

Liquid-phase Exfoliation of Graphite to Produce High-quality Graphene

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Abstract: Graphene has attracted intense interest due to its exceptional physical and chemical properties as well as its wide potential applications. For applications of two-dimensional graphene, commercially viable sources are necessary. Liquid-phase exfoliation of graphite is one of the most promising economical methods for the mass production of graphene. A number of methods have been developed to achieve exfoliation of graphite, each with advantages and disadvantages. Here, we present a brief overview of the main developments in this research area over the last few years. Particularly, we present and discuss the current status of liquid-phase exfoliation of graphene from pristine graphite, highlighting some of the obstacles that have been encountered along the way and the approaches proposed to overcome them.

Keywords: Liquid-phase exfoliation, Solvents assisted exfoliation, Surfactant assisted exfoliation, Graphene

INTRODUCTION

Following the astonishing discoveries of fullerenes and carbon nanotubes in earlier decades, the rise of graphene has recently triggered an exciting new area in the field of carbon nanoscience. Graphene, a one-atom thick two-dimensional molecule, can be formally considered as the most basic building block of all sp^2 carbon allotropes [Hu et al., 2010]. Graphene, with outstanding physical properties [Balandin et al., 2008, Lee et al., 2008, Novoselov et al., 2004] and enormous potential in practical uses [Allen et al., 2010, Geim et al., 2007, Rao et al., 2009], has become one of the most attractive nanomaterials.

The availability of graphene has been the prerequisites for its practical uses. Until now, several widely used methods of preparing graphene have been developed since graphene was first isolated by Novoselov and Geim using Scotch tape in 2004 [Novoselov et al., 2004]. Such as epitaxial growth of SiC [Robinson et al., 2010], chemical vapor deposition (CVD) [Li et al., 2009] and liquid-phase exfoliation (LPE) [Coleman et al., 2009, Hernandez et al., 2008, Lotya et al., 2010], and so on.

Extremely direct LPE of pristine graphite in solvents or surfactant solutions to give dispersed graphene, have attracted more attention in recent years [Buzaglo et al., 2013, Coleman et al., 2013, Chang et al., 2015, Lotya et al., 2009, Zhu et al., 2013]. These methods are cost-efficient, using inexpensive graphite, and potentially up-scalable to produce graphene free of defect or oxidation that other methods suffer. Dispersed graphene can be deposited on different substrates not available using CVD and epitaxial growth methods.

This review will summarize the recent progress in the LPE of pristine graphite in solvents or surfactant solutions. We will first describe the LPE mechanisms for pristine graphite. Then we describe a variety of successful LPE methods that we categorize into three major classes: organic solvents assisted exfoliation, surfactant assisted exfoliation and other exfoliation methods, presented in Sections 3, 4, and 5, respectively.

LIQUID-PHASE EXFOLIATION MECHANISMS

Graphite can be exfoliated in solvents or surfactant solutions by exploiting ultrasound to extract individual layers. For successful exfoliation, overcoming the van der Waals attractions between the adjacent layers of graphite is necessary.

One straightforward method 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. The matching of graphene and solvent surface energies is one criterion for a successful exfoliation process. Coleman and coworkers showed that the key parameter for suitable solvents is that the solvent-graphene interactions must be at least comparable to those existing between the stacked graphenes in graphite [Hernandez et al., 2008]. Based on this criterion, good solvents are characterized by surface tension in the region of 40-50 mJ/m².

Another way to reduce the strength of the van der Waals attractions is ultrasonication. During ultrasonication, shear forces and cavitation, i.e. the growth and collapse of the micrometer-sized bubbles or voids in liquids due to pressure fluctuations, act on the bulk material and induce exfoliation. In addition, surfactants by attached to the graphite layers induce

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repulsive electric double layers, can be helpful in achieving stable graphene dispersions in solvents [Coleman et al.,2009, Jin et al.,2009, Lotya et al.,2009].

ORGANIC SOLVENTS ASSISTED EXFOLIATION

The successful exfoliation relies on the proper choice of special solvents. The first successful LPE of graphite was achieved in the organic solvent NMP [Hernandez et al.,2008]. Graphene can be dispersed at concentrations of up to 0.01 mg/mL, and the monolayer yield was around 1 wt%, which could be improved to 7-12 wt% with further processing.

Some improvement was achieved through the use of different solvents. Another successful example of direct LPE of graphite by using perfluorinated aromatic solvents, such as pentafluorobenzonitrile, which is beneficial from the charge transfer through π - π stacking from the electron-rich graphene sheets to the electron-deficient aromatic molecules containing strong electron-drawing fluorine atoms [Bourlinos et al.,2009]. In a series of perfluorinated aromatic solvents, the concentrations of graphene dispersions ranged between 0.05 and 0.1 mg/mL. AFM analysis of average flake thickness was estimated to range between 0.6 and 2.0 nm, suggesting the existence of a few-layer thick graphene nanosheets.

In addition to the solvents discussed above ionic liquids (ILs) are another promising candidate. ILs often have surface energies close to that of graphene, which is the key prerequisite of solvents for direct exfoliation of graphite. The first ionic liquid used for this purpose was 1-butyl-3-methyl-imidazolium bis (trifluoro-methane-sulfonyl)imide. The concentration was at 0.95mg/mL with only one hour of tip sonication and the majority of graphene nanosheets were less than 5 atomic layers thick [Wang et al.,2010]. Noteworthy, in 2011 Mariani and co-workers [Nuvoli et al.,2011] suggested that graphene could be obtained by LPE of graphite powder in 1-hexyl-3-methyl-imidazolium hexafluorophosphate. The graphene concentration was estimated as being as high as 5.33 mg/mL. Quantitative analysis of the resulting nanosheets was again brief, noting only the presence of some nanosheets as wide as 4 μ m, with an average thickness of 2 nm, corresponding to 6-7 atomic layers. By considering 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 [Cai et al.,2012].

Alternatively, these solvents discussed above tend to have high boiling points (NMP 203 °C), making it difficult to remove solvents when processing graphene into films or composites [Hernandez et al.,2008]. Thus, dispersion of graphene in low boiling solvents is preferable. Several attempts of producing graphene by LPE in low boiling solvents have been reported. For example, Coleman and coworkers demonstrated the exfoliation of graphene at relatively high concentration in low boiling point solvents such as chloroform and isopropanol [Arlene et al.,2011]. It

is possible to achieve concentrations of up to 0.5 mg/mL. Feringa and co-workers reported that dispersion of graphene could be obtained in ethanol using solvent exchange from NMP, which enables broader application of dispersed graphene [Zhang et al.,2010].

Although advances in producing graphene by LPE from graphite have been rapid, a number of outstanding problems remain. Of these, probably the most important is the relatively low concentration of dispersed graphene that can be achieved. As such, to improve the yields of exfoliated graphene, exfoliation in mixed solvents has also been developed.

Hitherto several attempts of producing graphene by LPE in mixed solvents have been reported. For example, In 2014 Xu et al. reported the graphene concentration of the dispersion is as high as 0.15 mg/mL by LPE of graphite in NMP with addition of naphthalene (after sonication for 90 min) [Xu et al.,2014]. Naphthalene serves as a "molecular wedge" to intercalate into the edge of graphite, which plays a key role during sonication and significantly improves the production yield of graphene. In addition, Wang et al. reported the yield concentration was significantly increased with addition of NaOH [Liu et al.,2011]. Especially for the case of cyclohexanone, NaOH improves the yield concentration more than 20 times. They suggested that this improvement was due to NaOH intercalation into graphite, the resultant expansion of the interplanar spaces of the adjacent graphite layers, and thus their easier exfoliation. Furthermore, this finding may suggest a new method to preparing graphite intercalation compounds containing alkali hydroxide.

Jiang and co-workers reported that certain ordinary organic salts, such as edetate disodium, sodium tartrate, potassium sodium tartrate and sodium citrate were found to have universal and efficient assistant effect for LPE of graphite in common organic solvents to produce pristine graphene [Du et al.,2013]. These organic salts can markedly improve exfoliation efficiencies and high-concentration graphene dispersions close to 1mg/mL were easily obtained only after 2h short-time mild sonication. Experiments show that DMSO can be a better alternative as exfoliation medium than NMP and DMF in the presence of some common organic salts. Up to 123 times enhanced exfoliation efficiency was observed when sodium citrate was introduced into an exfoliation system consisting of natural graphite powder and dimethyl sulfoxide. TEM, AFM, et al. analysis showed graphite was successfully exfoliated into single or few-layer graphene nanosheets which were free of defects and oxides. DMSO is much cheaper than NMP, which is beneficial for large-scale production of pristine graphene.

Many studies have shown that the yields of exfoliated graphene increases with long-time sonication. A low-power bath sonicator was used to LPE graphite powder in DMF for up to 150 hours, yielding concentrations that were stable at 1mg/mL.

A similar procedure was applied in NMP, using 460 hours [Khan et al.,2010], yielding concentrations that were stable at 1.2mg/mL. Extremely high concentrations from 2 to 63mg/mL of graphene dispersions were achieved by redispersing dried exfoliated few-layer graphene[Khan et al.,2011]. These results demonstrate a clear advantage of long sonication times in low power bath sonicators. Such a time consuming approach requires high energy; in addition, with the increasing sonication time, the size of the flakes is severely reduced [Henrich et al.,2007], being a critical parameter for several applications. As such the time- and energy-consuming process would be unfavorable in practice.

SURFACTANT ASSISTED EXFOLIATION

Sonication provides high energy activation to overcome interlayer adhesion. Diffusion of surfactants to the newly exposed interfaces is needed to stabilize the exfoliation process against re-aggregation or flocculation. As such, the use of surfactants can promote the exfoliation of graphite into graphene. Dispersion of graphene in Water by using surfactants which opens perspective for the formation of biocompatible graphene based materials for biomedical applications. Practical results have been achieved by using various types of surfactants to exfoliate graphene by LPE in water.

Coleman and co-workers reported the first LPE of graphite in aqueous surfactant solutions by using the surfactant sodium dodecyl benzene sulfonate (SDBS) and provided very good physical characterizations of the dispersed materials [Lotya et al.,2009]. Statistical Raman analysis revealed a reasonable population of few-layer graphene, e.g. ~43% of flakes had ~5 layers. More importantly, ~3% of the flakes were found to be monolayer thick. Even more importantly, the sediment remaining after centrifugation can be recycled to improve the overall yield of graphene exfoliation. Recycling the sediment results in narrowing of the flake thickness distribution, shifting it toward thinner flakes with large quantities of bilayers and trilayers, 67% of flakes observed had 05 layers. However, the concentration was relatively low, typically <0.01 mg/mL.

In a continuation study [Lotya et al.,2010], in combination with low power sonication, LPE was improved to produce graphene dispersions at concentrations up to 0.3~0.52 and 2.58mg/mL by using the different surfactants sodium cholate and sodium deoxycholate respectively [Ramalingam et al.,2013]. Another extremely high concentrations (up to 7.1mg/mL) of stable aqueous dispersions of pristine graphene was achieved by by LPE using the very different surfactant sodium taurodeoxycholate under tip sonication [Sun et al.,2012]. TEM showed that about 8% of the graphene flakes consisted of monolayers and 82% of the flakes consisted of less than five layers. Noteworthy, at ambient temperature, the dispersions concentration could be significantly improved to about 12mg/mL by vacuum-

evaporation. As such, the method extends the scope for scalable liquid-phase processing of graphene for a wide range of applications.

Another effective LPE for the preparation of graphene by using the triblock copolymer Pluronic P-123 in aqueous solutions was reported by Guardia and co-workers [Guardia et al.,2011]. The best dispersions concentration could be as high as 1mg/mL with two hours of sonication. The same as exfoliation in organic solvents, the yields dispersions concentration in aqueous increases to 1.5mg/mL with an increase in sonication time to five hours. AFM evidence showd that almost all sheets were less than 5layers thick, with 10-15% monolayers, consistent with other investigations of surfactant-assisted LPE.

OTHER EXFOLIATION METHODS

Apart from above the relatively well-developed methods, several new and promising direct exfoliation of graphite in liquid phase methods have emerged.

Self-exfoliation in liquid phase. Graphene can also be selfexfoliated by induced strong repulsions between the interlayers.For example, Behabtu et al. demonstrated that graphite could be spontaneously exfoliated into single-layer graphene in chlorosulfonic acid, and dissolved at isotropic concentrations as high as 2mg/mL [Behabtu et al.,2010].

Supercritical fluid exfoliation. A supercritical CO₂ processing technique was reported for intercalating and exfoliating layered graphite to graphene. But AFM shows that the typical graphene sheet contains about 10 atomic layers [Pu et al.,2009]. Some improvement was achieved through the use of different supercritical fluids, with solubilities as high as 2-4 mg/mL obtained with DMF, NMP, and ethanol. In addition, about 90-95% of the exfoliated sheets are <8layers with approximately 6-10% monolayers [Rangappa et al.,2011].

CONCLUSION

Liquid-phase exfoliation of graphite is a potentially up-scalable method to scale up the production of graphene. Organic solvents assisted exfoliation and surfactant assisted exfoliation rely on using well-chosen solvents or surfactants to exfoliate and disperse graphene. Substantial effort has been made to improve the yield and degree of exfoliation, but the yield of single-layer graphene is still relatively low. As such developing more effective exfoliation systems or new methods to prepare high quality graphene more effectively are still of critical interest.

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