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3D nest-shaped Sb_2O_3/RGO composites based high-performance Lithium-ion batteries

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Experimental part

Graphite powder (325 mesh, with purity >99.99 %) and didodecyldimethylammonium bromide (DDAB) were purchased from Aladdin Industrial (Shanghai) Co., Ltd. All other chemicals (purchased from Beijing Chemical Co., Ltd.) used in this experiment were analytical grade and were used without further purification. Deionized water was used throughout the experiments.

GO was synthesized from natural graphite powder by a modified Hummer's method as originally presented by Kovtyukhova *et al.*[1,2] In order to obtain GO nanosheets dispersed in water, the solution was sonicated for 1 h before using. The concentration of the prepared GO suspension was attenuated to 1 mg mL^{-1}.

A facile wet chemical method was used to prepare the Sb_2O_3/RGO composite. In a typical synthesis, 0.2313 g (0.5 mol L^{-1}) DDAB was added to 25 mL of deionized water, after stirring for 1 h, 0.1808 g (0.1 mol L^{-1}) urea was added into the above solution under vigorous stirring for 0.5 h to form a homogeneous solution. Then, 5 mL GO (1 mg mL^{-1}) and Sodium borohydride ($NaBH_4$) were dispersed in the mixture by ultra-sonication for 0.5 h. Then, 0.2004 g (0.02 mol L^{-1}) $C_4H_4KO_7Sb$ as antimony source was added in with constant stirring for another 0.5 h. All of these above were done in room temperature and pressure. Afterward, the hybrid solution was stirred in an oil-bath and heated at 85 °C for 3 h. Finally, the resulting solution was cooled naturally to room temperature, and the black deposit was washed several times with deionized water and ethanol before dried at 60 °C for 12 h, and collected for further characterization. For comparison, Sb_2O_3 micro/nano particles were synthesized as well in the same procedure instead of 30 mL of deionized water without adding the GO.

The phase composition of the products were determined using a Rigaku Dmax 2200 X-ray diffraction (XRD), equipped with Cu Kα radiation of 1.5406 Å. The patterns were recorded at a scanning rate of 6° min^{-1} from 10° up to 80° (2θ). The morphology and size of the as-synthesized products were observed directly by Environmental scanning electron microscopy (SEM, Quanta 250 FEG). Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) studies were performed using JEOL JEM-2100F electron microscopes. Thermogravimetric analysis was performed using a Pyris Diamond TG analyzer (PerkinElemer Inc., U.S.A.), heated from 30 °C to 800 °C at 10 °C min^{-1} in air. The groups on the samples were studied by Fourier transform infrared spectrometer (FT-IR, Nicolet, iN10MX). Raman spectroscopy was performed on a laser Raman spectrometer (LabRAM HR800) using a visible laser (λ= 325 nm) at room temperature.

The electrochemical properties of the Sb_2O_3 and Sb_2O_3/RGO composite as anode electrodes in lithium-ion batteries were evaluated. The working electrodes were prepared by mixing active materials, acetylene black, and the binder (polytetrafluoroethylene) at a weight ratio of 80:10:10, dissolved in N-methyl-2-pyrrolidone (NMP) to form a slurry, which was then coated onto a copper foil (current collector). After dried at 90 °C for 12 h, coin cells (CR2430 type) were then assembled in an Ar-filled glove box, using Celgard 2325 as the separator, a solution of 1 M $LiPF_6$ in a mixture of ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 by volume) as electrolyte and metallic lithium foil as the counter electrode. The galvanostatic charge/discharge experiment and cyclic voltammograms were performed on a Land CT2001A battery testing system (Wuhan Jinnuo Electronics. Ltd., China) between 0.01

and 3.0 V (*vs.* Li/Li$^+$) at a rate of 50 mA g^{-1} at room temperature. The electrochemical impedance measurements were performed on CHI660D electrochemical workstation (Shanghai Chenhua Co. Ltd., China) in the 100 kHz to 0.1 Hz range. All above electrochemical measurements were taken at room temperature.

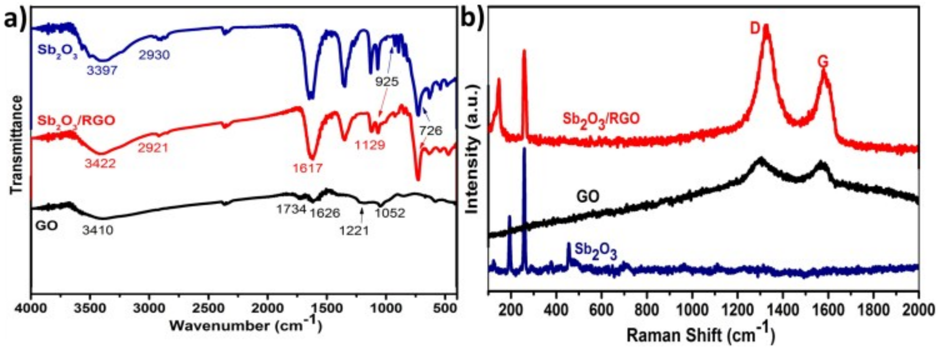

Fig. S1 a) Fourier transform infrared spectrum and b) Raman spectrum of GO, Sb_2O_3, and Sb_2O_3/RGO composite.

Fig. S1a presents the FTIR spectra of Sb_2O_3, Sb_2O_3/RGO composite and pristine GO. Two intense absorption bands are observed at 3340 and 2930 cm^{-1}, which are assigned to the -OH asymmetrical stretching vibration and symmetrical stretching vibration of physically adsorbed water in the sample, respectively. The FTIR spectrum of Sb_2O_3 shows two characteristic absorption bands at 925 and 726 cm^{-1} which can be assigned to the Sb-O stretching vibration mode.[3,4] The spectrum of GO shows a weak band at 1734 cm^{-1} assigned to C=O stretching vibrations from carbonyl and carboxylic groups, 1626 cm^{-1} assigned to C-C skeletal vibrations from non-oxidized graphene domains, 1221 cm^{-1} assigned to C-OH stretching vibrations, and 1052 cm^{-1} due to C-O stretching vibrations.[5] Obviously, these peaks are largely decreased in the Sb_2O_3/RGO composite, the results indicate that carboxyl and epoxy functional groups are eliminated and GO is transformed into RGO in the Sb_2O_3/RGO composite.

Raman spectroscopy is a powerful tool to identify the crystal phase and get the degree of structural defects. Fig. S1b is the Raman spectra of the Sb_2O_3, Sb_2O_3/RGO composite and pristine GO. The fundamental Raman scattering peaks for Sb_2O_3 micro/nano materials are observed at 123.5, 194.1, 259.1, 377.8, 455.1, and 711.7 cm^{-1}. No other antimony oxides are detected, indicating the high purity of it.[6,7] Besides these Raman modes of Sb_2O_3, two strong characteristic peaks, denote as the disorder peak (D band, at 1350 cm^{-1}) and the graphitic peak (G band, at 1580 cm^{-1}) are observed from the Sb_2O_3/RGO composite. Compared to the intensity ratio of the I_D/I_G in GO, the ratio from Sb_2O_3/RGO composite is increased, implying the decrease of oxygen functional groups, and GO is reduced to RGO successfully.

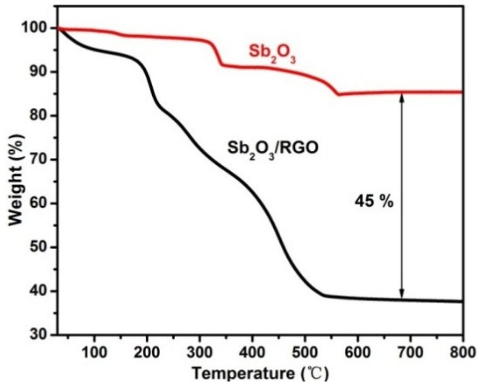

Fig. S2 TGA patterns of Sb_2O_3 and Sb_2O_3/RGO composite.

In order to observe the thermal stability of the material, and to quantify the mass percentage of graphene, the as-prepared Sb_2O_3 and Sb_2O_3/RGO composites are analysed by TGA. As shown in Fig. S2, both Sb_2O_3 and Sb_2O_3/RGO composite are mass loss between 100 and 600 °C. The residual part of Sb_2O_3 is around 85 wt.%, while Sb_2O_3/RGO is around 40 wt.% after weight loss. In addition to the loss of Sb_2O_3, a rapid mass loss occurs between 100 and 400 °C due to the decomposition of oxygen containing functional groups in graphene. When the temperature increases to 400 °C, the oxidation of graphene is starting. Finally, the mass percentage of graphene in the composite is estimated to be approximately 47 %.

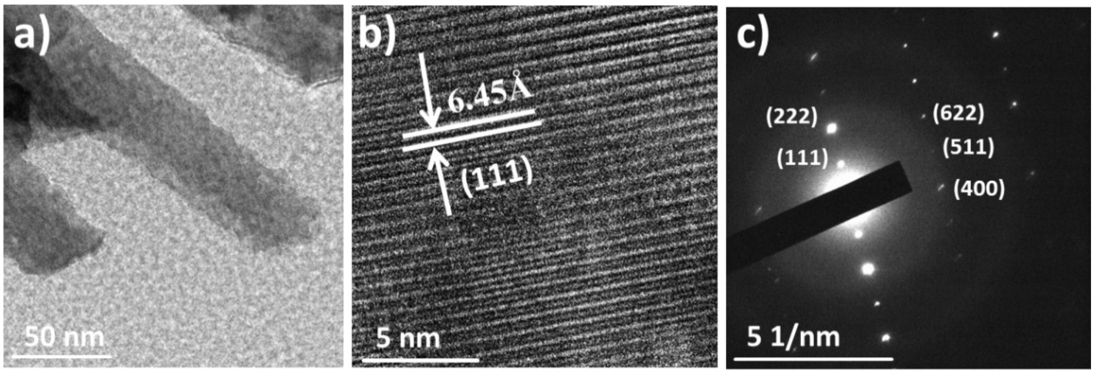

Fig. S3 TEM, HRTEM images and SAED pattern of Sb_2O_3 micro/nano materials.

Fig. S3a is a high-magnification TEM image of part of nest-shaped Sb_2O_3. The HRTEM image clearly shows that one set of lattice fringes is nearly 6.42 Å in Fig. S3b, which agree well with the results of the selected area electron diffraction (SAED) (in Fig. S3c), indicating that the nanorods have high single-crystalline structure and prefer to grow along the [111] crystallographic direction.

Notes and references

1 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**, 771-778.

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

3 A. E. Panasenko, L. A. Zemnukhova, L. N. Ignat’eva, T. A. Kaidalova, S. I. Kuznetsov, N. V. Polyakova and Y. V. Marchenko, *Inorg. Mater.,* 2009, **45**, 402-408.

4 A. H. Abdullah, N. H. M. Noor, I. Ramli and M. Hashim, *Mater. Chem. Phys.,* 2008, **111**, 201-204.

5 J. Peng and J. Weng, *Carbon,* 2015, **94**, 568-576.

6 I. A. Degen and G. A. Newman, *Spectrochim. Acta A-M.,* 1993, **49**, 859-887.

7 X. C. Ma, Z. D. Zhang, X. B. Li, Y. Du, F. Xu and Y. T. Qian, *J. Solid State Chem.,* 2004, **177**, 3824-3829.