Electronic Supplementary Material (ESI) for RSC Advances

Photochemical Synthesis of Fluorinated Graphene via A Simultaneous Fluorination and Reduction Route

Peiwei Gong[ab], *Zhaofeng Wang*[a], *Zhangpeng Li*[a], *Yongjuan Mi*[ab], *Jinfeng Sun*[ab],*Lengyuan Niu*[ab], *Honggang Wang*[a], *Jinqing Wang**[a], *and Shengrong Yang*[a]

a State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, 730000, P. R. China.

b Graduate University of Chinese Academy of Sciences, Beijing, 100080, P. R. China.

* Corresponding author,

jqwang@licp.cas.cn (J. Wang)

Fax: +86 931 8277088

Tel.: +86 931 4968076

1. Synthesis of fluorinated graphene (FG)

Graphene oxide (GO) was synthesized from natural graphite (300 μm, Qingdao Graphite Company) by a modified Hummers' method,[16] and then was subjected to dialysis to remove residual salts and acids. The purified GO was dispersed in water to make a 1 mg/mL suspension and exfoliated by ultrasonication (Kunshan, KQ5200DE). After sonication for 1 h, the mixer of 10 mL HF (40 wt %) and 40 mL GO suspension was irradiated under mercury lamp (Shanghai Yaming Company, GGY 150W), 10 cm away from the solution level. After 46 h of irradiation, the samples were left several hours for delamination and collected with filtration after being neutralized by $NaHCO_3$. Then, the samples were washed thoroughly by Milli-Q water (>18 MΩ·cm) several times, and dried through vacuum freeze for 48 h.

To estimate the yield, several parallel experiments were conducted under the same conditions and the products were collected and weighed. The average weight ratio of FG to reduced graphene oxide (RGO) is about 1/10. As a result of the photochemical process,[1,2] the average size of FG is about 1 μm, which is smaller than that of GO (for the sample used in our experiment, the average size of GO is about 2 μm).

2. Material Characterization

IFS 66 V/S Fourier transformation infrared (FTIR, Bruker, Germany) and X-ray photoelectron spectrometer (XPS, PHI-5702, Physical Electronics) were employed for element analyses. XPS was performed using a monochromated Al-Kα irradiation and the chamber pressure was about 3×10^{-8} Torr under testing conditions. Optical absorption spectrum was measured by Agilent 8453 photometer, and the crystal structure of samples was examined by powder X-ray diffraction (XRD, Rigaku D/MAX-2400 X-ray diffractometer with Ni-filtered Cu Kα radiation).

The surface morphology and structure were observed by a Nanoscope IIIa multimode atomic force microscope (AFM, Veeco) in tapping mode and a field-emission scanning electron microscopy (FE-SEM, JEOL JSM-6701F), respectively. Thermal gravimetric analysis (TGA) measurements were carried out by DSC/DTA-TG (Netzsch Ltd., Germany) and the electrochemical property of FG was measured by CHI 660C electrochemical workstation (Shanghai CH Instrument Company, China). Galvanostatic charge/discharge test was taken by Land Battery Test System (Wuhan Kingnuo Electronic Company, China).

3. Solubility and Stability of FG

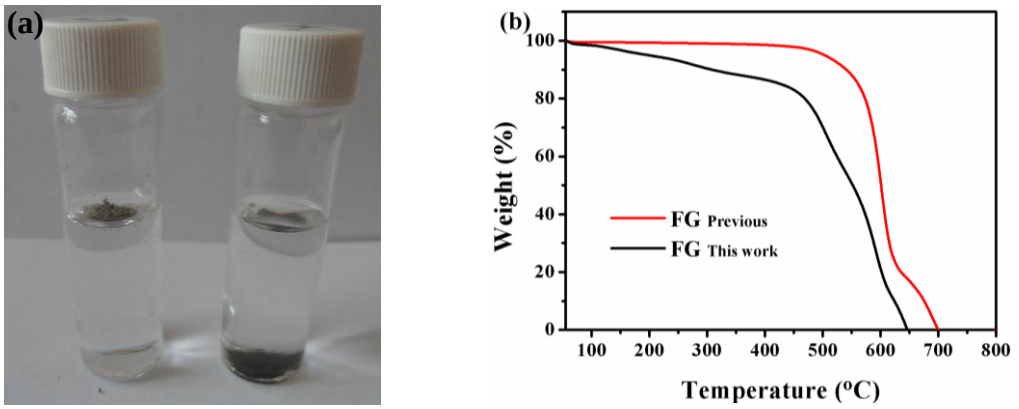

Fig. S1 (a) Digital images of FG dispersed in water (left) and ethanol (right), respectively. (b) TGA curves of FG obtained by heating the samples to 800 ^{o}C at a rate of 10 ^{o}C per min in flowing air.

To investigate the solubility of FG, 2 mg of samples was dispersed in water and ethanol, respectively. In agreement with previous reports,[3,4] although certain oxygen groups still remain on the graphene scaffold, the invasion of hydrophobic fluorine makes FG difficult being dispersed in water while FG precipitates in ethanol. And for the stability of FG, it is stable in air at room temperature and no detectable changes can be found without further treatment. Moreover, to precisely investigate its thermal stability, thermal gravimetric analysis (TGA) measurements were also carried out and TGA analyses reveal that the prepared FG is inert in air up to 400 ^{o}C. Meanwhile, we also measured the TGA curves of FG with the similar fluorine coverage (about 50%) but with less larger functional groups, which was prepared through our previously reported method.[3] Our TGA analyses indicate that the prepared FG is not as stable as our previously prepared FG samples, which might be caused by the larger functional groups and remaining oxygen groups.

4. Electrochemical Properties of FG

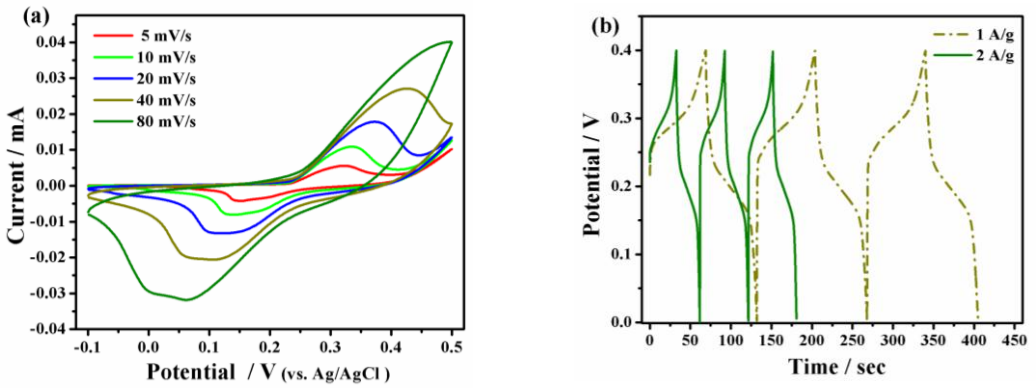

Fig. S2 (a) Cyclic voltammetry (CV) curves of FG electrode at different scan rates in 6 M KOH solution. (b) Charge–discharge behavior of FG electrode at different current densities.

The electrochemical property of FG has been investigated in 6 M KOH solution. CV curves at different scan rates of 5, 10, 20, 40, and 80 mV/s are presented in Fig. a and b. Obviously, the shape of CV curves gradually transforms with increasing scan rate and the galvanostatic charge/discharge experiments indicate that the obtained FG's capacitance could reach 157 F g^{-1} at a current density of 1 A g^{-1}.

Notes and references

1. X. J. Zhou, Y. Zhang, C. Wang, X. C. Wu, Y. Q. Yang, B. Zheng, H. X. Wu, S. W. Guo, and J. Y Zhang, *ACS Nano*, 2012, **6**, 6592-6599.

2. H. J. Sun, L. Wu, N. Gao, J. S. Ren and X. G. Qu, *ACS Appl. Mater. Interfaces*, 2013, **5**, 1174-1179.

3. P. W. Gong, Z. F. Wang, J. Q. Wang, H. G. Wang, Z. P. Li, Z. J. Fan, Y. Xu, X, X.

Han and S. R. Yang, *J. Mater. Chem.*, 2012, **22**, 16950-16956

4. K. J. Jeon, Z. Lee, E.Pollak, L. Moreschini, A. Bostwick, C. M. Park, R. Mendelsberg, V. Radmilovic, R. Kostecki, T. J. Richardson and E. Rotenberg, *ACS Nano*, 2011, **5**, 1042-1046.