Electronic Supplementary Material

A Hybrid Material of Graphene and Poly (3,4-ethyldioxythiophene) with High Conductivity, Flexibility and Transparency

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Supporting information to DOI 10.1007/s12274-009-9032-9

1. Materials and general information

Unless specifically indicated, all chemicals and reagents used in this study were purchased from commercial sources and used as received. Graphite was obtained from Qingdao Huarun Graphite Co. Hydrazine hydrate 80% was obtained from Tianjin Ruijinte Chemical Co., PEDOT-PSS (Clevios™ P AI 4083) was obtained from H. C. Starck., $Fe_2(SO_4)_3$ (99.998%) was obtained from Alfa Aesar. EDOT was obtained from Aldrich. Nylon membrane (0.22 μm) was obtained from Automatic Science (Tianjin) Instrument Co., LTD. FTIR spectra were obtained with a Bruker Tensor 27 instrument. All IR samples were prepared as pellets using spectroscopic grade KBr. UV–vis–NIR spectra were obtained with a Jasco V-570 spectrometer, and UV–vis spectra were recorded on a Varian Cary 300 spectrophotometer. Tapping mode atomic force microscopy (AFM) measurements were performed using Multimode SPM from Digital Instruments with a Nanoscope IIIa Controller and samples for AFM images were prepared by spin coating H_2O/DMF solutions of sulfonated graphene or graphene-PEDOT (0.2 mg/mL) on a freshly cleaved mica surface. The direct current (DC) conductivity of the graphene-PEDOT composites was determined using the standard two-point contact method on a rectangular sample, and the data were collected with a Keithley SCS 2400 SourceMeter instrument. The films were prepared by drop-casting the solution (12 mg/mL) onto quartz and then heated at 60 °C under vacuum for 12 h, with the thickness of the drop-casting film being tuned by varying the solution concentration or performing multiple coating steps. The film thickness was estimated using a profilometer (Ambios Technology XP-2).

2. Synthesis

Sulfonated graphene was prepared from graphene oxide in four steps: (1) pre-reduction of graphene oxide with sodium borohydride to remove the majority of the oxygen functionality; (2) sulfonation with the aryl diazonium salt of sulfanilic acid; (3) post-reduction with hydrazine to obtain lightly sulfonated graphene, soluble in water/DMF (2 mg/mL); (4) Further functionalization with sodium nitrite, sulfanilic acid, and azoisobutyronitride (AIBN) in fuming H_2SO_4 to obtain a more highly sulfonated graphene, which shows good solubility in both water and organic solvents (12 mg/mL). Pre-reduction is necessary both to achieve complete reduction (in step 3) and to enable the sulfonation reaction (step 2) by increasing the size of sp^2-carbon domains available for reaction with the aryldiazonium salt. Elemental analysis indicates that the S/C elemental ratio increased from 1/93 to 1/48 after the second sulfonation step.

Synthesis of lightly sulfonated graphene: The lightly sulfonated graphene with improved water solubility was synthesized using a modification of a literature method [21]. Graphene oxide was prepared using a modified Hummers method [11, 26]. In a typical procedure, graphene oxide (225 mg) was dispersed in water (225 mL). After

sonication for 1 h with an ultrasonic bath, a clear, brown dispersion of graphene oxide was formed. In the pre-reduction step, sodium borohydride (2.7 g, 71 mmol) in water (67.5 mL) was added to the dispersion of graphene oxide after its pH was adjusted to 9–10 with 5 wt% sodium carbonate solution. The mixture was then kept at 80 °C for 1.5 h under constant stirring. The mixture turned gradually from dark brown to black. After centrifuging and rinsing with water several times, the collected partially reduced graphene oxide was redispersed in water (225 mL) via mild sonication. The dizaonium salt [prepared following the procedure in Ref. [S-1] solution (2 g, 9 mmol aryl dizaonium salt in 200 mL water) and HCl solution (0.2 g, 1 mol/L) were added to the dispersion of partially reduced graphene oxide prepared above cooled in an ice bath under magnetic stirring. The mixture was stirred in the ice bath for 2 h, and then further stirred at room temperature for 12 h. After centrifuging and rinsing with water several times, the sulfonated graphene oxide product was then collected by centrifugation. It was again redispersed in water (225 mL). In the post-reduction step, hydrazine hydrate 80% (6 g) was added into the dispersion and the reaction mixture was kept at 100 °C for 24 h under constant magnetic stirring. After centrifuging and rinsing with water several times, the final product was collected and dried under vacuum to yield the lightly sulfonated graphene. Elemental analysis gave a S:C ratio of 1:93.

Synthesis of sulfonated graphene: The lightly sulfonated graphene (50 mg) was stirred in oleum (50 mL) in a 100 mL flask for 3 h. The mixture was then heated to 80 °C, and sodium nitrite (1.15 g, 17 mmol), sulfanilic acid (2.886 g, 17 mmol), and AIBN (0.137 g, 0.8 mmol) were added. The mixture was stirred for 2 h at 80 °C and, then poured slowly and carefully into more than 500 mL of water and filtered through a Nylon membrane (0.22 μm). The filter cake was washed with acetone and water, vacuum dried at 50 °C overnight, and the product collected. Elemental analysis gave a S:C ratio of 1:48.

AFM and a profilometer were used to probe the dispersion of sulfonated graphene in solvents, film morphology, and thickness. As determined by AFM (Fig. S-1), sulfonated graphene can be readily

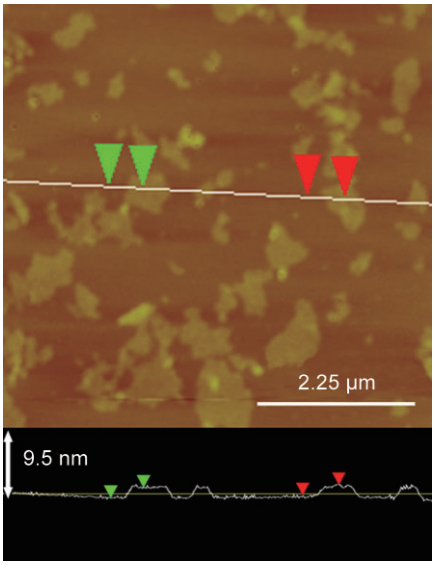
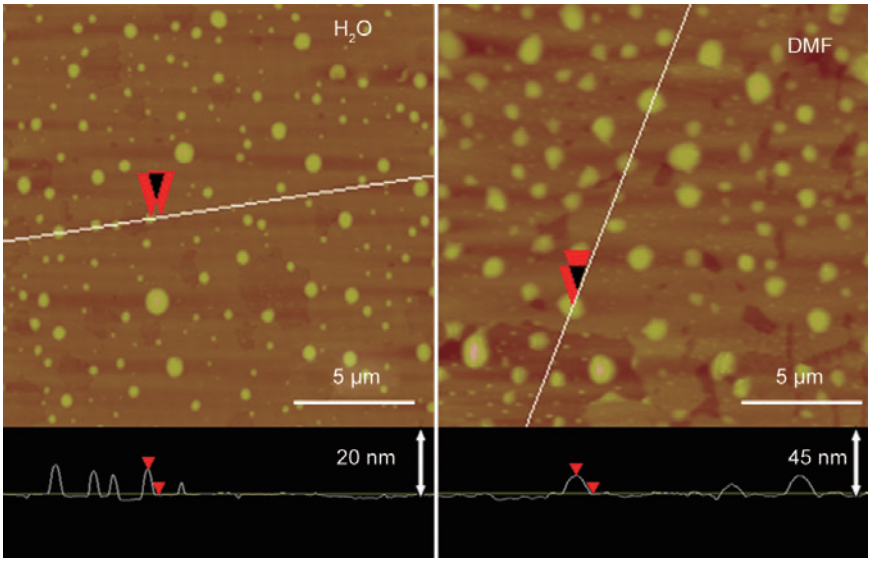


Figure S-1 AFM image of sulfonated graphene. The graphene material can be easily dispersed in a state of complete exfoliation consisting almost entirely of single-layered graphene sheets in water. The average thickness is 1.32 nm



(a) (b)

Figure S-2 (a) Tapping mode AFM height images of graphene-PEDOT sheets obtained by spin coating an aqueous solution of graphene-PEDOT (0.2 mg/mL) onto a mica substrate. Such films are 2–10 nm thick and continuous. (b) Tapping mode AFM height images of graphene-PEDOT sheets obtained by spin coating a DMF solution (0.2 mg/mL) onto a mica substrate. Analysis of a large number of AFM images revealed that most of the continuous sheets have dimensions of hundreds of nanometer with heights in the range 4–15 nm. The reason for these differences may lie (partially) in the different wettability of water and DMF

dispersed in water to form a stable dispersion, composed of completely exfoliated, functionalized individual graphene sheets. The AFM samples were prepared by spin coating the aqueous solutions (0.2 mg/mL) onto a mica substrate. The average thickness was 1.186 nm.

Synthesis of graphene-PEDOT: Sulfonated graphene was dispersed in water (10 mL), followed by the addition of anhydrous $Fe_2(SO_4)_3$ (10 mg, 0.025 mmol) and the monomer EDOT (100 mg, 0.70 mmol). The mixture was stirred for 48 h at 50 °C, and was then poured into methanol (100 mL), and stirred vigorously for 1 h. The resulting dark-blue precipitate was collected by centrifuging. The excess EDOT and other impurities were removed through five washing cycles that included sonication, filtration (discarding the filtrate), and re-suspending the solid in water (50 mL) each time. The same washing procedure was repeated five times using THF as solvent (50 mL). UV and thin-layer chromatography (TLC) were used to check the filtrate to ensure no EDOT was present in the final washing and no unreactive EDOT left in the final product. The resulting hybrid graphene-PEDOT was dried under vacuum. Elemental analysis gave a S:C ratio in the product of 1:11.

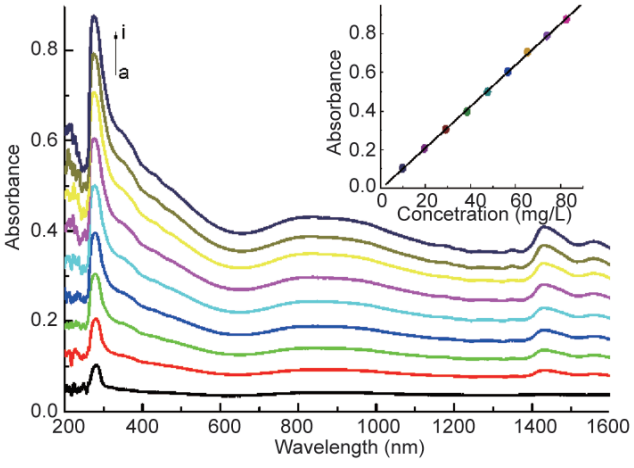


Figure S-3 Concentration dependence of UV absorption of graphene-PEDOT in DMF (concentrations are 9.9, 19.6, 29.1, 38.5, 47.6, 56.6, 65.4, 74.0, 82.6 mg/L, from a to i, respectively). The straight line in the plot in the inset is a linear least-squares fit to the data, indicating the hybrid graphene-PEDOT was dissolved homogeneously in the solvent

Reference

[S-1] Wang, X.; Liu, R.; Waje, M. M.; Chen, Z.; Yan, Y.; Bozhilov, K. N.; Feng, P. Sulfonated ordered mesoporous carbon as a stable and highly active protonic acid catalyst. *Chem. Mater.* **2007**, *19*, 2395–2397.