

Solvent-Based Exfoliation via Sonication of Graphitic Materials for Graphene Manufacture

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ABSTRACT: Graphene, a new 2D material, is gaining a lot of attention because of its remarkable mechanical, electrical, chemical, thermal, and optical properties. Graphene synthesis procedures can follow two different strategies named as “bottom up” and “top down”. In the first one, a carbonaceous carbon material is used to deposit graphene over a substrate and, in the second one, graphite is used as raw material to obtain graphene using different methods. Inside the top down strategy, exfoliation of carbon nanomaterials, both graphite and graphene oxide, is considered as a cheap and simple method to synthesize graphene. Graphite exfoliation can be conducted with both aqueous and organic methods. On the other hand, different alternatives to produce graphene using graphene oxide as the raw material can be followed, which are based on either the presonation of graphite, as a previous step for manufacturing graphene, or the sonication of the synthesized graphite oxide, leading to graphene oxide.

INTRODUCTION

Carbon, as a chemical element, is currently of great interest because of the large number of compounds with different structures and properties derived from it.¹ Among the different allotropic forms of carbon, the hardest and the softer materials known in nature are included: *graphite* (Figure 1a) and *diamond* (Figure 1b), respectively. New carbon allotropes have recently been discovered, such as *fullerenes* (Figure 1c), *carbon nanotubes* (Figure 1d) and *carbon nanofibers* (Figure 1e). The last carbon allotrope discovered has been *graphene* (Figure 1f).

Graphene is a two-dimensional (2D) carbon network comprising a hexagonal crystal structure and packed in a honeycomb structure.² Although it is known since 1960, it was in 2004 when Andre Geim and Konstantin Novoselov obtained graphene sheets isolated by the Scotch tape method.³ The extraordinary electronic, mechanical, thermal, chemical, and optical properties make graphene one of the most promising materials discovered to date.

Since 2004, many researches have been focusing their attention in developing a high purity, high yield, and easily scalable fabrication route to obtain graphene materials.⁴ Table 1 summarizes the relationships between the different graphene properties and the applications derived of them, whereas Figure 2 shows its most important applications.

Depending on its morphology (sheet or powder), graphene can be synthesized through a great variety of methods. Thus, based on the nature of the raw material, two different routes to synthesize graphene, namely, “bottom up” and “top down” (Figure 3) can be established. The first one, the bottom up route, comprises those methods which use carbonaceous gas sources to synthesize graphene. The top down methods are based on the attack of graphite (powder solid) to break its layers forming graphene sheets.⁵

The most important methods used to synthesize graphene comprised in the bottom up route are epitaxial growth on silicon carbide (SiC) and chemical vapor deposition (CVD). Epitaxial growth on silicon carbide allows the formation of graphene on SiC via silicon sublimation from the SiC surface

and the subsequent graphitization of the excess of carbon atoms left behind.⁶ By using this method, large-areas of both single crystals and few layers graphene can be directly grown over insulating substrates. Regarding the drawbacks, epitaxial growth on SiC requires specialized equipment which increases the cost of the graphene produced, its growth being limited to the SiC terrace size.⁷ Chemical vapor deposition leads to the graphene growth over metals substrate due to the pyrolysis of carbonaceous sources at high temperatures. Transition metals are actually used as catalysts, copper and nickel being the most popular ones.² For certain applications, the as-obtained graphene has to be transferred to arbitrary substrates.⁸ CVD is self-limiting to a single layer or few-layers and allows large single-crystal areas to be obtained. Important CVD disadvantages are the contamination during the transfer process and the subsequent damage to graphene sheets.⁷ Recently, substrate-free CVD synthesis of graphene has been reported, thus avoiding the use of metal substrates and their further removal.⁵

The most important top down methods to synthesize graphene are micromechanical cleavage, exfoliation of graphite intercalation compounds (GICs), arc discharge, unzipping carbon nanotubes (CNTs), graphene oxide exfoliation, and solvent-base exfoliation. Micromechanical cleavage involves the Scotch tape method, which led Novoselov and Geim to win the Nobel Prize in 2010.^{9,10} It consists of the cleavage of graphite using an adhesive tape to obtain graphene.⁷ This simple method can be used with several layered materials, although it has the disadvantage of both being inefficient for mass production and only obtaining few layers or multilayer graphene.⁷ Graphite exfoliation through the graphite intercalated compounds (GICs) method can be conducted by either the solvent-assisted exfoliation or the thermal exfoliation of GICs.

Received: September 18, 2015

Revised: December 17, 2015

Accepted: January 6, 2016

Published: January 6, 2016

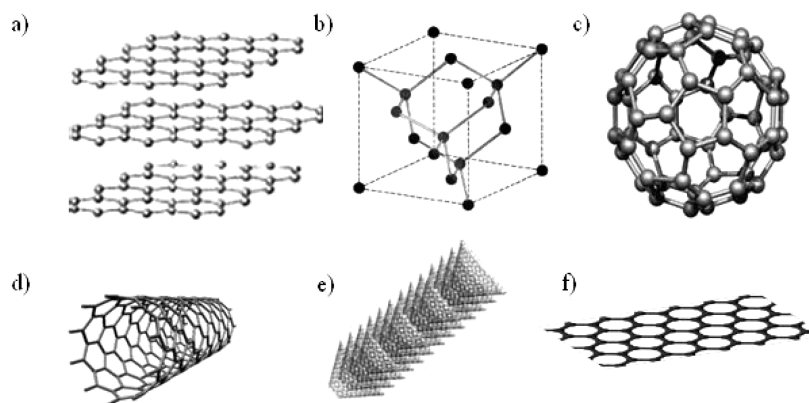


Figure 1. Structure of (a) graphite, (b) diamond, (c) fullerene, (d) carbon nanotube (CNTs), (e) carbon nanofibre (CNFs), (f) graphene.

Table 1. Graphene Properties and Applications

property	application	ref
high speed electron mobility	transistors lasers photo detectors	2,9
large specific surface area	sensors	84,85
conductance		
linear band structure (Dirac spectrum for massless fermions)	field effect transistors	10
high electrical conductivity	transparent conductive film	84
high speed electron mobility		
high optical transmittance		
high theoretical surface area	clean energy devices	84
electron transfer along it 2D surface		
anomalous quantum hall effect	ballistic transistors	86
irrelevant spin-orbit coupling	spin valve devices	9
high conductivity	conductive materials electrical batteries super capacitors	85
easy absorption of gases	contamination control	9
transparency (>99%)	displays	87
high electronic conductivity	touchscreens	
impermeability	coatings	88
high mechanical stress (hardness)	construction	2

With the former, GICs are sonicated in a solution to assist the exfoliation.¹¹ With the latter, graphite is exposed to strong acids in order to yield GICs, which are exfoliated by rapid thermal

heating or microwave radiation.¹² Although exfoliation is generally a very effective way to synthesize graphene, the exfoliation of GICs requires special processing techniques, the dimensions being constrained by the size of the initial crystal.⁷ Recently, arc discharge, consisting in a direct current passing between high purity graphite electrodes, has been used to synthesize few-layers graphene.^{13,14}

Graphene can be also synthesized by unzipping CNTs by using both physical methods (plasma etching^{15,16} and laser irradiation¹⁷) and chemical methods (strong oxidizing agents¹⁸).

On the other hand, the exfoliation and subsequent reduction of graphene oxide have gained great attention in graphene synthesis. Graphene oxide can be obtained by using different methods such as Brodie,^{19,20} Staudenmaier,^{21,22} Hummers,^{23,24} Modified Hummers²³ and Improve Hummers²³ methods. Among them, the Hummers method (with its modifications and improvements) remains as the one most broadly used because of its low cost. The most important disadvantage of graphene oxide exfoliation is the degradation of the electronic properties of the as-synthesized graphene. As in the exfoliation of GICs, the dimension of obtained graphene is constrained to the size of the initial crystals.⁷ Finally, solvent-based exfoliation comprises the sonication of graphite using different solvents. Several studies have been performed in order to find the most proper solvent as well as the optimum operation conditions for the sonication process.^{25–28} However, all of them are based on three different strategies according to the synthesis method used. The first one, known as normal force, is based on the exertion of a normal force to overcome the van der Waals attraction when two graphite

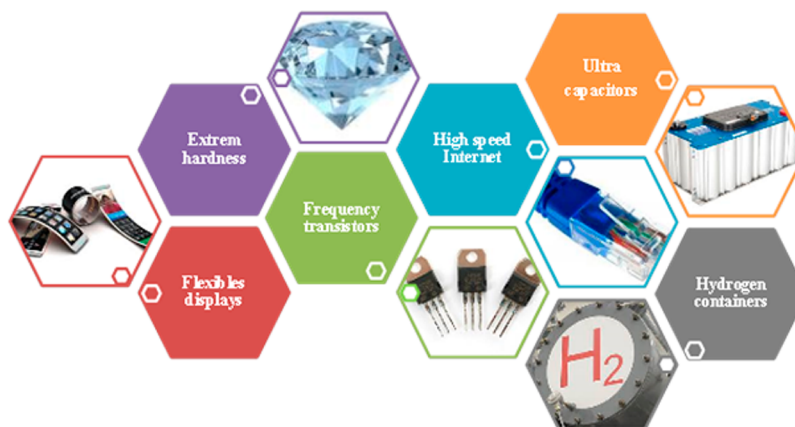


Figure 2. Graphene applications.



Figure 3. Bottom up and top down routes to synthesize graphene.

sheets are peeling. The second one, known as shear force, consists of the exertion of a lateral or shear force to promote the movement of two graphite sheets. The last one is based on the graphite fragmentation during graphite exfoliation, producing the breakage of graphite particles or sheets in smaller pieces. This last strategy has the disadvantage that the fragmentation reduces graphene lateral size so small-area graphene is obtained. However, it has the advantage of the easy exfoliation of the smaller graphite pieces due to the lower van der Waals interactions taking place between them.²⁵ Incorporating surfactants, polymers, and organic molecules during exfoliation could be useful to achieve more stable graphene dispersions.^{29–31} It has been demonstrated that, if surfactant are attached to graphite layers, stable colloidal dispersions can be obtained as a consequence of the repulsive steric forces between the exfoliated sheets.³²

This review discusses the most important results achieved in recent years in relation to the exfoliation of different carbon materials in both aqueous and organic dispersions to produce graphene. Note that several reviews have already summarized the progress of the liquid-phase exfoliation of graphite or graphite oxide to obtain graphene or graphene oxide, respectively.^{28,32–34}

From a different point of view, this review is focused on the exfoliation conditions as well as in the main characteristics of the obtained graphene, such as size, yield, or graphene type (multilayer, few-layer, bilayer, or monolayer). Exfoliation conditions are directly related with the characteristic of the obtained powder (graphene or graphene oxide) so, it is important to focus on the exfoliation parameters, including sonication conditions, centrifugation conditions, and the solvents which assist the sonication.

The present review is intended to provide an overview of recent investigations of the sonication-assisted method to produce graphene-based materials. It includes not only the exfoliation conditions, but also the solvent used to assist the sonication and the principal characteristics of the obtained product.

■ FROM GRAPHITE TO GRAPHENE POWDER VIA SOLVENT-BASED EXFOLIATION

Recent researches agree that graphene powder is a material with exceptional properties to be used for many applications,³⁵ such as advanced composites and polymers or coatings. According to literature, graphite exfoliation to obtain graphene

is considered an issue of great interest in the scientific field because it is the most promising large-scale method to produce graphene.^{36,37}

Graphene powder synthesis via solvent-based exfoliation of graphite has been studied for the last 50 years.³⁸ Two different strategies have been considered: direct sonication of a mixture of surfactant–water–graphite or direct sonication of a mixture of solvent–graphite. In the former, hydrophobic groups of graphite react with hydrophobic groups of a surfactant forming a stable solution. In the latter, graphite is directly sonicated in a solvent which may have similar surface energy than graphite, enabling a stable graphite solution.⁷ However, most of the investigations conducted were only able to obtain thin graphite sheets or small graphene fractions with many defects rather than large-scale monolayer graphene.³⁹

It was not until the year 2008 when the first researches, focused on graphite flakes sonication, achieved graphene.^{26,27} Blake et al. first, synthesized graphene using the micro-mechanical cleavage method over a microscope slide glass. They concluded that no industrial technology can rely on the micromechanical cleavage technique because only low quantities of graphene can be obtained. For this reason, they proposed an alternative approach based on the preparation of a graphene suspension by direct chemical exfoliation of graphite, which would be used to obtain transparent conductive films. For that purpose, natural graphite crystals were sonicated for 3 h using dimethylformamide (DMF) as the solvent, obtaining a suspension of thin graphitic platelets with a large proportion (up to 50%) of monolayer graphene flakes. Hernandez et al.²⁷ achieved the production of high quality graphene using *N*-methyl-pyrrolidone as the organic solvent. They obtained a scalable-method to produce high quality unoxidized monolayer graphene, with yields of about 1 wt %, which could potentially be improved to give yields of up to 12 wt % by using a starting graphite mass with sediment recycling. To get perfect structurally graphene, Hernandez et al. also investigated the exfoliation of pristine graphite in liquid-phase environments demonstrating that those solvents whose surface energy is close to that of graphite ($\sim 70\text{--}80\text{ mJ m}^{-2}$) enhanced the exfoliation and dispersion of pristine graphite.²⁷

Aqueous Dispersion. Water is considered the most suitable dispersive agent due to its nontoxicity and its abundance. However, both the hydrophobic nature of graphite sheets and

the water surface energy are far from the required range, which does not favor the formation of stable dispersions.²⁷ This fact means that aqueous colloidal dispersions of pristine graphite must be stabilized by using a surfactant, which allows exfoliated sheets to persist suspended.^{30,40–53} Thus, the addition of surfactants helps to decrease the water surface energy, making feasible graphite exfoliation. Following the works by Blake et al. and Hernandez et al.,^{26,27} several research groups have focused on the study of the most suitable surfactants to obtain stabilized aqueous colloidal graphene dispersions. Lotya et al.³⁰ focused their research on the production of graphene by exfoliation of graphite in water–surfactant mixture solutions. In 2009, they obtained, by using sodium dodecylbenzene sulfonate (SDBS) as the surfactant, large quantities of multilayer graphene presenting five layers or lesser (with a small proportion of monolayer graphene). The synthesis process was based on the stirring, sonication, and centrifugation of a mixture SDBS–water–graphite. High resolution transmission electron microscopy (HR-TEM), Raman, IR, and X-ray photoelectron techniques were used to characterize the obtained graphene, suggesting that low levels of defects or oxides appeared in the graphene basal plane structure. The obtained graphene films were conductive and could be made semitransparent. This work anticipated that the properties of these graphene films could be enhanced by improving the removal of the surfactant.³⁰ One year later, in 2010, the same investigation group proposed the production of graphene dispersions stabilized in water using sodium cholate (NaC) as the surfactant.⁴⁷ The optimization of the main dispersion parameters (initial graphite concentration, surfactant concentration, centrifugation rate, and sonication time) were studied to improve final concentration and dispersion quality. Thus, graphene dispersions were prepared by adding 5 mg/mL of initial graphite concentration to a NaC solution. The resulting solutions were sonicated for long times, using a continuous refilling of bath water. After sonication and before centrifugation (30 or 90 min, 500–2000 rpm), samples were left to stand overnight to allow the formation of any large unstable graphite aggregates. Obtained results showed that the dispersion concentration increased sublinearly with the sonication time, while high quality dispersions were obtained for higher centrifugation powers. With this process, about 10% of the sample was monolayer graphene and up to 80% of the flakes had less than five graphene layers. Raman spectroscopy showed that the relation between D and G bands (I_D/I_G ratio) increased with sonication time, which was consistent with the formation of new edges. However, an increase in the I_D/I_G ratio with centrifugation rotation rate may indicate an excess of defects in the samples. The dispersions could be placed into films with good electrical and mechanical properties, achieving a method which could be the base to develop new graphene-based composite materials requiring aqueous precursors.⁴⁷

Sim et al.⁵⁴ used both aqueous NaC and polyoxyethylene nonylphenyl ether (PNE) as surfactant agents for the graphite flakes exfoliation (sonication time in the range 6–36 h, 540 W sonication power and 26 °C sonication temperature). During the horn-type ultrasonication by using a NaC aqueous solution, graphite flakes were broken into single or few layers graphene. During the exfoliation process, the hydrophobic parts of NaC molecules were associated with the graphene, the resulting graphene–NaC complexes being stabilized through the hydrophilic parts of the NaC molecules. After centrifugation (1 h, 1000 rpm), the top part of the centrifuged solution was deposited over SiO₂ substrates once it was cleaned (to avoid any

residual surfactant rest), dried, and annealed at 250 °C for an hour. It was demonstrated that the annealing tends to reduce the intensity ratio between D and G bands (I_D/I_G) in RAMAN spectra, implying that some structural defects, which were introduced during the sonication, could be cured. Raman spectroscopy and atomic force microscopy (AFM) characterization clearly showed the production of single or a few-layers surfactant-functionalized graphene with sizes of about tens of nanometers that can be applied to the biocompatible functionalization of graphene.⁵⁴

Pyrene organic derivatives have been also fairly used as surfactants for chemical exfoliation of graphite into graphene. Dong et al.⁵⁵ studied the symmetry of breaking graphene monolayers by molecular decoration, by sonication (2 h at 70 W) of a mixture of tetrasodium 1,3,6,8-pyrenetetrasulfonic acid (Py-SO₄)–graphite–water, obtaining a high yield of monolayer graphene sheets with a single 2D peak. An et al.⁵⁶ investigated the stability of aqueous dispersions of non-covalently functionalized graphene obtained by sonication (45 min) of a mixture of 1-pyrenecarboxylic acid (Py-COOH)–graphite–ethanol–water. As result, around 10% of monolayer graphene was obtained but also few-layers graphene with an average yield of around 1 wt % and a size in the range from 100 nanometers to few micrometers. Anyway, the obtained graphene showed structural defects, which was demonstrated by the presence of a D peak in the RAMAN spectra. Zhang et al.⁴⁹ produced graphene sheets by graphite powder exfoliation via sonication in an ice bath (130 W) using an aqueous solution of pyrene molecules that had been previously functionalized with different water-soluble groups (e.g., water solutions of 1-pyrenemethylamine, (Py-NH₂) hydrochloride and 1,3,6,8-pyrenetetrasulfonic acid (Py-SO₃)). After the unexfoliated graphite removal by centrifugation (20 min, 4000 rpm), the free pyrene molecules were also removed by supernatant dialysis. The monolayer graphene obtained had an average thickness of 1.3 nm, while that of the bilayer graphene was 2.6 nm. UV–vis–NIR spectroscopy measurements show that graphene sheets could be synthesized without adding toxic chemicals for its further reduction. Raman spectroscopy suggests that the relation between D and G intensities was lower than that obtained for graphene sheets reduced by hydrazine. Graphene sheets were used to fabricate transparent conductive films, which could replace transparent conductive oxides in photovoltaic applications. Jang et al.⁵⁷ investigated the supercritical fluid exfoliation (SCF) of graphite. They used an aqueous solution of 1-pyrene sulfonic acid sodium salt (Py-SO₃) to exfoliate graphite powder dispersed in ethanol by ultrasonication in a water bath (30 min, 160 W). Then, the obtained dark solution was loaded into a steel reactor that was heated (2 h) at 450 °C maintaining constant shaking. After supercritical fluid exfoliation, the reactor was quenched in an ice water. Unreacted surfactants were removed by washing the product several times with distilled water and ethanol. It was proved that graphite exfoliation in the presence of a supercritical fluid (such as Py-SO₃) increased the yield of defect free monolayer or bilayer graphene nanosheets up to about 60% (four times higher than that obtained in absence of any supercritical fluid). Lee et al.⁴⁶ prepared graphene dispersions by sonicating a mixture, consisting of a water/methanol solution, graphite powder and a pyrene-based amphiphile molecule (Amphiphilic-Py), in which the aromatic segment was based on four pyrenes units and a laterally grafted oligoether Dendron. The dispersion thus prepared was centrifuged (1300 rpm, 20 min) obtaining supernatant graphene sheets with a concentration of 1.5 mg/mL (higher concentration

than those reported for graphene sheets prepared by exfoliation).^{30,45} Detailed characterization of the obtained product determined that the exfoliation process led to single-layer and bilayer graphene sheets with some structural defects but with good electrical properties. It was also demonstrated that by using the aromatic amphiphile as surfactant, it was possible to selectively functionalize only 2D graphene sheets among the different carbon allotropes in aqueous solution, thereby yielding water-soluble graphene. Yang et al.⁵⁰ proposed the graphite powder exfoliation in aqueous solutions of 1-pyrenesulfonic acid sodium salt (Py-SO₃) by sonication (80 min). After centrifugation (1000 rpm, 20 min), the Py-SO₃ excess was washed several times and the supernatant graphene was resuspended in water. Finally, residual graphite flakes were removed by mild centrifugation (1000 rpm, 20 min) in order to obtain the final graphene dispersion, which showed to have around 70% of few-layer graphene (<7 layers). This work also demonstrated that the exfoliation yield strongly decreased when four pyrene groups (Py-4SO₃) were used instead of one (Py-1SO₃).

In 2013, Yi et al.⁵⁸ reported the graphene dispersion preparation using the tailoring Hansen solubility parameters strategy by sonication (2–12 h) of graphite in an acetone–water solution (75:25 wt %). After centrifugation (500–4000 rpm, 30 min), the obtained dispersion consisted of about 50% of defect-free graphene with a thickness less than 1 nm and lateral sizes between 0.6 and 0.8 nm. In previous investigations the same research group⁵⁹ described the graphene dispersion preparation by sonication (1 h) using the Hansen solubility parameters theory in order to optimized water–alcohol mixture ratio (60:40 wt %). After centrifugation (1 Krpm) and the standing of the samples for 2 weeks, the resulted graphene dispersion contains about 8% monolayer and 86% few-layer graphene, where graphite lattice parameters remain and basal planes are largely free of structural disorder. Furthermore, in 2014 this research group led by Wang⁶⁰ demonstrated that the addition of ethanol in water–surfactant solutions can lead to high concentration graphene dispersion, enhancing the exfoliation efficiency and the graphene concentration up to three times.

In 2014, Zhou et al.⁶¹ in turn reported graphene production by liquid-phase graphite exfoliation by sonication (6 h, 900 W) using an aqueous solution consisting of tetrafluoroborate (TEA), sodium hydroxide, and thionin acetate salt. After centrifugation (5000 rpm, 15 min) and several water/ethanol washings, the obtained graphene was irradiated and ultrasonicated (2 h, 250 W). Around 70% of the functionalized and structurally defective graphene with a thickness around 1 nm was obtained.

Bose et al.⁴⁴ prepared noncovalently functionalized graphene by sonicating (30 min) graphite flakes in a solution composed of 9-anthracene carboxylic acid (9-ACA) and ethanol. Subsequently, distilled water was added to the solution and again ultrasonicated (24 h). 9-ACA traces and ethanol excess were removed by decantation while the residue was cleaned and ultrasonicated with distilled water (3 h). As a result, stable a graphene dispersion was obtained with a yield of 2.3%.

Recently, Yeon et al.⁶² reported the surfactant-assisted exfoliation of graphite in an aqueous solution with sodium dodecyl sulfate by sonication (1 h, 665 W, 40 kHz) followed by a centrifugation (500 rpm, 15 min). The surface tension dependence on the concentration of different alcohols was measured in order to achieve the optimal surface tension for graphite exfoliation. Higher graphene concentration was obtained using

low surfactant concentration by adjusting the surface tension, obtaining thicker than a few tens of graphene layers.

Figure 4 summarizes the number of graphene layers obtained using different aqueous solutions, whereas Table 2 lists the

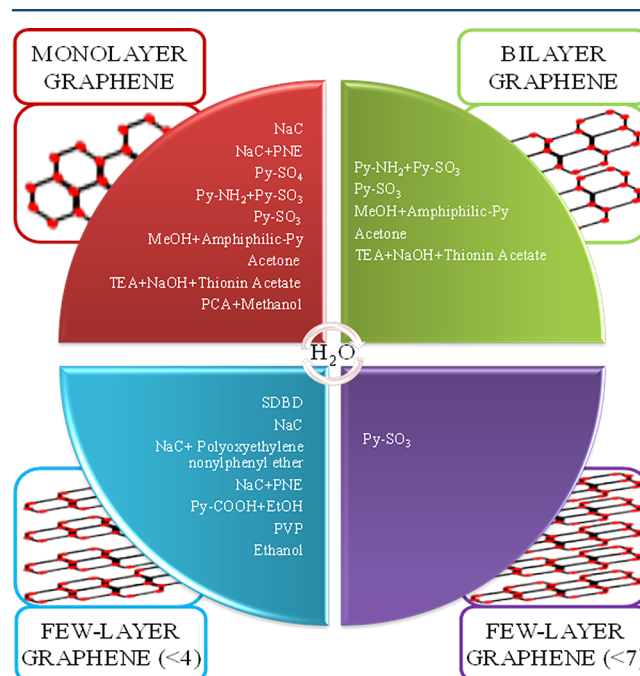


Figure 4. Graphene layers according to the kind of aqueous solution used in the sonication procedure.

synthesis conditions and the more relevant results in the preparation of graphene by aqueous solution dispersions.

Organic Dispersions. Because of its hydrophobic character, organic solvents have been considered for many years to be the most suitable candidates to prepare stable graphite dispersions.⁶³ Thus, they can contribute with an appropriate surface tension in the solution, similar to that of surfactants in aqueous dispersions.^{27,40–42}

NMP (1-methyl-2-pyrrolidone) is considered to be the most suitable organic solvent to obtain stable graphite suspensions, not only because of its surface tension value but also because of the stability that it brings to the final graphene dispersion.^{64,65} Hernandez et al.²⁷ carried out a detailed study of graphite dispersions by sonication (30 min) using NMP as the organic solvent. After centrifugation (500 rpm, 90 min), a yield of 0.01 mg/mL and about 28% monolayer graphene with dimensions from hundreds of nanometers to tens of micrometers were obtained. Liu et al.⁶⁶ reported a method to prepare high concentrations of exfoliated graphene sheets solutions. This way, a mixture containing graphite powder and NMP was sonicated for 2 h. Then, a SBS/NMP (2 wt %) solution was slowly added. The as-obtained mixture was subjected to a new sonication process (6 h), thus facilitating the SBS adsorption by the exfoliated graphite and obtaining a stable solution, which was then centrifuged (12000 rpm, 90 min). Finally, the supernatant was pipetted out, filtered in a polytetrafluoroethylene membrane, and was rinsed with THF and chloroform before drying. As a result, a high concentration and a high yield of graphene sheets with individual SBS chains climbing on its edges were obtained. Wang et al.⁶⁷ sonicated (6 h) a mixture composed of graphite powder and NMP. After centrifuging

Table 2. Synthesis Conditions and More Relevant Results in the Preparation of Graphene by Aqueous Solution Dispersions

starting material	solvents	exfoliation conditions	aqueous solution dispersions	results	ref
graphite powder	H ₂ O + TEA tetrafluoroborate + NaOH + thionin acetate salt	sonication, 6 h, 900 W; centrifugation, 15 min; 5000 rpm; 250 W.		Thickness, 1 nm (70% of graphene). Few defects and functional groups graphene.	61
graphite powder	H ₂ O + PVP	sonication, 9 h, 135 W; centrifugation, 30 min; 1500 rpm		Smooth planar structure and no multilayers protruding for their edges sheets. Lateral sizes, from micrometer (large) to submicrometer (small) range.	42
graphite flakes	NaC + H ₂ O	sonication, high times; 16 W; centrifugation, 500 and 2000 rpm; 30 or 90 min		Stable dispersions at concentration up to 0.3 mg/mL. Yield, monolayer number of fraction of 10% (1 wt %). 80% of material have <5 layers.	47
graphite powder	H ₂ O + acetone	sonication, 2–12 h; centrifugation, 30 min; 500–4000 rpm		Thickness, < 1 nm (50% of sample). Lateral sizes, 0.6–0.8 nm. Free of basal defects graphene.	58
graphite flakes	H ₂ O + NaC + polyoxyethylene nonylphenyl ether	sonication, 6–36 h, 540 W; centrifugation, 1 h, 10000 rpm		Surfactant-functionalized graphene of a single or a few layers. Lateral Sizes, approximately tens of nm.	54
graphite powder	H ₂ O + SDBS	sonication, 30 min; centrifugation, 90 min; 500 rpm		Large quantities of multilayer graphene (<5 layers) and smaller quantities of monolayer graphene	30
graphite powder	pyrenecarboxylic acid (PCA) + methanol + H ₂ O	sonication, 45 min		Lateral size, from 100 nm to few microns. Ten % of monolayer graphene. Yield, 1 wt %.	56
graphite flakes	ethanol + H ₂ O	sonication, 50/60 Hz; 30–180 min; Centrifugation, 1000 rpm; 30 min		Lateral Sizes, From a few hundred nm to a few microns. Thickness, Few nm (2 nm the majority of the graphene sheet). Mixture of single, bilayer and few-layer graphene. Surface area, ~ 1023.8 m ² /g	89
graphite	H ₂ O	sonication, 20 kHz; 3–72 h		Longer sonication time, lower thickness of graphene, (72 h, 100 nm). Combination of single, bilayer and multilayer graphene	90

(4000 rpm, 10 min), they obtained both single and few-layer graphene sheets with concentrations of about 0.5 mg/mL and yields of about 1 wt %. Recently, Xu et al.⁶⁸ considered the liquid-phase exfoliation of graphite by using different organic solvents, NMP, *N,N*-dimethylformamide (DMF), 1,2-dichlorobenzene (ODCB), or *c*-butyrolactone (GBL) and naphthalene, which served as a molecular-wedge to the graphite edge intercalation. Thus, a mixture composed by graphite, the corresponding organic solvent, and naphthalene was sonicated (90 min, low power) and then centrifuged (30 min, 3000 rpm). Finally, different graphene films were prepared over polyvinylidene fluoride membranes (PVDF) using vacuum, in which was found the presence of few-layer graphene almost without defects at a concentration up to 0.15 mg/mL. Simultaneously, Hossain et al.⁶⁹ carried out the liquid-phase organic exfoliation of thermal pretreated graphite by using NMP as the organic solvent. The experimental procedure was as follows: graphite powder was introduced in a reactor at 900 °C for 5 h at 44 psi under N₂ atmosphere, followed by a cooling step until 250 °C (cooling rate: 4 °C/min), and then in a beaker containing NMP placed on a Si oil bath. The mixture was stirred at 180 °C under N₂ atmosphere and later sonicated (3 h). The mixture was left to settle for 140 h. After that, 80% of the sample could be collected and left to stand again, ending with a drying step (300 °C, 4 h). Finally, mono-, bi-, and multilayer graphene with a yield of 14% and a concentration of 5.25 mg/mL was obtained. Wu et al.⁷⁰ used the graphene obtained by the solvent exfoliation strategy to create graphene electrodes. The experimental procedure consisted of dispersing graphite in NMP and then sonicating the mixture (100 W) during different times. The resulting dispersions were directly used for electrodes modification. Obtained results showed that the exfoliation process improved with prolonged ultrasonic times, leading to different concentrations depending on the value of this parameter: for example, 0.16 mg/mL (after 12 h of sonication) and 1.50 mg/mL (after 48 h of sonication).

Many other organic solvents have been also investigated. In 2011, Young-Choi et al.⁷¹ reported the dispersion of graphite powder in 1-propanol by sonication (20 min, 320 W) obtaining a graphene product with lateral size from a few to tens of nanometers and a thickness between 1 and 5 μm (10 monolayer per each graphene flake). They limited the sonication time to 20 min because, according to their previous results, longer sonication times damaged the graphite sheets while their lateral size decreased. The high volatility of the organic solvent (1-propanol) makes this procedure useful for the prompt production of graphene dispersions without residual solvents. Ahmad et al.⁷² prepared colloidal graphene dispersion by sonication (200 W, up to 49 h) of graphite powder in different organic solvents: tetrahydrofuran (THF), *N*-methylpyrrolidone (NMP), isopropanol and γ -butyrolactone (GBL). Dispersions were left to stand (24 h) to allow the formation of any unstable aggregates and centrifuged (15000 rpm, 30 min). They observed that the time required for settling of the graphene product was of about 1 week when THF and isopropanol were used, and 2 weeks, when NMP and GBL were employed. Results revealed that the nature of the organic solvent has an influence on the formation of a stable layer dispersion of graphene. Multilayered, wrinkled, and overlapping graphene sheets were obtained when isopropyl alcohol and THF were used as organic solvents while less thick and predominantly folded graphene sheets were obtained by using NMP and GBL.

Most of the solvents led to graphene samples with a lateral size between 2 and 4 μm .

Niu et al.⁷³ reported the use of aqueous solutions of inorganic salts before the liquid-phase exfoliation of graphite using organic solvents. First, mixtures composed by graphite, sodium dodecylbenzenesulfonate (SDBS), and the inorganic salt (NaCl or CuCl_2) were prepared and stirred at 100 $^\circ\text{C}$. Then, the corresponding organic solvent (*N,N*-dimethylformamide (DMF), ethanol (EtOH), and *N*-methyl-2-pyrrolidone (NMP)) was added to the mixture, which was sonicated (2–3 h) and vacuum filtered. Finally, the obtained product was washed several times with deionized water to remove both salt and SDBS excess and redispersed in deionized water to reach an aqueous dispersion with a concentration of 5 mg/mL, which was then centrifuged (3000 rpm, 5 min). After an exhaustive product characterization, it was concluded that about 86% of the as-obtained graphene presented between 1 and 5 layers with a lateral size between 1 and 60 μm . This size was dependent on the inorganic salt used: NaCl (1–30 μm) and CuCl_2 (1–60 μm). The final product presented excellent properties to be used in the manufacture of high-performance electronic devices and graphene-reinforced composites. As the authors claimed, their method constituted a low-cost, environmental friendly, and oxidation-free way to synthesize graphene by graphite exfoliation.

Recently Gayathri et al.⁷⁴ reported the synthesis of graphene by sonication during different times (in the range 1–8 h) of a mixture composed of graphite and ortho-dichlorobenzene (O-DCB) (organic solvent). After sonication, dispersions were centrifuged (3500 rpm, 20 min). According to their results, the longer was the sonication time, the higher was the graphene sheets concentration. Anyway, homogeneous dispersions (stable up to 6 months) containing uniformly distributed graphene with sizes about 800 nm were obtained. RAMAN characterization showed that the number of graphene sheets in the samples decreased with increasing sonication times.

Figure 5 summarizes the graphene layers obtained using different organic solutions, whereas Table 3 lists the synthesis conditions and the more relevant results in the preparation of graphene by organic solution dispersions.

Graphene Oxide (GO) Dispersion. While graphite is a 3-dimensional carbon-based material made up of millions of layers of graphene, graphite oxide is a little different. By the oxidation of graphite using strong oxidizing agents, oxygenated functionalities are introduced in the graphite structure, which not only expand the layer separation but also add a hydrophilic nature to the resulting material. This property enables the graphite oxide to be exfoliated in water using sonication, ultimately producing single or few-layer graphene, known as graphene oxide (GO). The main difference between graphite oxide and graphene oxide is the number of layers. Thus, graphite oxide is a multilayer system, whereas graphene oxide is constituted by few-layer flakes and monolayer flakes.⁷⁵ To obtain graphene, it is necessary to carry out the GO reduction using any of the existing methods (chemical, thermal, or multistep reduction⁷⁵). The as-obtained product is usually called reduced graphene oxide (RGO) or functionalized graphene instead of graphene, because of a complete reduction, and consequently, the complete elimination of the oxygenated groups is not totally achieved.⁵

The first reported method to prepare graphite oxide was named the Brodie method.^{19,21} It was followed then by the Staundenmaier method,²¹ which was an improvement of

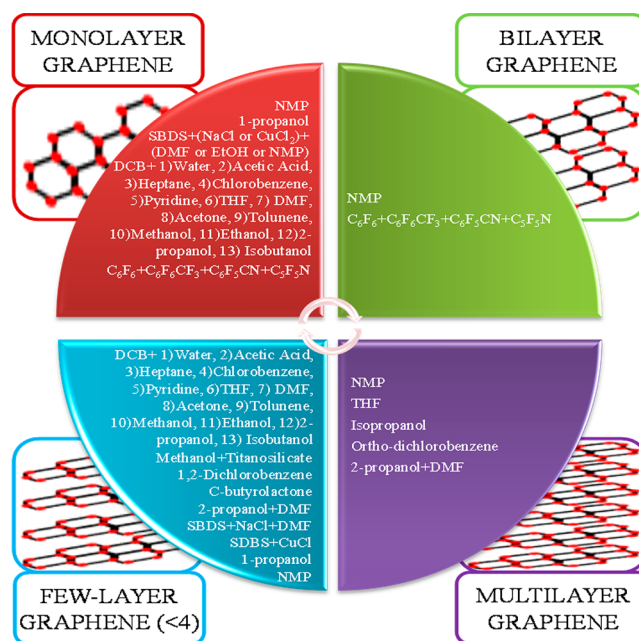


Figure 5. Graphene layers according to the kind of organic surfactant used in the sonication procedure.

Brodie's one. Decades later, Hummers and his colleagues developed a completely different method to synthesize graphite oxide.^{23,24} Recently, some improvements were developed to the Hummers method, obtaining two different methods: Hummers Modified and Hummers Improved (or Tour) methods.²³ Recently a new route to synthesized graphene oxide in 1 h using K_2FeO_4 as a oxidant agent was reported by Li et al.⁷⁶

Pantelic et al.⁷⁷ synthesized graphite oxide using the Hummers method, which was exfoliated to graphene oxide by sonication (35 kHz, during 30–60 min) at room temperature by adding the oxidized graphite (1.5 mg/mL) to Ω -filtered water (pH = 7). Using lower parent material concentrations, the above-mentioned sonication and a low speed concentration (980–6000 rpm) are enough to exfoliate graphite oxide. However, using coarse graphite as the raw material, a pre-exfoliation step (5 min) of graphite was required to ensure a sufficiently homogeneous concentration prior to the final exfoliation. Suitable graphene oxide coatings were obtained with an optical density/absorption ratio of 2 at 230 nm. The exfoliated graphene oxide solutions had a lifetime between 2 and 3 weeks.

Wojtoniszag et al.⁷⁸ studied the toxicity of graphene oxide, synthesized from graphite oxide using the modified Hummers method, and reduced graphene oxide. The exfoliation of the graphite oxide to graphene oxide was performed by ultrasonication of the former in water, leading to a homogeneous graphene oxide–water slurry (0.1 mg/mL). RGO was obtained by the GO reduction with glucose. The stability of the dispersions of these two materials in phosphate buffered solution containing three types of dispersants, polyethylene glycol (PEG), sodium deoxycholate (DOC), and polyethylene glycol–polypropylene glycol–polyethylene glycol (Pluronic 123), was studied. IR spectrum of graphene oxide suggested that graphite was successfully oxidized to GO. X-ray diffraction (XRD) indicated that the interlayer distance of GO was enhanced if compared with that of graphite due to the introduction of oxygen-containing functional groups into the carbon structure during the oxidation step. TEM images of GO

Table 3. Synthesis Conditions and More Relevant Results in the Preparation of Graphene by Organic Solution Dispersions

starting material	organic solution dispersions		ref
	solvents	exfoliation conditions	
graphite powder	2-propanol (IPA) + DMF	sonication, 2–240 min; 100 W; centrifugation, 37 kHz; 15–90 min; 10000 rpm	91
graphite powder	NMP	sonication, 30 min; centrifugation, 90 min; 500 rpm	27
graphite powder	hexafluorobenzene+ octafluorotoluene + pentafluoronitrobenzene + pentafluorobenzonitrile + pentafluoropyridine + pyridine	sonication, 1 h; 135 W	92
graphite powder	NMP	sonication, 12–48 h; 40 kHz; 100 W	70
graphite	methanol + titanosilicate JDF-1	sonication, 2 h ($T_a < 35\text{ }^\circ\text{C}$)	93
graphite	DCB + (1) water; (2)acetic acid; (3) heptane; (4) chlorobenzene; (5) pyridine; (6) THF; (7) DMF; (8) acetone; (9) toluene; (10) methanol; (11) ethanol; (12) 2-propanol; (13) isobutyl alcohol	sonication, 1 h; centrifugation, 500–4000 rpm	94

results

Thickness, 9–66 nm (68% of flakes). 11–14 nm (most of the flakes).

High quality, unoxidized monolayer graphene. Twenty-eight % of flakes have yields ~1 wt % with 1–5 nm. Lateral sized, tens of micrometers. Thickness, few micrometers.

Thickness, 0.5–1 nm Multilayered structure solutions. Obtaining of stable colloids containing solubilized graphene.

Exfoliation of graphite improves with prologues of ultrasonic time. Lateral sizes decrease from 510 to 368 nm because the sonication time was extended from 12 to 48 h.

<4 layer defects free graphene. Thickness, 1.3 nm. Specific Surface Area, 20 m²/g.

Suspension highly enriched in monolayer and few-layer graphene sheets. 90% few-layer graphene (<5 layers); 10 % monolayer graphene dispersibility (>0.1 mg/mL) thickness, 90% of graphene (>2.5 nm). lateral size, 0.1–5 μ

indicated that the material tended to wrinkle. Regarding the toxicity of these materials, it was observed that GO and RGO exhibited toxicity to mice fibroblast cell and toxicity degree depended on the concentration and type of dispersant. An increase of the GO concentration in PEG led to cell viability.

Tran et al.⁷⁹ studied the influence of the grain size of the graphite precursor on the synthesis of GO. First, graphite oxide was synthesized using a simplified and modified Brodie method.⁸⁰ Then, a mixture of this product with deionized water was sonicated (2 h) in order to obtain graphene oxide. XRD analysis showed that the material with the larger grain was hard to oxidize if compared with that with the smaller one. In addition, XRD analysis showed that the larger is the size of the parent material, the better the crystallinity and layer alignment of the GO produced. On the other hand, it was observed that for shorter oxidation times (5 min) smaller grain presented better dispersibility than larger ones, which precipitated at the bottom of the vial. For longer oxidation times (24 h), the dispersibility was not a function of the grain size. Finally, it was observed that the GO with the smallest size was the most hydrophilic, presenting the best dispersibility in deionized water.

Krishnamoorthy et al.⁸¹ reported the graphite oxide (modified Hummers method) exfoliation into GO by ultrasound (30 min) using distilled water as the solvent. A sonochemical reduction (using hydrazine in the presence of ultrasound irradiation, 2 h) of GO was used to produce graphene nanosheets. The main difference between the graphite oxide and the GO was that the number of individual layers present in both materials. Graphite oxide had more number of layers, while GO presented monolayers or few-layers of oxidized graphite.⁸² The TEM image showed that graphene sheets were of high transparency with the presence of defects. FTIR suggested the presence of oxygenated groups in GO and, in a minor extension due to the reduction process, in RGO. The same trend was observed from XPS analysis. This technique showed however that low reduction times (2 h) were not sufficient to achieve the complete reduction of GO.

Botas et al.⁸³ reported the preparation of graphite oxide from natural graphite and synthetic graphite using the Hummers method in purified water (1 mg/mL) at 60 °C (sonication conditions: 26 W, 42 kHz, and 0.5–24 h). XPS analysis of the GO prepared confirmed that regardless of the parent material the composition was similar (C/O ratio). However, GO prepared from natural graphite presented a higher proportion of sp³ C–C bonds. In addition, it was found that, although the amount of GO sheets increased with the sonication time, the natural graphite exfoliated more rapidly from the very beginning, reaching a maximum yield after 6 h. For shorter sonication times, natural graphite showed more numbers of larger monolayer sheets than the synthetic one.

Different scalable methods for large-area graphene synthesis already exist, such as CVD or solvothermal method. In addition to them, solvent-assisted exfoliation is considered a promising method for the scalable production of graphene or graphene oxide. With the use of this method, mild synthesis conditions are required, performing a very simple procedure, which could be easily automated. Furthermore, the required investment to carry out the experimental installation is low if compared with other synthesis methods.

The present review summarizes the exfoliation conditions related to the carbon nanomaterials sonication to produce graphene because of its greater importance in recent years

among the scientific community. Two different strategies, called “bottom up” and “top down” can be followed. The latter is considered a cheap, simple, and scalable method to synthesize graphene. Graphite exfoliation can be conducted in both aqueous and organic solvents. On the other hand, different alternatives to produce graphene using graphene oxide as the raw material can be followed. These alternatives are based on either the presonication of graphite as a previous step for manufacturing graphene, or the sonication of the synthesized graphite oxide, leading to graphene oxide.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We gratefully acknowledge the Spanish Ministry of Economy and Competiveness (project CTQ2013-45030-R) for the financial support of this work.

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