Electronic Supplementary Material (ESI) for RSC Advances.
This journal is © The Royal Society of Chemistry 2014

Chemically edge-connected multilayer graphene-based architecture with enhanced thermal stability and dispersibility: experimental evidence of making the impossible possible

Juanjuan Gao,[a] Shupeng Zhang,*[a] Xinfang Zhang,[a] Chunpei Yu,[a] Huili Ye,[a] Yueyue Qian,[a] and Haiou Song*[b]

Supplementary Information

1. Experimental

1.1 Materials

Natural graphite was obtained frome Qingdao Zhongtian Company. Polystyrene (PS), cyclodextrins (CDs) and others chemical reagents were analytical grade and used as received without further purification.

1.2 Fabrication of chemically modified GO

1.2.1 Synthesis of GO-CD_β

Graphite oxide used in this work was synthesized from graphite using the modified Hummers method as described elsewhere.[1-3] As a typical example, the sample prepared with powdery graphite oxide and β-cyclodextrins (CD_β) is labeled as GO-CD_β for easy expression. The synthesis procedure for a typical well-dispersed GO-CD_β compound was carried out as follows: 200 mg of graphite oxide was added into 15 mL of *N, N*-dimethylforamdie under ultrasonication for 7 h and in this process graphite oxide was completely exfoliated down to individual sheets to form a stably dispersed GO/DMF solution.[3] The stable suspension of GO/DMF refluxed in the presence of 40 mL of $SOCl_2$, at 70 °C for 24 h, using a $CaCl_2$ guard tube. At the end of the reaction, the excess $SOCl_2$ was removed by distillation. [4, 5]

The obtained reactive intermediate（GO-Cl）was mixed with 4 g CD_β dissolved in 22 mL of DMF and conducted at 100 °C for 2 days. The mixture was then washed several times with DMF and ethanol to remove any impurities by filtration. Finally, the product (GO-CD_β) was dried at 70 °C in vacuum oven.

1.2.2 Synthesis of so-called GO-CDs-PS by conventional method

For the preparation of GO-CD_β-PS, 0.2 g of GO-CD_β was first dispersed in DMF (10 mL) by ultrasonication. 0.2 g of PS was also dissolved in DMF. Then, a dispersion of GO-CD_β was dropwise added to the PS solution and stirred vigorously for 2 d at 100 ℃. The mixture was then washed several times with $CHCl_3$ and ethanol to remove any impurities by filtration. Finally, the product was dried at 70 °C in vacuum oven.

For the preparation of the GO-CD_{α}-PS, all procedure is identical except the raw material is switched from CD_{β} to CD_{α}.

1.2.3 Synthesis of GO-CDs-PS by one-pot approach

For the preparation of GO-CD_{β}-PS, 0.2 g of PS and 4 g of CD_{β} were dissolved in DMF (42 mL) at the same time (Mxiture 1). The obtained reactive intermediate（GO-Cl）was added with 10 mL of DMF. Then, the mixture 1 was dropwise added to the GO-Cl solution and stirred vigorously for 2 d at 100 ℃. The mixture was then washed several times with $CHCl_3$ and ethanol to remove any impurities by filtration. Finally, the final product (GO-CD_{β}-PS) was dried at 70 ℃ in vacuum oven.

For the preparation of the GO-CD_{α}-PS, 0.2 g of PS and 0.2 g of CD_{α} were dissolved in DMF (30 mL) at the same time (Mxiture 2). The obtained reactive intermediate（GO-Cl）was added with 10 mL of DMF. Then, the mixture 2 was dropwise added to the GO-Cl solution and stirred vigorously for 2 days at 100 ℃. The mixture was then washed several times with $CHCl_3$ and ethanol to remove any impurities by filtration. Finally, the final product (GO-CD_{α}-PS) was dried at 70 ℃ in vacuum oven.

1.2.4 Fabrication of the film of PS/2 wt‰ GO-CD_{α}-PS and PS/2 wt‰ GO-CD_{β}-PS

In our case, PS, GO-CD_{α}-PS and GO-CD_{β}-PS can all be readily dispersed in $CHCl_3$, which will help to achieve molecular level dispersion by solution blending.[6] For the preparation of PS/2 wt‰ GO-CD_{α}-PS composite film, the 2 ‰ *wt.* GO-CD_{α}-PS nanofillers were first dispersed in $CHCl_3$ by ultrasonication. 1 g of PS was also dissolved in $CHCl_3$. Then, a dispersion of GO-CD_{α}-PS was dropwise added to the PS solution and stirred vigorously for 12 h. At last, the composite solution was casted and dried at room temperature for 1 day and then in a vacuum oven for 24 h at 60 ℃. For the preparation of the PS/2 wt‰ GO-CD_{β}-PS composite film, all procedure is identical except the nanofillers are switched.

1.3 Characterization

FT-IR spectroscopy of GO-based hybrid materials were collected on a Nicolet IS-10 FT-IR spectrometer equipped with a Smart OMNI sampler with a high purity Ge crytal. Raman spectra of samples were measured from 800 to 2000 cm^{-1} on a LabRAM ARAMIS (HORIBA Jobin Yvon S.A.S.)

using an excitation wavelength of 532 nm. XRD analyses were performed on a Bruker D8 Advance diffractometer with Cu-Kα radiation. The diffraction data was recorded for 2θ angles between 5° and 60°. Scanning electron microscope (SEM) images were preformed on a JEOL JSM- 6380LV SEM. Thermogravimetric analyses (TGA) were preformed on a Mettler TGA/SDTA851e thermogravimetric analyzer over the temperature range of 50-800 °C at a heating rate of 20 °C/min in a dry nitrogen atmosphere.

2. Results and discussion

2.1 FT-IR

A strong and broad absorption at 3337 cm^{-1} originated from O-H stretching vibrations can be observed in Fig. 1A (trace a). The characteristic stretching adsorption bands corresponding to the carbonyl groups (C=O) in COOH units situated at edges of GO sheets can be observed at around 1728 cm^{-1}, [7, 8] whereas the bands due to C-O in alcoholic or epoxy groups (COH/COC) appear in the range of 1048 cm^{-1}. In addition, the peak at 1624 cm^{-1} can be attributed to the O–H bending vibration, epoxide groups or skeletal ring vibrations of graphitic domains.[5]

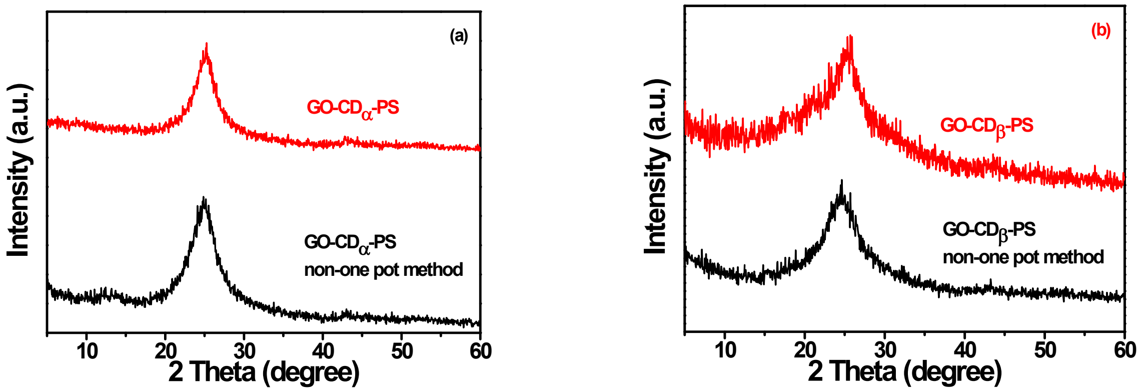

Fig. S1. XRD patterns of (a) GO-CD$_{\alpha}$-PS and GO-CD$_{\alpha}$-PS prepared by non-one pot method. (b) GO-CD$_{\beta}$-PS and GO-CD$_{\beta}$-PS prepared by non-one pot method.

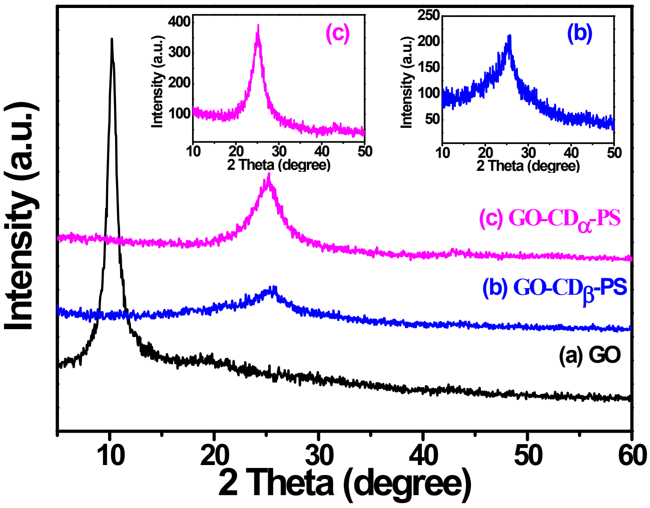

Fig. S2 XRD patterns of (a) GO, (b) GO-CD$_\beta$-PS, (c) GO-CD$_\alpha$-PS

The strong peak of 2θ at 10.2° in the GO could be clearly observed, indicating the presence of close stacked layers of graphene oxide with functional groups containing oxygen, formed during oxidation.

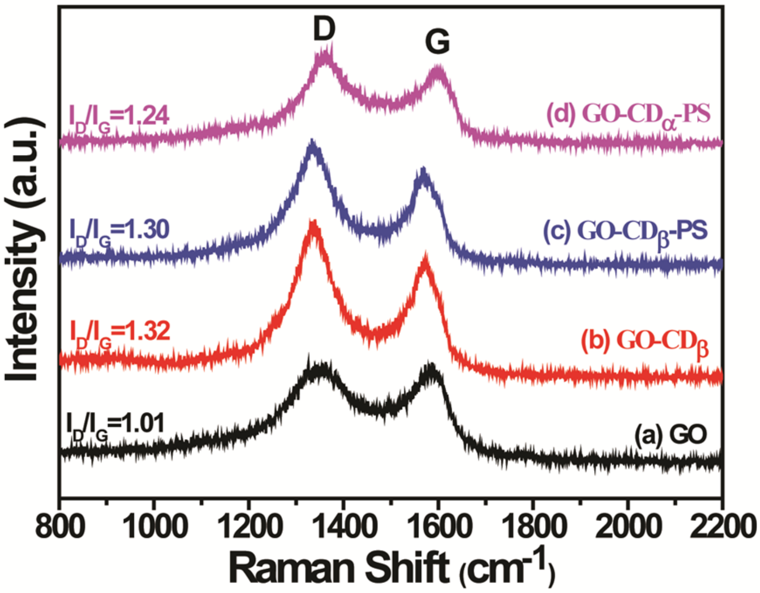

Fig. S3 Raman spectra depicting G and D bands of GO (a), GO-CD$_\beta$ (b), GO-CD$_\beta$-PS (c), GO-CD$_\alpha$-PS (d)

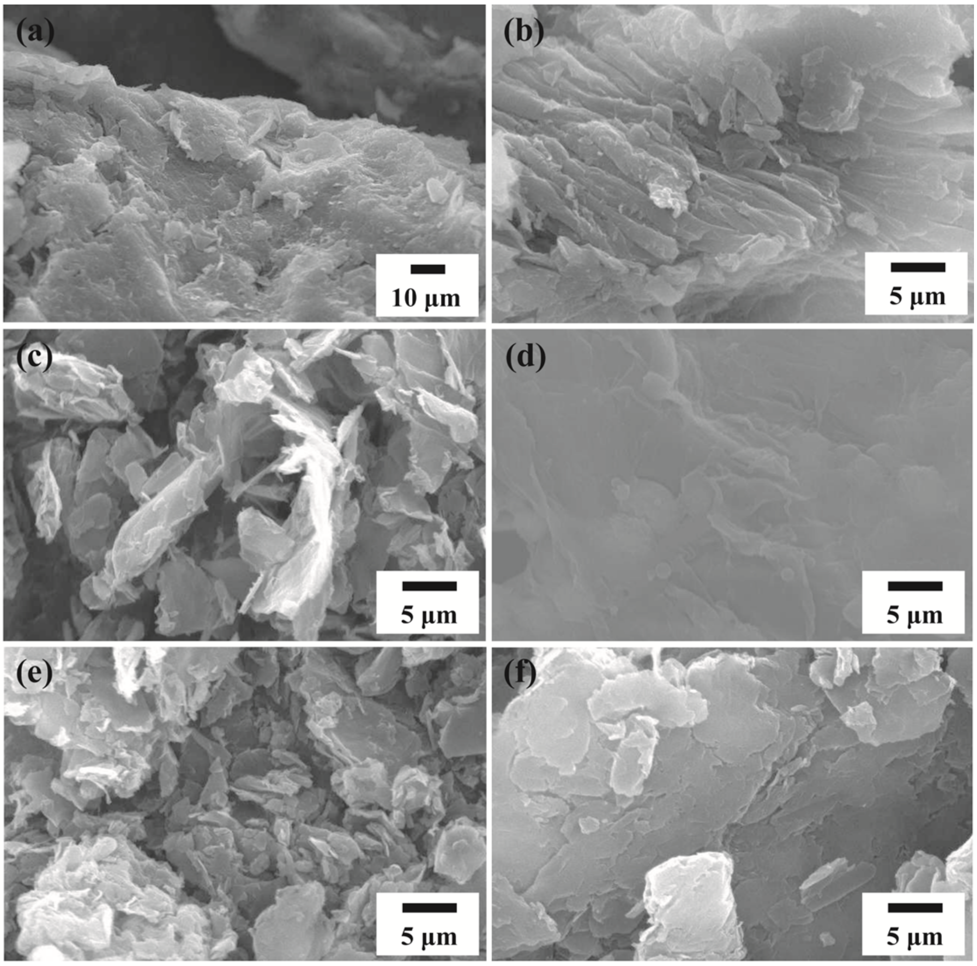

Fig. S4 SEM images of (a and b) GO, (c) GO-CD$_\beta$, (d) PS, (e) GO-CD$_\beta$-PS, (f) GO-CD$_\alpha$-PS

Reference

S1. W. S. Hummers and R. E. Offeman，*J. Am. Chem. Soc.*，1958，**80**, 1339.

S2. N. I. Kovtyukhova，P. J. Ollivier，B. R. Martin，T. E. Mallouk，S. A. Chizhik，E. V. Buzaneva and A. D. Gorchinskiy，*Chem. Mater.*，1999，**11**，771.

S3. S. Stankovich，D. Dikin，R. Piner，K. Kohlhaas，A. Kleinhammes，Y. Jia，Y. Wu，S. Nguyen and R. Ruoff，*Carbon*，2007，**45** ，1558.

S4. S. Niyogi，E. Bekyarova，M. E. Itkis，J. L. McWilliams，M. A. Hamon and R. C. Haddon，*J. Am. Chem. Soc.*，2006，**128**，7720.

S5. S. Zhang，P. Xiong，X. Yang and X. Wang，*Nanoscale*，2011，**3**，2169.

S6. S.P. Zhang and H.O. Song，*New J. Chem.*，2012，**36**，1733.

S7. A. Lerf，H. He，M. Forster and J. Klinowski，*J. Phys. Chem. B*，1998，**102**，4477.

S8. D. R. Dreyer，S. Park，C. W. Bielawski and R. S. Ruoff，*Chem. Soc. Rev.*，2010，**39**，228.