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Organic Functionalization of Graphene in Dispersions

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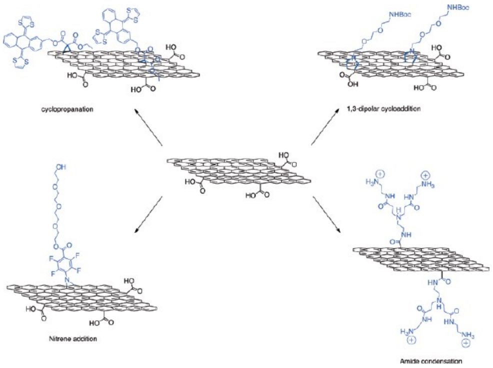

Graphene is considered a promising material for a range of new applications from flexible electronics to functional nanodevices, such as biosensors or intelligent coatings. Therefore researchers need to develop protocols for the mass production of graphene. One possible method is the exfoliation of graphite to form stable dispersions in organic solvents or even water. In addition, researchers need to find effective ways to control defects and locally induced chemical changes. We expect that traditional organic chemistry can provide solutions to many of these challenges. In this Account, we describe our efforts toward the production of stable dispersions of graphene in a variety of solvents at relatively high concentrations and summarize representative examples of the organic reactions that we have carried out using these stable dispersions.

The sonication procedures used to solubilize graphene can often damage these materials. To mitigate these effects, we developed a new methodology that uses mechanochemical activation by ball-milling to exfoliate graphite through interactions with melamine (2,4,6-triamine-1,3,5-triazine) under solid conditions. Alternatively, the addition of reducing agents during sonication leads to larger graphene layers in DMF. Interestingly, the treatment with ferrocene aldehyde, used as a radical trap, induces the formation of multiwalled carbon nanotubes. The resulting graphene sheets, stabilized by the interactions with the solvent, are suitable materials for performing organic reactions.

Relatively few organic reactions have been performed in stable dispersions of graphene, but organic functionalization of these materials offers the opportunity to tune their properties. In addition, thermal treatments can remove the appended organic moieties, restoring the intrinsic properties of pristine graphene. We describe a few examples of organic functionalization reactions of graphene, including 1,3-dipolar cycloadditions, amide condensations, nitrene additions, and radical reactions. The design of novel protocols for further organic functionalization should increase our knowledge of the fundamental chemistry of graphene and spur the further development and application of these materials.

Introduction

Graphene is a layer of carbon atoms, just one atom thick, structured in a honeycomb lattice. Thanks to its 2D nature, graphene has a host of unique electronic properties not seen in thicker carbon films or other carbon nanostructures. For instance, graphene is characterized by conduction electrons that travel near to the speed of light and have zero mass, the so-called Dirac fermions.[1] Besides, graphene is the thinnest known material and the strongest ever measured, shows record thermal conductivity and stiffness, is impermeable to gases, and has the right proportion between brittleness and ductility.[2] Although the physics of graphene has been extensively explored and remains at the center of the attention, its chemistry and in particular its reactivity and covalent functionalization have persisted largely unexplored, probably because of the lack of

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samples suitable for traditional chemistry and for the intrinsic difficulty to characterize the resulting products. Graphene possesses a zero band gap and functionalization of graphene with organic and inorganic materials may offer an alternative approach to control its electrical properties. In addition, chemically manipulated graphene samples can be incorporated more easily into new functional materials.

So far, several methods have been established for graphene preparation, such as micromechanical cleavage,[3] chemical vapor deposition,[4] graphitization of silicon carbide,[5] anodic bonding,[6] unzipping of carbon nanotubes,[7] organic synthesis,[8] reduction of graphene oxide,[9] polymer-coated graphene,[10] liquid phase exfoliation of graphite,[11] electrochemical exfoliation of graphite,[12] graphite intercalation,[13,14] and ball-milling processing of graphite.[15] Until now, most protocols remain as demonstration techniques, mainly for basic research and for providing proof of concept devices. However, the recent progress in making stable dispersions[9−14] allows the production of graphene on a more preparative scale, opening the way to solution/dispersion chemistry. Therefore, it is expected that many problems in graphene processing could be, at least partially, solved, such as, scalability, dispersibility, stability, and the control of the electronic structure by introducing chemical changes locally. Then, the physical properties of graphene might be exploited in a more controlled manner or even modulated by engineering its structure at the atomic and molecular level. The chemical manipulation of graphene is expected to stimulate the development of several new applications in many different fields. These applications include composites,[16] supercapacitors,[17] batteries,[18] fuel cells,[19] inks,[20] flexible touch screen displays,[21] inteligent coatings,[22] sensors,[23] photonics and optoelectronic devices.[24]

In this Account, we describe our recent efforts toward (1) obtaining graphene stable suspensions suitable for chemical modification and (2) organic functionalization approaches performed in stable dispersions of graphene that modify its structural, electronic, and chemical properties. Even if functionalization methodologies used for fullerenes[25] and carbon nanotubes[26] have been applied to graphene, significant differences arise due to the single atomic layer configuration (a wide open double-side surface). We will not consider graphene oxide here, because the properties of this species seem to be quite different from those of a quasi-perfect layer of graphene.

Stable Dispersions of Graphene Layers

Chemistry can play an important role in future developments of graphene technology. To this scope, the major challenges include (i) large-mass-scale production, (ii) high concentration of graphene layers well-dispersed in solvents with different characteristics, (iii) stable dispersions over long periods of time, (iv) the effective control of defects in graphene, (v) production of stable graphene derivatives, and (vi) locally induced chemical changes. Until now, few methodologies have been developed to fulfill all these requirements. Graphene oxide[9] and polymer-stabilized graphene nanoribbon[10] dispersions can be produced in large scale and are stable over time, but unfortunately these materials are chemically different from pure graphene.[27]

One technique to obtain stable dispersions of pure graphene is the exfoliation of graphite through ultrasonication, known as liquid phase exfoliated graphene. Essentially, the technique consists of the sonication of graphite in organic solvents able to stabilize colloidal graphene.[28] After that, graphene is separated from larger graphitic particles by centrifugation. During the process, ultrasound waves break the basal structure and produce graphitic carbon fragments of variable sizes, which are later intercalated by solvent molecules producing its exfoliation.[29] The surface energy of the solvent should match the surface energy of graphite in order to minimize the enthalpic cost of mixing,[11] solvents therefore may have surface tensions between 40 and 50 mJ m^{-2}. Two organic solvents successfully used for the exfoliation of graphite are *N*-methyl-2-pyrrolidone (NMP) and *N*,*N*-dimethylformamide (DMF). Dispersions generated in these solvents initially reached graphene concentrations up to 0.01 mg/mL and 1 wt % monolayer.[11] Upon increase of the sonication time, the concentration increased up to 1.2 mg/mL with 4 wt % monolayer.[30] However, harsh ultrasonication treatments result in graphene layers with a higher number of defects and reduction of the layer size. These defects mostly consist of oxidized carbon atoms at the edges of the layer in the form of epoxide, carbonyl, or carboxylic groups.

Although NMP and DMF produce acceptable results in obtaining stable dispersions of graphene, they present the inconvenience that they are expensive and require special care during handling. In addition, they possess high boiling points that prevent evaporation making difficult any future processing, for example, deposition on surfaces. Dispersions of graphene have been later produced in mixtures of water−surfactant,[31] *ortho*-dichlorobenzene (ODCB),[32] perfluorinated aromatic molecules,[33] pyridine,[33] and benzylamine.[34]

The exfoliation of graphene sheets from a graphite anode in ionic liquids (ILs) represents another possibility.[12] The mechanism of exfoliation was attributed to a complex interplay of anodic oxidation of water and anionic intercalation from the IL. Different nanostructured carbon materials could be generated by controlling the water content and the type of counterion in the IL used as electrolyte. In addition to the graphene sheets, water-soluble fluorescent carbon nanoparticles and nanoribbons could be generated during the exfoliation.

Graphite intercalation compounds (GIC) offer a valuable approach to single-layer graphene sheets, based on the favorably expanded interlayer spacing. It was recently demonstrated that alkali metal GICs spontaneously exfoliate in NMP yielding air-sensitive solutions of negatively charged graphene sheets and ribbons.[13] The graphene sheets could be deposited from these solutions onto a variety of substrates. An alternative treatment can be performed by adding natural graphite to a solution of a sodium/potassium alloy in 1,2-dimethoxyethane (DME) as inert solvent.[14] In analogy to carbon nanotube chemistry,[35] reductive treatment of graphite with solvated electrons causes activation of the graphite associated with a subsequent exfoliation into graphene. This procedure only requires the addition of electrons to the graphene layers avoiding any kind of sonication. Homogeneous colloidal dispersions of graphene, which do not present irreversible lattice damage, are produced. This procedure guarantees a facile reaction of *in situ* generated graphene with electrophiles as a result of the excess negative charge present on the layers.[14]

Large quantities of inexpensive materials like graphite and melamine can be used for massive and fast production of few layer graphenes with low concentration of defects. The methodology uses mechanochemical activation by ball-milling to exfoliate graphite through interactions with melamine (2,4,6-triamine-1,3,5-triazine) in solid conditions (Figure 1).[15] The milling treatments can be modulated in order to achieve graphene flakes with desired sizes. Once graphite is exfoliated by the milling treatment, the resulting solid mixtures can be dispersed in water or DMF to produce relatively concentrated dispersions. The as-prepared dispersions are stable at room temperature for weeks and can be washed by filtration to remove melamine. Graphene samples can be redispersed in virtually any solvent, a possibility that opens the way to chemical functionalization.

Reducing the Damage on Graphene Layers During Sonication Treatments

As already mentioned, the long sonication periods needed to improve graphene concentrations, reduce the size of graphene layers, and increase the number of defects. This fact can be attributed to the formation of oxidizing radicals, such as peroxyl radicals, in air-sonicated solutions. Thus, in the attempt to reduce the damage caused by ultrasonication treatments, we sonicated graphite in DMF with the addition of reducing agents, such as ferrocene aldehyde or tiopronin, see Figure 2.[36,37]

Fc-CHO is a reducing agent that can inhibit reactions promoted by oxygen, peroxides, and radicals.[38] The addition of Fc-CHO during sonication of graphite in DMF considerably reduces the degree of oxidation of the exfoliated graphene as demonstrated by XPS and Raman spectroscopy analysis. This process results in larger graphene layers compared with those produced in pure DMF and yields concentrations as high as 0.03 mg/mL, Figure 3a.

In addition, we observed that Fc-CHO facilitates the formation of multiwalled carbon nanotubes (MWNT). The formation of MWNT occurs by sealing unstable pieces of graphene layers smaller than a specific size, Figure 3b. Thus, Fc-CHO first reduces the concentration of radical species, which cut graphene into small fragments, then localizes itself at the edges of graphene and templates the rolling up of a sheet to form a nanoscroll where it remains trapped; finally it accepts and donates unpaired electrons to the graphene edges and converts the less stable scroll into a MWNT. Hence, not only does the sonication of graphite upon the addition of Fc-CHO produce stable graphene dispersions that can be used for further functionalization, but also the results obtained in this study can be useful to understand how solvents disperse graphene and the processes that take place during ultrasonication.

Further, we demonstrated that the damage created in graphene sheets during exfoliation of graphite by ultrasonication in DMF is significantly reduced upon addition of *N*-2-mercaptopropionylglycine (tiopronin).[37] The degree of oxidation of the exfoliated graphene sheets is decreased as demonstrated by XPS and Raman spectroscopy analysis. Higher concentrations were calculated from the UV–vis absorption (at 660 nm), and larger graphene sheets were observed by TEM. HR-TEM confirms the low density of defects present in the resulting graphene layers. Our results confirm that ultrasonication in organic solvents generates free radicals, which can enable or

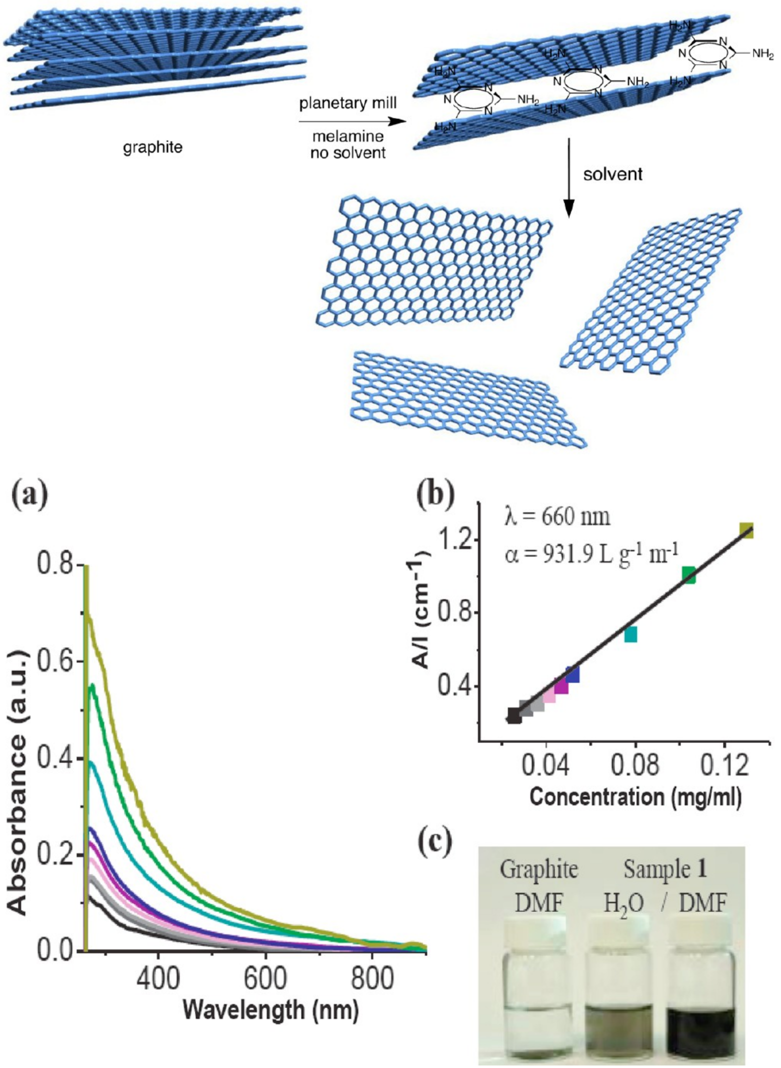


FIGURE 1. (top) Schematic representation for the exfoliation of graphite by ball-milling process. (bottom) (a) UV–vis spectra of graphene dispersed in DMF at increasing concentrations; (b) optical absorbance ($\lambda = 660$ nm) as a function of the concentration showing Lambert–Beer behavior; (c) dispersions of graphite and graphene in DMF and water.

be involved in secondary reactions. The addition of reducing agents/radical traps during sonication treatments significantly reduces the damage created on graphene layers.

Graphene Covalent Reactivity

In principle, graphene can be functionalized at the two surface faces and at the edges. The results indicate that functional moieties attack both graphene faces, altering the energetics, allowing chemical bonds that would be unstable if only one surface were exposed.[39,40] Even though graphene has been considered as an inert material toward chemical attack, some groups have observed a considerable reactivity of the graphene layer.[41−43] In some instances, this process might result in unpaired electrons, which would be created at sites adjacent to the point of covalent bonding, enhancing the reactivity there and leading to a chain reaction from the initial point of attack.[44] Under this perspective, the graphene edges are considered more reactive than the inner surface faces. It is also expected that zigzag edges will display higher reactivity compared with the armchair ones. However, it is technically challenging to control the edge structure, so, in practice, graphene contains a combination of the two basic types of edge configuration, which makes it difficult to control the functionalization process.[45] Defects are considered additional reactive sites, which usually facilitate graphene functionalization at both surface faces and edges. All the current methods for graphene production yield layers with defects, including structural imperfections and chemical impurities randomly distributed.[46] Thus,

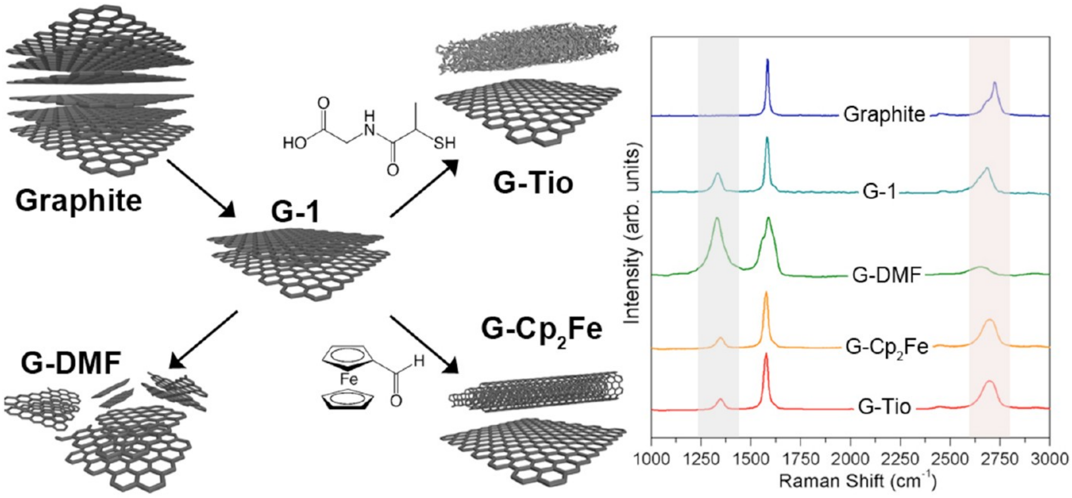


FIGURE 2. Schematic representation of the products obtained during ultrasonication of graphite in DMF with the addition of reducing agents, ferrocene aldehyde, or tiopronin. Comparison of the Raman spectra (collected with excitation at 633 nm) of graphite and of the graphene products of our sonication procedure. G-1 is the starting material (graphite sonicated for 30 min during cycles of 30−30 s off/on), G-DMF is a sample sonicated for 3 h without the addition of any reducing agent, G-Cp$_2$Fe is a sample sonicated for 3 h with the addition of ferrocene aldehyde, and G-Tio is a sample sonicated for 3 h with the addition of tiopronin. Spectra are scaled to have an identical height of the G peak at ~1580 cm^{-1}.

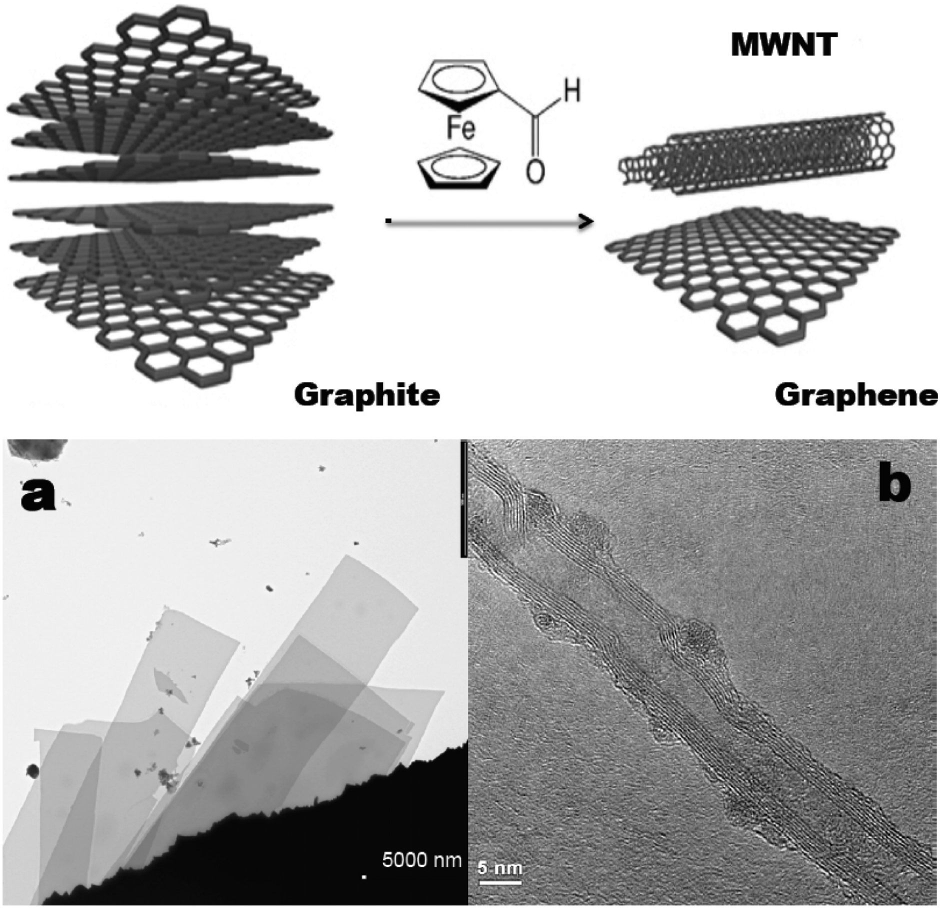
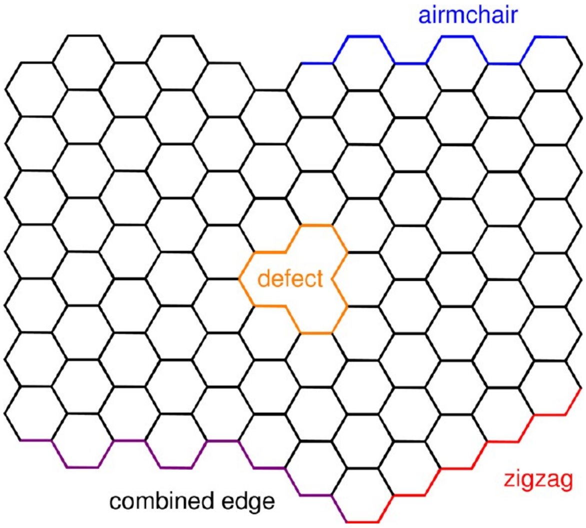


FIGURE 3. Sonication of graphite with the addition of ferrocene aldehyde produces higher concentration of large graphene sheets (a) and the formation of MWNTs (b).

SCHEME 1. Schematic Representation of Reactive Sites in Graphene Sheets: Surface Faces, Edges and Defects



chemical reactions are expected to occur at both faces and edges, Scheme 1.

Reactivity also depends on the fact that graphene is not flat but exhibits nanometer-scale corrugations.[47] The associated strain and curvature can markedly influence the local reactivity. Finally, several methods for the production of graphene lead to graphene layers with different size, shape, chemical composition, and environment. All of them have different requirements for chemical functionalization. Herein, we describe the covalent functionalization of graphene layers performed in stable dispersions.

Covalent Functionalization of Stable Dispersion of Graphene

There have been several examples of covalent attachment of reactive species to graphene flakes. These approaches include 1,3-dipolar cycloadditions, nitrene, and radical reactions. On the basis of the perfect structure of a graphene monolayer, one might postulate a very low reactivity of these molecular sheets. However, since reaction is observed, often under standard conditions, it is possible that reaction occurs preferably at defect sites. Usually, sonication under air generates oxidation of the graphene layers at the rim.[11] Often, carboxylic groups are generated, which can be used to anchor amino derivatives through amide condensation reactions.

Our group performed the 1,3-dipolar cycloaddition reaction of azomethine ylides on graphene produced by sonication of graphite in NMP (Scheme 2).[42] By condensing paraformaldehyde with an N-modified glycine, we produced pyrrolidine rings distributed on the surface of graphene. The reaction is very versatile, and the outcome is in agreement with the results previously observed with fullerenes and carbon nanotubes.[48,49] In order to identify the reactive sites on the graphene layers, we introduced free amino groups at the end of the aliphatic chain (Scheme 3). Gold nanorods (AuNR) are known to bind free amino groups, and therefore, we added AuNR to the amino-functionalized graphene. The results show that the reaction takes place not only at the edges or in their proximity but also at C=C bonds in the interior of the graphene plane. In fact, we were able to visualize a distribution of gold nanorods spread over the whole surface of the graphene surface (Figure 4).

This methodology allows the integration of the outstanding properties of graphene with those of other interesting materials, such as photoactive, electroactive, or bioactive units. For instance, porphyrins were covalently attached to graphene, using the same cycloaddition approach. Two types of hybrid materials, using free or palladium tetraphenylporphyrin, were obtained from pristine graphene through one-pot cycloaddition reactions.[50] The quenching of fluorescence and reduced excited state lifetimes suggest photoinduced energy/electron transfer between graphene and the covalently attached porphyrin units.

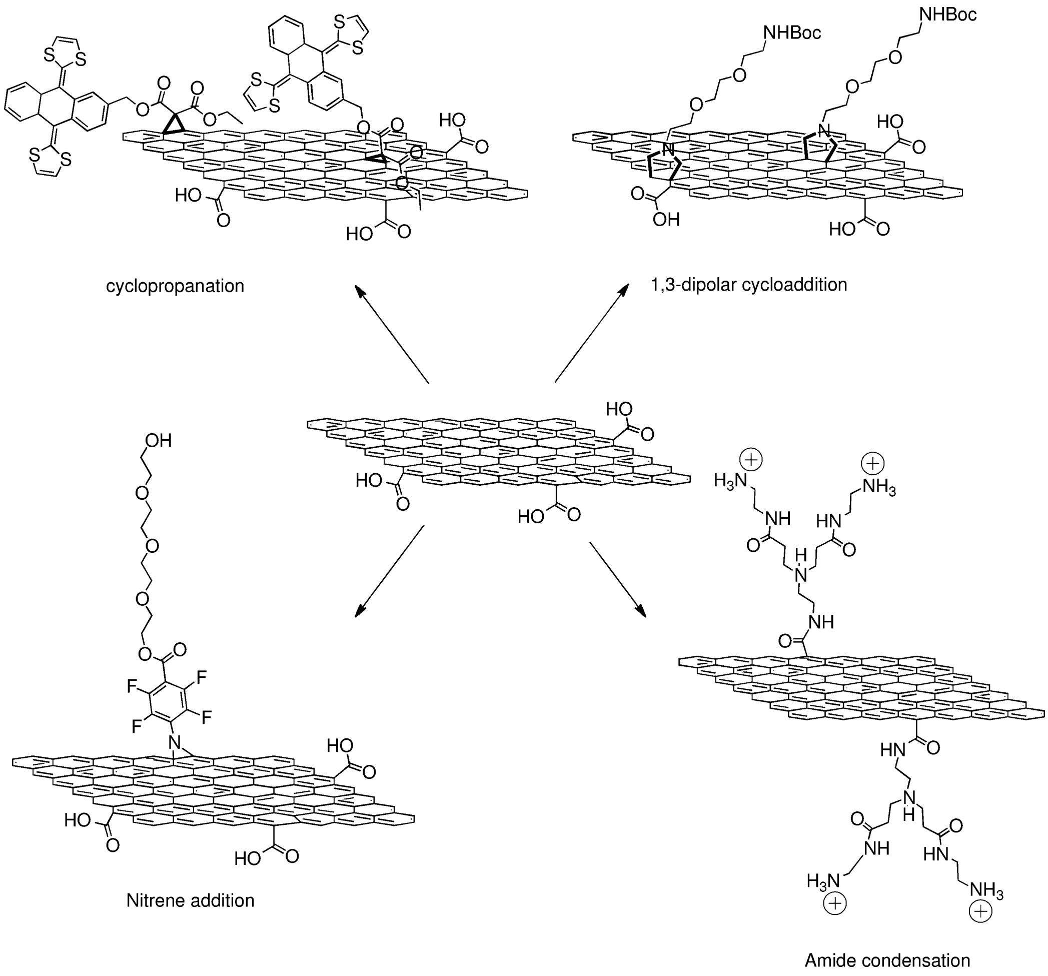
Using a similar approach, functionalization of graphene sheets was obtained by addition of an azomethine ylide formed by condensation of 3,4-dihydroxybenzaldehyde and sarcosine.[51] It was also reported that the hydroxyl groups increase the graphene dispersibility in polar solvents, such as ethanol and DMF.[51]

In order to differentiate between functionalization at all reactive sites and at the rim of the graphene sheets only, we performed two-well established organic reactions, namely 1,3-dipolar cycloaddition and amide condensation reaction. Following this strategy, we introduced poly amido amine (PAMAM) dendron moieties with amino terminal groups at the surface faces (Scheme 4) or at the edges of graphene layers (Scheme 5).[43]

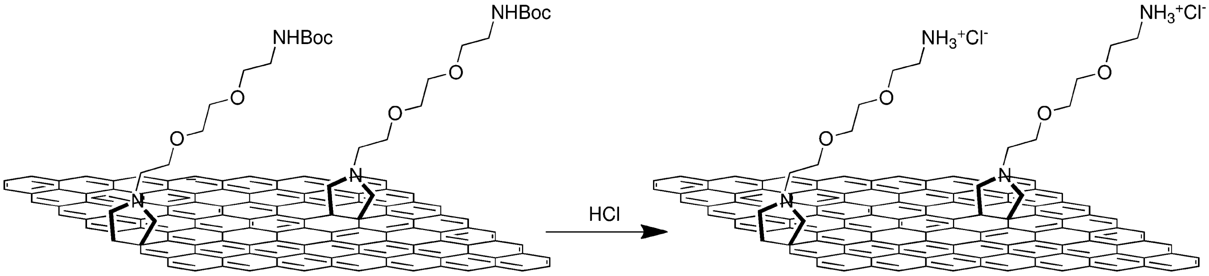
These free amino groups recognize gold nanoparticles used as contrast markers in the identification of the reactive sites. In the case of 1,3-dipolar cycloadditions, the functionalized material exhibited gold nanoparticles distributed all over the graphene surfaces, while in the amidation reaction, particles were deposited mainly at the edges of the graphene layers, Figure 5.

Our experimental results confirm that 1,3-dipolar cycloaddition produces highly functionalized material, inducing higher dispersibility of graphene layers in DMF and water. Instead, in the amide condensation reaction, we

SCHEME 2. Organic Reactions Performed in Graphene Dispersions



SCHEME 3. Graphene Functionalized by the 1,3-Dipolar Cycloaddition Reaction, Deprotection Step



confirmed that carboxylic groups generated during the ultrasonication process are mainly present at the edges of the exfoliated graphene. The low concentration of functional groups in this latter material induces its reaggregation as the concentration is increased. In principle, by use of this approach, diverse functional groups can be attached selectively at the graphene edges or at the surface faces. The nature of the functional groups can increase the dispersibility in suitable solvents or serve as anchors for other nanostructures to tune the properties of the resulting graphene hybrid materials.

Other examples of functionalization of graphene in dispersions include the formation of very reactive intermediate species, such as nitrenes or free radicals. Perfluorophenyl azide (PFPA) was added to a dispersion of graphene exfoliated in ODCB. Upon photochemical or thermal treatment, the azide was converted to the highly reactive singlet perfluorophenyl nitrene, which adds to the C−C double bonds

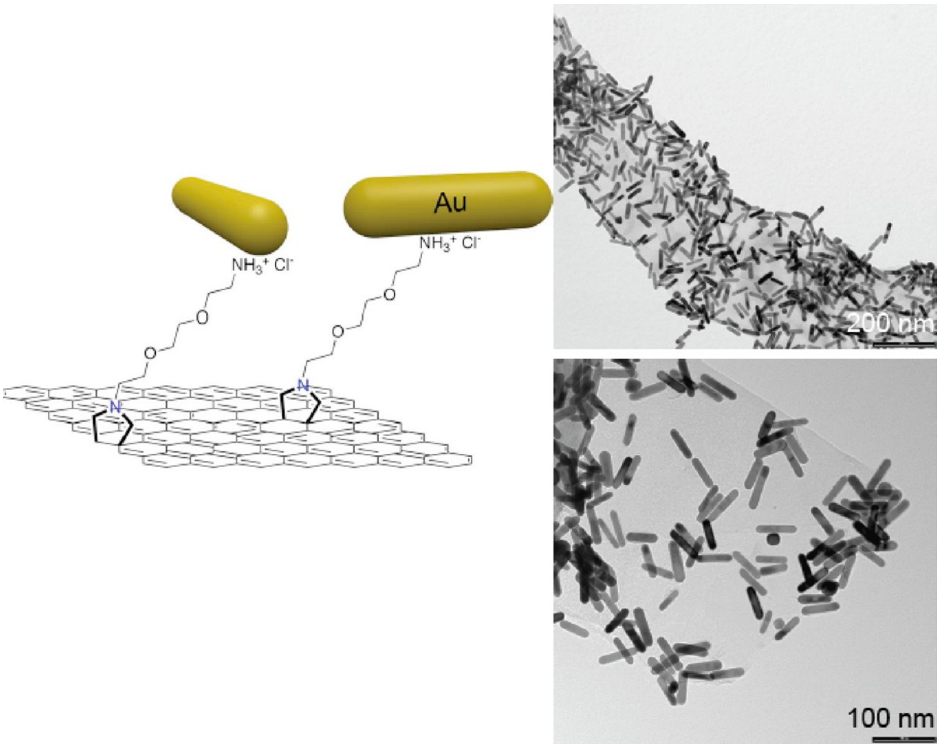
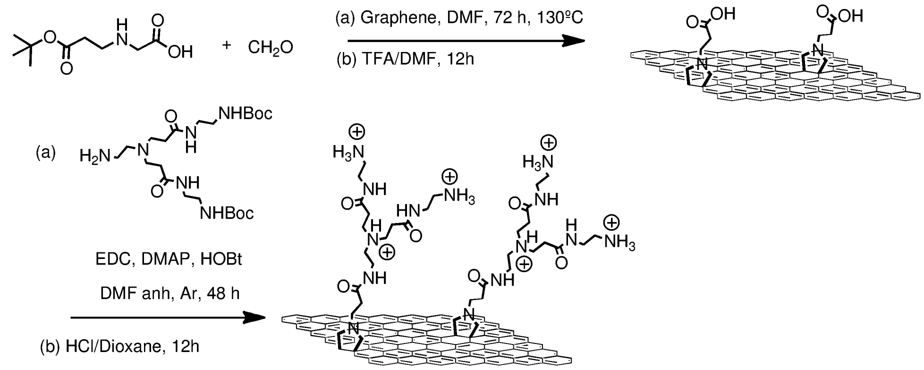


FIGURE 4. Au nanorods are used as contrast markers for the identification of reactive sites. On the right, TEM photographs of the graphene layers covered with Au nanorods.

SCHEME 4. Functionalization of Graphene Layers with PAMAM Dendrons by 1,3-Dipolar Cycloaddition



of graphene to form aziridine derivatives.[52] The resulting materials were dispersible in organic solvents or water depending on the nature of the functional groups present on PFPA.

Polystyrene-functionalized graphene was obtained via a single-step sonochemical method, starting from graphite flakes and styrene, which serves both as a solvent for the exfoliation of graphite and as a reactive monomer for polymerization.[53] These polymer-functionalized graphenes are very stable and can be easily dispersed in common organic solvents. The graphitic structure of these functionalized graphenes is not extensively affected. This material has a great potential for graphene-based composite materials.

An electro-active extended tetrathiafulvalene (exTTF) moiety was attached to exfoliated graphene using a cyclopropanation reaction under microwave treatment. For this hybrid nanomaterial, the formation of a radical ion pair that includes one-electron oxidation of exTTF and one-electron reduction of graphene was suggested with an energy gap calculated as 1.23 eV.[34]

The chemical exfoliation of graphite, in association with an in situ covalent functionalization, performed by coupling reductive graphite activation with oxidative arylation by aryldiazonium salts in a one-pot procedure was recently reported.[14] The covalent functionalization protects the single layer graphene from reaggregation. Through variation

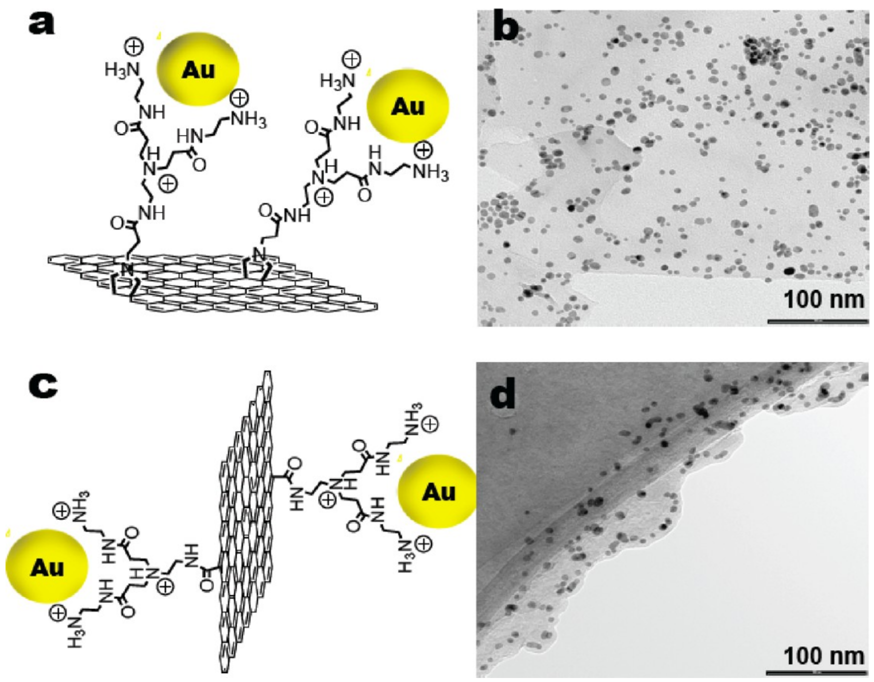
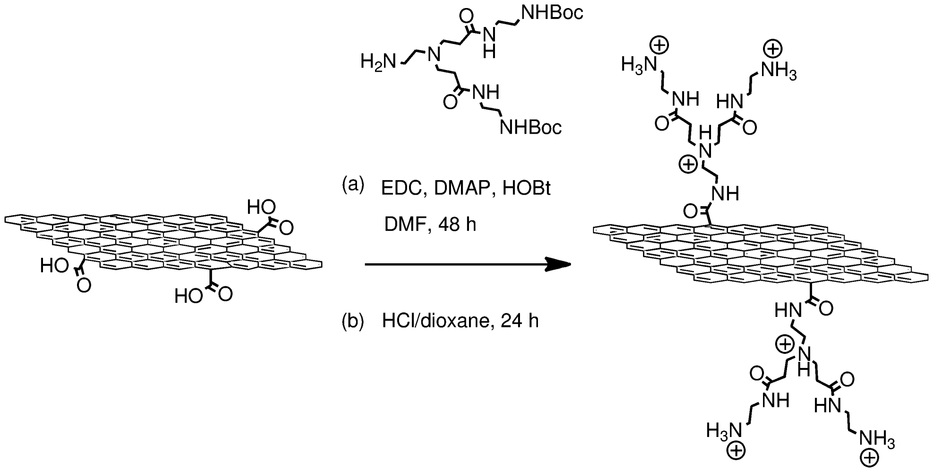


FIGURE 5. (left) Graphene layers functionalized with Au nanoparticles; (right) TEM photographs of the corresponding left composites.

SCHEME 5. Functionalization of Graphene Layers with PAMAM Dendrons by Amide Condensation Reaction



of the diazonium salt concentration, it was possible to control the amount of functionalization. The use of reversibly attached functional groups is expected to provide improved and tailor-made properties, such as customizable solubility, electron mobility, and sensor activity, important for high-performance applications.

Conclusions

Fundamental understanding of the chemistry of graphene is required for its development in future technologies. Improvement of functionalization protocols for the controlled chemical modification of graphene depends on a number of key challenges, including its production, defects, edges, reactivity, control of stoichiometry, dispersibility, and stability. Here, we have described the recent strategies in the preparation of stable dispersions of graphene that allow its wet organic functionalization. In the production of stable dispersions of graphene, the wide-ranging advantage of the sonication treatments is that they produce dispersible materials that comprise mainly few-layer or monolayer graphenes. The resulting graphene sheets, stabilized by the interactions with the solvent, are suitable materials for performing organic reactions. Until now, only a few organic reactions have been performed in stable dispersions of graphene. However, organic functionalization has demonstrated high potential in tuning graphene properties.

Additionally, organic moieties can be removed by thermal treatments restoring the intrinsic properties of pristine graphene. The design of novel protocols for the organic functionalization is expected to increase our knowledge in the fundamental chemistry of graphene, allowing exciting future developments.

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BIOGRAPHICAL INFORMATION

Mildred Quintana received her B.Sc. and Ph.D. degrees from the Universidad Autónoma Metropolitana-Iztapalapa (Mexico) in 2001 and 2005, respectively. Then, she worked in the Instituto de Física of the Universidad Autónoma de San Luis Potosí (IF-UASLP, Mexico, 2005-2007) and at the University of Trieste (with Professor Maurizio Prato, Italy, 2007-2011) as a Postdoctoral Fellow. In 2011, she was elected Profesor-Investigador at the IF-UASLP. Her research interest lies in the synthesis and functionalization of nanostructured materials and their properties and application.

Ester Vázquez obtained her Ph.D. degree from the University of Castilla-la Mancha (UCLM) in 2000. She carried out her postdoctoral training in Trieste, working with Professor Maurizio Prato, in the frame of a European Research Training Network. She joined the Faculty of Chemistry at UCLM in 2001, being promoted to Associate Professor in 2010. In 2009, she received the "Ibn Wafid de Toledo" Price for young researchers of Castilla-La Mancha. Her research interests focus on the modification of carbon nanostructures using non-conventional methodologies.

Maurizio Prato graduated in Padova, Italy, where he started his academic career in the Department of Organic Chemistry. He then moved to Trieste in 1992 as an Associate Professor, becoming Full Professor in 2000. In 2008, he received an ERC Advanced Grant. In 2010, he was elected Member of the "Accademia Nazionale dei Lincei".

FOOTNOTES

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The authors declare no competing financial interest.

REFERENCES

1 Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Katsnelson, M. I.; Grigorieva, V.; Dubonos, S. V.; Firsov, A. A. Two-Dimensional Gas of Massless Dirac Fermions in Graphene. *Nature* **2005**, *408*, 197–200.

2 Geim, A. K. Graphene: Status and Prospects. *Science* **2009**, *324*, 1530–1534.

3 Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, Y.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. Electric Field Effect in Anatomically Thin Carbon Films. *Science* **2004**, *306*, 666–669.

4 Reina, A.; Jia, X.; Ho, J.; Nezich, D.; Son, H.; Bulovic, V.; Dresselhaus, M. S.; Kong, J. Large Area, Few-Layer Graphene Films by Chemical Vapor Deposition. *Nano Lett.* **2009**, *9*, 30–35.

5 Emtsev, K. V.; Bostwick, A.; Horn, K.; Jobst, J.; Kellogg, G. L.; Lay, L.; McChesney, J. L.; Ohta, T.; Reshanov, S. A.; Röhrl, J.; Rotenberg, E.; Schmid, A. K.; Waldmann, D.; Weber, H. B.; Seyller, T. Towards Wafer-Size Graphene Layers by Atmospheric Pressure Graphitization of Silicon Carbide. *Nat. Mater.* **2009**, *8*, 203–207.

6 Balan, A.; Kamar, R.; Boukhicha, M.; Beyssac, O.; Bouillard, J. C.; Taverna, D.; Sacks, W.; Marangolo, M.; Lacaze, E.; Gohler, R.; Escoffier, W.; Poumiroi, J. M.; Shukla, A. Anodic Bonded Graphene. *J. Phys. D: Appl. Phys.* **2010**, *43*, 374013.

7 Kosynkin, D. V.; Higginbotham, A. L.; Sinitskii, A.; Lomeda, J. R.; Dimiev, A.; Price, K.; Tour, J. M. Longitudinal Unzipping of Carbon Nanotubes to Form Graphene Nanoribbons. *Nature* **2009**, *458*, 872–876.

8 Yang, X.; Dou, X.; Rouhanipour, A.; Zhi, L.; Räder, H. J.; Müller, K. Two-Dimensional Graphene Nanoribbons. *J. Am. Chem. Soc.* **2008**, *130*, 4216–4217.

9 Zhu, Y.; Murali, S.; Stoller, M. D.; Ganesh, K. J.; Cai, W.; Ferreira, P. J.; Pirkle, A.; Wallace, R. M.; Cychosz, K. A.; Thommes, M.; Su, D.; Stach, E. A.; Ruoff, R. S. Carbon-Based Supercapacitors Produced by Activation of Graphene. *Science* **2011**, *332*, 1537–1541.

10 Li, X.; Wang, X.; Zhang, L.; Dai, H. Chemically Derived, Ultrasmooth Graphene Nanoribbon Semiconductors. *Science* **2008**, *319*, 1229–1232.

11 Hernandez, Y.; Nicolsi, V.; Loyta, M.; Blighe, F. M.; Sun, Z.; De, S.; McGovern, I. T.; Holland, B.; Byrne, M.; GuńKo, Y. K.; Boland, J. J.; Niraj, P.; Duesberg, G.; Krishnamurty, S.; Goodhue, R.; Hutchinson, J.; Scardaci, V.; Ferrari, A. C.; Coleman, J. N. High-Yield Production of Graphene by Liquid-Phase Exfoliation of Graphite. *Nat. Nanotechnol.* **2008**, *3*, 563–568.

12 Lu, J.; Yang, J.; Wang, J.; Lim, A.; Wang, S.; Loh, K. P. One-Pot Synthesis of Fluorescent Carbon Nanoribbons, Nanoparticles, and Graphene by the Exfoliation of Graphite in Ionic Liquids. *ACS Nano* **2009**, *3*, 2376–2375.

13 Valles, C.; Drummond, C.; Saadaoui, H.; Furtado, C. A.; He, M.; Roubeau, O.; Ortolani, L.; Monthioux, M.; Pénicaud, A. Solutions of Negative Charged Graphene Sheets and Ribbons. *J. Am. Chem. Soc.* **2008**, *130*, 15802–15804.

14 Englert, J. M.; Dotzer, C.; Yang, G.; Schmid, M.; Papp, C.; Gottfried, J. M.; Steinrück, H.-P.; Spiecker, E.; Hauke, F.; Hirsch, A. Covalent Bulk Functionalization of Graphene. *Nat. Chem.* **2011**, *3*, 279–286.

15 León, V.; Quintana, M.; Herrero, M. A.; Fierro, J. L. G.; de la Hoz, A.; Prato, M.; Vázquez, E. Few-Layers Graphenes Using Melamine and Ball Milling Processing. *Chem. Commun.* **2011**, *47*, 10936–10938.

16 (a) Stankovich, S.; Dikin, D. A.; Dommett, H. B.; Kohlhaas, K. M.; Zimney, E. J.; Stach, E. A.; Piner, R. D.; Nguyen, S. T.; Ruoff, R. S. Graphene-Based Composite Materials. *Nature* **2006**, *442*, 282–286. (b) Bai, S.; Shen, X. Graphene-Inorganic Nanocomposites. *RSC Adv.* **2012**, *2*, 64–98.

17 Wu, Qiou.; Xu, Y.; Yao, Z.; Liu, A.; Shi, G. Supercapacitors Based on Flexible Graphene/Polyaniline Nanofiber Composite Films. *ACS Nano* **2010**, *4*, 1963–1970.

18 Yoo, E.; Kim, J.; Hosono, E.; Zhou, H.; Kudo, T.; Honma, I. Large Reversible Li Storage of Graphene Nanosheet Families for Use in Rechargeable Lithium Ion Batteries. *Nano Lett.* **2008**, *8*, 2277–2282.

19 Qu, L.; Liu, Y.; Baek, J.-B.; Dai, L. Nitrogen-Doped Graphene as Efficient Metal-Free Electrocatalyst for Oxygen Reduction in Fuel Cells. *ACS Nano* **2010**, *4*, 1321–1326.

20 Lucechinger, N. A.; Athanassious, E. K.; Stark, W. J. Graphene Stabilized Copper Nanoparticles as an Air-Stable Substitute for Silver and Gold in Low-Cost Ink-Jet Printable Electronics. *Nanotechnology* **2008**, *19*, No. 445201.

21 Wang, S.; Ang, P. K.; Wang, Z.; Tang, A. L. L.; Thong, J. T. L.; Loh, K. P. High Mobility, Printable, and Solution-Processed Graphene Electronics. *Nano Lett.* **2010**, *10*, 92–98.

22 Lee, V.; Whittaker, L.; Jaye, C.; Baroudi, K. M.; Fischer, D. A.; Banerjee, S. Large-Area Chemically Modified Graphene Films: Electrophoretic Deposition and Characterization by Soft X-ray Absorption Spectroscopy. *Chem. Mater.* **2009**, *21*, 3905–3916.

23 Mohanty, N.; Berry, V. Graphene-Based Single-Bacterium Resolution Biodevice and DNA Transistor: Interfacing Graphene Derivatives with Nanoscale and Microscale Biocomponents. *Nano Lett.* **2008**, *8*, 4469–4476.

24 Bonaccorso, F.; Sun, Z.; Hassan, T.; Ferrari, C. Graphene Pothonics and Optoelectronics. *Nat. Photonics* **2010**, *4*, 611–622.

25 Montellano-Lopez, A.; A., M.-A.; Prato, M. Materials Chemistry of Fullerene C60 Derivatives. *J. Mater. Chem.* **2011**, *21*, 1305–1318.

26 Singh, P.; Campidelli, S.; Giordani, S.; Bonifazi, D.; Bianco, A.; Prato, M. Organic Functionalisation and Characterisation of Single-Walled Carbon Nanotubes. *Chem. Soc. Rev.* **2009**, *38*, 2214–2230.

27 Park, S.; Ruoff, R. S. Chemical Methods for the Production of Graphenes. *Nat. Nanotechnol.* **2009**, *4*, 217–224.

28 Shin, C. J.; Lin, S.; Strano, M. S. Understanding the Stabilization of Liquid-Phase-Exfoliated Graphene in Polar Solvents: Molecular Dynamic Simulations and Kinetic Theory of Colloid Aggregation. *J. Am. Chem. Soc.* **2010**, *132*, 14638–14648.

29 Cravotto, G.; Cintas, P. Sonication-Assisted Fabrication and Post-Synthetic Modifications of Graphene Like Materials. *Chem.—Eur. J.* **2010**, 5246–5259.

30 Khan, U.; ÓNeil, A.; Loyta, M.; De, S.; Coleman, J. N. High-Concentration Solvent Exfoliation of Graphene. *Small* **2010**, *6*, 864–871.

31 Loyta, M.; Hernandez, Y.; King, P. J.; Smith, R. J.; Nicolosi, V.; Karlsson, L. S.; Blighe, F. M.; De., S.; Wang, Z.; McGovern, I. T.; Duesberg, G. S.; Coleman, J. N. Liquid Phase Production

of Graphene by Exfoliation of Graphite in Surfactant/Water Solutions. *J. Am. Chem. Soc.* **2009**, *131*, 3611–3620.

32 Hamilton, C. E.; Lomeda, J. R.; Sun, Z.; Tour, J. M.; Barron, A. R. High-Yield Organic Dispersions of Unfunctionalized Graphene. *Nano Lett.* **2009**, *9*, 3460–3462.

33 Bourlinos, A. B.; Georgakilas, V.; Zboril, R.; Steriotis, T. A.; Stubos, A. K. Liquid-Phase Exfoliation of Graphite Towards Solubilized Graphenes. *Small* **2009**, *5*, 1841–1845.

34 Economopoulos, S. P.; Rotas, G.; Miyata, Y.; Shinohara, H.; Tagmatarchis, N. Exfoliation and Chemical Modification Using Microwave Irradiation Affording Highly Functionalized Graphene. *ACS Nano* **2010**, *4*, 7499–7507.

35 Syrgiannis, Z.; Gebhardt, B.; Dotzer, C.; Hauke, F.; Graupner, R.; Hirsh, A. Reductive Retrofunctionalization of Single-Walled Carbon Nanotubes. *Angew. Chem., Int. Ed.* **2010**, *49*, 3322–3325.

36 Quintana, M.; Grzelczak, M.; Spyro, K.; Calvaresi, M.; Bals, S.; Kooi, B.; Van Tendeloo, G.; Rudolf, P.; Zerbetto, F.; Prato, M. A Simple Road for the Transformation of Few Layer Graphene into MWNTs. *J. Am. Chem. Soc.* **2012**, 10.1021/ja303131j.

37 Quintana, M.; Grzelczak, M.; Spyro, K.; Bals, S.; Kooi, B.; Van Tendeloo, G.; Rudolf, P.; Prato, M. Unpublished.

38 Fukuzumi, S.; Shimoisako, K.; Suenobo, T.; Watanabe, Y. Mechanism of Hydrogen, Oxygen, and Electron Transfer Reactivity of Cumylperoxy Radical. *J. Am. Chem. Soc.* **2003**, *125*, 9074–9082.

39 Elias, D. C.; Nair, R. R.; Mohiuddin, T. M. G.; Morozov, S. V.; Blake, P.; Halsall, M. P.; Ferrari, A. C.; Boukhvalov, D. W.; Katsnelson, M. I.; Geim, A. K.; Novoselov, K. S. Control of Graphene's Properties by Reversible Hydrogenation: Evidence for Graphane. *Science* **2009**, *323*, 610–613.

40 Sofo, J. O.; Chaudhari, A. S.; Barber, G. D. Graphane: A Two-Dimensional Hydrocarbon. *Phys. Rev. B* **2007**, *75*, No. 153401.

41 Sharma, R.; Baik, J. H.; Perera, J. C.; Strano, M. S. Anomalous Large Reactivity of Single Graphene Layer and Edges Towards Electron Transfer Chemistries. *Nano Lett.* **2010**, *10*, 398–405.

42 Quintana, M.; Spyro, K.; Grzelczak, M.; Browne, W. R.; Rudolf, P.; Prato, M. Functionalization of Graphene via 1,3-Dipolar Cycloaddition. *ACS Nano* **2010**, *4*, 3527–3533.

43 Quintana, M.; Montellano, A.; del Rio, E. A.; Van Tendeloo, G.; Bittencourt, C.; Prato, M. Selective Organic Functionalization of Graphene Bulk or Graphene Edges. *Chem. Commun.* **2011**, *47*, 9330–9332.

44 Loh, K. P.; Bao, Q.; Ang, P. K.; Yang, J. The Chemistry of Graphene. *J. Mater. Chem.* **2010**, *2*, 2277–2289.

45 Yan, L.; Zheng, Y. B.; Zhao, F.; Li, S.; Gao, X.; Xu, B.; Weiss, P. S.; Zhao, Y. Chemistry and Physics of a Single Atomic Layer: Strategies and Challenges for Functionalization of Graphene and Graphene-Based Materials. *Chem. Soc. Rev.* **2012**, *41*, 97–114.

46 Banhart, F.; Kotakoski, J.; Krasheninnikov, A. V. Structural Defects in Graphene. *ACS Nano* **2010**, *5*, 26–41.

47 Meyer, J. C.; Geim, A. K.; Katsnelson, M. I.; Novoselov, K. S.; Booth, T. J.; Roth, S. The Structure of Suspended Graphene Sheets. *Nature* **2007**, *446*, 60–63.

48 Prato, M.; Maggini, M. Fulleropyrrolidines: A Family of Full-Fledged Fullerene Derivatives. *Acc. Chem. Res.* **1998**, *31*, 519–526.

49 Georgakilas, V.; Kordatos, K.; Prato, M.; Guldi, D. M.; Holzinger, M.; Hirsch, A. Organic Functionalization of Carbon Nanotubes. *J. Am. Chem. Soc.* **2002**, *124*, 760–761.

50 Zhang, X.; Hou, L.; Cnossen, A.; Coelman, A. C.; Ivashenko, O.; Rudolf, R.; Van Wees, B. J.; Brown, W. R.; Feringa, B. L. One-Pot Functionalization of Graphene with Porphyrin through Cycloaddition Reactions. *Chem.—Eur. J.* **2011**, *17*, 8957–8964.

51 Georgakilas, V.; Bourlinos, A.; Zboril, R.; Steriolis, T. A.; Dallas, P.; Stubos, K. A.; Trapalis, C. Organic Functionalization of Graphenes. *Chem. Commun.* **2010**, *46*, 1766–1768.

52 Liu, L. H.; Lerner, M. M.; Yan, M. Derivatization of Pristine Graphene with Well-Defined Chemical Functionalities. *Nano Lett.* **2010**, *10*, 3754–3756.

53 Xu, H.; Suslick, K. S. Sonochemical Preparation of Functionalized Graphenes. *J. Am. Chem. Soc.* **2011**, *133*, 9148–9151.