



Environmentally Friendly Approaches Toward the Production of Processable Graphene by Exfoliation of Graphite Using Ionic Liquid

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A facile, low-cost and environmentally friendly method was developed to prepare processable graphene materials by direct exfoliation of expandable graphite flakes under wet ball milling conditions in ionic liquids. The graphene nano-sheets obtained in this method were characterized by AFM, Raman spectroscopy, UV-NIR. Thin-film field-effect transistors made from this graphene sheets exhibit ambipolar effect, an average hole mobility of $\sim 0.29 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, electron mobility of $\sim 0.57 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was obtained.

Keywords: Graphene, Ionic Liquid, Ball Milling, Field-Effect, Ambipolar Effect.

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1. INTRODUCTION

Graphene, a two-dimensional monatomic thin sheet with a large lateral dimension sp^2 -hybridized carbon nano-structure¹ has many attractions to offer in terms of superior mechanical, thermal, electrical and optical properties.² Graphene is an ideal candidate for use in a wide range of potential applications, such as transistors, sensors, supercapacitors, and hydrogen storage.³ However, the widespread exploitation of graphene in technological applications will depend, in the first instance, on the availability of efficient and inexpensive methodologies that allow the preparation and manipulation of this material on a large scale.

Ionic liquids (ILs) have been proposed as “green” alternatives to conventional solvents because of their unique properties like negligible vapor pressure, thermal stabilities, wide solubility, low viscosity, and recyclability.^{4,5} The high dielectric constant of ILs provides shielding for the stacking interactions caused by van der Waals interaction and helps to disperse carbon nanomaterials effectively.⁶ Most importantly, ILs have surface tensions closely matching the surface energy of graphite, which is a key prerequisite of solvents for direct exfoliation of graphite.⁷ Such advantages over most solvents make ILs the ideal systems for synthesis of graphene.

Herein, we report a simple, efficient, low-cost, environmentally friendly approach to fabricate graphene by the direct exfoliation of expandable graphite flakes under wet ball milling conditions into a dispersion of graphene in 1-butyl-3-methyl-imidazolium bis(trifluoromethanesulfonyl)imide ([BMIM][Tf₂N]). This method affords a stable suspension of graphene/[BMIM][Tf₂N] in NMP with high concentrations. We also demonstrate a potential application for this new graphene with preliminary data using the graphene/[BMIM][Tf₂N] as semiconductor for field-effect transistors.

2. EXPERIMENTAL DETAILS

Expandable graphite flakes was obtained from Qingdao Huarun graphite Co. [BMIM][Tf₂N] (99.998%) was obtained from Hebei Normal University. Planet-Ball-Grinding machine were obtained with a Nanjing University QM 001.

Expandable graphite flakes (5 g) were dispersed in [BMIM][Tf₂N] (5 g) and the mixture was subjected to mill for a total of 60 h. The resulting mixture (100 mg) was dispersed homogeneously in NMP (100 mL) by 0.5 h sonication, the suspension was left for 36 h at ambient conditions in order to settle out any insoluble particles and the supernatant containing graphene/[BMIM][Tf₂N] were carefully collected and retained for use.²⁰

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The graphene/[BMIM][Tf₂N] product was then collected by centrifugation.

AFM measurements were performed using Multimode SPM from Digital Instruments with Nanoscope IIIa Controller. Raman spectra were measured by a Renishaw inVia Raman microscope with the 514-nm line of an Ar ion laser as an excitation source.

OFET devices on SiO₂/Si substrates were fabricated and transistor characterization was performed using a Keithley 2612 under ambient conditions.

3. RESULTS AND DISCUSSION

The procedures to prepare the ILs-stabilized graphene sheet (graphene/[BMIM][Tf₂N]) are illustrated in Figure 1. Atomic force microscopic (AFM) was used to quantify the exfoliation of expandable graphite flakes. The thickness of graphene/[BMIM][Tf₂N] sheet is approximately 0.66 nm, which is consistent with the value referred for a single-layer graphene reported previously,²¹ suggesting graphite was completely exfoliated.

Raman scattering is strongly sensitive to the electronic structure and it has proved to be an essential tool to characterize graphene. As shown in Figure 2, the graphene/[BMIM][Tf₂N] structural change during the preparation of graphene by exfoliation of graphite under wet ball milling is reflected in the Raman spectra. The *D*-band is associated with disorder-induced scattering resulting from imperfections or loss of hexagonal symmetry of disordered graphite. The *G*-band corresponds to an *E*_{2g} mode of graphite and is related to vibration of sp²-bonded carbon atoms in a two-dimensional hexagonal lattice.⁸ For comparison, we also shown raman spectrum of graphene oxide by chemical exfoliation of graphite based on the early Hummers method.⁹ For graphite, the main peak at 1581 cm⁻¹ (*G*-band) can be observed, which is assigned to the first-order scattering of the *E*_{2g} mode.¹⁰ In the Raman spectrum of graphene/[BMIM][Tf₂N], the *D/G* intensity ratio is decreased compared to graphene oxide, which indicates that suggests a increase in the average size of the sp² domains. A frequency shift (19 cm⁻¹) toward a higher wavenumber and a broadened bandwidth of the *G*-band

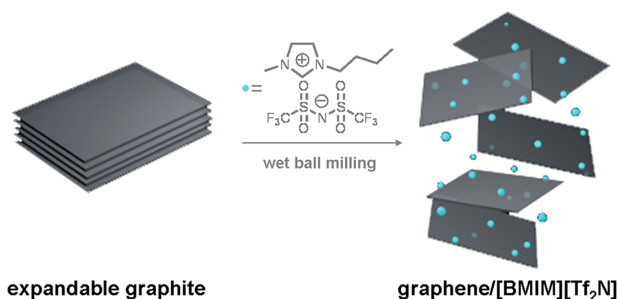


Fig. 1. Schematic illustration of the production of processable graphene by exfoliation of graphite using ionic liquid.

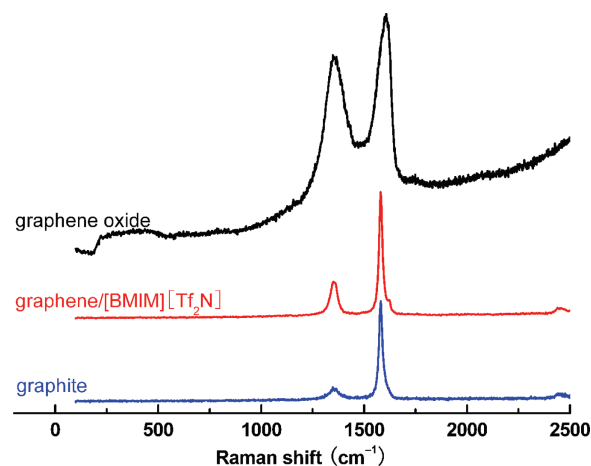


Fig. 2. The Raman spectra of expandable graphite flakes, graphene/[BMIM][Tf₂N], and graphene oxide. The graphene/[BMIM][Tf₂N] *D/G* intensity ratio is decreased compared to graphene oxide, which indicates that suggests a increase in the average size of the sp² domains.

are found in graphene oxide compared with graphite and graphene/[BMIM][Tf₂N], also indicating the decrease of in-plane graphene size during the chemical reaction process, possibly due to the extensive oxidation.¹¹

The prevention of aggregation is of particular importance for processability and applications of graphene because most of its attractive properties are only associated with individual graphene sheets. Solution-phase UV Vis NIR spectroscopy (Fig. 3) can be used to determine the solubility of graphene/[BMIM][Tf₂N] in NMP. The absorptions (at 346 nm) for the graphene/[BMIM][Tf₂N] were plotted against concentration (Fig. 3 inset) and a good linear relationship was obtained with an *R* value of 0.998.⁷ Assuming the applicability of Beer's law, from the slope of the linear least-squares fit we estimated the

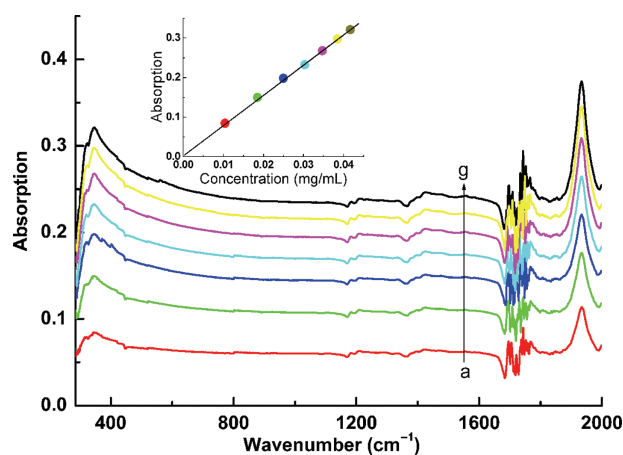


Fig. 3. Concentration dependence of the UV absorption of graphene/[BMIM][Tf₂N] in NMP (concentrations are 10, 18, 25, 30, 35, 39, and 42 mgL⁻¹, from a to g, respectively). The plot of optical density at 346 nm versus concentration is shown in the inset. The straight line is a linear least-squares fit to the data, which indicates that the hybrid graphene/[BMIM][Tf₂N] is homogeneously dissolved in NMP.

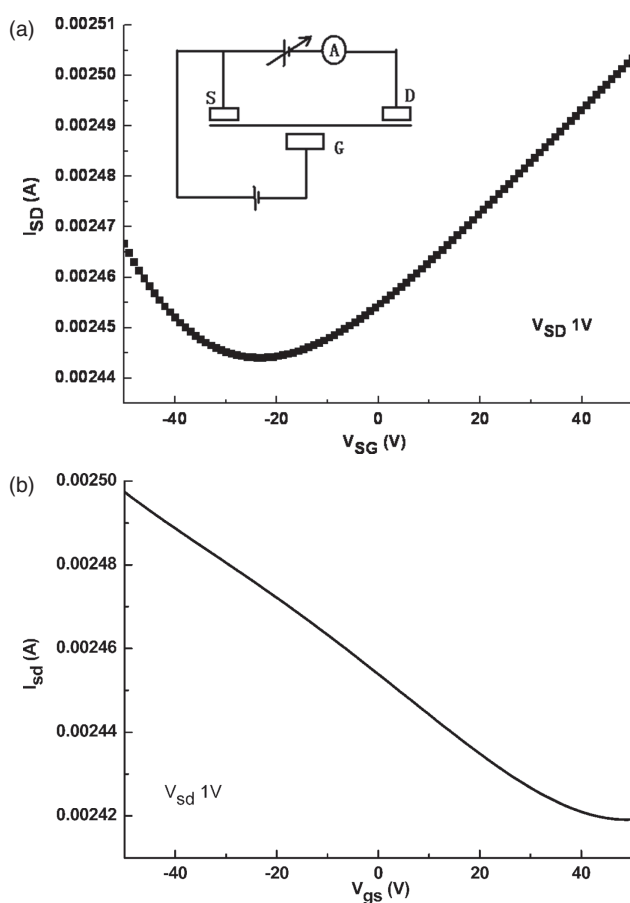


Fig. 4. (a) Electrical transport characteristics of the graphene/[BMIM][Tf₂N]. By applying a gate voltage of up to ± 50 V (provided by a Si back gate with 300 nm oxide thickness), source/drain voltage of 1 V, an average hole mobility of ~ 0.29 cm² V⁻¹ s⁻¹, electron mobility of ~ 0.57 cm² V⁻¹ s⁻¹ with on/off ratio of ~ 1 was obtained. Inset: Schematic of a transistor with Au as the source/drain electrodes on SiO₂/Si substrates. Channel length of ~ 40 μ m and width of ~ 1.2 cm. (b) Transfer characteristics of *p*-type graphene/[BMIM][Tf₂N], an average hole mobility of ~ 0.29 cm² V⁻¹ s⁻¹.

effective extinction coefficient of graphene/[BMIM][Tf₂N] to be 0.008 L mg⁻¹ cm⁻¹ at this position. The absorbance of solutions of graphene/[BMIM][Tf₂N] at other wavelengths was also consistent with the Beer's law. These results demonstrate that the dispersion of the graphene/[BMIM][Tf₂N] was homogeneous and no effects could be associated with concentration-dependent aggregation of graphene sheets.

For further electrical property measurements, we have fabricated graphene/[BMIM][Tf₂N] transistors with Au as the source/drain electrodes on SiO₂/Si substrates (Fig. 4(a) inset). Typical ambipolar transfer characteristics of the graphene/[BMIM][Tf₂N] transistors at ambient conditions are illustrated in Figure 4(a). We measured more than fifty devices at ambient conditions. By applying a gate voltage of up to ± 50 V, source/drain voltage of 1 V, an average hole mobility of ~ 0.29 cm² V⁻¹ s⁻¹, electron mobility of ~ 0.57 cm² V⁻¹ s⁻¹ with on/off ratio of ~ 1 was

obtained. The graphene/[BMIM][Tf₂N] transistors showed hole/electron mobility comparable with the similar transistors using reduced graphene oxide as semiconductor.¹² The graphene/[BMIM][Tf₂N] transistors represents only *p*-type field-effect by the long exposure to the air, maybe due to the doping of oxygen (Fig. 4(b)),¹³ an average hole mobility of ~ 0.29 cm² V⁻¹ s⁻¹. Also the transfer characteristics show ambipolar transistors with large hysteresis, which is probably caused by adsorbed water molecules.^{14,15} Efforts are underway to improve the quality of the graphene/[BMIM][Tf₂N] by tuning the fabrication conditions, and the graphene/[BMIM][Tf₂N] transistor properties.

4. CONCLUSIONS

In conclusion, graphite in ionic liquids was first directly exfoliated into graphene aided by wet ball milling. The good dispersion of well-exfoliated graphene/[BMIM][Tf₂N] in NMP was obtained followed by centrifugation. We demonstrate the existence of ionic liquid functionalized graphene by using IR and AFM characterizations. According to Raman studies, this simple method prevents high levels of oxidation. The top-gated FETs utilizing graphene/[BMIM][Tf₂N] was fabricated, and the devices exhibit ambipolar behavior. As a very common industrial technique, the ball milling method can be easily scaled up to mass production, offering a promising opportunity to produce graphene in volumes needed for real-life world applications.

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