Electronic Supplementary Information

Fast synthesis of SnO$_2$/graphene composites by reducing graphene oxide with stannous ions

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I Experimental Section

Graphite powders were purchased from Alfa Aesar China (Tianjin) Co. Ltd., with an average particle diameter of 47 μm. All other chemicals were of analytical grade and used as received without any purification process. The water was Millipore Milli-Q grade with a resistivity larger than 18 MΩ cm⁻¹.

Graphene oxide (GO) was prepared from graphite powders according to a modified Hummers’ method. Exfoliation was carried out by sonicating GO dispersion (2 mg/mL) under ambient condition for 2 h. We prepared a mixture of GO, tin dichloride and urea with the concentration of 0.4 mg/mL, 0.025 and 0.05 M, respectively. Next, the mixture was refluxed under ambient for 5 min with a microwave heater. Finally, after washed with deionized water and ethanol for 5 times and dried in oven at 363 K for 12 h, composites containing SnO₂ and graphene sheets (Sn-GSs Ⅰ) were collected. To obtain pure graphene sheets (GSs), Sn-GSs Ⅰ were processed by HCl (0.1 M) to remove SnO₂. After washed repeatedly with deionized water and isolated by centrifugation, graphene sheets (GSs) were dried at 353 K for 12 h. As a comparison, in a control experiment, the mixture without tin dichloride was refluxed for 5 min with a microwave heater. And the final product was marked as GOX. To investigate the electrochemical properties of the composites as anode materials for lithium ion batteries, Sn-GSs Ⅰ were treated in Ar at 773 K for 2 h and the products were marked as Sn-GSs Ⅱ.

The composites were characterized by a powder X-ray diffraction (XRD) on SIEMENS D5000 X-ray diffractometer with Cu Kα irradiation (λ=0.15406 nm). The
microstructure and morphology of composites were analyzed by a Hitachi S4800 scanning electron microscope (SEM), and a JEOL-2010 transmission electron microscope (TEM) at a 200 kV accelerating voltage. Fourier transform infrared (FT-IR) spectra were obtained on a WQF-410 Fourier transform infrared spectrophotometer (Beijing Secondary Optical Instruments, China). Thermogravimetric analysis (TGA) data were achieved on a Netzsch STA449C. Raman spectra were obtained using a confocal microprobe Raman system (LabRam-010, 632 nm as excitation source). UV-vis absorption spectra were recorded using a TU-1900 UV-vis double-beam spectrophotometer.

Electrochemical properties of products were measured using CR2016-type coin cells. In a process of fabricating the lithium ion batteries, electrodes were prepared by compressing a mixture of active materials (Sn-GSs II) (80 wt %), carbon black (10 wt %), and polyvinylidene fluoride (PVDF, 10 wt %) on pure copper foils. The mass of active materials on each anode is ca. 0.8 mg. A Celgard 2400 microporous polypropylene membrane was used as a separator. The electrolyte consists of a solution of 1 M LiPF₆ in ethylene carbonate/dimethyl carbonate/diethyl carbonate (1:1:1, in wt %). Pure lithium foils were used as counter electrodes. These cells were assembled in an argon-filled glovebox with water and oxygen contents less than 1 ppm. The discharge and charge measurements were carried on an Arbin BT2000 system with the cut off potentials being 0.005 V for discharge and 2 V for charge.
II TG of Sn-GSs

Figure S1. TG and DSC curves of Sn-GSs in air with a heating rate of 10 K/min.
III FESEM images of Sn-GSs II on copper foils

Figure S2. FESEM images of Sn-GSs II on copper foils before cycles (a, b), after 50 cycles (c, d) and after 100 cycles (e, f).

References

