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Dispersion of graphene sheets in ionic liquid [bmim][PF$_6$] stabilized by an ionic liquid polymer†

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Received (in Cambridge, UK) 22nd July 2009, Accepted 17th November 2009
First published as an Advance Article on the web 1st December 2009
DOI: 10.1039/b914763b

Downloaded by University of South Dakota on 08 November 2012
Published on 01 December 2009 on http://pubs.rsc.org | doi:10.1039/B914763B

Dispersion of graphene sheets in ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate was successfully achieved with the aid of a polymerized ionic liquid (PIL).

Graphene, a one atom thick and two-dimensional honeycomb lattice, has attracted enormous attention in recent years from both the experimental and theoretical scientific communities because of its unique mechanical, electronic, and thermal properties.[1] This special nanostructure has great potential applications in many technological fields, such as nanocomposites,[2] nanoelectronics,[3] and biosensors.[4] Different methods, such as mechanical exfoliation,[5] thermal expansion,[6] epitaxial growth,[7] and chemical vapour deposition[8] has been developed for preparing graphene. Recently, many attempts to produce graphene sheets in a large quantity *via* chemical reduction of dispersed graphite oxide have been reported. For example, Xu *et al.* demonstrated that pyrenebutyric acid could be used to non-covalently functionalize graphene sheets *via* strong π–π interactions between pyrenyl rings and basal planes of graphene sheets.[9] Li and co-workers reported that chemically converted graphene sheets obtained from graphite could readily form stable aqueous colloids through electronic stabilization in the presence of ammonia.[10] More recently, Müllen and Feng described a method to disperse graphene sheets in organic solvent supported by ionic interactions.[11] In addition, covalent functionalization of graphene sheets with sulfonate, imidazolium or poly(vinyl alcohol) was also achieved, which could be dispersed in water and some organic solvents.[12]

Ionic liquids (ILs), which are organic salts with a melting point below 100 °C, have attracted much attention owing to their unique properties, such as extremely low vapor pressure, wide liquid temperature range, high ionic conductivity, wide electrochemical window, good thermal stability, nonflammability, and designable properties.[13] They have been widely investigated for organic chemical reactions,[14a] electrochemical applications,[14b,c] and synthesis of inorganic nanomaterials.[14d] Recently, imidazolium-based ILs have been used as media[15a] or stabilizers[15b] for the dispersion of carbon nanotubes.[15]

It would be reasonable to expect that the fluids formed from graphene sheets and ILs will open up some possibilities for new applications in different fields, such as being utilized as an electrolyte in dye sensitized solar cells, and being used to stabilize metal nanoparticles in catalysis, because both of them have some unique properties. Dispersion of graphene sheets in ILs is the key for exploring the applications, but this is challenging. In this communication, we report an approach to disperse graphene sheets stably in 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF$_6$], Scheme S1). The key of this method is the use of an IL polymer poly(1-vinyl-3-butylimidazolium chloride) (PIL, Scheme S1) as the stabilizer, which could not only easily dissolve in [bmim][PF$_6$], but also interacted strongly with graphene sheets through non-covalent π–π interactions. Furthermore, it was demonstrated that the dispersion of a small amount of graphene sheets in [bmim][PF$_6$] could enhance the conductivity of the IL considerably. To the best of our knowledge, this is the first work to disperse of graphene sheets in an IL.

The detailed procedures to prepare the PIL-stabilized graphene sheet (PIL-G) dispersion in the IL are described in the Notes.‡ In brief, the dispersion of graphite oxide (GO) in water was first prepared from graphite by modified Hummers method (ESI†).[16] Then, the PIL was added into the aqueous dispersion of GO followed by reduction of GO with hydrazine monohydrate. The resulting PIL-G aqueous dispersion was mixed with [bmim][PF$_6$], and the PIL-G was extracted into the IL phase due to the excellent compatibility of the PIL and IL. The dispersion of PIL-G in the IL was obtained after the mixture was dried until the mass was independent of drying time.

Fig. 1 illustrates the photographs of the PIL-G aqueous dispersion before and after mixing with [bmim][PF$_6$]. Two other amphiphilic polymers, namely poly(vinyl pyrrolidone) (PVP, Scheme S1†) and poly(sodium 4-styrenesulfonate) (PSS, Scheme S1†), which have been used to stabilize graphene sheets in water,[4b,17] were also utilized as stabilizers for the dispersion of graphene sheets with the same procedures. Obviously, all the polymers could stabilize the graphene sheets in water (Fig. 1a–c). The mixtures separated into an aqueous phase (top phase) and an IL-rich phase (bottom phase) after the ceasing of shaking because the IL is hydrophobic. Interestingly, the PIL-G entered the IL phase (Fig. 1d), while graphene sheets stabilized by PVP and PSS remained in aqueous phase (Fig. 1e and f) because they are not compatible with the IL. This phenomenon shows that the PIL not only possesses excellent stabilizing ability for graphene sheets, but also has better solubility in the IL. Therefore, we can conclude that the existence of PIL is essential for the dispersion of graphene sheets in the IL, although the presence of polymeric dispersing agents is undesirable for some applications.[10,12a,18]

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† Electronic supplementary information (ESI) available: Chemicals used, synthesis of 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF$_6$]), graphite oxide (GO), and poly(1-vinyl-3-butylimidazolium chloride) (PIL), chemical structures of the IL and polymers used, and Fig. S1–S4. See DOI: 10.1039/b914763b

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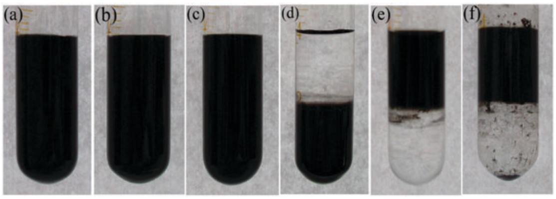

Fig. 1 Photographs (a), (b) and (c) correspond to aqueous dispersions of the graphene sheets (0.8 mg mL^{-1}) stabilized by PIL, PVP and PSS, respectively, and the weight ratio of the stabilizers to graphene sheets was 12.5; photographs (d), (e) and (f) correspond to (a), (b) and (c) after being mixed with [bmim][PF$_6$] of equal volume by shaking vigorously and then depositing for 20 min.

The dried dispersion of PIL-G in the IL was diluted by [bmim][PF$_6$] to prepare the dispersions of different concentrations. The photographs of the freshly prepared samples and those of the samples after depositing for two months are presented in the ESI (Fig. S1†). As expected, the color of these dispersions became darker as the concentration of graphene sheets in the IL increased (Fig. S1†). The photographs also show that the color of the samples was not changed noticeably after depositing for two months, indicating that the dispersion was very stable. In order to get some quantitative results, we measured the UV-vis absorbance of PIL functionalized graphene sheets in [bmim][PF$_6$] with different concentrations, which are shown in Fig. 2. The absorbance of the PIL is negligible at 550 nm (Fig. S2†), *i.e.*, the absorbance at this wavelength in the inset of Fig. 2 resulted from the graphene sheets in the dispersions. Obviously, the absorbance of the graphene sheets in the IL obeys Beer's law. This indicates that the dispersion of the graphene sheets in [bmim][PF$_6$] was homogeneous and no effects could be associated with concentration-dependent aggregation of graphene sheets.[19] Our experiments also showed that the absorbance of the samples was not changed noticeably after two months, in agreement with the direct observation.

The GO and PIL-G were characterized by atomic force microscopic (AFM) technique. The samples were prepared by depositing a drop of the above diluted aqueous dispersion on a new cleaved mica surface and dried in air. The average thickness of a GO sheet was ~0.84 nm (Fig. S3†), which was consistent with that in the previous reports,[9,20] suggesting that the graphite oxide was completely exfoliated. After reduction of the GO sheets with hydrazine monohydrate, some of the PIL was adsorbed on the surface of the graphene sheets by non-covalent π–π interactions between the imidazolium rings of the PIL and graphene sheets. The thickness of single PIL-G sheet was about 3.0 nm (Fig. 3), similar to that of DNA-stabilized graphene sheets.[21] The graphene sheets were thicker than that of the theoretical thickness of a single graphene layer (0.34 nm) due to the adsorption of the PIL molecules. The physical adsorption of PIL along the surface of the graphene sheets was further verified by X-ray photoelectron spectroscopy (XPS) analysis (Fig. S4†). The Cl 2p spectrum of PIL-G exhibited an intensive peak (Fig. S4d†), suggesting that the PIL still existed on the surface of graphene sheets after the pre-treatment.

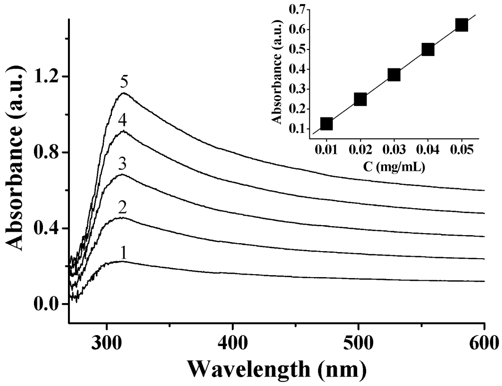

Fig. 2 UV-vis absorption spectra of PIL functionalized graphene sheets dispersed in [bmim][PF$_6$] with different concentrations: (1) 0.01 mg mL^{-1}, (2) 0.02 mg mL^{-1}, (3) 0.03 mg mL^{-1}, (4) 0.04 mg mL^{-1}, and (5) 0.05 mg mL^{-1}; dependence of the absorbance on concentration at 550 nm (inset); the weight ratio of the PIL and graphene sheets was 12.5, and the reference solution used in the measurement was neat [bmim][PF$_6$].

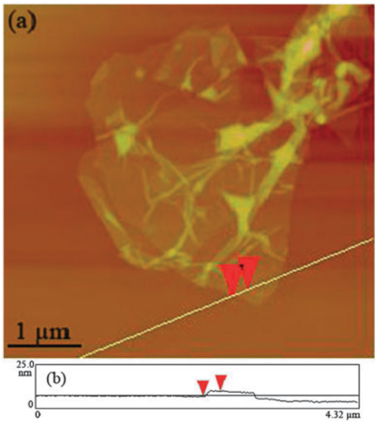

Fig. 3 (a) Tapping mode AFM image of PIL stabilized graphene sheets. (b) Height profile along the line displayed in (a).

We measured the conductivity of [bmim][PF$_6$], PIL-[bmim][PF$_6$] solution (PIL-IL), and PIL-G-[bmim][PF$_6$] dispersion (PIL-G-IL) at various temperatures ranging from 293.15 to 323.15 K using the same apparatus and procedures to determine the conductivity of different IL solutions.[22] The results are presented in Fig. 4.

The conductivity of the neat [bmim][PF$_6$] determined in this work agreed well with that reported by other authors in the

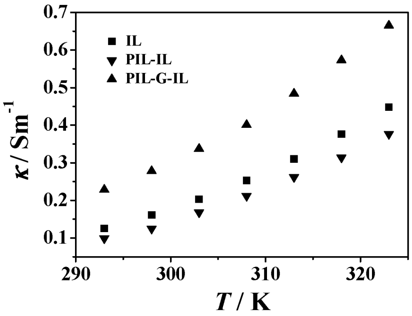

Fig. 4 The conductivity of the IL, PIL-IL solution (10 mg L^{-1}), and PIL-G-IL solution at various temperatures; the concentrations of the graphene and PIL in the PIL-G-IL solution were 0.8 mg mL^{-1} and 10 mg mL^{-1}, respectively.

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whole temperature range.[23] As illustrated in Fig. 4, the conductivity of [bmim][PF$_6$] decreased after introduction of the PIL, which may result mainly from the increase of viscosity of the IL after adding the PIL. Interestingly, the dispersion of PIL-G in [bmim][PF$_6$] resulted in considerable increase in the conductivity of the IL, even though the content of the graphene sheets was as low as 0.8 mg mL^{-1}. This may be mainly attributed to the extraordinary electronic transport property of graphene sheets, the homogeneous distribution of graphene sheets in the ionic liquid matrix, and the π–π interaction between the imidazolium rings of [bmim][PF$_6$] and graphene sheets.[24]

In conclusion, uniform dispersion of graphene sheets in [bmim][PF$_6$] was successfully achieved with the aid of PIL. The obtained PIL-G-IL solution exhibited higher conductivity than the pure ionic liquid. We believe that the combination of ILs and graphene sheets have great potential applications in some fields, such as solar cells, lubricating materials, energy-storage devices, and catalysis, and even some special applications because both graphene and ILs have unique properties.

The authors are grateful to the National Natural Science Foundation of China (20633080), Ministry of Science and Technology of China (2009CB930802), and the Chinese Academy of Sciences (KJCX2.YW.H16) for their financial support.

Notes and references

‡ *Preparation of aqueous dispersion of graphene sheets stabilized by the polymers*: We only describe procedures to prepare aqueous dispersion of graphene sheets stabilized by the PIL because others were prepared using the similar procedures. In the experiment, 2.0 mL of GO aqueous solution (5.0 mg mL^{-1}) was diluted to 10 mL (1.0 mg mL^{-1}) with double distilled water, and then the exfoliation of GO aqueous solution was achieved by sonicating the mixture in a water bath (KQ-100, 40 kHz) for 5 min. The obtained brown dispersion was centrifuged at 4000 rpm for 30 min to remove any unexfoliated GO. Then, 100 mg of PIL was mixed with 10 mL of GO dispersion (0.8 mg mL^{-1}) in a test tube and vigorously shaken for a few minutes. The resulting homogeneous dispersion was transferred into a 25 ml flask by pipette, followed by reduction with hydrazine monohydrate (10 μL) at 100 °C for 1 h. Finally, a stable dispersion of graphene sheets in aqueous solution was obtained.

Preparation of PIL-stabilized graphene sheet dispersion in [bmim][PF$_6$]: 2.0 mL of the stable dispersion (PIL-G) obtained above and 2.0 mL of [bmim][PF$_6$] were first added into a test tube, and mixed entirely by vigorously shaking followed by deposition. The PIL-G was extracted into the IL phase (Fig. 1d) and the water was vaporized and the PIL-G dispersion in IL was dried under vacuum at 70 °C for 24 h.

The photos of the samples were taken by a digital camera (Olympus C-4000). The UV-vis spectra were recorded with a TU-1901 spectrophotometer (Beijing General Instrument Company). An X-ray photoelectron spectroscopy (XPS) study was carried out with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W AlKα radiation. The base pressure was about 3×10^{-9} mbar and the binding energies were referenced to C1s line at 284.8 eV from adventitious carbon. Atomic force microscopic (AFM) study was performed with NanoScope IIIa (Veeco, US) operating in the tapping mode. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV-400. Molecular weight of poly(1-vinyl-3-butylimidazolium choloride) was measured with a gel permeation chromatography (GPC) system equipped with a Waters 2414 differential refractive index detector, a Waters 1515 HPLC pump and three Waters styragel columns (HT3, HT4 and HT5) using DMF as eluent at a flow rate of 1 mL min^{-1} at 50 °C. The calibration curve was obtained by applying polystyrene standards. The apparatus and procedures for the conductivity measurement were the same as that reported previously.[22]

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