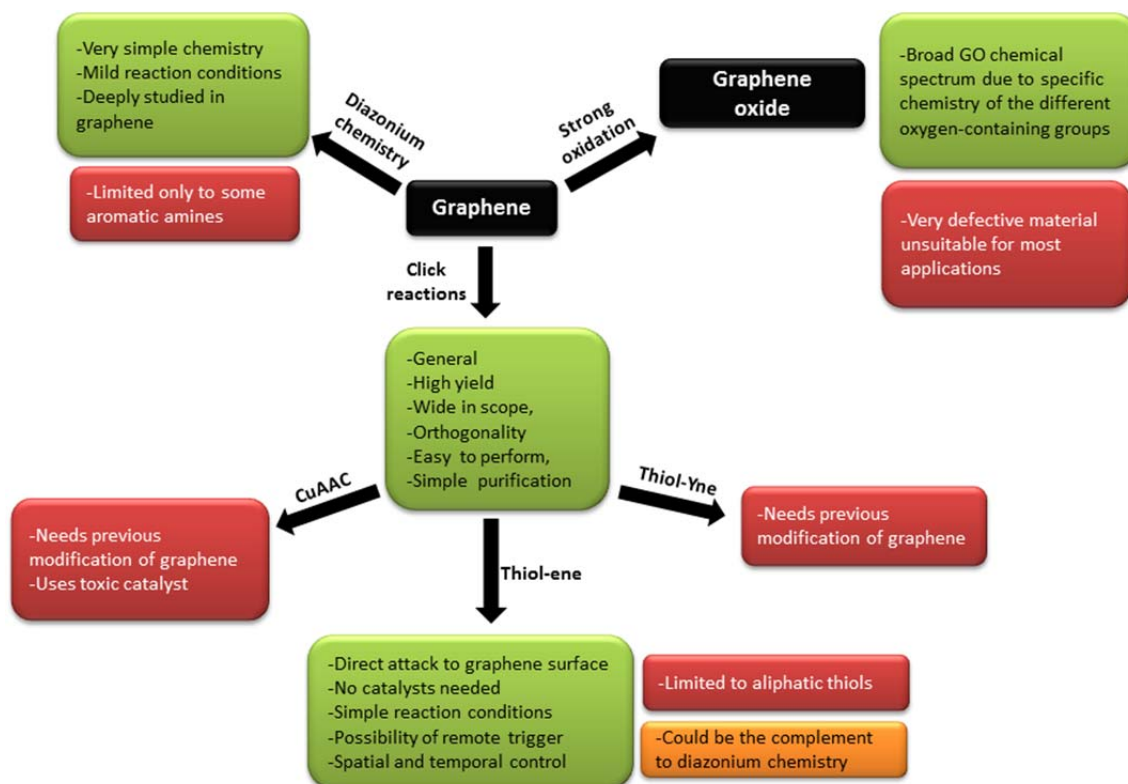
The functionalization of graphene is no doubt the key to achieve stable graphene dispersions leading to better processability for new materials, and to assist the combination/incorporation with other classes of compound to produce high performance multifunctional materials.<sup>55</sup>

Effective covalent functionalization of graphene is not free of problems due to the low intrinsic reactivity of graphene, which is lower than that of other carbon nanoforms such as fullerene and carbon nanotubes, principally because of the absence of tension in the basal planes.<sup>3</sup> However, the extensive previous work developed with its structurally similar older cousins has paved the way for the chemical modification of graphene, and many research teams have succeeded in graphene functionalization.

Here, I focus uniquely on the different types of chemical reactions attempted with graphene. Microwave-assisted functionalization of graphene that can be directly associated to atypical or non-conventional synthetic methods are beyond the aim of this manuscript and the reader is referred to a very recent review by Vazquez et al.<sup>28</sup>

Although different cycloaddition reactions have recently been reported,<sup>6, 7, 56-59</sup> the most employed approaches for graphene modification involve the chemistry of graphene oxide (GO),<sup>5, 11, 60-62</sup> especially esterification/amidation reactions at the carboxylic groups, and the coupling of diazonium salts<sup>8, 9, 63</sup> to the  $sp^2$  network (Figure 3). The former requires the previous formation of GO, achieved under extreme oxidizing conditions that generates a high density of structural defects in the  $sp^2$  network. At present, the focus is on preserving the quality of the starting material where diazonium chemistry approaches are the most popular. In this reaction, graphene reduces an azo compound provoking the elimination of a molecule of nitrogen with the formation of a highly reactive aryl radical that instantly attacks the graphene lattice forming a covalent bond.<sup>63</sup> However, the scope for diazonium chemistry is limited to a handful of organic aromatic compounds since aliphatic diazonium salts are quite unstable and the development of a general strategy for the preparation of graphene based materials in an almost combinatorial manner is still very challenging.

Click chemistry comprises a series of chemical reactions that are modular, of high yield, wide in scope, orthogonal, simple to perform, that employ easily removable or benign solvents and either avoid the formation of by-products or generate easily removed species, amongst other characteristics (Figure 3). Developed by Sharpless and co-workers<sup>64</sup> and originally associated to the synthesis of biomolecules, the concept of click chemistry has been extended to polymers and, more recently, to carbon nanostructures. Although when applied to these materials not all of the stringent aforementioned criteria are met, the use of this simple synthetic protocol with graphene is expected to significantly increase the number of graphene-based materials that can be prepared, some of which are otherwise inaccessible.



**Figure 3.** Scheme showing the principal features of the most employed chemical procedures to functionalise graphene.

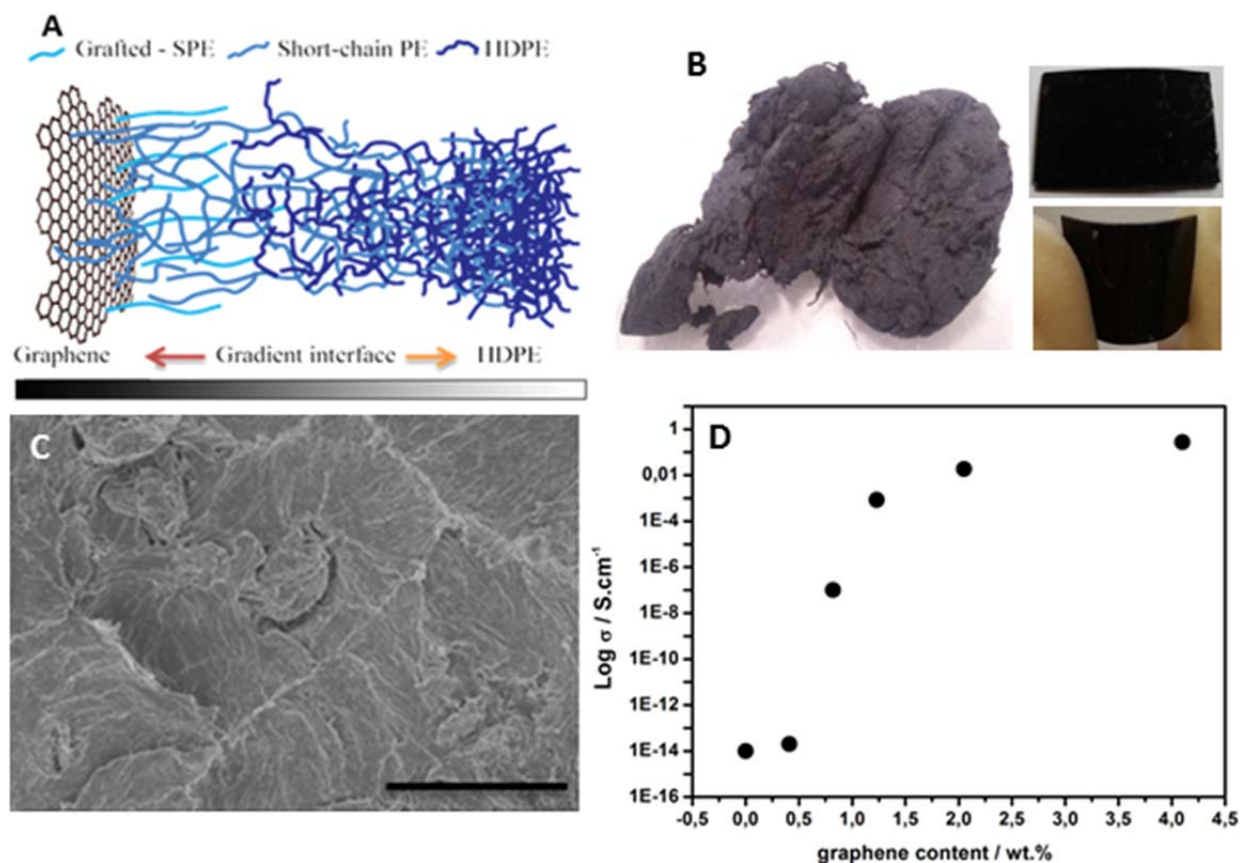
Until recently, the only click reaction used on graphene was Cu(I) catalyzed alkyne-azide coupling.<sup>65,66,67, 68,69</sup> The triazole formed in this reaction is essentially chemically inert to

reaction conditions, e.g. oxidation, reduction, and hydrolysis, and has an intermediate polarity.<sup>70</sup> First reported in 2010, this reaction has mainly been employed to combine graphene with different polymers.<sup>3</sup> The application of this reaction to graphene requires furnishing graphene with one of the two functional groups involved (alkyne or azide), thus requiring additional synthetic steps. Moreover, the main drawback of this reaction is the use of a toxic metal catalyst. Metal-free click reactions have been addressed; of these thiol-ene click chemistry appears to be the most promising due to its robustness and versatility.<sup>71, 72</sup>

The radical mediated thiol-ene reaction proceeds under simple and mild reaction conditions and is based on the decomposition of a radical precursor by the action of heat (thermally) or light (photochemically), creating thiol radicals that attack double or triple bonds. These features enable the reaction to be remotely triggered as well as spatial and temporally controlled, which is not possible with other click chemistry approaches.<sup>71, 72</sup> The combination of graphene with these features of thiol-ene click reactions is expected to revolutionize the field of graphene-based materials science, greatly increasing the number of materials that can be prepared, thus having direct impact potential in areas such as nano or biotechnology.

Research on the use of thiol-ene and thiol-yne reactions in graphene is in its early stages, and only few examples are available. In our group we have succeeded in the modification of graphene with brushes of short-chain polyethylene tailored towards the preparation of nanocomposites of graphene and high density polyethylene (HDPE).<sup>73, 74</sup> We have studied the coupling of a thiol-terminated polyethylene to pristine and alkyne-modified graphene. While the latter permits the incorporation of two thiol groups per triple bond, leading to higher degree of functionalization, the former is conducted directly on the graphene lattice where steric hindrance is more important. However, this is of significance since no previous modification of graphene is required and the lower the degree of modification, the lower the

extent of disruption of the  $sp^2$  structure, whilst moderately improving solubility. For instance, the incorporation of polymer brushes to graphene by the thiol-ene approach produces a graphene derivative with slight solubility in *o*-dichlorobenzene and conductivity in the same order of magnitude as the starting graphene.



**Figure 4.** (A) Scheme describing the gradient interface effect of HDPE/Graphene nanocomposites. (B) Images of the raw nanocomposite (left) and as films prepared from it by hot-pressing (right). (C) SEM images of the nanocomposite with 0.75 wt. % of graphene. The scale bar corresponds to 20 μm. (D) Variation in the electrical conductivity of the nanocomposites as a function of graphene content. Some parts of this figure are reproduced from Ref. <sup>73</sup> with permission from The Royal Society of Chemistry.

Graphene modified with short-chain polyethylene brushes improved the incorporation of graphene into HDPE matrix due to an enhancement of the interfacial interaction between graphene and the polymer. Thus, using a two-step mixing strategy based on what we define as a “gradient interface” (Figure 4A), we succeeded in the preparation of graphene-based HDPE

nanocomposites with improved mechanical properties as well as thermal and electrical conductivity. The rubbery grey material (Fig. 4B, left) obtained after the two-step mixing can be transformed into flexible films by hot-pressing (Figure 4B, right) and was cryo-fractured to analyse the dispersion of the filler into the matrix. Figure 4C shows a SEM image of a nanocomposite with 0.75 wt. % of graphene, where the filler laminates appear to be perfectly dispersed in the polymer matrix throughout the sampled area. This good filler/polymer compatibilization led to nanocomposites with low percolation threshold and reasonably good conductivity values (Figure 4D), which are the main challenges when nanocomposites of insulating polymers with highly conductive fillers are required.

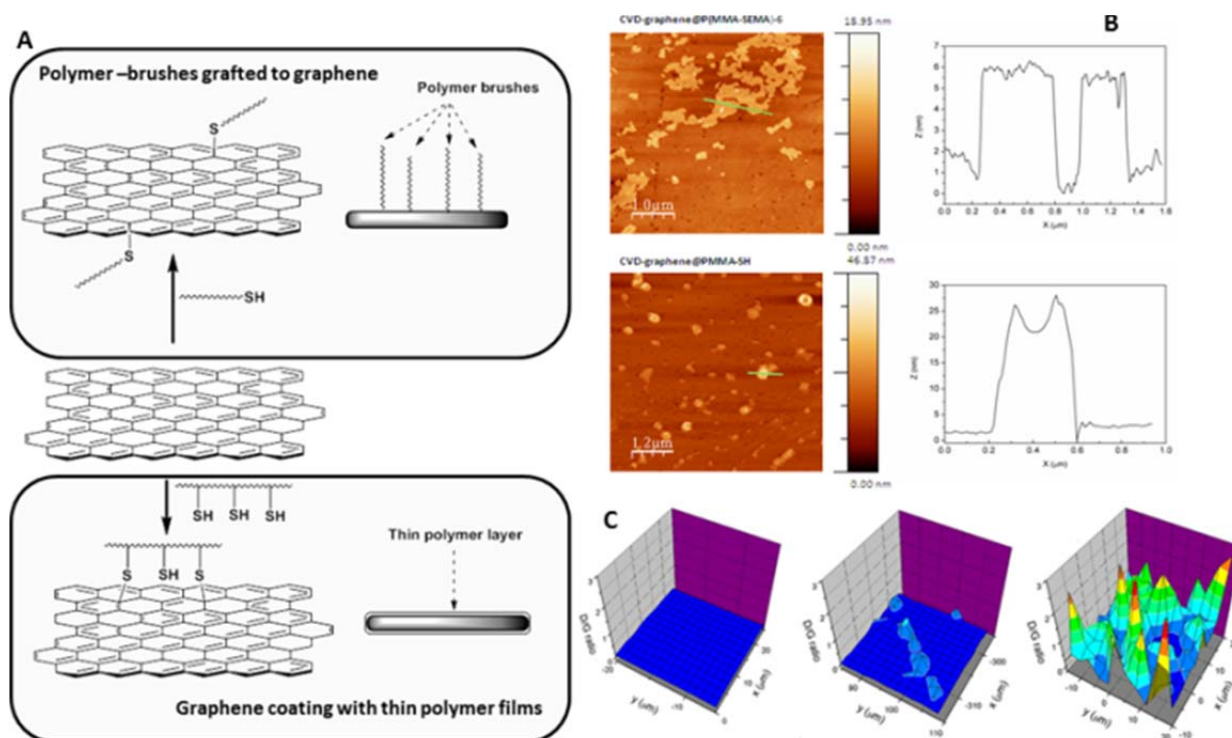
Despite the brush-like method where a unique reactive group is located at the end of the polymer chains, controlling the concentration of these clickable groups and their distribution along the polymer chains represents an interesting alternative for property modulation, since the presence of multiple clickable groups widely distributed along the polymer chains could allow the formation of multiple graphene-polymer bonds. Importantly the distribution and concentration of these groups can be controlled easily by copolymerization through managing parameters such as the nature of the monomers, the feed composition or type of polymerization (ATRP, RAFT, etc.) employed.

The case of poly(methyl methacrylate)(PMMA) is especially interesting, for example, with regard to the importance of antistatic paints in transportation or aerospace industries. We have recently reported the modification of graphene with both brushes and thin films of PMMA (Figure 5A).<sup>75</sup> The reactions were conducted on both CVD-grown and powdered samples in order to monitor the type modification of graphene (single or multiple layer) and to evaluate the bulk properties of the nanocomposites, respectively. AFM images of the CVD-graphene modified with a PMMA and a PMMA copolymer derivative<sup>76</sup> with one (polymer brushes) or



multiple polymer/graphene bonds (denominated a multidentate polymer) clearly show the differences between both methods. In the case of brush-like modification, spots of different diameter and irregular height ranging from ca. 20 to 50 nm are formed because of the collapse of the polymer chains during drying (Figure 5B, bottom).<sup>77</sup> In the case of multidentate approach, a homogeneous layer of around 5 nm height distributed over several microns of material was observed, confirming the formation of a thin polymer coating onto the graphene surface (Figure 5B, top). Figure 5C shows mapping data of the  $I_D/I_G$  ratio in the form of isometric projections constructed from spectra recorded from pristine CVD graphene and graphene modified by both approaches. The starting pristine graphene has very few defects with values of D/G between 0.06 - 0.17 (Fig. 5C, left). In the case of the brush-like modification the sample looks more defective, and D/G values raised to ca. 0.9 (Fig. 5C, middle). However, when a multidentate polymer is used dramatic changes occurred due to much higher extent of modification with values of D/G > 2.5 in several regions, conclusively confirming the existence of multiple connection points between the polymer chains and the graphene surface.





**Figure 5.** (A) Schematic showing the modification of graphene with polymer brushes and thin films. (B) Tapping mode AFM images of CVD-graphene functionalised with brushes (bottom) or thin polymer layers (top) with their corresponding height profiles along the indicated lines. (C) Raman maps (isometric projections) of the D/G ratio for CVD-graphene (left) and brush-like (middle) and multidentate modification (right). Some parts of this figure are reproduced from Ref. <sup>75</sup> with permission from The Royal Society of Chemistry.

The same reaction conducted on powdered graphene produced materials with good solubility in organic solvents. The brush-like modified graphene displayed higher solubility because of the freedom of the polymeric chains to interact with the solvent, while in the case of the multidentate polymer; the polymer-graphene interaction is more intimate. Nevertheless, only when the multidentate modified graphene is used as filler in PMMA nanocomposites measurable conductivity values were obtained, suggesting the importance of the thin coating in compatibilizing graphene with the polymer.

## Summary and Outlook.

With respect to the preparation of graphene, the features inherent to electrochemical methods provide an economic alternative, at a scale intermediate between academic and industrial requirements. Some effort is still required on the scale-up issues of this technology. It is expected that the future direction will focus on optimizing the electrochemical parameters through varying the electrode source, the nature of the electrolyte (where ionic liquids or ternary eutectic melts may play an important role), and the potential and time applied, etc. Hopefully the strategies outlined here can serve to stimulate researchers to consider electrochemical methods as a serious and flexible alternative to already established graphene production methods.

Regarding the functionalization of graphene, the thiol-ene click approach provides a powerful chemical tool for future combinatorial preparation of graphene-based materials. The reaction proceeds directly on the graphene surface without any previous modification, and is not limited to aromatic compounds as is the case for diazonium coupling. Although the reaction needs thiol moieties, these may be incorporated into the target molecules to be connected to graphene through facile organic reactions. In the near future efforts will focus on extending the scope of this reaction to molecules other than those presented herein, as well as to evaluate the possibility of connecting graphene with other materials, i.e. metallic nanoparticles, biological agents, etc. leading to the preparation “a la carte” of multifunctional materials. In this sense the scope of using such click approaches in graphene-based materials is only limited by ones imagination.

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