



Regular Article

Direct exfoliation of graphite in water with addition of ammonia solution



Han Ma^{a,b}, Zhigang Shen^{a,b,*}, Min Yi^c, Shuang Ben^d, Shuaishuai Liang^e, Lei Liu^b, Yixiang Zhang^b, Xiaojing Zhang^b, Shulin Ma^b

^aSchool of Materials Science and Engineering, Beihang University, Beijing 100191, China

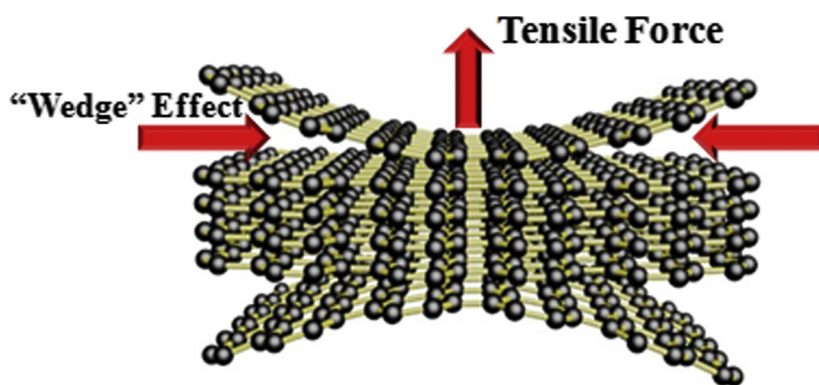
^bBeijing Key Laboratory for Powder Technology Research and Development, Beihang University, Beijing 100191, China

^cInstitute of Materials Science, Technische Universität Darmstadt, Darmstadt 64287, Germany

^dSchool of Chemistry and Environment, Beihang University, Beijing 100191, China

^eState Key Laboratory of Tribology, Tsinghua University, Beijing 100084, China

GRAPHICAL ABSTRACT



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ABSTRACT

To bring graphene closer to its real-world applications, finding a green, low-cost, environment-friendly and less toxic solvent for production of high-quality graphene is highly demanded. However, water, the most widely used green solvent, is generally considered to be a poor solvent for hydrophobic graphene. In this study, we exfoliate graphene nanosheets directly in basic water without surfactants, polymers or organic solvents. The addition of a small amount of ammonia solution achieves the exfoliation of few-layer graphene nanosheets from pristine graphite. Diverse characterization methods are employed to investigate the morphology and quality of as-prepared graphene sheets. The release of gaseous ammonia plays the key role in exfoliation of graphene. The concentration of stable graphene dispersions can reach 0.058 mg/mL.

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* Corresponding author at: School of Materials Science and Engineering, Beihang University, Beijing 100191, China.

E-mail addresses: hawkinsma1218@gmail.com (H. Ma), shenzhg@buaa.edu.cn (Z. Shen), minyibhu@gmail.com (M. Yi), 347872954@qq.com (S. Ben), doubleleung@sina.com (S. Liang), liulei0111@qq.com (L. Liu), buaazyx@hotmail.com (Y. Zhang), zhangxiaojing@buaa.edu.cn (X. Zhang), mshl@buaa.edu.cn (S. Ma).

1. Introduction

Graphene, one kind of two-dimensional nanomaterial, has attracted much attention in a series of application fields. Constituted by the honeycomb C–C network, graphene possesses extraordinary mechanical [1], electronic [2], thermal [3] and optical properties [4], and thus holds great promise in a wide range of applications including energy storage [5], composite [6] and catalysis [7]. However, despite its huge potential and bright prospects, the scalable production of graphene remains a huge challenge.

The common methods for preparation of graphene mainly include micromechanical cleavage [8], chemical vapor deposition (CVD) [9], epitaxial growth [10], reduction of graphene oxide [11] and liquid exfoliation of graphite [12,13]. Among them, reduction of graphene oxide (GO) is typically regarded as the strategy that is most suitable for mass production of graphene. GO can be easily dispersed in water to form stable colloids owing to abundant oxygenated functional groups attached to its basal plane and edges [14]. After the reduction process, GO can be converted to reduced graphene oxide (RGO) as these groups are eliminated. However, this approach has its own disadvantages. Though oxidation-reduction method can achieve high graphene concentrations, the reduction process is not green for the usage of highly toxic reducing agents like hydrazine [15], and reactions at an extremely high temperature [11]. Besides, the oxygen-contained functional groups, which make GO electrically insulate, cannot be reduced completely [14]. The residual defects after reduction also render the properties of as-prepared RGO inferior to those of pristine graphene.

In contrast, liquid exfoliation of graphite in suitable solvents provides a simple and cost-efficient route to graphene preparation. Specifically, the Van der Waals force between graphite internal layers is overcome by applied mechanical interactions, e.g. ultrasonic cavitation [16]. Significantly, such method can maintain the structural integrity of pristine graphene to a large extent, and thus outperform the oxidation-reduction method. However, liquid exfoliation is not without drawbacks. It has been demonstrated that organic solvents, like NMP [12] and DMF [17], are excellent solvents for producing graphene due to their suitable surface energy, but they suffer from high cost, toxicity, high boiling point and a lack of user-friendliness, etc. On the other hand, to exfoliate graphite in aqueous solutions, surfactants are often introduced to stabilize graphene suspensions, as depicted in many reports [18,19]. Such surfactants or organic solvents are quite difficult to eliminate completely, thus exerting negative effects on the properties that make graphene unique. To solve this problem, searching green, volatile and low-cost solvents for preparing graphene is of great importance.

Water is the most common and widely used solvent that offers advantages such as low boiling point and good environmental compatibility. Unfortunately, it is well known that water is a poor solvent for graphene due to its hydrophobic nature. Recently, significant efforts have been devoted on this issue. To maximize the surface charge, Li et al. [20] used ammonia solution to modulate the pH value, resulting in stable aqueous dispersions of chemical converted graphene (CCG) with a high concentration of ~ 0.5 mg/mL without the assistance of polymers or surfactants, but this method still suffers from the highly toxic hydrazine. Yi et al. [21] demonstrated that graphene produced by liquid exfoliation in organic solvent can be stably dispersed in pure water. Additionally, smaller graphene flakes results in more stable dispersion. Generally, both works proved possible dispersability of graphene in aqueous environment based on electrostatic repulsion between flakes. Furthermore, some researchers attempt to directly exfoliate pristine graphite in water. For example, Ricardo et al. [22] prepared multi-layer graphene by directly exfoliating graphite in the aqueous

solution of NaOH, but the maximum value of graphene concentration was only 0.02 mg/mL. Kim et al. [23] achieved direct exfoliation of graphite and storage of graphene nanosheets in pure water via temperature control (333 K), but the concentration of graphene only reached 7.5 $\mu\text{g}/\text{ml}$ after a quite long sonication process (60 h). Therefore, scalable production of graphene nanosheets in water still remains a big challenge.

In this work, to prepare water-dispersed graphene, we propose a facile, green, cost-efficient and in situ approach, in which the addition of a small amount of ammonia solution allows for exfoliation of graphite in water. We find that graphite can be exfoliated to few-layered graphene nanosheets, while the use of organic solvents, polymers and surfactants is not required. The volatile nature of aqueous ammonia makes it easy to evaporate during the processing of the graphene dispersion. Our findings not only offer new options of solvents for liquid exfoliation, but also pave the way for scalable production of graphene in water-based systems.

2. Experimental

2.1. Materials

The pristine graphite powder was purchased from Alfar Aesar (325 mesh, Product Number 43209). The deionized (DI) water was obtained from Beijing Kebaiao Biotech. Co., Ltd. The ammonia solution (25–28%) was bought from Xilong Chemical Co., Ltd. All the materials were used as received.

2.2. Preparation of graphene

The schematic process flow is shown in Fig. S1. In a typical experiment, 200 mL of DI water was poured into a wide-mouth bottle with the volume of 500 mL, in which 40 μL of aqueous solution of ammonia was utilized to adjust the pH value to around 9. 4000 mg of graphite powder was added into the basic water to achieve an initial concentration of 20 mg/mL. The mixture of graphite and water was sonicated for 2 h at a fixed position in one sonic bath (1730 T, 120 W, 40 kHz, Beijing Kexi Ultrasonic Instrument Co., Ltd., China). During the sonication process, a piece of preservative film was covered on the sealed cap of the bottle to prevent ammonia evaporation. After sonication, the as-prepared dispersion was allowed to stand for 2 h. Then the upper dispersion was centrifuged at 2000 rpm for 30 min with a 80-2 Centrifuge (Jintan Zhongda Apparatus Co., Ltd., China) to remove large flakes and unexfoliated graphitic particles. Eventually, the supernatant of the centrifugation tubes was carefully assembled as the graphene dispersion. A thin film of graphene was prepared via vacuum filtration of the graphene dispersion through a porous membrane (mixed cellulose esters, pore size 0.22 μm). Parameters mentioned above, including pH value, sonication time, initial concentration of graphite and centrifugation rate, were altered to investigate effects of them. All of the experiments were performed at ambient conditions.

2.3. Characterization

Transmission electron microscope (TEM) and high-resolution TEM (HRTEM) images were taken with a JEOL 2100 operating at 200 kV. TEM samples were prepared by pipetting a few drops of dispersions onto holey carbon grids. Atomic force microscope (AFM) analyses were performed using a CSPM5500 (Beijing Nano-Instruments Ltd., China) to investigate thickness and lateral size of graphene. AFM samples were prepared by pipetting several microliters of graphene dispersion onto mica substrates. The concentration of graphene, C, was calculated following Lambert-Beer

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