Electronic Supplementary Information (ESI)

Covalent Functionalization of Polydisperse Chemically Converted Graphene Sheets with Amine-Terminated Ionic Liquid

Experimental Section

Chemicals. Graphite powders (320 mesh) were of spectroscopically pure reagent and obtained from Shanghai Chemicals, China. 3-bromopropylamine hydrobromide (≥98%) was obtained from Aldrich. 1-methylimidazole (≥ 98%, Linhai Kaile Chemicals, China) was distilled at reduced pressure before use. potassium hydroxide (KOH, 82%) was obtained from Tianjin Chemicals, China. ethyl acetate (99.7%, Beijing Chemicals) were used as received. Unless otherwise stated, other reagents were of analytical grade and were used as received. All aqueous solutions were prepared with ultra-pure water (>18 MΩ) from a Milli-Q Plus system (Millipore).

Instruments. Atomic force microscope (AFM) images were obtained by a Digital Instruments Nanoscope IIIa (Santa Barbara, CA). X-ray diffraction (XRD) spectra were obtained using a D8 ADVANCE (Germany) using Cu-Kα (1.5406 Å) radiation. X-ray photoelectron spectroscopy (XPS) analysis was carried on an ESCALAB MK II X-ray photoelectron spectrometer. Fourier transform infrared spectroscopy (FTIR) was recorded on a CaF_2 substrate containing the interesting materials in the solid state with a Bruker Tensor 27 Spectrometer (4 cm^{-1}). Thermogravimetric analysis (TGA) were measured under a nitrogen atmosphere with a Perkin Elmer Thermal Analyzer at a heating rate of 5 °C min^{-1}. Transmission electron microscopy (TEM) pictures were imaged by JEOL 2000 transmission electron microscope operating at 200 kV. ^1H NMR spectrum was obtained on a Varian Unity-400 (400 MHz) NMR spectrometer with tetramethylsilane (TMS) as an internal standard.

Preparation of graphene oxide (GO). Graphene oxide (GO) was prepared by oxidizing natural graphite powder (SP, 320 mesh) based on a modified Hummers method as originally presented by Kovtyukhova and colleagues.[1,2] As-prepared graphene oxide was suspended in ultra-pure water to give a brown dispersion, which was subjected to dialysis to completely remove residual salts and acids for 4 days.[3] The resulting purified graphene oxide powders were collected by centrifugation and air-dried. Graphene oxide powders were dispersed in water to create a 0.05 wt% dispersion. Then the dispersion were exfoliated through ultrasonication for 1 h, which the bulk graphene oxide powders were transformed into GO nanoplatelets.

Preparation of unfunctionalized chemically converted graphene (u-CCG) nanosheets. Unfunctionalized chemically converted graphene (CCG) was synthesized from as-purified graphene oxide nanosheets.[3,4] Briefly, 20 mL graphene oxide sheets (in water, 0.05 wt%) was mixed with 20 mL water, 0.012 mL hydrazine solution (50% in water, Beijing Yili Chemicals, China) and 0.142 mL ammonia solution (25% in water, Beijing Chemicals, China) in a 100 mL glass vial. After being vigorously shaken or stirred for a few minutes, the GO nanosheets were reduced to graphene nanoplatelets by refluxing the mixture for 24 h under a oil bath (95 °C). The final products were then centrifuged, washed, and finally air-dried.

Preparation of IL-NH_2. In the typical procedure according to the literature,[5] 3-bromopropylamine hydrobromide (1.1000 g, 5 mmol) and 1-methylimidazole (0.395 mL, 5 mmol) were added to 12.5 mL ethanol, forming a colorless solution which was refluxed under nitrogen for 24 h. The resulting turbid mixture was purified by re-crystallization from ethanol, with ethyl acetate as anti-solvent. Finally, the resulting white powder was dried under

vacuum at 60 °C overnight and then purified. ^{1}H NMR (D_2O): □=8.738ppm (S,1H), 7.484 ppm (S,1H), 7.424 ppm (S,1H), 4.283 ppm (t,2H), 3.022 ppm (t,2H), and 2.232 ppm (m,2H). IL-NH_2 is soluble in DMF and DMSO, and well soluble in water, and stable in air.

Preparation of Polydisperse chemically converted graphene nanosheets. p-CCG was synthesized by an epoxide ring-opening reaction between graphene oxide (GO) and the 1-(3-aminopropyl)-3-methylimidazolium bromide (IL-NH_2). Firstly, IL-NH_2 (10 mg) was added into 10mL of GO homogeneous and transparent dispersion in water (0.5mg/mL), and then the salt effect of the GO sheets occurred, owing to the presence of ionic liquid. Secondly, KOH (10 mg) was added into the above turbid mixture and then the mixture was subjected to ultrsonication for 30 minutes. After the ultrsonication, the turbid mixture was transformed into homogeneous and transparent solution. Finally, the homogeneous solution was vigorously stirred at 80 °C for 24 h. The resulting p-CCG was subsequently centrifuged, washed with ethanol and water, and air-dryed. It is well known that the ring-opening reaction of epoxides can be catalyzed by acid and base. In control experiment, the hydrochloric acid (HCl) was chosen as the acid catalyst. It is found that the turbid mixture is still turbid after adding the HCl into the turbid mixture of GO and IL-NH_2. The inhomogeneity of the mixture results in the failure of the functionalization.

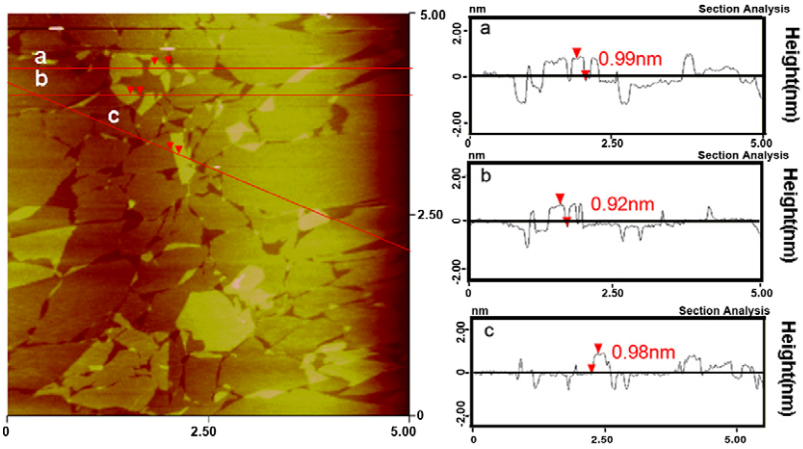

Fig. S1. (left) AFM image of GO dispersion in water (0.25mg/mL) on freshly cleaved mica surface through drop-casting. and (right) Height profile along the lines shown in AFM image.

The sample for AFM measurement was prepared by ultrasonic treatment of GO (in water) dispersions of 0.25 mg mL^{-1}.The sample was prepared through drop-casting on freshly cleaved mica surface. The mica was dried at ambient conditions for 24 h, and was directly examined using atomic force microscope. Individual GO sheets were imaged using AFM as shown in Fig. S1. On average, the interlayer space of the GO sheets is ca.0.96 nm, indicating that exfoliation of graphite down to individual GO nanosheets was indeed achieved.[6] While a pristine graphite sheet is atomically flat with a well-known van der Waals thickness of ca. 0.34 nm,[7] the GO is expected to be thicker mainly owing to the presence of epoxy groups above and below the GO plane.[8] Moreover, it is unavoidable that some solvent molecules still be kept in the interlayer of GO sheets after dried at ambient conditions for 24 h and these molecules will also contribute to the interlayer space of GO sheets. So the interlayer space of GO sheets obtained in AFM analysis is larger than that obtained in XRD analysis (Fig. S2, dry GO powders were directly used in XRD analysis).

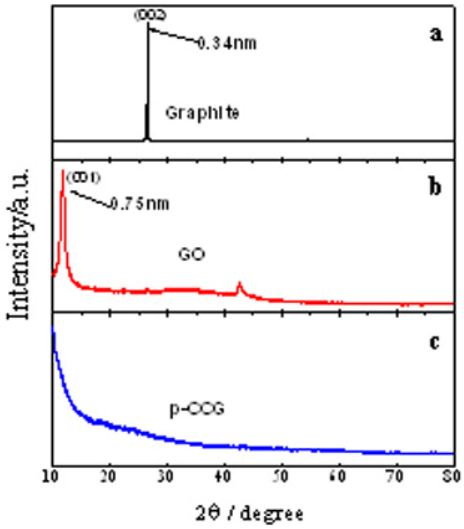

Fig. S2. The XRD pattern of (a) natural graphite, (b) GO, and (c) p-CCG.

The dry GO powders were directly used in the X-ray diffraction (XRD) analysis (Fig. S2). The XRD analysis exhibits that the (002) diffraction peak of graphite (Fig.S2a) appears at ca. 26.6°, and the interlay space is ca. 0.34 nm. After oxidation, the interlay space of GO (11.8°, 0.75 nm) is larger than that of the pure graphite, as a result of the introduction of oxygenated functional groups on carbon sheets.

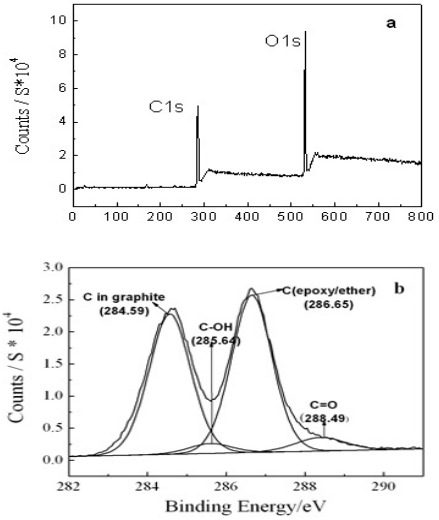

Fig. S3. (a) The survey XPS data of GO, and (b) the higher resolution data of the GO.

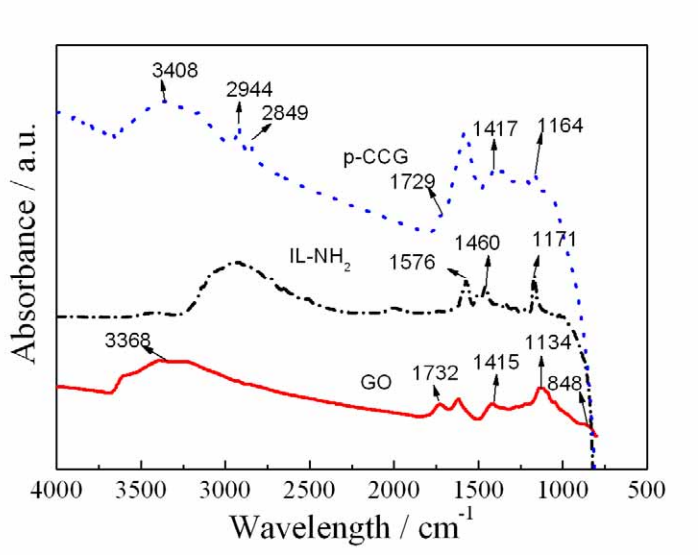

Fig. S4. FTIR spectra of GO (solid), IL-NH_2 (dashed), and p-CCG (dotted).

Fourier transform infrared spectroscopy (FTIR) was performed to characterize the resulting graphene nanosheets. The characteristic band of the carboxylic group in GO appeared at ca. 1732 cm^{-1} (C=O stretching) (Fig.S4, solid).[3, 9] The C-O vibrations of epoxy groups in GO appeared at ca. 1134 cm^{-1} and 848 cm^{-1}. As shown in Fig.S4 (dotted), the doublet at 2849 cm^{-1} and 2944 cm^{-1} corresponds to symmetric $\nu_s(CH_2)$ and asymmetric $\nu_{as}(CH_2)$ of the IL-NH_2 units which have been grafted on the CCG nanosheets basal plane. Moreover, the CH_3(N) stretching, CH_2(N) stretching, and ring in-plane asymmetric stretching arising from imidazolium ring were also observed at ca. 1164 cm^{-1},[5] which further confirmed the successful attachment of amine-terminated IL-NH_2 to GO nanosheets.

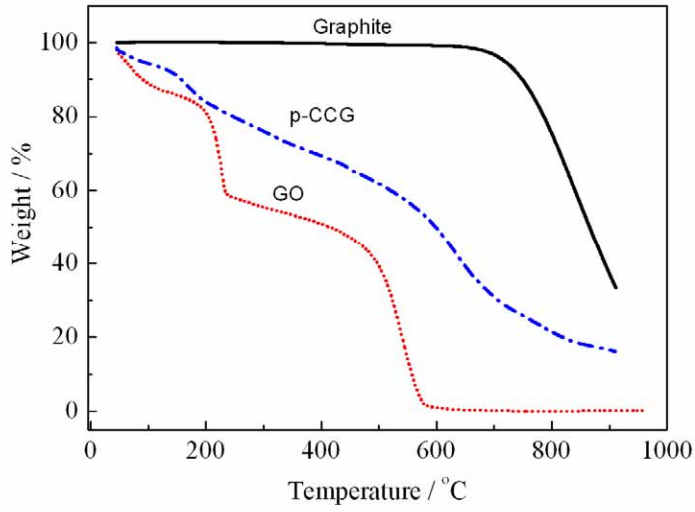

Fig. S5. TGA curves of graphite (solid), p-CCG (dashed), and GO (dotted).

As shown in Fig. S5, the TGA were performed on natural graphite (solid), p-CCG (dashed), and GO (dotted) heated in a TGA instrument to 900°C at heating rate 5 °C min^{-1} under N_2. It was observed that GO is thermally unstable and starts to lose mass upon heating even below 100 °C, and there are two significant drops in mass around 226 and 541 °C. The former is decomposition of the labile oxygen-containing functional groups, yielding CO, CO_2, and steam,[6] and

the latter is attributed to pyrolysis of the carbon skeleton of GO. After the removal of the thermally labile oxygen functional groups via the functionalization of CCG sheets with IL-NH_2, the p-CCG shows a 7 wt % and 1 wt % loss due to the decomposition of the IL-NH_2 groups around 170 °C and 450 °C, respectively. High temperature bulk pyrolysis of p-CCG is similar to graphite around 650 °C.

References

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