Supporting Information

Dispersion of Graphene Sheets in Ionic Liquid [bmim][PF_6] Stabilized by an Ionic Liquid Polymer

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1. Experimental

Materials. Natural graphite flake (325 mesh), 1-vinylimidazole, and hydrazine monohydrate (>99%) were purchased from Alfa Aesar. Poly(sodium 4-styrenesulfonate) (PSS, M_w = 70,000, Scheme S1) was purchased from Aldrich. N-methylimidazolium was produced by Linhai Kaile Chemical Factory, and distilled prior to use. Poly(vinyl pyrrolidone) (PVP, M_w = 30,000, Scheme S1) and other chemicals (A. R. grade) were purchased from Beijing Chemical Reagent Company.

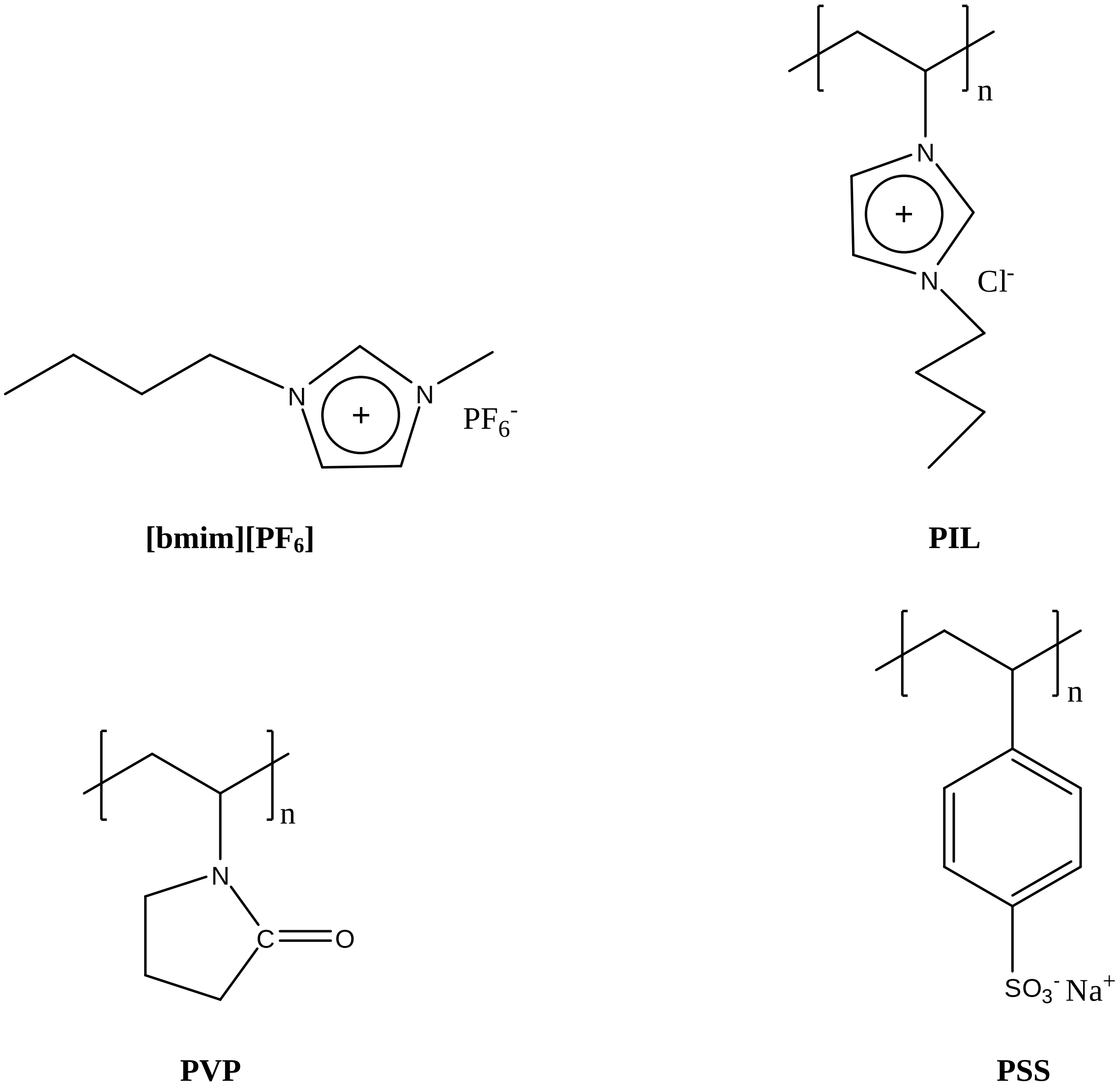
Synthesis of 1-butyl-3-methylimidazolium hexafluorophosphate [bmim][PF_6]. The ionic liquid (Scheme S1) was used as a solvent to disperse graphene sheets, which was prepared according to the method reported by Dupont et al.[S1]

Synthesis of graphite oxide. The graphite oxide was synthesized from natural graphite flake by a modified Hummers method.[S2, S3] In the experiment, concentrated H_2SO_4 (15 mL) was mixed with $K_2S_2O_8$ (3.0 g) and P_2O_5 (3.0 g) at 90 ^{o}C in a 150 mL beaker, and then the mixture was cooled to 80 ^{o}C. 3.6 g of natural graphite flake was slowly added to the above solution with stirring. The mixture was kept at 80 ^{o}C for 4.5 h. Afterwards, the mixture was diluted with 600 mL double distilled water and left to stand for 12 h. Then the mixture was filtered and washed with excess double distilled water using a 0.2 micron Nylon Millipore filter until the pH of the filtrate was neutral. The solid product was dried in air for one day. Then, a half of this pretreated graphite flake was added to cold (3 ^{o}C) concentrated H_2SO_4 (70 mL). While keeping the reaction temperature less than 10 ^{o}C, $KMnO_4$ (9.0 g) was added slowly until completely dissolved. This mixture was stirred at 35 °C for 2 h. 150 mL double distilled water was added to the mixture slowly and the reaction temperature was kept less than 50 °C using an ice bath. Then the mixture was stirred for 2 h followed by adding additional 420 mL double distilled water. Successively, 10 mL 30% H_2O_2 was added to the mixture, resulting in a brilliant yellow color along with bubbling. The mixture was deposited overnight and then the clear supernatant was decanted. The remaining mixture was centrifuged and washed with 750 mL of 10% HCl solution and 1000 mL double distilled water. The resulting graphite oxide was then diluted into a 400 mL brown dispersion, which was subjected to dialysis to completely remove residual salts and acids. Finally, 0.5% w/w dispersion was obtained by dialysis for one week, and the dispersion was used to prepare all the following dispersions.

Synthesis of poly(1-vinyl-3-butylimidazolium chloride) (PIL). The IL 1-Vinyl-3-butylimidazolium chloride ([Vbim][Cl]) was synthesized according to the literature methods.[S4, S5] In the experiment, 1-vinylimidazole (12.0g, 127 mmol) and 1-chlorobutane (37.0g, 400 mmol) were added to a three-necked flask in an oil bath at 70 °C under nitrogen atmosphere. The mixture was stirred vigorously for 75 h. After cooling to room temperature, the top liquid was decanted and the bottom viscous liquid was diluted in ethanol, and then precipitated in ethyl acetate. The resulting solid was filtered and dried under vacuum at 50 °C overnight to afford [Vbim][Cl] as a white solid. Next, the polymerization of [Vbim][Cl] was performed using the similar procedures to prepare the polymer supported ILs.[S4, S5] In the experiment, [Vbim][Cl] (3.0g), AIBN (0.015g) and chloroform (30 mL) were added into a three-necked flask in an oil bath at 60 °C under nitrogen atmosphere. After stirring for 18 h, the reaction mixture was cooled to room temperature, and then precipitated in ethyl ether. The residual [Vbim][Cl] was removed by dialysis for two days. Then the solution was concentrated with a rotary evaporator at 70 °C. Finally, the product PIL was obtained after being dried under vacuum and its molecular weight was measured to be 26,316 by GPC analysis.

1-Vinyl-3-butylimidazolium chloride ([Vbim][Cl]). ^{1}H NMR (400 MHz, D_2O) δ =0.97 (t, J (H, H) = 7.2 Hz, 3H), 1.38 (m, 2H), 1.92 (m, 2H), 4.29 (t, J (H, H) = 7.2 Hz, 2H), 5.47 (dd, J (H, H) = 8.8, 2.8 Hz, 1H), 5.84 (dd, J (H, H) = 15.6, 2.8 Hz, 1H), 7.18 (dd, J (H, H) = 15.6, 8.8 Hz, 1H), 7.62 (s, 1H), 7.81 (s, 1H). ^{13}C-NMR (100MHz, D_2O) δ = 12.70, 18.71, 31.14, 49.71, 109.35, 119.47, 122.92, 128.28, 134.11.

2. Structures of [bmim][PF_6], PIL, PVP and PSS



Scheme S1. Structures of IL and polymers used.

3. Results

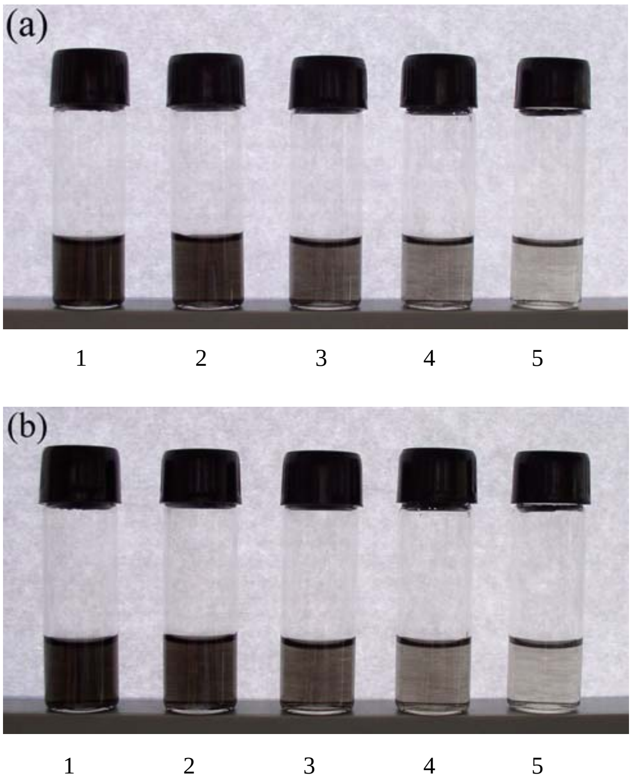


Figure S1. (a) Vials 1, 2, 3, 4, and 5 show PIL-G dispersed in [bmim][PF_6] with a content of 0.05, 0.04, 0.03, 0.02, and 0.01 mg/mL, respectively, the weight ratio of the PIL and graphene sheets was 12.5; (b) Vials 1-5 correspond to vials of (a) after being deposited for two months.

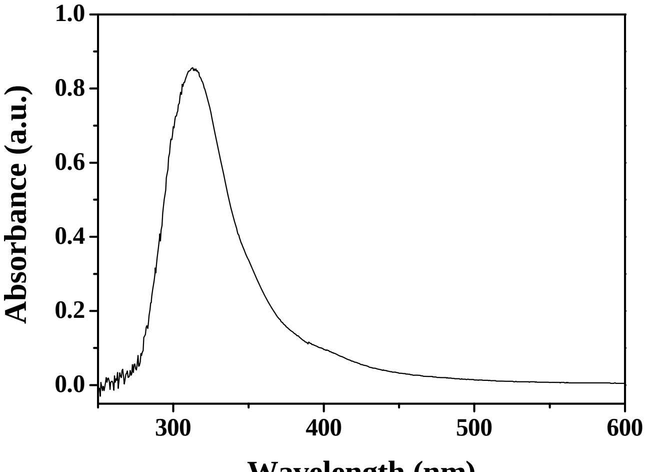


Figure S2. UV-vis absorption spectra of PIL dissolved in [bmim][PF_6] (10.0 mg/mL), and the reference solution used in the measurement was neat [bmim][PF_6].

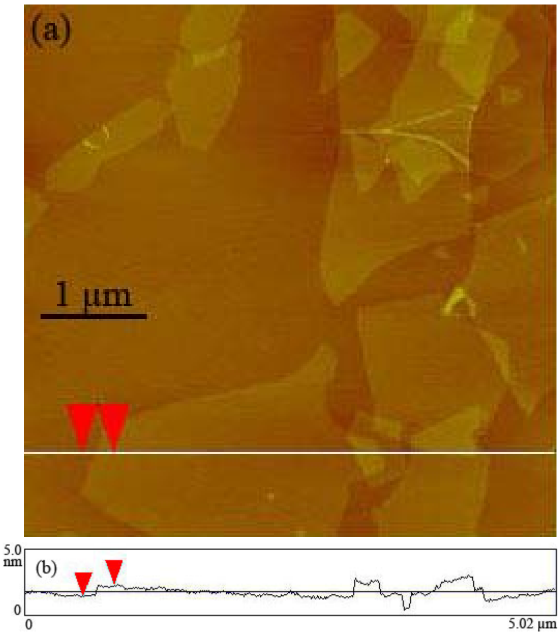


Figure S3. (a) Tapping mode AFM image of GO on freshly cleaved mica. (b) Height profile along the line displayed in (a).

GO, reduced graphite oxide (r-GO), and PIL-G were analyzed by X-ray photoelectron spectroscopy (XPS), which were pretreated by filtration under vacuum and washing with double distilled water and then drying under vacuum. The results are presented in Figure S4. The main peak centered at 284.8 eV corresponded to extensively delocalized sp^2-hybridized carbon atoms. The separated peaks with binding energies of 285.4, 285.9, 286.8, 287.9, and 289.0 eV were attributed to carbon atoms in C-N, C=N, C-O, C=O, and O-C=O species, respectively.[S6] The oxygen functionalities in the GO were reduced significantly after the reduction process, which can be known by comparing the C1s XPS spectra of GO (Figure S4a), r-GO(Figure S4b) or PIL-G(Figure S4c), indicating that significant de-oxygenation took place in the process of reduction. In fact, it is impossible to reduce GO completely.[S7] The Cl 2p spectrum of PIL-G exhibited an intensive peak, while the Cl 2p spectrum of the reduced GO displayed no obvious signal (Figure S4d), suggesting that the PIL still existed on the surface of graphene sheets after the pretreatment.

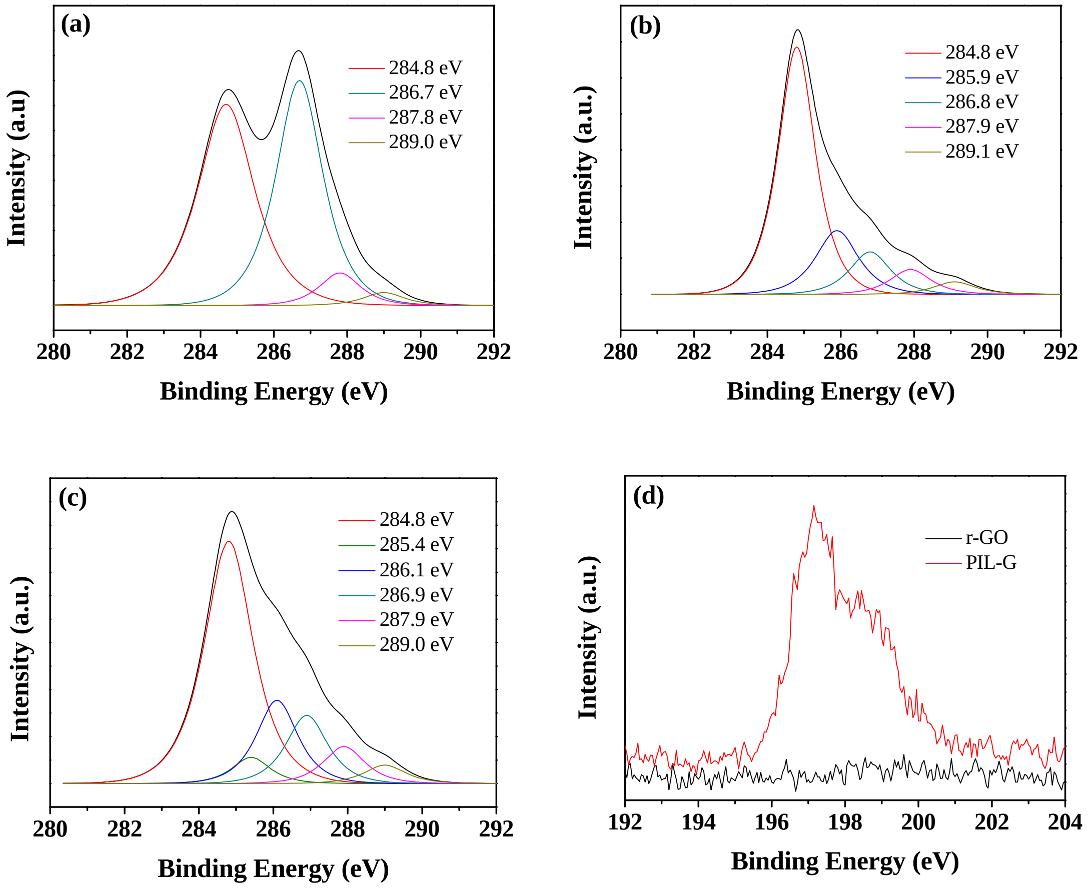


Figure S4. The XPS C 1s spectra of (a) graphite oxide (GO), (b) reduced graphite oxide (r-GO), and (c) PIL stabilized graphene sheets (PIL-G). (d) The XPS Cl 2p spectra of r-GO and PIL-G.

References:

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