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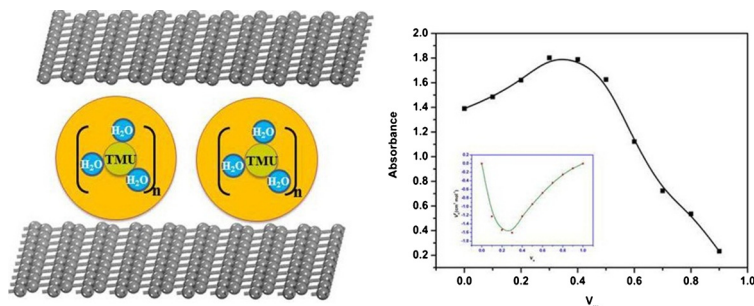
Efficient liquid-phase exfoliation of few-layer graphene in aqueous 1, 1, 3, 3-tetramethylurea solution



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GRAPHICAL ABSTRACT



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ABSTRACT

Liquid-phase exfoliation of graphite is a promising method to produce graphene in large quantities. Selection of the solvent is the most important factor in determining the productivity of liquid-phase exfoliation and stability of the graphene dispersion. However, only low concentrations of graphene dispersion have been achieved in most of the solvents, and the solvents usually employed are toxic up to now. To address the performance and environmental safety issues of solvent, renewable solvents water and 1, 1, 3, 3-tetramethylurea (TMU) are explored as a mixture to exfoliate graphite into graphene in the present work. It is found that water-TMU mixed solvent is a powerful solvent to obtain a few-layer graphene, and the yield at the water volume fraction of 0.3 was 4.5 times that in neat *N*-methylpyrrolidinone (NMP). The solvent-cosolvent interactions (water-TMU heteroassociation) are a critical factor in the liquid-phase exfoliation of graphene. The results reported in this work may provide a guide to rational design of a sustainable solvent system and to improve the yield and stability of the exfoliated graphene.

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1. Introduction

Graphene is a carbon allotrope and exhibits fascinating electronic, optical, thermal and mechanical properties, which makes it promising for various applications in electronic and optoelectronic devices, chemical sensors, nanocomposites, and energy storage [1–5]. While the successful preparation of graphene by

mechanical exfoliation has attracted intense interest [6], it is still challenging to produce graphene with high purity in a bulk quantity. Therefore, developing new strategies for the scalable production of graphene with high quality may lead to important advances in both fundamental studies and innovative applications.

Compared to other methods such as mechanical exfoliation, epitaxial growth, chemical vapor deposition, and organic synthesis, liquid-phase exfoliation with assistant of ultra-sonication is one of the most promising ways to produce graphene with the advantage of cheap, versatile, simple to execute and scale [7]. The yields and

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stability of the exfoliated graphene sheets prepared by liquid-phase exfoliation are two key factors for its commercialization [8]. Obviously, solvent plays a paramount role in successful exfoliation. Dichlorobenzene was the first solvent introduced for the preparation of high quality few-layer graphene by liquid-phase exfoliation assisted with sonication [9]. Since then, a number of solvents have been developed for the exfoliation of high quality graphene. The actively employed solvents are *N*-methylpyrrolidone (NMP), *N,N*-dimethylformamide (DMF), 1-methyl-2-pyrrolidone, naphthalene, dimethyl sulfoxide (DMSO), oligomer, ionic liquids, poly(ionic liquid)s, and so forth [10]. However, these solvents are generally toxic, expensive or have high boiling point, which hinder the application of liquid-phase exfoliation of graphene [11].

In order to avoid these disadvantages, mixed-solvent strategy in which two or more mediocre solvents with low or no toxicity and low price have recently been synergized to form strong solvents for facile liquid-phase exfoliation of graphene [12–14]. For example, the mixtures of water with organic compounds (such as ethanol, tetrahydrofuran, acetone, isopropanol, NMP, DMF, or DMSO) have been developed for the production of graphene [12–18]. Nevertheless, in these mixed solvents, the yield of the as prepared graphene is low and the stability of the exfoliated graphene is poor. Therefore, new mixed solvents are urgently needed which are low/no toxic, stable, and easy to reuse, and have high performance for the exfoliation of graphene.

Herein we report a new strategy for the efficient exfoliation of bulk graphite by using water and 1, 1, 3, 3-tetramethylurea (TMU) as the mixed solvents, where water is a green solvent, and TMU has low toxic and high ability to dissolve aromatic compounds, which is expected to be a good solvent for high yield preparation of graphene. It is noted that these mixtures are powerful solvent for the exfoliation of graphene. Thus, the effect of the component properties and microstructure of water-TMU mixed solvents on the yield, stability and quality of graphene is analyzed, and the fundamental factors governing the degree of liquid exfoliation and stability of the exfoliated graphene have been discussed from the interactions of graphene–mixed solvent and solvent–cosolvent.

2. Experiment section

2.1. Materials

1, 1, 3, 3-Tetramethylurea (TMU, 99.0%) and *N*-methyl pyrrolidone (NMP, 99.0%) were purchased from Aladdin Co., Ltd (Shanghai, China). Graphite (average size 100 mesh) and highly oriented pyrolytic graphite (HOPG) were bought from Macklin Co., Ltd (Shanghai, China). Deionized water was used in all the experiments.

2.2. Exfoliation

Standard 25 mL centrifuge tubes were used for the exfoliation assisted by sonication and followed by centrifuge processes to avoid material loss during transfer to centrifuge tubes. In a typical exfoliation experiment, 20 mg of graphite and 10 mL of the solvent were placed in a centrifuge tube. Then the mixture was put into an ultrasonic instrument operated at a power of 400 W for 2 h to produce a black turbid liquid at 25 °C. The black turbid liquid was centrifuged for 30 min (15 min \times 2) under 2000 rpm. The top two thirds of the dispersion were taken by a pipette and retained for the next use.

2.3. Materials characterizations

Characterizations of the starting materials and as-produced graphene were performed by absorbance spectroscopy, transmission electron microscopy (TEM), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), and micro-Raman spectroscopy.

In order to determine the productivity resulting from different contents of mixed solvents, the optical absorbance (A) of the dispersion was measured at 660 nm with a spectrophotometer (Shanghai 752 N) after correction of the scattering background by using corresponding water-TMU mixed solvent as blank [19]. The concentration of graphene in the liquid could be calculated using the Lambert-Beer law, which relates the absorbance to the optical absorption coefficient α , the graphene concentration c , and the path length l of the light beam as follows: $A = \alpha cl$. The c value can be obtained from the weight of graphene after filtration of the given volume dispersion with a filter of 0.22 μm pore size under reduced pressure. Then, accurate value of optical absorption coefficient α has been calculated from the measured absorbance A and the corresponding concentration at a given path length.

High-resolution transmission electron microscopy (HR-TEM) images were taken from a JEOL 2010 electron microscope at an accelerating voltage of 200 kV. The samples were prepared by dropping a given concentration of supernatants on the holey carbon grids. The X-ray photoelectron spectra (XPS) measurements were carried out on a Thermo Scientific K-Alpha electron energy spectrometer using Al K α (1486.6 eV) as the X-ray excitation source. Atomic force microscope experiments were performed on a Bruker Dimension Icon microscope in tapping mode by dropping diluted supernatant onto freshly cleaved Si substrates. Raman spectrum was determined by a Raman spectrometer (XploRA, HORIBA JobinYvon) with an excitation wavelength of 532 nm.

The FTIR spectra of water-TMU mixed solvents as a function of water volume fraction were recorded on a Perkin-Elmer Spectrum 400 Fourier transform infrared spectrometer. All the spectra were recorded at 25 °C, and background corrections were performed before every measurement.

2.4. Contact angle measurements

Contact angle of water-TMU mixed solvent at varying volume fractions of water was determined by using a video-based optical contact angle meter (Kruss DSA 25, Germany). The contact angle values were reported by fitting the contact angle photographs with appropriate software. The sampling of the liquid drops on HOPG surface was performed with a micropipette, and one spot was used once for the measurement. All the contact angle measurements were conducted at ambient temperature. Each contact angle value was the result of an average of three independent measurements.

2.5. Surface tension measurements

Surface tensions of water-TMU mixed solvents were determined by a DCA 315 tensiometer (Cahn Instruments) with a platinum plate ($20 \times 15 \times 0.127 \text{ mm}^3$) at 25.0 °C. The temperature around the sample cell was controlled by circulating water from a HAAKE DC30-K20 thermostat (Thermo Electron, Germany), and the temperature was maintained to be within ± 0.1 °C. All the measurements were repeated three times to allow the determination of an average surface tension value. The tensiometer was calibrated with double distilled water according to the procedure provided by the manufacturer, and the uncertainty of the surface tension data was estimated to be around $\pm 0.1 \text{ mJ m}^{-2}$.

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