Flexible Graphene Films via the Filtration of Water-Soluble Noncovalent Functionalized Graphene Sheets

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The unique electronic property of graphene sheets[1–3] provides potential applications in synthesizing nanocomposites[4] and fabricating various microelectrical devices, such as field-effect transistors,[5] ultrasensitive sensors,[6] and electromechanical resonators.[7] Several effective techniques have been developed for preparing graphene sheets. Among them, mechanical exfoliation can produce pure graphene for fundamental sudies.[1] Epitaxial graphene sheets have been prepared by treatment of silicon carbide wafers at high temperatures.[2] Reduction of exfoliated graphite oxide can produce a large amount of graphene sheets, and they can be stabilized by amphiphilic polymers to form a stable dispersion.[8] Functional graphene sheets were produced by thermal expansion of graphite oxide,[9] and stable dispersions of graphene chemically modified by alkylamine were also obtained.[10] Recently, a method of dispersing graphene sheets was developed by utilizing the hydrophilic carboxyl groups on graphene surface.[11] The functionalization of graphene has been considered to be important for improving their solubility and self-assembly properties[10,12] and applications in devices.[6] However, up to date, noncovalent functionalization of graphene sheets through $\pi-\pi$ interactions using aromatic organic molecules has rarely been addressed in the literature, although there are plenty of publications in the field of carbon nanotubes.[13] In this communication, we prepared stable aqueous dispersions of graphene sheets using a water-soluble pyrene derivative, 1-pyrenebutyrate (PB$^-$), as a stabilizer since the pyrene moiety has been reported to have strong affinity with the basal plane of graphite via π-stacking.[14] On the basis of this dispersion, a large area flexible graphene film with a conductivity of 2×10^2 S/m was obtained by filtration.

In a typical experiment, graphite oxide (GO) was synthesized from natural graphite powder by a modified Hummers method (Supporting Information).[12b,15] To prepare a PB$^-$-functionalized graphene dispersion, 20 mg (0.5 mmol) of NaOH and 29 mg (0.1 mmol) of pyrenebutyric acid were added to 20 mL (0.1 mg mL^{-1}) of GO dispersion, and then the mixture was reduced with hydrazine monohydrate (100 μL, 2 mmol) at 80 °C for 24 h. After reduction, a homogeneous black dispersion with a small amount of black precipitate was obtained. The original dispersion was centrifuged to remove the precipitate to yield a stable black supernatant (Figure 1, right). The stable black supernatant was filtered through a cellulose acetate membrane (0.22 μm pore size) to produce a film consisting of PB$^-$-functionalized graphene (PB$^-$-G) sheets, and the film was repeatedly washed with deionized water. The filtrate was detected to contain PB$^-$ by UV–visible spectroscopy, indicating that an excess free PB$^-$ existed in the original dispersion. In comparison, the reduction of GO dispersion without PB$^-$ stabilizer produced black reduced graphite oxide (r-GO),
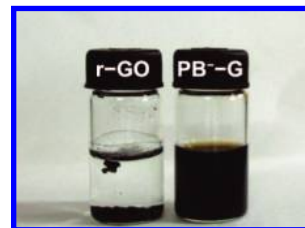

Figure 1. Images of water dispersions (0.1 mg mL^{-1}) of reduced graphite oxide (left) and PB$^-$-functionalized graphene (right).
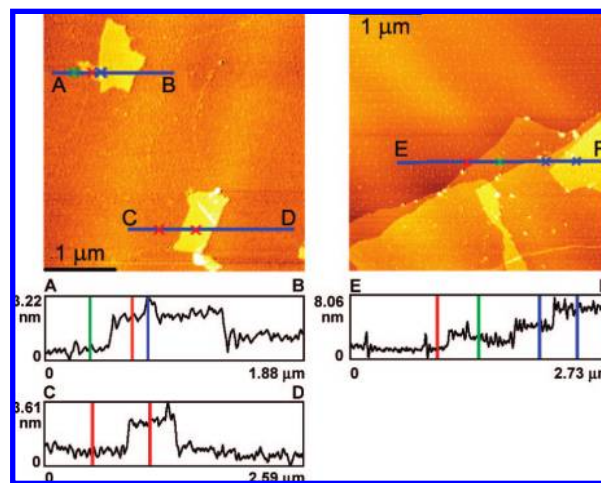

Figure 2. Tapping mode AFM images of exfoliated graphite oxide (left) and PB$^-$-functionalized graphene (right) on mica.

precipitating to the bottom of the solution (Figure 1, left). GO, r-GO, and PB$^-$-G have been carefully characterized by X-ray diffraction (XRD), FT-infrared, Raman, and X-ray photoelectron spectroscopies (Figures S1–S4). The results confirmed that GO has been well deoxygenated in r-GO and PB$^-$-G.

Figure 2 shows the atomic force microscopic (AFM) images of GO and PB$^-$-G. The samples used for AFM studies were prepared by depositing the corresponding dispersions on new cleaved mica surfaces and dried under vacuum at room temperature. The cross-sectional view of the typical AFM image of the exfoliated GO (Figure 2, left) indicated that the average thickness of GO sheets is ~1.3 nm, being somewhat larger than the interlayer spacing of GO (0.78 nm) measured by XRD (Figure S1). Similar results have also been observed for the thickness of single GO sheets by other AFM studies.[10,13] On the other hand, the mean thickness of single PB$^-$-G was determined to be ~1.7 nm (Figure 2, right). If we assume that
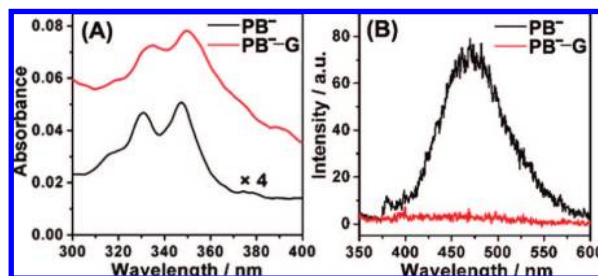
Figure 3. (A) Absorption and (B) fluorescence ($\lambda_{ex} = 340$ nm) spectra of PB$^-$-G and PB$^-$ film deposited on glass substrate from aqueous solution.

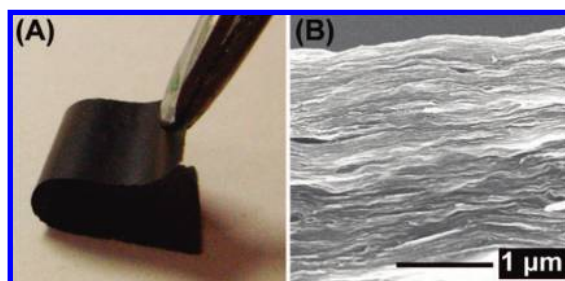**Figure 4.** (A) Photograph of a 6 μm thick PB$^-$-G film (1 $\times$ 3 cm). SEM side view image of a 2.5 μm thick PB$^-$-G film.

monolayered PB$^-$ molecules covered both sides of graphene sheet with offset face-to-face orientation via $\pi-\pi$ interactions, the estimated distance between PB$^-$ and the graphene sheet is $\sim$0.35 nm.[16,17] Accordingly, the average thickness of the graphene sheet in the PB$^-$-G layer can be derived to be $\sim$1 nm. This value is almost triple the interplanar spacing of graphene ($\sim$0.34 nm). Considering there is a low content of unreacted functional groups in PB$^-$-G, possible multilayer adsorption of PB$^-$ molecules onto the graphene surface, and the overestimate of sheet thickness in AFM measurements,[9,10,12b] we can expect that these sheets are uniformly graphene monolayers. Furthermore, from points E to F in the right picture of Figure 2, the height of the sample showed three stages with similar increment of 1.7 nm, corresponding to one, two, and three layers of PB$^-$-G sheets, respectively.

Figure 3 illustrates the absorption and fluorescence spectra of PB$^-$ and PB$^-$-G thin films coated on glass sheets. As can be seen from Figure 3A, the main absorption peaks of the PB$^-$-G film appear at 334 and 350 nm, respectively, which are red-shifted by 3 nm in comparison with those of the PB$^-$ film. This is mainly due to the $\pi-\pi$ interactions between the graphene sheets and the large aromatic ring of PB$^-$. In the fluorescence spectra (Figure 3B), the characteristic emission band of the PB$^-$ film at 470 nm is ascribed to its excimer emission.[18] Meanwhile, this emission was extensively quenched in PB$^-$-G film, indicating an effective electron or energy transfer between these two components.

Filtration of 0.1 mg L^{-1} aqueous PB$^-$-G dispersion through a membrane filter yielded a free-standing and flexible PB$^-$-G film (Figure 4A). The thickness of the film can be adjusted by the volume and concentration of PB$^-$-G dispersion. The cross-sectional view of the PB$^-$-G film imaged via scanning electron microscopy (SEM) clearly indicated its well-packed layered structures (Figure 4B). XRD pattern of the PB$^-$-G film also confirmed its layered structures (Figure S5). The characteristic

2θ peak appearing at 25.4° corresponds to the layer-to-layer distance (d-spacing) of $\sim$0.35 nm, which was very close to the d-spacing (0.335 nm) of natural graphite. The modulus and tensile strength of a 30 μm thick film were tested to be about 4.2 GPa and 8.4 MPa, respectively (Figure S6), being comparable to those of flexible graphite foils composed of stacked platelets of expanded graphite.[19] The conductivity of the PB$^-$-G film was measured to about 2×10^2 S/m, almost 7 orders of magnitude larger than that of a GO film (6×10^{-5} S/m) prepared by the same procedure. Furthermore, the soluble graphene described above can be used as an electrocatalytic layer for modifying the fluorine-doped tin oxide (FTO) counter electrode of a dye-sensitized TiO$_2$ solar cell and improve its performance significantly (Figure S7).

In summary, graphene sheets prepared by the reduction of graphene oxide can be noncovalently functionalized with PB$^-$, and the resulting PB$^-$-G can be stably dispersed in water. Large area flexible PB$^-$-G films with layered structures have been successfully prepared by filtration. The conductivity of the film is 7 orders of magnitude larger than that of the GO precursor. The simple method developed here can be extended to synthesize various functionalized graphene dispersions by using other stabilizers with large planar aromatic rings and provides a general route for preparing conducting films based on graphene.

Supporting Information Available: Detailed experimental procedures and additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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