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Supplementary Information for

Controlled functionalization of graphene with carboxyl moieties toward multiple applications

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Experimental Section

Materials:

Graphite powder was obtained from Tianjin Chemicals Company (China), and the pristine graphene (G) was produced by using a modified interlayer catalytic exfoliation of ferric chloride-graphite intercalation compounds.[1,2] The preparation of CG involved a controlled oxidation treatment of the G by using sodium chlorate ($NaClO_3$), concentrated sulfuric acid (H_2SO_4), and hydrogen peroxide (H_2O_2). Briefly, 40 mL H_2SO_4 (98%) and a small amount (typically, ~1 mL) of H_2O_2 (30%) solution were mixed and stirred at 0 ℃ for several minutes. Then the as-produced G (60 mg) and 360 mg $NaClO_3$ were added into the above mixed solution. The mixture was stirred at room temperature for additional 8 h, followed by repeated centrifugation and washing with water, thus obtaining dispersible functionalized graphene (denoted as CG). Furthermore, the preparation of HG and GO from graphene was based on a chlorate system ($NaClO_3$ and H_2SO_4), and a permanganate system ($KMnO_4$ and H_2SO_4), respectively, as reported recently by our group. Briefly, for the HG synthesis, typically, the as-produced G (60 mg) and a small amount of $NaClO_3$ (typically, 300 mg) were put into 20 mL H_2SO_4 (98%). The mixture was stirred at room temperature for 8 h, followed by repeated centrifugation and washing with water, thus obtaining highly dispersible HG; for the GO synthesis, the as-produced G (60 mg) and a small amount of $KMnO_4$ (typically, 180 mg) were put into 20 mL H_2SO_4 (98%), The mixture was stirred at room temperature for 8 h, followed by repeated centrifugation and washing with water, thus obtaining GO. It should be mentioned that, for these functionalized graphene (CG, HG, GO), the layer number and size of CG generally inherit that of the pristine G, which bears a single-layer and/or few-layer feature, as well as a slightly wide size range with an average sheet area of 150 μm^2.

Assembly of Sn(OH)Cl nanoparticles:

10 g tin(II) chloride dihydrate ($SnCl_2•2H_2O$) were dissolved in 100 mL water containing 5 mL dilute hydrochloric acid (HCl) solution. The CG or control samples (HG, GO) were added into the above mixture, stirred for 10 min, and collected by centrifugation. Upon drying at 60 ℃ for 2 h, the Sn(OH)Cl nanoparticles assembled onto CG and also control samples were obtained.

Fabrication of TCFs:

1 mL of CG aqueous solution was dropped on the edge area of a poly(ethylene terephthalate) (PET) substrate, and a Meyer rod (0.2 mm, Pushen) was pulled over the solution at a speed of 150 mm s^{-1}, leaving an uniform film that was dried with flowing air. The RCG TCF was obtained by immersing the above film in a hydrogen iodide (HI) acid solution (55%) for 2 h, followed by repeated washing with ethanol and drying at 80 ℃. The RGO TCF and RHG TCF were fabricated by the same rod-coating route and reduction method.

Contact angle measurements:

A certain amount of CG, and control samples (HG, GO) were made into thin films upon vacuum filtration. The RCG, RHG, and RGO were obtained by immersing the above films in a hydrogen iodide (HI) acid solution (55%) for 2 h, followed by repeated washing with ethanol and drying at 80 ℃. All the samples were flattened by a pressure about 20 MPa.

Characterization:

The morphology and structure of the samples were characterized by scanning electron microscopy (SEM, Hitachi S4800), transmission electron microscopy (TEM, Tecnai F20 U-TWIN and Tecnai G2 20 STWIN), and atomic force microscopy (AFM, Dimension 3100). The X-ray diffraction (XRD) instrument type is D/MAX-TTRIII (CBO). FTIR spectra were taken on a Bruker Vector-22 FTIR spectrometer at room temperature. Raman spectra were collected using a Renishaw inVia Raman microscope with a laser wavelength of 514.5 nm. For TCF characterizations, the sheet resistance was measured on a four-probe electro-resistance analyzer (RTS-9), and the transmission curves were recorded on a Perkin-Elmer UV-Vis-NIR spectrometer (Lambda 950). The hydrophilic properties of the smaples were measured on a contact angle instrument (Kruss DSA 100).

Fig. S1-S2 and Table S1

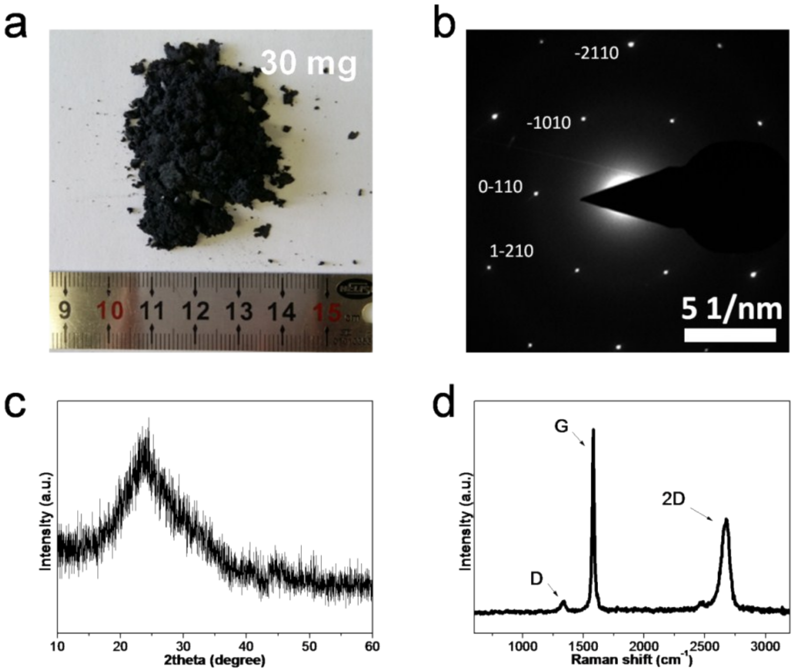

Fig. S1 Characterization of the pristine graphene (G) produced by a modified interlayer catalytic exfoliation of ferric chloride-graphite intercalation compounds. (a) Optical image. (b) selected area electron diffraction (SAED) pattern. (c) XRD pattern. (d) Raman spectrum.

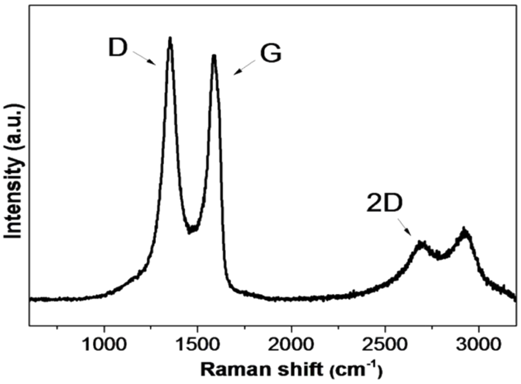

Fig. S2 Raman spectrum of GO.

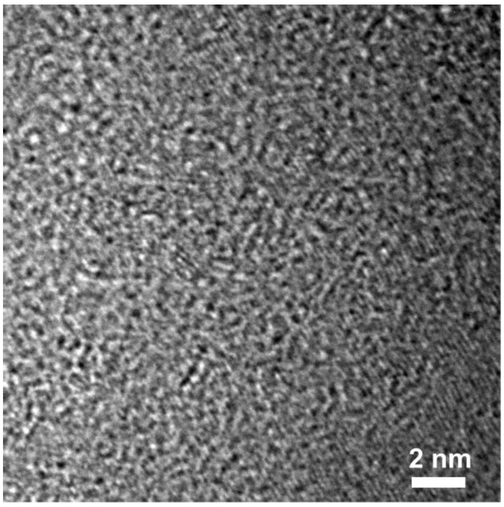

Fig. S3 Typical high-resolution TEM image of CG.

Sample	C (%)	O (%)
G	96.726	3.274
HG	78.555	21.445
GO	61.061	38.939
CG	82.058	17.942

Table S1 Atomic percentage of carbon and oxygen detected by XPS, in G, HG, GO and CG.

References

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[2] X. Geng, Y. Guo, D. Li, W. Li, C. Zhu, X. Wei, M. Chen, S. Gao, S. Qiu, Y. Gong, L. Wu, M. Long, M. Sun, G. Pan, L. Liu, Sci. Rep., 2013, 3, 464.