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Liquid-phase exfoliation of graphene in organic solvents with addition of naphthalene

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ABSTRACT

We report a facile method for the production of graphene sheets through liquid-phase exfoliation of graphite in organic solvents with addition of naphthalene. The production yield of graphene is significantly increased with the addition of naphthalene in most solvents tested in this work. 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. The graphene concentration of the dispersion in 1-methyl-2-pyrrolidinone is as high as 0.15 mg/mL (after sonication for 90 min), which allows this method to easily produce films and composites for a range of applications.

1. Introduction

Graphene is the strongest and toughest material known to man, and it offers extraordinary electronic, thermal and mechanical properties and is expected to find a variety of applications [1–3]. There are many methods for generating graphene and chemically modified graphene from graphite and derivatives of graphite, each with different advantages and disadvantages [4–9]. Recently, the most commonly used approach involves the oxidation of graphite to graphene oxide (GO), followed by chemical reduction, but the resultant graphene sheets contain high levels of defects [10,11]. For many applications, however, pristine graphene (defect-free) are required. Toward this end, the exfoliation of graphene in a liquid phase has shown its superiority for both scaling-up and application of graphene [12–16]. It is believed that the liquid-phase exfoliation of graphene is potentially important for the production of conducting inks and top-down approaches to electronics. Numerous studies have reported the solution-phase dispersion of pristine, unfunctionalized graphene because there are no defects and oxide groups in the pristine graphene, which is essential for its application in the electronics [17–22].

Highly polar solvents such as 1-methyl-2-pyrrolidinone (NMP), N,N-dimethylformamide (DMF), 1,2-dichlorobenzene (ODCB), and γ-butyrolactone (GBL) et al. have been chosen for the liquid-phase exfoliation process. The selection of these solvents was based primarily on the trial-and-error experimentation [20,23–26]. Solvents that are efficient in dispersing graphene can be selected on the basis of their Hildebrand solubility parameters, Hansen solubility parameters, and surface tensions (or surface free energy). It is known that good solvents for graphite exfoliation have surface tensions in the region of 40–50 mJ/m^2 [20,27]. The graphene–solvent interaction should be sufficiently strong to compensate for the enormous van der Waals attractive interaction between the graphene sheets. This method, however, has a serious drawback of an extremely low yield efficiency of graphene, typically <0.01 mg/mL [20]. This method (to improve the graphene concentration) commonly requires long-time ($\sim$400 h) sonication, which may not be allowed in commercial production. Moreover, the excessive sonication leads to the destruction of graphene. Undoubtedly, how to improve the yield efficiency without destruction of the structure of graphene is a key point in this research area. Many research groups have made a considerable progress in exfoliating graphene with the strategy of mixed solvents [28–30], solvent exchange [31], solvothermal-assisted exfoliation [32,33], and addition of intercalants [34–39].

The representative intercalants are pyrene derivatives [35,37]. The noncovalent π–π stacking mechanism does not disrupt the graphene crystal structure (its sp^2 hybridization) nor degrade the physical and chemical properties of graphene. However, it takes long time and involves complex steps to remove the superfluous pyrene derivatives in the graphene dispersions during the

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exfoliation process [34]. There have been reports about the adsorption of naphthalene onto multi-walled carbon nanotubes with the π–π interaction [40,41]. We suggest that similar effects may be exploited between the naphthalene and graphene in organic solvents. Herein, we report a new approach to improving the liquid-phase exfoliation efficiency of graphite in organic solvents. With addition of naphthalene, the graphene yield is significantly increased. Naphthalene intercalates into the graphite and expands the interplanar space between the adjacent graphitic layers during the sonication process.

2. Experimental details

2.1. Materials

All reagents and solvents were purchased from Aldrich Chemical Inc. and used as received. The SEM image of graphite powder (Product Number: 496596-113G, particle size <45 μm, assay ⩾99.99%) is shown in Fig. S1.

2.2. Exfoliation

The graphite was dispersed in various solvents (cylindrical vial, 20 mL solvent) at a concentration of 5 mg/mL. Typically, 25 mg of naphthalene powders were added in the graphite dispersion. The mixture was then sonicated in a low-power ultrasonic bath (JEIOTECH UC-10) for 90 min. The resultant dispersion was centrifuged using a centrifuge (GYROZEN-1236MGR) at 3000 rpm for 30 min. After centrifugation, decantation was carried out by pipetting off the top half of the dispersion. Thin films were prepared by vacuum filtration onto polyvinylidene fluoride (PVDF) membranes (pore size 100 nm).

2.3. Characterization

UV–visible spectra were recorded on a UV–visible spectrophotometer (SPECORD 210 PLUS-223F1107) using a quartz cell with a 1 cm optical path. By measuring the absorbance of graphene dispersion at 660 nm, the concentration of the exfoliated graphene dispersion was determined from the Lambert–Beer law, using $A/l = \alpha_{660}C$ with $\alpha_{660} = 2460$ mL/mg/m. Raman spectra were taken on a confocal Raman microscope (alpha 300S, WITec) with a 532 nm wavelength incident laser light. Field emission transmission electron microscope (FE-TEM) images were taken on a JEM-2100 (JEOL) with an operating voltage of 200 kV. X-ray diffraction (XRD) patterns were recorded on a Rigaku RAD-3C diffractometer (35 kV, 20 m A, Japan) with Cu Ka radiation ($\lambda = 1.548$ Å) at a scan rate of 2°/min, in the 2θ angles ranging from 10° to 70°. The morphology and size of graphene were measured using a field-emission scanning electron microscope (FE-SEM, JEOL, JSM-6500FE). Fourier transform infrared (FTIR) spectra were recorded on a FTIR spectrometer (KBr disk method; NEXUS) at wavenumbers in the range 400–4000 cm^{-1}. Thermogravimetric analysis (TGA) was conducted in nitrogen atmosphere at a heating rate of 10 °C/min using a TA Hi-Res TGA 2950 thermogravimetric analyzer. X-ray photoelectron spectroscopy (XPS) measurement was performed on an ESCALB-MKII250 photoelectron spectrometer (VG Co.) with Al Kα X-ray radiation as the X-ray source for excitation.

3. Results and discussion

3.1. TEM characterization

As shown in Fig. 1, graphite was exfoliated in organic solvents with the addition of naphthalene (see Fig. S1 in the Supplementary material). The exfoliation of graphite using the π–π stacking interaction with naphthalene is depicted in Fig. 1 down: naphthalene acts as a "molecular wedge" to intercalate into the edge of graphite, which facilitates the exfoliation of graphite during sonication significantly improving the production yield of graphene.

Transmission electron microscopy (TEM) study has been carried out to ascertain the degree of exfoliation and quality of the graphene sheets. Fig. 2a and b shows the representative TEM images of few-layer graphene sheet with folded characteristics. The high-resolution TEM (HRTEM) image of the folded edge in Fig. 2d indicates that the graphene sample is a tri-layer graphene sheet. The prepared graphene sheet has a high quality and crystallinity, which is clearly demonstrated by a perfect crystal lattice in HRTEM image. Selected area electron diffraction (SAED) pattern (Fig. 2c) corresponding to Fig. 2b, with the zone axis of [0001] shows that the prepared graphene is single-crystalline. These patterns show the typical sixfold symmetry as expected for graphene, allowing us to label the peaks with the Miller-Bravais (*hkil*) indices, as shown in Fig. 2c.

Additional TEM images of graphene are shown in the Supplementary material, Figs. S2 and S3. Fig. S3a shows the folded graphene with an angle of ∼30°. This indicates that the flakes are aggregated when the graphene dispersion is casted and dried on a TEM grid, the resultant stacking is ordered AB (Bernal) stacking with the lowest energy state [42]. Fig. S3b and c shows the representative rolling structure in the graphene sheets. The graphene sheets have more folded and rolling structures during the exfoliation process with the addition of naphthalene due to the π–π interaction between naphthalene and graphene.

3.2. Graphene production yield

Figs. 3 and 4 show the production yield of graphene sheets dispersed in organic solvents with or without the addition of naphthalene. It can be seen that the addition of naphthalene results in a significant increase in the graphene concentration in most solvents tested. For the commonly used solvent NMP, the graphene concentration is ∼0.15 mg/mL in the presence of naphthalene, which is twice higher than that in the absence of naphthalene (∼0.08 mg/mL). In Fig. 3, for the case of NMP, 1,3-dimethyl-2-imidazolidinone (DMEU), cyclohexanone (CYC), benzylamine (BA), propylene carbonate (PC) and γ-butyrolactone (GBL), the addition of naphthalene increases the graphene concentration almost 2–4 times. However, naphthalene has a small effect on the graphene concentration for DMF, ODCB, 1-propanol (1-Pro) and 2-propanol (2-Pro). It is believed that the Hildebrand solubility parameter, Hansen solubility parameter, and surface tension (or surface free energy) of a solvent have a great effect on the graphene–solvent interaction. Good solvents for graphite exfoliation are characterized by surface tensions in the region of 40–50 mJ/m^2 [20,27].

When naphthalene is added in the graphene dispersion, the naphthalene–solvent interaction should be carefully considered, which may greatly affect the production yield of graphene. The molecular structure of naphthalene consists of a fused pair of benzene rings. If the molecular structure of a solvent is similar to that of the naphthalene, the naphthalene–solvent interaction will be strong. NMP, DMEU, CYC, BA, PC and GBL where the addition of naphthalene significantly increases the graphene yield have a ring structure similar to naphthalene. Among DMF, ODCB, 1-Pro and 2-Pro where the addition of naphthalene has a small effect on the graphene yield, only ODCB has a ring structure. Accordingly, ODCB, being an aromatic, interacts with naphthalene via a strong π–π interaction. When a larger amount of naphthalene (>100 mg) is added in the ODCB exfoliation process, however, no graphene is produced (Fig. S4). This may be attributed to a stronger