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An amphiphilic pyrene sheet for selective functionalization of graphene†

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We have demonstrated that the aromatic amphiphile consisting of a hydrophilic dendron and an aromatic segment with a planar conformation can selectively exfoliate graphite powder into single- and double-layer graphene sheets in aqueous solution through hydrophilic functionalization of graphene surfaces.

One of the most significant recent highlights in the field of carbon allotropes such as fullerene, single wall nanotubes, and graphite is how to attain their processability without sacrificing their intrinsic properties for practical application.[1] In particular, exfoliation of graphite into single layers, graphene sheets, has attracted considerable attention because of the unusual electronic properties of monolayers of the graphite lattice.[2] Among the many exfoliation methods, dissolution of graphite into certain solvents such as *N*-methyl pyrrolidine (NMP), dimethylformamide (DMF), and *o*-dichlorobenzene (ODCB) is particularly interesting because graphite could be directly exfoliated into monolayer sheets, preserving their intrinsic electrical properties.[3] As an alternative strategy, surfactant molecules in aqueous solutions have been demonstrated to allow graphite flakes to exfoliate directly with concentrations up to 1 mg mL^{-1}.[4] Another recent example for direct exfoliation of graphite is provided by surface functionalization of graphene sheets with aromatic carboxylic acids in aqueous solutions.[5] The aqueous dispersions of graphene sheets in these cases originate from noncovalent functionalization of graphene with hydrophilic carboxylic acid through aromatic interactions between graphene surfaces and fused aromatic units. The carboxylic acid groups positioned at the out of plane graphene surface stabilize aqueous dispersions of the graphene flakes. In addition, fused aromatic segments render single-wall carbon nanotubes (SWNTs) with stable aqueous dispersions through noncovalent functionalization of the side walls.[6] For selective dispersions of the 2-D graphene sheet out of all graphite allotropes in aqueous solution, however, elaborate molecular design of amphiphilic molecules is required. Recently, we have shown that aromatic amphiphiles generate stable aqueous dispersions of fullerene or SWNTs through aromatic and hydrophobic interactions depending on the shape and conformation of the aromatic segments.[7] These results stimulated us to synthesize a sheet-like aromatic amphiphile that would selectively adhere to a 2-D graphene surface through efficient aromatic interactions.

In this communication, we present the design and synthesis of an amphiphilic molecule based on an aromatic molecular sheet that assembles selectively onto 2-D graphene surfaces through nondestructive π–π stacking interactions (Fig. 1). The amphiphilic molecule that functionalizes graphene surfaces consists of an aromatic segment based on four pyrene units and a laterally-grafted oligoether dendron. The aromatic segment may adopt a 2-D sheet-like conformation on graphene surfaces to maximize aromatic interactions with the basal plane of graphene and the hydrophilic dendron would be protruded away from the graphene surface to generate hydrophilic outerlayers, consequently facilitating the dispersion of graphene sheets in aqueous solution. The amphiphilic molecule was synthesized in a stepwise fashion according to the procedure reported previously.[8] The resulting aromatic amphiphile was characterized by NMR spectroscopy, elemental

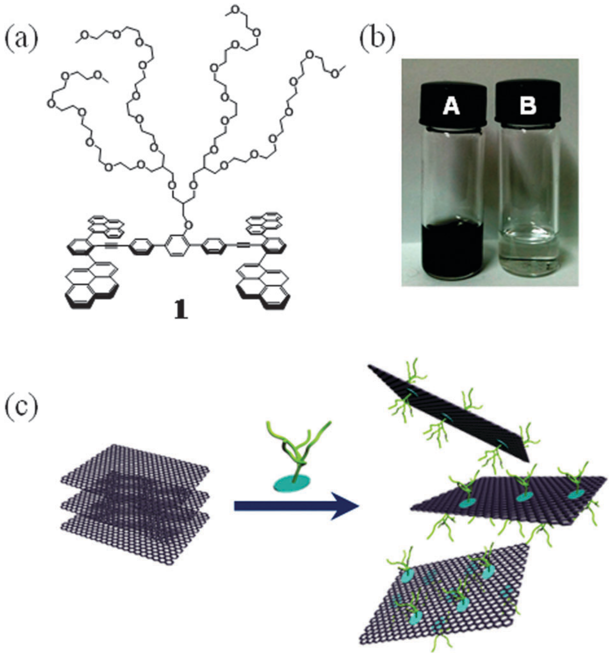

Fig. 1 (a) Chemical structure of amphiphile **1**. (b) Photograph of graphene (A) and SWNT (B) in aqueous solution of **1**. (c) Schematic representation of graphene dispersion.

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analysis, and MALDI-TOF mass spectroscopy and was shown to be in full agreement with the structure presented.

To investigate the capability of amphiphile **1** to exfoliate graphite into graphene in aqueous solution, we prepared graphene dispersions by sonicating a mixture solution (H_2O/MeOH = 7 : 3 v/v) of graphite powder and amphiphile **1**. The resulting dispersions were centrifuged at 1300 rpm for 20 min and the supernatant containing graphene sheets was collected, in which the concentration was measured to be 1.5 mg mL^{-1}, a much higher concentration than those reported for graphene sheets prepared by direct exfoliation.[4,9] As shown in Fig. 1b, sonication of graphite powder in amphiphile **1** solution afforded a dark black dispersion even after centrifugation. Such a dispersion showed to be very stable without any noticeable sedimentation and aggregation over a period of 2 months. Remarkably, the comparative study with SWNTs under the same conditions showed that the black SWNT powder was not dispersed in amphiphile **1** solution (Fig. 1b), indicating that **1** is unable to disperse SWNTs but exfoliates selectively only 2-D graphene in aqueous solution. Indeed, the flat conformation of the aromatic segment of **1** provides a large surface mismatch with the highly curved SWNT to frustrate efficient π–π stacking interactions, thereby unable to exfoliate curved carbon allotropes. This result demonstrates that the 2-D planar conformation of the aromatic segment in the molecular architecture is essential for selective exfoliation of graphene through efficient π–π stacking interactions.[5]

The aromatic π–π stacking interactions between the pyrene units of **1** and graphene were confirmed by UV absorption and fluorescence spectra (Fig. 2). The absorption maximum of **1** in the graphene dispersion at 325 nm showed to be red shifted together with the strong hypochromic effect with respect to that of the solution in the absence of graphene, indicative of extended π-conjugation of the aromatic segment in the presence of graphene. When the graphene dispersion was excited at 325 nm, the fluorescence intensity of **1** was significantly suppressed because of fluorescence quenching, indicative of strong π–π stacking interactions between the aromatic segments and graphene surfaces.[10]

The dispersion of graphene by **1** in aqueous solution was also investigated by AFM, TEM, and SEM measurements (Fig. 3). The AFM image revealed graphene flakes composed of a single layer sheet with a thickness of ~2 nm, which is consistent with heights for single layers reported previously.[11] This value corresponds to the face-on arrangement of the amphiphilic molecules on both sides of graphene sheets, thereby forming a sandwich-like structure. TEM and SEM images showed that the sizes of the exfoliated graphene sheets are 2–4 μm in diameter.

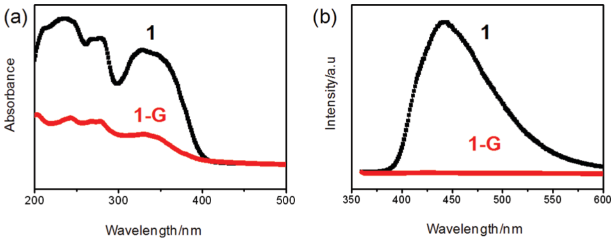

Fig. 2 (a) Absorption and (b) emission spectra of **1** and **1**-G in 0.2 wt% (MeOH/H_2O); λ_{ex} = 340 nm.

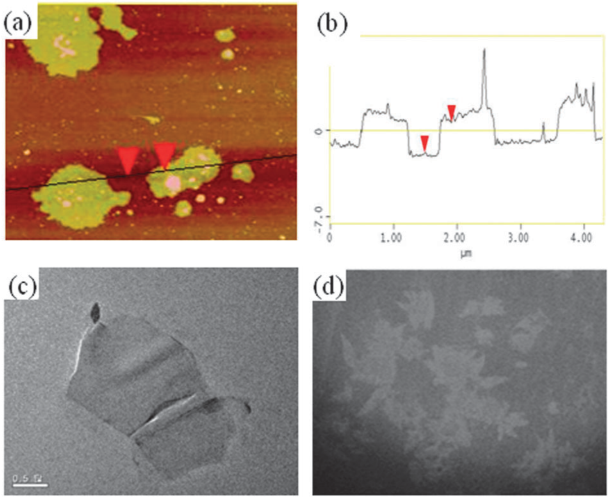

Fig. 3 (a) AFM image of **1**-graphene sheet on SiO_2/Si wafer after spin-coating and annealing at 200 °C, (b) the height profile of the AFM image, (c) TEM image from **1**-graphene dispersion on a carbon grid, (d) SEM image of **1**-graphene dispersion on Si after spin-coating.

The direct exfoliation of graphite into graphene was further evidenced by Raman scattering which is sensitive to the electronic structure of graphene.[12] Fig. 4 shows typical Raman spectra of graphene sheets which are characterized by a G-band at 1580 cm^{-1} and a 2D-band at 2680 cm^{-1}. The most prominent Raman feature is that the peak intensity of the 2D-band is much larger than the G-band (the intensity ratio, G/2D = 0.3), indicating the exfoliation of graphite into single layer and double layer sheets.[12a] In addition, the 2D-band showed to be a single and symmetrical Lorentzian peak at 2680 cm^{-1}, in contrast to that of HOPG that is split into two different subpeaks, one small peak at 2678 cm^{-1} and the other large peak at 2723 cm^{-1}, which further confirms the single-layer feature of graphene. These two Raman features demonstrate that graphene in aqueous solution of **1** predominantly consists of single- and double layer graphene sheets. The electrical properties of dried thin films obtained from the graphene dispersions were investigated by transparent resistance measurements. The sheet resistance of the graphene film with 87% transparency is measured to be ~5 kΩ sq^{-1} while that of 97% transparency is ~34 kΩ sq^{-1}, indicating much better electrical properties than those reported for graphene sheets

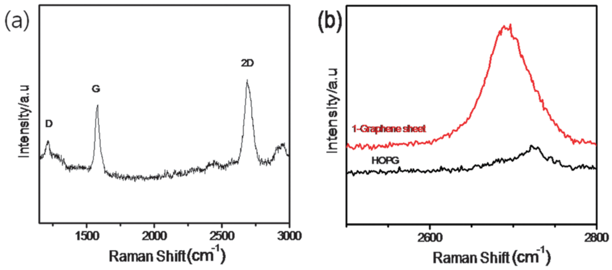

Fig. 4 (a) Raman spectrum of the annealed (400 °C) **1**-G sheet on SiO_2/Si after spin-coating and (b) the 2D single peak compared to HOPG.

prepared in surfactant solutions and polymer solutions.[4a,9a] We believe that this outstanding electrical property arises from the exfoliation into defect-free graphene sheets, which will provide applications of graphene for a transparent flexible electrode.

The results described here demonstrate that an aromatic amphiphile based on a conformationally flexible aromatic segment including four pyrene units readily exfoliates graphite flakes into graphene sheets in aqueous solution with concentrations up to 1.5 mg mL^{-1}. The graphene dispersions arise from hydrophilic functionalization of graphene surfaces with an aromatic amphiphile based on an oligoether dendron through a combination of amphiphilicity and π–π stacking interactions. On the other hand, curved carbon allotropes such as SWNTs are unable to be dispersed in aqueous solution of **1**, demonstrating that the amphiphile selectively recognizes only 2-D graphene sheets. The graphene sheets of the film are transparent and show a good electrical property as evidenced by transparent resistance measurements. The most notable feature of the aromatic amphiphile synthesized here is its ability to selectively functionalize only 2D graphene sheets among carbon allotropes with different shapes in aqueous solution, thereby yielding water-soluble graphene. The selective dispersions of graphene arise from its capability to adopt a planar conformation on 2D graphene surfaces that provides strong mismatch in shape for highly curved spherical and tubular structures. We anticipate that our strategy provides new opportunities for separation of graphene from carbon allotropes and fabrication of graphene-based composite materials that require aqueous environments such as cytocompatible nanomaterials through readily available noncovalent functionalization of graphene surfaces.[9a,13,14]

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