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Direct exfoliation of graphene in ionic liquids with aromatic groups

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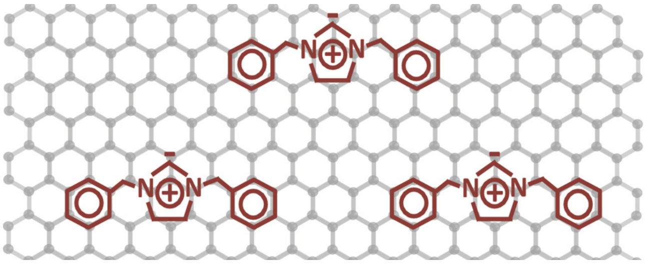
HIGHLIGHTS

- Imidazolium ionic liquids with phenyl groups disperse graphene noncovalently without stabilizers.
- The graphene concentration is higher in diphenyl than in monophenyl substituted ionic liquids.
- DFT calculations show phenyl-graphene π–π interactions help stabilize graphene–IL dispersions.

GRAPHICAL ABSTRACT



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ABSTRACT

Novel ionic liquids (ILs) were designed and synthesized to contain aromatic groups on the imidazolium cation that non-covalently interact with graphene surfaces. This route enables the dispersion of pristine graphene without covalent functionalization or an additive stabilizer; such dispersions are stable against aggregation and display high concentration values. We find that ILs without these aromatic groups are less effective in graphene dispersion, and the dispersed graphene concentration increases with increasing interaction between the cation and graphene surface. Density functional theory (DFT-D3) calculations support the experimental observations and provide a foundation for predictive modeling of IL design for optimal graphene dispersions.

1. Introduction

Graphene (*i.e.* single-layer graphite sheets) is a form of two-dimensional sp^2 hybridized carbon [1,2]. The unique properties of graphene include mechanical strength, electrical conductivity, and thermal conductivity [1–3], which collectively hold promise for use in a wide range of applications, including composites [4], thin conductive films [5,6], and supercapacitors [7,8]. Graphene was first identified by micromechanical cleavage of graphite in 2004 [2], but other techniques have been developed to increase graphene production scalability. In the current paper, we focus on the major problem of producing graphene from graphite using liquid phase exfoliation without dispersants or oxidation [9,10].

Graphene layers are held together by van der Waals forces in graphite; this creates problems both in exfoliating graphene from graphite as well as keeping graphene dispersed in a liquid medium rather than aggregating. The most common approach to solving this problem of producing graphene from graphite involves oxidizing the graphite to produce graphite oxide, which may then be exfoliated to yield dispersions of graphene oxide. Graphene oxide (GO) may subsequently be chemically or thermally treated to remove the

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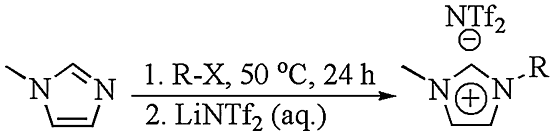

Scheme 1. Generic synthesis of the asymmetric ILs.

covalent functional groups and produce reduced graphene oxide (rGO) [6,11–15]. Alternatively, graphene may be produced through exfoliation (through sonication or high shear) of graphite powder in a solution of stabilizer molecules such as micelle-forming surfactants, polymers, and aromatic hydrocarbons [16–18]. (A summary of these methods is given in Table S1 in the Supplementary Materials.) However, it is highly desirable to directly disperse graphene in liquids with no stabilizer or additive of any kind, because such additives may have adverse effects on the mechanical or electrical properties of graphene-based films, sensors, or composites. Only a few candidate solvents have been identified for such direct exfoliation and dispersion [19], and one of the most promising are ionic liquids [20].

Ionic liquids (ILs) are organic molten salts with melting point temperatures below 100 °C, which have been used extensively as solvents. ILs are non-volatile [21], thermally stable [22], non-flammable, recyclable [23], and capable of dissolving a range of solutes. Furthermore, their properties (such as miscibility and viscosity) can be tuned *via* chemical changes to the cation or anion [24]. Additionally, ILs are attractive because of their status as green solvents due to their low vapor pressures and ease of recycling, in contrast to common organic solvents [9].

Prior reports have indicated that ILs can disperse graphene directly [25,26]. The mechanisms behind IL–graphene interactions are just beginning to be understood [27]. However, the existing literature gives little insight into effective IL design for graphene dispersion. In the present investigation, we produce novel ILs with controlled differences in chemical functionality and demonstrate that these ILs can be used to directly disperse graphene at high concentrations.

2. Materials and methods

2.1. Materials

Expanded graphite (EG) was graciously provided by Asbury Carbons (CAS# 7782-42-5, Grade 3772). All the other chemical reagents and solvents were purchased from commercial sources (Sigma–Aldrich, Acros Organics, 3M) and were used as received. All reactions were run using oven-dried glassware under nitrogen atmosphere. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on JEOL 400 spectrometer and collected as solutions of deuterochloroform (bromide ionic liquids) or deuteroacetone (bistriflate ionic liquids).

Four different types of ILs were synthesized: 1-benzyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([BnzC$_1$im][NTf$_2$], IL-1), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([bmim][NTf$_2$], IL-2), 1-benzyl-3-methylimidazolium bromide ([BnzC$_1$im][Br], IL-3), and 1,3-bis(phenylmethyl) imidazolium bis(trifluoromethylsulfonyl)amide ([(Bnz)$_2$im][NTf$_2$], IL-4). Their chemical structures are presented in Table 1. The synthetic procedures of the ILs have been published elsewhere [28–30]. They follow Scheme 1 for the asymmetric compounds and Scheme 2 for the symmetric compound.

2.2. Preparation of graphene dispersions

Expanded graphite (10 mg mL^{-1}) was added to the IL and then tip-sonicated at an output wattage of 10 W for 1 h in an ice-water bath. The resulting dispersion was then centrifuged (Centrific Centrifuge 225, Fischer Scientific) at ~5000 rpm for 6 h to remove large aggregates. The supernatant was collected and used for further characterization. Four different ILs varying in chemical composition (anion and cation) were investigated with the final graphene yields summarized in Table 1. The supernatant containing graphene in IL-4 was collected as shown in the inset of Fig. 1a. The concentration of graphene was measured by vacuum filtration. Dichloromethane was used to wash the excess IL from the filter paper, and the weight difference was used to calculate a graphene concentration. The absorbance was measured by a Shimadzu UV–vis spectrophotometer 2550 in the 200–800 nm wavelength range. The Lambert-Beer law, $A = \alpha LC$, where the absorbance A is proportional to the product of concentration C and path length L, was utilized to measure the extinction coefficient α of the IL stabilized graphene dispersion. The pure IL was used as a blank to eliminate the background effect. The absorbance spectrum of graphene dispersion is shown in Fig. S2 in the Supplementary Materials, and the extinction coefficient was computed to be 3181 mL mg^{-1} m^{-1} for IL-4. The value of the extinction coefficient is comparable to that of another system reported in literature ($\alpha = 1172$ mL mg^{-1} m^{-1} for graphene in l-hexyl-3-methylimidazolium hexafluorophosphate) [25].

2.3. Characterization of graphene/ionic liquid dispersions

To determine the surface area of EG, physisorption analysis was performed. An Autosorb iQ machine (Quantachrome Instruments) was utilized to conduct the experiment. Initially EG was degassed for 15 h at 90–100 °C. After degassing, the nitrogen adsorption–desorption isotherm was acquired. The surface area of the sample was determined by applying the multipoint Brunauer–Emmett–Teller (BET) method to the isotherm.

In order to measure the degree of exfoliation, Raman spectroscopy was used. A Thermo Scientific^{TM} DXR Raman microscope was utilized. The filtered sample was used to measure the Raman spectrum using a 532 nm laser.

To measure the number of layers of graphene in a typical dispersed flake, transmission electron microscopy (TEM) was performed. The TEM sample was prepared by drop-casting the dispersion on a lacey carbon coated 200-mesh copper grid and then washing with ethanol to remove the IL. A Hitachi H8100 TEM was utilized to image the sample with the accelerating voltage set as 75 kV.

To confirm that the prepared sample is graphene, X-diffraction (XRD) was performed on the vacuum filtered film. The instrument used for the analysis of the graphene sample was a Rigaku MiniFlex II powder diffractometer with a Cu source and a scintillation detector. The X-ray source was operated at a power setting of 30 kV and 15 mA. The data was collected with a step size of 0.005° and a collection time of 4 s per step.

In order to quantify the atomic percentage of the elements in the vacuum filtered film of graphene and IL-4, X-ray photoelectron spectroscopy (XPS) was performed with a 5000 VersaProbe Electron Spectroscopy for Chemical Analysis (ESCA) spectrometer. A focused monochromatic X-ray beam of 1486.6 eV was utilized to do this characterization. Four different runs were performed on the film at different spots.

The thickness of the graphene film on filter paper was measured by scanning electron microscope (SEM) (Hitachi S-4300). The filtered sample was mounted on double sided carbon tape and the accelerating voltage set at 2 kV.

The electrical resistivity was measured by the standard two-point probe method. The vacuum filtered sample was used to measure the resistivity by a high resistance meter (Model-HR2, AlphaLab, Inc.). A number of measurements were performed on