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FEATURE ARTICLE

Methods of graphite exfoliation

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For applications of two-dimensional graphene, commercially viable sources are necessary. Exfoliation from bulk, stacked graphite is the most economical way to achieve large quantities of single layer graphene. A number of methods have been developed to achieve exfoliation of graphite, each with advantages and disadvantages. In this review, we describe current exfoliation methods and techniques used to produce single layer materials from graphite precursors.

1 Introduction

Graphene,[1,2] a single atomic layer of sp^2-bonded carbon atoms arranged in a honeycomb lattice, exhibits remarkable electronic, thermal and mechanical properties.[3–5] A variety of applications have been demonstrated for graphene materials, such as structural nanocomposites,[6–8] catalyst supports,[9] electronic devices,[10] and energy storage in batteries and supercapacitors.[11,12]

Several methods of preparing graphene sheets have been developed since graphene was first isolated by Novoselov and Geim using Scotch tape in 2004.[1] Chemical vapour deposition (CVD)[13] and epitaxial growth,[14,15] for instance, yield graphene with a relatively small number of defects, making these

techniques promising for applications in electronic devices. However, these surface-based techniques do not scale well for applications requiring macroscopic quantities of graphene. Significantly larger amounts of graphene can be produced by physical and chemical exfoliation of bulk graphite.[16,17] These methods are cost-efficient, using inexpensive graphite, and versatile, as they can be combined with other chemical treatments, *e.g.* chemical functionalization,[18] to produce a variety of graphene and graphene-based materials, such as graphene oxide (GO) and reduced graphene oxide, RGO (also called 'functionalized graphene sheets', FGS, or 'chemical modified graphene', CMG).

This review will discuss the bulk production of graphene *via* exfoliation, focusing on the exfoliation techniques and yields. We will first describe the exfoliation mechanisms for different starting materials, including graphite oxide, pristine graphite, graphite intercalation compounds, and expanded graphite. We then describe a variety of successful exfoliation techniques that we categorize into three major classes: mechanical exfoliation,

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thermal exfoliation, and other methods, presented in Sections 2, 3, and 4, respectively.

1.1 Mechanisms

The stacked parallel layers in bulk graphite are separated by 3.41 Å. Although the van der Waals attraction between the layers is weak enough to let them slide past each other in the direction perpendicular to the *c*-axis, the attraction is strong enough to make complete exfoliation into individual layers difficult. The first attempt by Brodie to produce single-layer graphene sheets by exfoliation dates as far back as 1859.[19] Since then, many attempts have been made at large-scale production of graphene with little success.[20–23] The isolation of graphene using the Scotch tape method[1] prompted new efforts to produce two-dimensional materials by exfoliation.

For successful exfoliation, overcoming the van der Waals attractions between the adjacent layers is necessary. One method is to decrease these attractions by expanding the distance between the adjacent layers *via* oxidation and chemical intercalating reactions.[6,17,24] This reduces these forces significantly, as the potential energy associated with van der Waals forces is inversely proportional to the interatomic separation.[25] For example, during the oxidation of graphite, functional groups such as hydroxyl and epoxide are inserted and bonded to the graphitic layers. The resulting material features disordered graphitic stacking with the *d*-spacing increased from 3.4 Å to around 7.0 Å,[16,26] which facilitates exfoliation significantly.

Another way to reduce the strength of the van der Waals attractions is liquid immersion. The potential energy between adjacent layers is given by the dispersive London interactions, which are significantly reduced with respect to vacuum in the presence of a solvent.[25] Coleman *et al.*[27] showed that by matching the refractive indices of the material and the solvents, the potential may approach zero. Based on this criterion, solvents with a surface tension of around 40 mJ m^{-2} were suggested for the dispersion of carbon nanotubes and graphene. Consequently, solvents like dimethylformamide (DMF) and *N*-methyl-2-pyrrolidone (NMP) are widely used to facilitate the exfoliation of graphite.

Exfoliation is often achieved by introducing additional external forces to overcome the attractive van der Waals interactions between layers. The commonly used techniques are ultrasonication and thermal treatment. During ultrasonication, shear forces and cavitation (the growth and collapse of micrometer-sized bubbles) act on the bulk material and induce exfoliation. In the thermal process of graphite oxide and graphite intercalation compounds, the pressure due to the decomposition of the functional groups and intercalates between layers overcomes the van der Waals attractions and results in exfoliation.

The association of graphene with surfactants, polymers, and organic molecules[18,24,28,29] can be helpful in achieving stable graphene dispersions in solvents. Surfactants attached to the graphite layers induce repulsive electric double layers, resulting in stable colloidal graphene suspension;[27] polymers and organic molecules provide repulsive steric forces between exfoliated sheets, preventing aggregation or reassociation.[27] Recently, structured solvent mixtures were also shown to prevent restacking and allow for the formation of stable suspensions.[30]

1.2 Precursor materials

When graphite is directly exfoliated, the resulting graphene sheets are of high quality with good crystallinity, low defect densities, and high conductivities. However, the yield from pristine graphite is usually low.[31,32] For example, the sonication of graphite in organic solvents normally produces graphene with a yield of less than 1 wt%.[31] Exfoliated graphene can also be obtained from graphite intercalation compounds (GICs) and expanded graphite (EG). GICs are graphite compounds where atoms or molecules such as alkali metal atoms or acid molecules are intercalated between the graphitic layers. They thus have an increased interlayer spacing relative to graphite,[33] which weakens the van der Waals interactions and facilitates the exfoliation. Rapid heating of intercalated GICs produces EG, which contains partially oxidized graphitic platelets.[34] Compared to direct

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exfoliation of graphite, EG and GICs have a better yield of single sheets; however, graphene sheets obtained from these precursors contain some defects.

Graphite oxide, obtained by oxidation of graphite,[19–21] has proven to be an excellent precursor to prepare single sheets. During oxidation, the introduction of functional groups reduces interlayer interactions, thereby promoting complete exfoliation of single-layer GO. While pure graphene is highly hydrophobic, GO sheets are hydrophilic due to oxygen functional groups on the carbon sheets. They are therefore dispersible in a wide range of solvents, which makes GO sheets easy to process and provides better surface affinity in nanocomposite applications. However, GO sheets exhibit inferior thermal/electrical conductivity and mechanical properties compared to pristine graphene[3,35,36] due to the presence of defects in the basal plane. Reduction of GO to graphene can be carried out to restore some conductivity, but structural weakness remains due to permanent defects in the lattice structure.[35]

2 Mechanical exfoliation

The application of mechanical forces to solutions of layered materials *via* stirring, shaking, or ultrasonication has become one of the most important approaches to exfoliate stacked materials. Newer techniques also utilize carefully chosen solvents that interact favourably with the material to be exfoliated, reducing the energy penalty of exfoliation and reducing re-aggregation of exfoliated sheets. Intercalating agents, surfactants, and chemical functionalization are also used to diminish van der Waals interactions and keep exfoliated products suspended in solution. The success of these different methods is detailed below for graphite oxide (Section 2.1) and graphite (Section 2.2).

2.1 Graphite oxide

2.1.1 Sonication in solvents. Graphite oxide can be exfoliated in water by sonication due to the presence of polar functional groups and the increased *d*-spacing of the material.[16,17,37,38] For many applications, however, GO sheets need to be dispersed in organic solvents; techniques to directly exfoliate graphite oxide in such solvents have thus been an important area of research. Typical applications include the GO-based polymer nano-composites obtained *via* solution processing.[6–8]

The first experimental demonstration of graphite oxide exfoliation in organic solvents involved functionalization of graphite oxide with isocyanate.[39] This reaction reduces the amount of hydrogen bonding in the oxide layer by converting potential hydrogen bond donors, such as hydroxyl groups, into amides or carbamate esters. These reactions allow for the exfoliation of graphite oxide to monolayers at 1 mg mL^{-1} concentrations in the organic solvents dimethylformamide (DMF) and *N*-methyl-2-pyrrolidone (NMP), while reducing the solubility of GO in water. Later work demonstrated the dispersion of poly(*tert*-butyl acrylate)-functionalized GO in toluene at 1 mg mL^{-1}.[40] The surfactant didodecyldimethylammonium bromide (DDAB), commonly used to disperse carbon nanotubes, has also been used to disperse GO in chloroform at concentrations on the order of 1 mg mL^{-1},[41] showing that even non-covalent functionalization can be effective for this purpose.

Recently, however, direct exfoliation of graphite oxide in certain organic solvents has been demonstrated without additional functionalization or additives, simplifying the process. Graphite oxide has also been directly exfoliated with moderate sonication in DMF, NMP, tetrahydrofuran (THF), and ethylene glycol.[42] Stable dispersions can typically be made for concentrations on the order of 1 mg mL^{-1} for organic solvents and 7 mg mL^{-1} for dispersions in water,[43] with almost all sheets existing as monolayers and diameters on the order of 1 μm.

Exfoliated graphene oxide is electrically insulating with a measured conductivity of 0.02 S m^{-1}.[37] Chemical reduction of graphene oxide with hydrazine hydrate partially restores conductivity to a value of 2420 S m^{-1}.[37]

2.1.2 Stirring and shaking. The strong cavitation induced by sonication is known to help separate the layers of graphite oxide, but it also fractures the sheets and is thus problematic for applications requiring monolayers with large diameters. A possible alternative to sonication is to stir or shake graphite oxide after oxidation, which can exfoliate the layers while maintaining their lateral size. Stirring graphite oxide stacks with a starting lateral size of 50 μm was shown to yield GO monolayers with diameters up to 40 μm, though no average size was reported.[44] This is a significant improvement over GO prepared *via* sonication, which typically yields diameters in the hundreds of nanometers and rarely exceeds a few microns. Recent work has increased the lateral size of GO monolayers even further by using graphite flakes with a larger initial size.[45] Starting with graphite flakes on the order of 300 μm, a protocol of oxidation and shaking leads to GO sheets with an average lateral size of 100 μm and a maximum lateral size of 200 μm. Interestingly, this same protocol applied to the starting material with 25 μm lateral size produced GO sheets with lateral sizes around 15 μm.

2.2 Graphite

In some ways, mechanical exfoliation of graphite is similar to the exfoliation of graphite oxide, involving strong mechanical forces to separate sheets from bulk material and various strategies to keep the separated sheets suspended rather than flocculating. However, the tighter interlayer spacing of graphite and the lack of mutually repulsive oxide layers makes direct exfoliation of graphite significantly more difficult in comparison to graphite oxide; intercalating agents were thus used to facilitate exfoliation. Furthermore, graphene sheets are strongly hydrophobic, so that exfoliation in polar solvents like water usually requires the use of surfactants or other aids.

2.2.1 Organic solvents assisted sonication. The first successful sonication-based exfoliation of graphite was achieved in the organic solvent NMP.[31] The sheets obtained were chemically unmodified, pristine graphene; after centrifugation to remove the unexfoliated bulk material, samples consisted of 28% graphene monolayers and nearly 100% graphene nanosheets less than 6 atomic layers thick. Maximum lateral sizes were on the order of a few microns, similar to values reported for sonicated GO. Unfortunately, solubility was low, at 0.01 mg mL^{-1}, and the yield was also low, at around 1 wt%. The authors suggested that the yield could be increased by serially re-sonicating and

re-centrifugating the unexfoliated bulk material. Due to the relatively pristine nature of the obtained graphene, films made from these sheets have conductivities of $\sim$6500 S m^{-1}.

Some improvement was achieved through the use of different solvents, with solubilities as high as 0.03 mg mL^{-1} obtained with *ortho*-dichlorobenzene,[46] and as high as 0.1 mg mL^{-1} with per-fluorinated aromatic solvents like pentafluorobenzonitrile.[32] The largest improvement was made by using benzylamine and extending the sonication time from approximately 1 hour used in previous studies to 4–6 hours, which lead to stable dispersions with concentrations of 0.5 mg mL^{-1}.[47] Though these studies showed improved stability, none of them provides a quantitative investigation of the average lateral size or thickness of the sheets obtained instead relying on qualitative TEM analysis to show the presence of monolayers and few-layer stacks.

A significant improvement in direct, sonication-assisted exfoliation of pristine graphene has been achieved by using drastically longer sonication times.[48] A low-power bath sonicator was used to sonicate graphite powder in NMP for up to 460 hours, yielding 4 wt% monolayer sheets and solutions that were stable at 1.2 mg mL^{-1}. More than 90% of the nanosheets obtained were less than 6 layers thick, and approximately 20% were mono-layers. The average lateral sheet size was found to decrease over time with sonication, but asymptotically approached 1 μm. A similar procedure was applied later, using 150 hours of bath sonication in DMF, yielding solutions stable at 1 mg mL^{-1}, though unfortunately sheets obtained this way were only characterized qualitatively by TEM to consist of a few layers, with no quantitative analysis of lateral size or thickness.[49] These results demonstrate a clear advantage of long sonication times in low-power bath sonicators, although this approach has not yet been fully explored. Extremely high concentrations from 2 to 63 mg mL^{-1} of graphene dispersions were achieved by redispersing dried exfoliated few-layer graphene.[50]

2.2.2 Surfactant-assisted sonication. Exfoliating graphene in water is particularly challenging due to the hydrophobic nature of the sheets, but surfactants can alleviate this problem and help exfoliated sheets to remain suspended. Lotya *et al.*[28] reported the first sonication-based exfoliation of graphite in aqueous surfactant solutions using the surfactant sodium dodecyl benzene sulfonate (SDBS). However, the concentration was relatively low, typically <0.01 mg mL^{-1}. AFM and TEM evidence showed that the majority of sheets were less than 6 layers thick, though less than 10% were monolayers. Monolayer height was around 1 nm, likely due to the persistence of surfactant molecules on the sheets. Vacuum deposited films made from the obtained graphene have a relatively low DC conductivity of 35 S m^{-1} because of the presence of the surfactant, which increases to 1500 S m^{-1} after removal of the surfactant. In combination with low power sonication for long times (up to 400 h), this method was improved to produce graphene dispersions at concentrations up to 0.3 mg mL^{-1}.[51]

Since this initial work, a variety of alternative surfactants have been used, including cationic surfactants like cetyl-trimethylammonium bromide (CTAB),[52] natural surfactants like sodium cholate and sodium deoxycholate bile salts,[53–55] and a bolaamphiphile.[56] These different approaches have typically yielded some surfactant-coated monolayer graphene, yields as
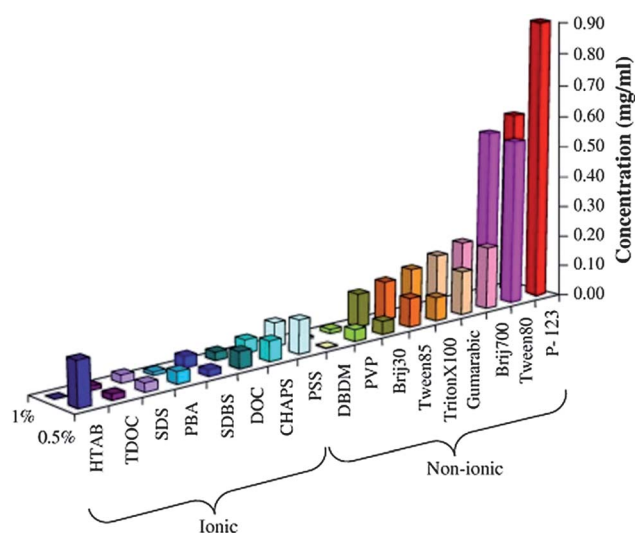

Fig. 1 Surfactants can facilitate the exfoliation of graphite to pristine graphene, and can be removed from the final material if necessary. Non-ionic surfactants have proven especially promising. Reprinted with permission from ref. 57. Copyright (2011) Elsevier.

high as 10%, and typically lead to concentrations on the order of 0.1 mg mL^{-1}. In a rigorous investigation, a variety of ionic and non-ionic surfactants were explored, testing their ability to aid sonication-based exfoliation and dispersion of graphene in water.[57] Generally, non-ionic surfactants significantly outperformed their ionic counterparts (Fig. 1). The best result, a dispersion of $\sim$1 mg mL^{-1} graphene after just two hours of sonication, was achieved using the triblock copolymer Pluronic® P-123. Interestingly, an increase in sonication time to 5 hours yielded solutions in P-123 at 1.5 mg mL^{-1}, consistent with the benefits of the extended sonication time seen for exfoliation in organic solvents. It has been shown that ionic surfactants adsorb onto graphene and impart an effective charge, providing electrostatic repulsion to prevent graphene from aggregation. In the case of non-ionic surfactants, which have a hydrophobic tail and a long hydrophilic part, steric repulsions stabilize graphene. However, additional repulsive interactions were found for non-ionic surfactants, which have been attributed to the presence of acid groups and ether linkages interacting with water and to the presence of a negative zeta potential value due to adsorbed impurities.[58] AFM analysis revealed that sheets obtained with the best surfactants had lateral sizes in the hundreds of nanometers, where almost all sheets were less than 5 layers thick, with 10–15% monolayers, consistent with other investigations of surfactant-assisted and sonication-based exfoliation. The concentration of 1.5 mg mL^{-1} is higher than that obtained by un-aided sonication in any organic solvent.[57] In terms of graphene size and thickness, ionic and non-ionic surfactants yielded similar results.[58] Films assembled from these graphene dispersions in surfactants showed a wide range of conductivities from 190 S m^{-1} to $\sim$10^4 S m^{-1}.[55,57]

2.2.3 Ionic liquids and sonication. Ionic liquids, semi-organic salts existing as liquids below 100 °C, often have surface energies close to that of graphene, and have emerged as promising solvents to aid sonication-based graphite exfoliation. The first ionic liquid used for this purpose was 1-butyl-3-methylimidazolium

bis(trifluoro-methane-sulfonyl)imide, which led to 0.95 mg mL^{-1} stable dispersions of nanosheets with only one hour of sonication.[59] Lateral sizes of the sheets were on the order of several microns, and the majority of sheets were less than 5 atomic layers thick. However, no rigorous analysis of these parameters was carried out. Recently, a protocol of grinding graphite with mortar and pestle before sonicating in 1-hexyl-3-methylimidazolium hexafluorophosphate for 24 hours yielded stable dispersions at an unprecedented 5.33 mg mL^{-1}. Quantitative analysis of the resulting nanosheets was again brief, noting only the presence of some nanosheets as wide as 4 μm, with an average thickness of 2 nm, corresponding to 6–7 atomic layers. Given the extremely high concentration of these suspensions, ionic liquids will continue to be investigated for graphite exfoliation, though questions remain about their ability to produce large quantities of monolayers.[60]

3 Thermal exfoliation techniques

Thermal exfoliation techniques are also capable of achieving near-complete exfoliation into single-layer materials. These approaches are in contrast to much earlier attempts at thermally exfoliating and expanding graphite, which only achieved partial exfoliation.[34,61–65] Compared to mechanical exfoliation methods (Section 2), thermal exfoliation has many advantages. First, thermal exfoliation is generally faster. For example, using high temperature processes, exfoliation can occur within seconds.[16,26] Furthermore, most thermal exfoliation methods produce graphene in a gaseous environment, avoiding the use of liquids. For some applications, such as electrodes in lithium batteries, dry graphene is required. When graphite oxide is used as the starting material, thermal exfoliation usually results in simultaneous exfoliation and reduction of graphene.

During the heating process, the functional groups attached to the graphitic layers decompose and produce gases that build up a pressure between adjacent graphitic layers. Exfoliation occurs when this pressure exceeds the van der Waals interlayer attractions.[26] For successful build-up of the pressure, the starting materials are required to have interlayer functional groups. For this reason, graphite oxide (Section 3.1), expanded graphite, and intercalated graphite compounds (Section 3.2) are usually used instead of pure graphite as starting materials for thermal exfoliation.

3.1 Thermal exfoliation of graphite oxide

3.1.1 High temperature thermal exfoliation. Successful thermal exfoliation of graphite oxide to produce single layer graphene sheets was first reported by Schniepp et al.[16] Dried graphite oxide was loaded into a quartz tube and purged with argon. The quartz tube was then quickly inserted into a furnace preheated to 1050 °C, and within 30 seconds, exfoliation of graphite oxide occurred. McAllister et al.[26] later provided a detailed analysis of the exfoliation mechanism and proposed that thermal exfoliation only occurred when the decomposition rate of the functional groups of graphite oxide surpassed the diffusion rate of the evolved gases, thus creating a high enough pressure to overcome the van der Waals interaction between graphene layers. They also suggested that a critical temperature of 550 °C
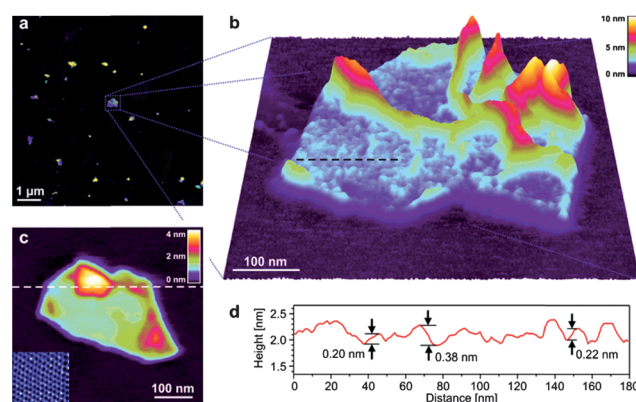

Fig. 2 Thermally exfoliated graphene. (a) Tapping-mode AFM topography image showing particles obtained by thermal exfoliation of graphite oxide. (b) An individual graphene sheet with a wrinkled and rough surface structure. (c) Contact-mode AFM scan of a different flake on the same sample. The cross-section through the sheet shown in (c) exhibits a height minimum of 1.1 nm. Reprinted with permission from ref. 16. Copyright (2006) American Chemical Society.

must be exceeded for a quick exfoliation to occur. Following dispersion in solvents, wrinkled graphene sheets with a minimum thickness of 1.1 nm were revealed (Fig. 2). A statistical analysis showed that 80% of the observed flakes were single-layer sheets, and the surface area of exfoliated graphene was determined to be in the range 700–1500 m^2 g^{-1} using the Brunauer, Emmett, and Teller (BET) method with conductivities ranging from 1×10^3 to 2.3×10^3 S m^{-1}.

Using the same exfoliation strategy of quick heating in a furnace preheated to 1050 °C, Wu et al.[66] compared the exfoliation results of five graphite starting materials. The authors found that the smaller the lateral size and the lower the crystallinity of the starting graphite, the better the exfoliation. The surface areas after exfoliation ranged from 50–350 m^2 g^{-1}, suggesting incomplete exfoliation. The graphene sheets obtained were of high quality with an electrical conductivity of $\sim 10^5$ S m^{-1}.

A detonation process[67] was also reported to exfoliate graphite oxide. A mixture of graphite oxide and picric acid, an explosive, were sealed in a vessel. Fast decomposition of the explosive produced a high temperature of around 900 °C and a powerful shockwave[68] of about 20 MPa, which exfoliated the graphite sheets. The exfoliated graphene sheets contained 2–5 layers with dimensions of a few micrometers.

Other rapid heating methods to exfoliate graphite oxide, including microwave irradiation and arc discharge, were also investigated. Using microwave heating, the exfoliation of graphite oxide occurred in less than 1 min,[69] producing exfoliated graphene with surface areas of 463 m^2 g^{-1}. These microwave exfoliated graphene sheets had a conductivity of 274 S m^{-1}. Interestingly, this microwave treated graphene exfoliated further after chemical activation with KOH. Specific surface area values of 3100 m^2 g^{-1} were achieved; the conductivity was $\sim$500 S m^{-1}.[70] It is suspected that this activated material is highly exfoliated and that its sheets exhibit an extensive amount of holes and pores. Park et al. reported a surface area of 586 m^2 g^{-1} for a mixture of graphite oxide and graphite nanosheets (GNS) that was irradiated with microwaves in a hydrogen atmosphere.[71] The

GNS acted as the microwave collector and caused rapid heating of graphite oxide. Similarly, Hu *et al.* demonstrated enhanced exfoliation of graphite oxide by mixing graphene and graphite oxide precursor.[72] They showed that the existence of π–π conjugated regions in graphite oxide facilitates microwave exfoliation of graphite oxide. Wu *et al.*[73] demonstrated effective exfoliation of graphene sheets using hydrogen arc discharge, in which the temperature instantaneously increases to more than 2000 °C. The graphene sheets obtained exhibited an electrical conductivity of ∼2 × 10^5 S m^{-1}. After dispersion and centrifugation, 80% of the graphene sheets were single layers with a thickness of 0.9–1.1 nm; the monolayer yield was around 18 wt%.

Two successful methods used to expedite exfoliation are insertion of intercalators[74] and mechanical grinding in ionic liquids.[29] Acetic anhydride was used as an intercalating agent, which decomposed into carbon dioxide and water vapour when subjected to high temperature.[74] Graphene sheets with thicknesses of 0.7–1.3 nm were also obtained by combining grinding and thermal exfoliation;[29] yields were not reported in these studies.

3.1.2 Low temperature thermal exfoliation. McAllister *et al.*[26] suggested a critical temperature of 550 °C for rapid exfoliation of graphite oxide, which they observed within seconds. Later, low temperature thermal exfoliation[75] was achieved by heating graphite oxide at 250 °C, 300 °C, and 400 °C in air for 5 minutes. The exfoliated sheets had specific surface areas in the range 328–418 m^2 g^{-1}, with the higher temperature resulting in higher surface areas. This is in line with thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) of graphite oxide showing that decomposition of the oxygen-containing groups in graphite oxide occurs between 200 and 300 °C.[26,29,76,77] Exfoliation was further reported in atmospheres other than air, for instance in argon at 275–295 °C (ref. 78) and in hydrogen at 200 °C.[79] The latter yielded a specific surface area of 442 m^2 g^{-1}, close to the value reported for exfoliation in air.

Vacuum was used with the intent of further enhancing exfoliation yields of graphite oxide at a temperature of 200 °C.[77] A pressure of <1 Pa surrounding the graphite oxide particles increased the net repulsive forces between the layers due to the release of functional groups. The schematics of the mechanism are shown in Fig. 3. Statistical analysis revealed that over 60% of the sheets were single layers. An even lower temperature of 135 °C in a vacuum oven was shown to produce graphene with a high specific surface area of 759 m^2 g^{-1}.[80]

3.2 Thermal exfoliation of graphite compounds

Direct thermal exfoliation of graphite typically involves expanded graphite (EG) or graphite intercalation compounds (GICs) as starting materials. These compounds have less functionalization than graphite oxide, which usually features a carbon to oxygen ratio of 2 : 1, yet they still have enough functionalization and/or expanded interlayer distance for successful thermal exfoliation. In the following, we review typical approaches to exfoliate these graphitic compounds, including techniques common to both graphite and graphite oxide.

3.2.1 Rapid heating methods. Li *et al.*[81] reported exfoliation of expandable graphite by a rapid heating to 1000 °C in forming
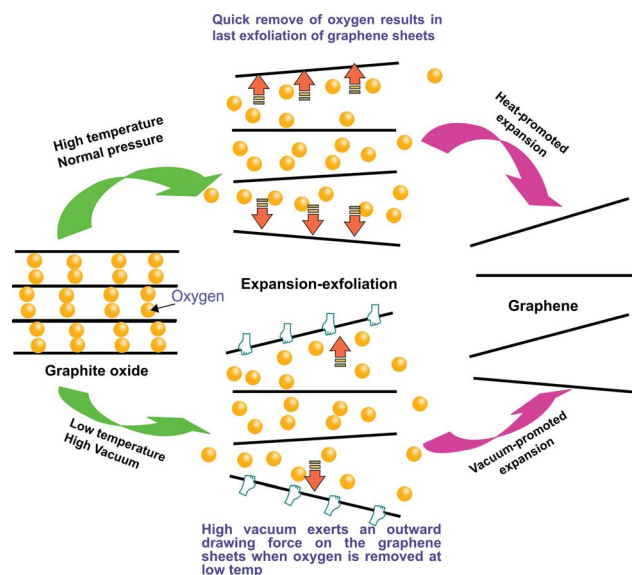

Fig. 3 Schematics showing exfoliation of graphite oxide in high temperature under atmospheric pressure (top) and in low-temperature (as low as 200 °C) under high vacuum (bottom). Reprinted with permission from ref. 77. Copyright (2009) American Chemical Society.

gas (3% hydrogen in argon). Single and few-layer graphene in ribbon and sheet form was found in suspension after dispersion and centrifugation. However, the yield was low; only 0.5% of the starting material had remained in the resulting supernatant. The authors believe that the rapid heating step, which causes violent formation of gas from the intercalant, is critical and responsible for the formation of the monolayer and few-layer graphene. The produced graphene ribbons are semiconductors with band gaps of varying size.

To improve the yield, a process combining thermal exfoliation and intercalation of graphite was described by Li *et al.*[82] The expandable graphite was first exfoliated by rapid heating. However, most of the exfoliated graphite was still in multilayer form. The exfoliated graphite was then intercalated with oleum (fuming sulphuric acid) and inserted by tetrabutylammonium hydroxide (TBA) in DMF, which further expanded the distance between adjacent graphite layers as shown in Fig. 4a. After sonication in the presence of a surfactant, a homogeneous suspension of graphene with around 90% monolayers was formed. Compared to graphene obtained from exfoliating graphite oxide, the graphene sheets from this expandable graphite are of high quality without significant defects (Fig. 4b and c).

Gu *et al.*[65] described a 900 °C rapid heating exfoliation of GICs made from natural graphite by intercalation with concentrated sulphuric acid and hydrogen peroxide. However, the obtained graphene sheets contained multiple graphitic layers, thus a re-exfoliation process of graphite was proposed.[83] The expanded graphite obtained after thermal expansion was re-intercalated and re-exfoliated under the same conditions, followed by ultrasonication and centrifugation, as shown in Fig. 5a. It was estimated that the number fraction of single layer graphene was above 50% with an overall yield of around 4–5 wt%. Graphene sheets made from these methods are of high
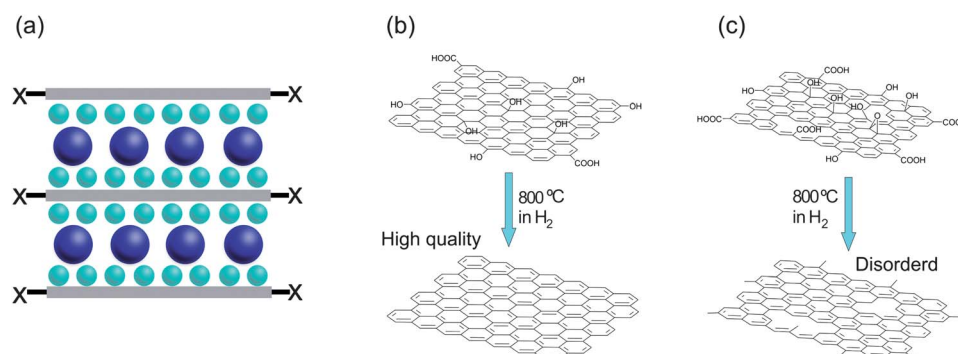
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Fig. 4 (a) Schematics of graphite exfoliation after reintercalation with sulphuric acid molecules (teal spheres) and insertion of tetrabutylammonium hydroxide (blue spheres). (b) and (c) Structures of graphene sheets after thermal exfoliation of expanded graphite (b) and graphite oxide (c). Reprinted with permission from Macmillan Publishers Ltd: [Nature Nanotechnology] ref. 82. Copyright (2008).

order and free of defects, as demonstrated by Raman spectroscopy (Fig. 5b).[65]

Thermal expansion of GICs using an inductively coupled thermal plasma (thermal ICP) was reported by Choi *et al.*[84] Thermal ICP was able to heat the GIC particles to >5000 K over a millisecond time period and rapidly vaporize the intercalated species. Acoustic cavitation was then used to produce graphene sheets with a low degree of defects (Fig. 6c). The conductivities ranged from 6.6×10^3 S m^{-1} to 8×10^3 S m^{-1}. A survey of particles by Raman spectroscopy revealed that 12% of the sheets were monolayers.

3.2.2 Microwave irradiation and solvothermal exfoliation. Microwaves were successfully used to exfoliate several different precursors in liquid or gas environments. Janowska *et al.*[85] reported exfoliation of EG in an aqueous ammonia solution under microwave irradiation in the temperature range 120–200 °C. The graphene sheets produced were less than 10 layers thick with a yield of around 8 wt%. The authors proposed that the excellent wetting behaviour of the ammonia solution on graphite facilitated its infiltration of graphite, resulting in exfoliation. The spontaneous decomposition of the ammonia solution (NH_4OH) to gaseous NH_3 and H_2O by microwave radiation also contributed to the exfoliation process. Simple microwave irradiation was also used to exfoliate EG;[86,87] after ultrasonication in a

solvent for better dispersion, graphene concentrations of 2.8–3.9 wt% were achieved.[87]

Qian *et al.*[88] reported solvothermal exfoliation of expanded graphite using the highly polar solvent acetonitrile (ACN). After centrifugation, the yield of monolayer and bilayer graphene (thickness: 0.5–1.2 nm) was as high as 10–12 wt%.

Direct exfoliation of pristine graphite into graphene was demonstrated by solvothermal treatment in NMP.[89] As shown in Fig. 7, the obtained graphene retains its unique intrinsic properties; no stabilizer or impurity was introduced during the process. The authors proposed that the solvothermal treatment increased the internal pressure and temperature, reducing the free energy of mixing. Both the high temperature and pressure promoted the intercalation of the graphitic layers by solvent molecules and weakened the layer interaction, facilitating exfoliation. However, the report did not provide information on the yield or the degree of the exfoliation.

A significant variation was developed with a solvothermal process using oleyl amine as a solvent and intercalating reagent for exfoliation of EG.[90] After dispersion and centrifugation, a high yield of 60% monolayer sheets was achieved, with surface areas of individual graphene sheets as high as 300 μm^2. The authors attributed the successful exfoliation to the ionic interactions between oleyl amine and the strong acids between graphitic layers, which prompted the intercalation of oleyl amine
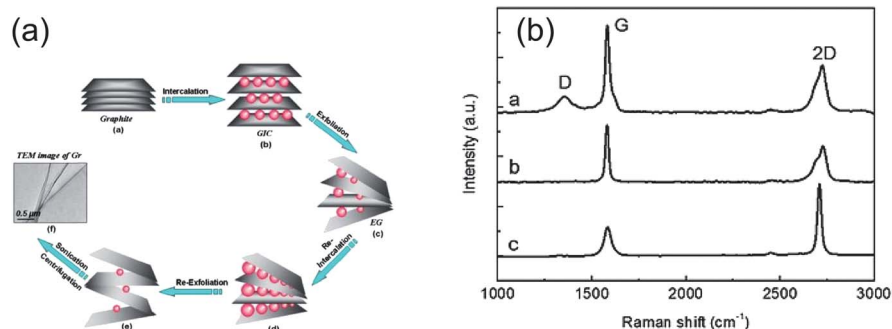

Fig. 5 (a) Schematic of the re-intercalation and re-exfoliation steps in the synthesis of graphene sheets. Reprinted with permission from ref. 83. Copyright (2011) Elsevier. (b) Raman spectra of the starting material GICs (curve a), thermal exfoliated graphite (curve b) and graphene after dispersion (curve c). Reproduced from ref. 65.
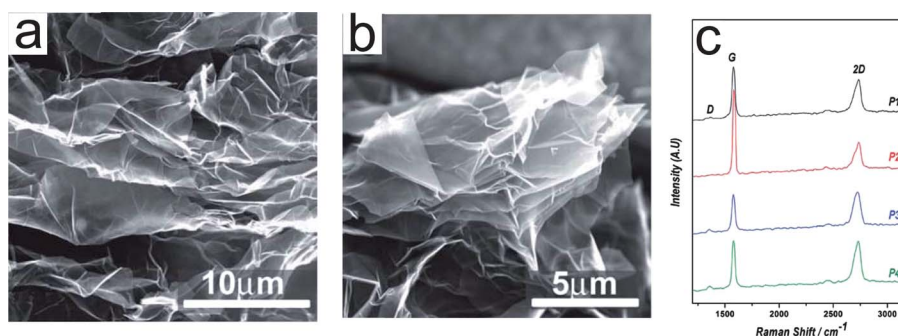
Fig. 6 (a) and (b) SEM images of expanded graphite after thermal ICP treatment. (c) Raman spectra of four graphene sheets after deposition on a Si wafer. Reproduced from ref. 84.
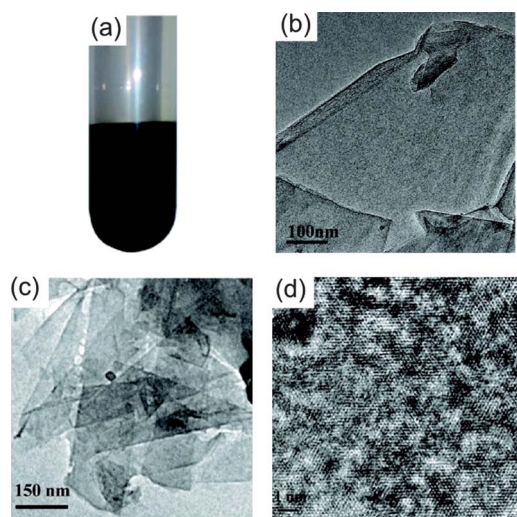

Fig. 7 (a) Optical image showing a dark suspension of graphene in NMP after thermal treatment. (b) TEM image of a piece of graphene monolayer. (c) TEM image of multilayer graphene flakes. (d) HRTEM image of a graphene monolayer with atomic resolution. Reprinted with permission from ref. 89. Copyright (2010) American Chemical Society.

molecules into expanded graphite. The high temperature and pressure induced by solvothermal treatment may have facilitated the exfoliation.

3.3 Thermal exfoliation summary

Thermal exfoliation has proven to be a very efficient method for the preparation of graphene. Although the sheets produced by thermal exfoliation of graphite oxide exhibit a wrinkled and defective structure, this process allows recovering some of the electrical conductivity lost by oxidation. Various heating sources, temperatures and assistive strategies have been employed, leading to great variance in the degree of exfoliation between methods. Both high temperature exfoliation of graphite oxide based on rapid heating in a furnace[16] and low temperature exfoliation under vacuum[90] have so far yielded the highest surface areas of all methods. The exfoliation of expanded graphite and graphite intercalation compounds, which yielded high quality graphene sheets with ordered and defect free structures, is very promising. Intercalation techniques have been widely combined with thermal treatments and have proven effective in increasing exfoliation yields.

4 Other methods

In addition to the relatively well-developed thermal and mechanical methods described in the sections above, several new and promising exfoliation methods have emerged. Although less extensively studied, these techniques show promise.

4.1 Electrochemical exfoliation

When a voltage is applied to graphite rods serving as electrodes in a conductive solution, the rods may corrode and yield graphene nanosheets functionalized by the solvent. This presents a new method for exfoliating and functionalizing graphene with different functional groups, while potentially lessening the number of lattice defects introduced by common oxidation methods like the Hummers method. The first electrochemical exfoliation functionalized graphene with ionic liquids such as methyl imidazolium hexafluorophosphate.[91] When a static potential was applied, the anode corroded, yielding imidazolium-functionalized flakes that were easily dispersed in organic solvents (but not in water) *via* sonication. The flakes were not analyzed before sonication, but those obtained after sonication were 1.1 nm thick on average, likely representing monolayers with the extra thickness being added by functionalization. Importantly, imidazolium functionalization is expected to reduce the electrical conductivity of graphene less than the addition of oxide groups. This was partially demonstrated by the improved conductivity of polystyrene nanocomposites made with imidazolium-functionalized graphene.

The electrochemical method was more thoroughly investigated by mixing different amounts of water with water-miscible ionic
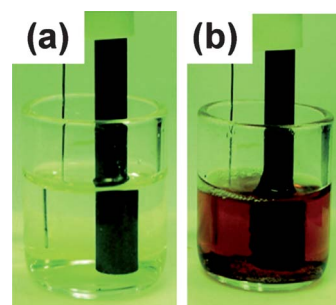

Fig. 8 A voltage applied across graphite rods in a conductive solvent can lead to exfoliation with functionalization. Reprinted with permission from ref. 92. Copyright (2009) American Chemical Society.

liquids (Fig. 8).[92] When a voltage was applied to a solution with <10% water content, ionic liquid-functionalized graphene sheets were generated as seen in previous work. When the voltage was applied to a solution with >10% water content, however, a variety of oxidized graphene products were produced, including 8–10 nm thick nanosheets, graphene nanoribbons, and graphene nanosheets. The researchers proposed that in this case water was oxidized at the anode, generating hydroxyl and oxygen radicals that attacked the edges of individual sheets. The attached radicals opened the sheets enough for the ionic liquid to intercalate, which depolarized and expanded the anode to begin corrosion.

When sulfuric acid was used as an electrolyte in place of ionic liquids, graphene nanosheets with large lateral size, ranging from several micrometers to tens of micrometers, were produced.[93] KOH was added to sulfuric acid to reduce the acidity and minimize, though not eliminate, oxidation. All sheets were thinner than 3 nm, and more than 65% of the sheets were thinner than 2 nm. Over 60% of the sheets were bilayers with AB stacking, and though oxidized, they were found to have significantly higher electron mobility than most reduced graphene oxide. The total yield of the graphene thin sheets was found to be 5–8 wt%.

Overall, electrochemical exfoliation represents a new and promising method of graphite exfoliation. It can be implemented quickly, in some cases within one hour, and has been tuned to yield graphene sheets of different sizes that are functionalized with different chemistries.

4.2 Thermal quenching of graphite

Thermal stress from rapid temperature changes has been proposed as another mechanism to separate layers in graphite. The first attempt at this technique involved quenching hot, highly oriented pyrolytic graphite (HOPG) in an aqueous ammonium hydrogen carbonate solution.[94] The HOPG was bent to introduce cracks and rapidly heated to 1000 °C, then quickly quenched to room temperature in a bath of cool water containing 1.0 wt% ammonium hydrogen carbonate, which was found to be significantly more effective than quenching in pure water. The process yielded sheets with thicknesses between 0.4 and 2 nm and diameters in the range 1–80 μm. The total yield and the distribution of sheet sizes were not reported. The use of more loosely packed, expanded graphite (EG) as a starting material improved upon the technique,[95] leading to a 15 wt% yield of nanosheets less than 5 layers thick after one round of quenching and an 80 wt% yield of such sheets after 5 sequential rounds of quenching, with 10% of this product consisting of monolayers. Lateral sizes were on the order of 5–10 μm; quenching in pure water was significantly less effective than in ammonia or hydrazine hydrate solutions.

Thermal stress has also been used to exfoliate synthesized graphite products.[96] Microwave synthesis was used to carbonize metal phthalocyanine compounds at 450 °C, producing synthetic stacked graphite structures. The stacks were then exfoliated by rapid cooling to 28 °C, 4 °C, and −105 °C. Cooling to 28 °C and 4 °C led to end products with 8 and 4 layers of thickness, respectively; cooling to −105 °C led to a monolayer yield as high as 60%; as many as 90% of the particles were single or double layers of pure graphene. This temperature dependence shows

great promise for producing large amounts of monolayer graphene.

4.3 Supercritical fluid exfoliation

A final method of separating graphite layers is to intercalate them with a supercritical fluid, which is expanded to push the graphene layers apart. This technique is potentially very fast, and has yielded pristine graphene nanosheets. The first supercritical exfoliation of intercalated graphite using CO yielded sheets of a few micrometers in diameter, but the smallest sheet thickness was 3.8 nm, corresponding to about 10 layers.[97] Much better results were achieved in a later study using DMF, NMP, and ethanol instead of CO in combination with a brief initial sonication of the materials.[98] All three solvents led to well-dispersed solutions at 2–4 mg mL^{-1}, where all sheets had less than 10 layers, including 10% monolayers. Subsequent efforts improved this method using 1-pyrene sulfonic acid sodium salt (1-PSA) surfactants during expansion, improving the percentage of monolayers from 10% to 60%.[98] Given the significant number of pristine monolayers attained and the ease of processing, these supercritical fluid techniques are very promising.

5 Conclusions

Bulk exfoliation of graphite is of great importance, as many applications rely on large scale production of exfoliated materials with controlled properties. Mechanical and thermal exfoliation of graphite oxide and graphite are established as the two major techniques. Substantial effort has been made to improve the yield and degree of exfoliation, but the yield of monolayer graphene is still quite low; in many cases centrifugation is thus used to remove unexfoliated material. Exfoliation methods with higher yields are still of critical interest.

Furthermore, once graphene sheets are exfoliated in solvents, they tend to aggregate due to van der Waals attraction, which compromises the efforts made during exfoliation. A better understanding of colloidal suspensions of graphene will promote the exfoliation of graphene in solvents and achieve suspensions with higher concentrations.

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