Supplementary information

High-rate lithium-sulfur batteries promoted by reduced graphene

oxide coating

Nianwu Li,^{†ab} Mingbo Zheng,^{†b} Hongling Lu,^a Zibo Hu,^b Chenfei Shen,^{ab} Xiaofeng Chang,^a Guangbin Ji,^a Jieming Cao^{*a} and Yi Shi^{*b}

^a Nanomaterials Research Institute, College of Materials Science and Technology, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, China. E-mail address: jmcao@nuaa.edu.cn

^b National Laboratory of Microstructures, School of Electronic Science and Engineering, Nanjing University, Nanjing 210093, China. E-mail address: yshi@nju.edu.cn

[†] These authors contributed equally to this work.

1. Experiment

1.1 Preparation of the thermally exfoliated graphene nanosheet–sulfur (TG–S) sample Graphite oxide was synthesized by oxidation of graphite using improved hummers' method.¹ The thermally exfoliated graphene nanosheet (TG) was prepared according to our previous report.² Typically, GO was put into a quartz tube preheated to 300 °C and held at this temperature for 5 min. After that the sample was heated to 900 °C under N₂ atmosphere for 3 h with a heating rate of 10 °C/min, and nominated as TG. The as-prepared TG (100 mg) was mixed with 1 g of the sublimed sulfur and was ground for 30 minutes in an agate mortar and pestle. The mixture was heated to 150 °C and held at this temperature for 10 h. During the process, the melted sulfur easily diffused into the interior porous structure of the TG. Then the temperature was increased to 250 °C and kept for 2 h to vaporize the sulfur covering on the outside surface of TG. The heat treatment was performed under N₂ protection. After that the TG–S sample was obtained.

1.2 Preparation of reduced graphene oxide (RGO) coated TG-S nanocomposite.

To obtained graphene oxide (GO) solution, 10 mg of graphite oxide was dissolved in 20 ml of distilled water by intensive sonication and magnetic stirring. The solution was heated to 70 °C in water bath. The as-prepared TG–S nanocomposite was dispersed in 1 ml ethanol and 9 ml distilled water, and 100 mg of Na₂S₂O₃ was dissolved to the suspension with sonication and magnetic stirring. The TG–S and Na₂S₂O₃ suspension was added to the as-prepared GO solution, and then 1 ml of 1 M hydrochloric acid was added to the mixture. Afterwards the mixture was filtered, washed with distilled water. Finally, the RGO coated TG–S nanocomposite (RGO–TG–S) was obtained by drying at 70 °C under vacuum for 12 h. For a control experiment, a control nanocomposite was prepared by mixing 6.3% conducting carbon with 100% TG-S nanocomposite (equal carbon proportion with the RGO-TG-S nanocomposite).

2. Material characterization

X-ray powder diffraction (XRD) patterns were recorded on a Bruker D8 powder X-ray diffractometer (Germany). The morphology of the as-prepared samples was observed using a Hitachi S-4800 field-emission scanning electron microscope (FE-SEM) at an acceleration voltage of 10.0 kV. The N₂ adsorption-desorption analysis was measured on the Micromeritics ASAP 2010 instrument. Thermal analysis was carried out on NETZSCH STA 409C thermal analyzer (Germany), in which the sample was heated in alumina crucible under N₂ flow to 600 °C at a heating rate of 10 °C min⁻¹.

3. Electrochemical test

The cathode slurry was prepared by mixing 70 wt% RGO-TG-S nanocomposite, 20 wt% conducting carbon, and 10 wt% polyvinylidene difluoride (PVDF) in N-Methylprrolidone (NMP) solvent dispersant. Positive electrodes were produced by coating the slurry on aluminum foil and drying at 60 °C for 12 h. Each current collector contained between 0.9 mg cm⁻² to 1.0 mg cm⁻² active material. Preliminary cell tests were done with a 2032 coin-type cells, which were fabricated in an argon-filled glove box using lithium metal as the counter electrode and a microporous polvethvlene separator. The electrolyte solution was Μ 1 bis-(trifluoromethane)sulfonimide lithium (LiTFSI) in a mixed solvent of dimethoxyethane (DME) and dioxolane (DOL) with a volume ratio of 1 : 1. This electrolyte was chosen to optimize high-rate behavior because of its lower viscosity³ and high ionic conductivity.⁴ The charge-discharge performance of the cells was tested with LAND CT-2001A instrument (Wuhan, China), and potential window was controlled between 1.0 and 3.0 V at room temperature. The specific capacity was calculated on the mass of elemental sulfur.

4. Figure



Electronic Supplementary Material (ESI) for Chemical Communications This journal is $\ensuremath{\mathbb{C}}$ The Royal Society of Chemistry 2012



Fig. S1 N_2 sorption isotherms (a) and pore size distribution curves (b) of TG and TG-S nanocomposite.



Fig. S2 The corresponding elemental mapping of carbon (a) and sulfur (b) of the Fig 2c. (c) EDS spectrum of the TG-S nanocomposite shown in Fig. 2c. The Peaks at 1.00, 8.00, and 9.00 KeV correspond to Cu (a Cu slice was used as the material carrier in the EDS detection).



Fig. S3 Thermal analysis curves of the TG-S and RGO-TG-S nanocomposite.



Fig. S4 Cycle performance of the control nanomposite at 0.2 A g^{-1} . The control nanomposite was prepared by mixing 6.3% conducting carbon with 100% TG-S nanocomposite (to ensure 63% sulfur and 37% carbon in the control nanocomposite, which are the same as those in the RGO-TG-S nanocomposite). The nanocomposite displays a specific discharge capacity of 805 mAh g^{-1} after 2 cycles and retains a reversible capacity of 563 mAh g^{-1} after 35 cycles. The coulombic efficiency is about 90.7% during 35 cycles.



Fig. S5 Cycle performance of the RGO-TG-S nanocomposite at 0.2 A g^{-1} . The nanocomposite retains a reversible capacity of 803 mAh g^{-1} after 160 cycles. The coulombic efficiency is about 100.0 % during 160 cycles.

References

- D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L. B. Alemany, W. Lu and J. M. Tour, ACS Nano, 2010, 4, 4806.
- 2. Q. Du, M. Zheng, L. Zhang, Y. Wang, J. Chen, L. Xue and W. Dai, Electrochim. Acta, 2010, 55, 3897.
- 3. G. He, X. Ji and L. Nazar, Energy Environ. Sci., 2011, 4, 2878.
- 4. C. Liang, N. J. Dudeny and J. Y. Howe, Chem. Mater., 2009, 21, 4724.