

Exfoliation of graphene via wet chemical routes



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ABSTRACT

Graphene is a two-dimensional material that has fascinating electrical and optical properties, and this material has provided chemists with great possibilities and challenges. Interests in graphene's exceptional physical and chemical properties and in its potential for applications have generated thousands of publications and have accelerated the pace of graphene research. Although considerable scientific progress has been achieved, the key to commercializing graphene lies in the cost-effective and scalable production of this material. Graphene can be produced using a variety of wet chemical methods, such as chemical oxidation followed by exfoliation, liquid-phase and electrochemical assisted exfoliation etc. from inexpensive and abundant sources such as graphite. This review article summarizes the recent progress toward the preparation of graphene through wet chemical routes and discusses their remaining challenges. In particular, the quality and yield of graphene sheets produced using these exfoliation protocols will be emphasized.

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1. Introduction

Graphene is an atomically thin layer of sp^2 -hybridized carbon atoms arranged in a honeycomb lattice, and it exhibits remarkable electronic, thermal and mechanical properties [1–3]. Over the past decade, graphene has emerged as an exciting new material with the potential to impact many areas of science and technology. In fact, the research in this field started in the 1840s, when the intercalation compounds of graphite were first reported [4]. However, the observation of graphitic carbon monolayers by scientists dates back to the 1960s, when SiC was heated to 2150 °C [5]. The exfoliation of graphite into individual graphene sheets remained out of reach until 2004, when the isolation of graphene using a simple scotch tape method was reported [6,7]. The isolated graphene was found to exhibit a high charge carrier mobility ($2 \times 10^5 \text{ cm}^2/\text{Vs}$) [8], high thermal conductivity ($\sim 5000 \text{ W/mK}$) [9], exceptional Young's modulus ($\sim 1.0 \text{ TPa}$) [10] and large theoretical specific surface area ($2630 \text{ m}^2/\text{g}$) [11]. Moreover, a single graphene layer absorbs only 2.3% of incident light and therefore has a transparency of 97.7% [12]. The combination of high electrical conductivity, chemical and thermal stability, and excellent stretchability provides

considerable advantages for the use of graphene in electronic devices such as solar cells [13], organic light-emitting diodes [14], field-effect transistors [15,16], photodetectors [17,18], and touch screens [19]. Moreover, graphene has also been demonstrated to be a promising electrode material for fuel cells [20,21], supercapacitors [22–24] and lithium-ion batteries [25] because of its excellent electrical conductivity and high surface area.

Pristine graphene can be obtained through micromechanical cleavage [6]. Unfortunately, this method only yields an extremely small amount of sample, which is only useful for fundamental research. Chemical vapor deposition (CVD) [26] can produce graphene over a large area and with a relatively small number of defects, making this protocol promising for electronic device applications that utilize the high transparency and high electrical conductivity of graphene. Nevertheless, this metallic surface-mediated method cannot be readily scaled up for the bulk production of graphene for applications. Considering the natural abundance of graphite flakes, the wet chemical approaches for graphite exfoliation may be feasible for the large-scale production of graphene. Moreover, the wet chemical methods are also versatile in terms of covalent and non-covalent functionalization, which can generate a variety of graphene and graphene-based materials.

This review article will discuss the bulk production of graphene via wet chemical exfoliation methods which typically involve the processes of chemical reaction, electrochemical reaction or solvent/surfactant assisted functionalization and exfoliation in the

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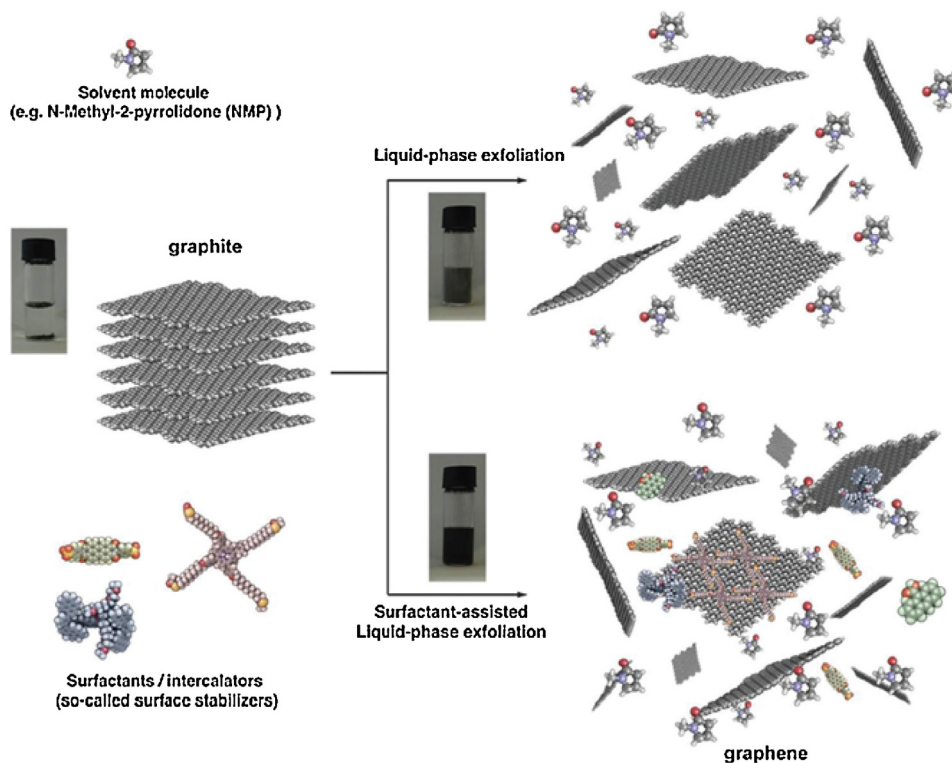


Fig. 1. Schematic representation of the liquid-phase exfoliation (LPE) process of graphite in the absence (top-right) and presence (bottom-right) of surfactant molecules. Reproduced from Ref. [43] with permission from the Royal Chemical Society.

solutions, with the major focus on the exfoliation protocols, yields and quality of graphene sheets. Some of the recent developments on the well-known graphite exfoliation processes, namely, liquid-phase exfoliation, reduction of graphite oxide and electrochemical exfoliation techniques, as well as their challenges will be discussed in detail. The dry chemical exfoliation methods from graphite, like ball-milling assisted by chemical functionalization [27] will not be discussed due to the low efficiency and/or scalability compared to the wet chemical exfoliation methods.

2. Liquid-phase exfoliation (LPE)

Liquid-phase exfoliation (LPE) typically involves a dispersion of graphite in a solvent mediated by an exfoliation process to extract individual layers (Fig. 1) [28–30]. The successful exfoliation of graphene layers requires overcoming the van der Waals forces between the adjacent layers. One of the most effective and straightforward methods for reducing the strength of the van der Waals forces is to immerse graphite into a liquid medium, where the potential energy between adjacent layers receives contributions from dispersive London interactions, which in the presence of a solvent are significantly lower than that in vacuum. The surface energy of graphene has been estimated to be 46.7 mN/m [31]. Therefore, solvents with a surface tension of ~ 40 mN/m, such as N-methylpyrrolidone (NMP, 40 mN/m), N,N'-dimethylformamide (DMF, 37.1 mN/m), γ -butyrolactone (GBL, 35.4 mN/m), and *ortho*-dichlorobenzene (*o*-DCB, 37 mN/m), are the best media for the exfoliation of graphite because they minimize the interfacial tension between the solvent and the graphene layer. The first successful LPE of graphite was achieved in NMP [28]. The obtained graphene sheets are considered to be pristine graphene because no chemical functionalization is involved. After centrifuging to remove the unexfoliated bulk material, the remaining samples consist of 28% monolayer graphene. A thin film fabricated from LPE graphene presents a conductivity value of ~ 6500 S/m.

Unfortunately, the overall yield of monolayer graphene is very low, approximately 1 wt% with a concentration of 0.01 mg/mL. Further optimization of the solvents led to some improvements in the dispersibility of graphene. For instance, concentrations as high as 0.03 mg/mL, 0.1 mg/mL and 0.5 mg/mL were achieved using *o*-DCB [32] and perfluorinated aromatic solvents such as pentafluorobenzonitrile [33] and benzylamine [34], respectively. However, due to the long ultrasonication process, the lateral dimension of LPE graphene is relatively small (< 3 μm). Nevertheless, despite the low yield and small flake size, LPE graphene is of high quality, and the field-effect mobility measured for an ink-jet-printed graphene film was reported to be as high as 95 cm^2/Vs [35].

Several attempts have been made to increase the concentration and the yield of LPE graphene by functionalization with small organic molecules during the exfoliation process. For example, large graphene flakes can be produced by the addition of *N*-2-mercapto-propionyl glycine (tiopronin) during the exfoliation of graphite in DMF [36]. It is hypothesized that ultrasonication in organic solvents generates free radicals, such as peroxy radicals. These radical species are strong enough to oxidize graphene sheets, initially at the edges and inner defects, thereby cutting the graphene into small pieces. The addition of tiopronin during the LPE process can inhibit reactions promoted by oxygen, peroxides and radicals, thereby preventing the graphene sheets from breaking into small pieces to some extent. As-prepared LPE graphene yielded a concentration of 0.027 mg/mL, with the majority of the graphene sheets in the size range of 2–5 μm . In another attempt, LPE graphene in chloroform was covalently functionalized with 4-*tert*-butylphenyldiazonium tetrafluoroborate (BPD) [37]. As a result, concentrations of 1.2 $\mu\text{g}/\text{mL}$ for medium BPD-functionalized and 27 $\mu\text{g}/\text{mL}$ for highly BPD-functionalized graphene were obtained. The intact graphene layers could be fully restored by thermal treatment of the functionalized graphene material. Recently, Samori and co-workers reported that simple alkane molecules, such as

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