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Graphene oxide oxidizes stannous to synthesize tin sulfide-graphene nanocomposites with small crystal size for high performance lithium ions batteries

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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.[1-2] Exfoliation was carried out by sonicating GO dispersion (2 mg/mL) under ambient condition for 2 h. To synthesize SnS_x-graphene (SnS_x-G) nanocomposites, we prepared a mixture of GO, tin dichloride and thiourea with concentrations of 0.5 mg/mL, 15 mM and 60 mM, respectively. Secondly, the flask was then purged with N_2 for 30 min to eliminate oxygen in the mixture. Thirdly, above suspension was transferred into a Teflon-lined stainless steel autoclave and maintained at 453 K for 12 h. After that, the autoclave was cooled to room temperature naturally and the products were washed with ethanol and distilled water for several times, following dried in oven at 333 K for 12 h. They were noted as SnS_x-G. As a comparison, in a control experiment, the mixture without GO was processed at the same condition for 12 h. After wished by ethanol and distilled water, the final sample was collected and marked as SnS_x-1.

To obtain pure graphene sheets (GSs), SnS_x-G were processed by HCl (0.1 M) to remove SnS_x. After washed repeatedly with deionized water and isolated by centrifugation, GSs were dried at 353 K for 12 h.

The composites were characterized by a powder X-ray diffraction (XRD) on SIEMENS D5000 X-ray diffractometer with Cu K_α 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).

Electrochemical properties of products were measured using CR2016-type coin cells.[3] In a process of fabricating the lithium ion batteries, electrodes were prepared by compressing a mixture of active materials (bare SnS or SnS_x-G) (80 wt %), carbon black (10 wt %) and carboxyl methyl cellulose (CMC, 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 $LiPF_6$ 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 glove-box 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 0.02 V for discharge and 2.5 V for charge.

II Thermogravimetric analysis

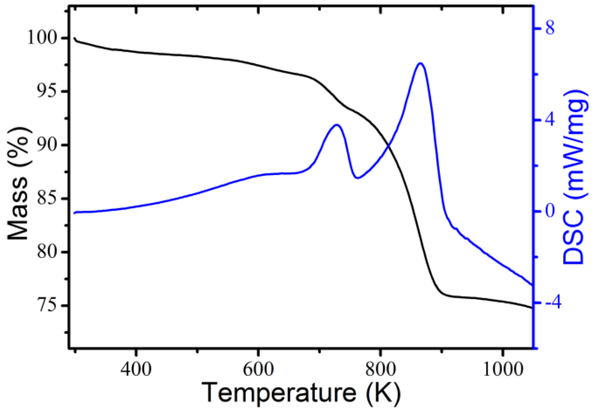

Figure S1. TG and DSC curves of SnS_x-G

TGA measurement was carried out at a heating rate of 10 K min^{-1} from 300 to 1050 K with an air flow rate of 10 mL min^{-1}. The TGA curve displayed two obvious weight loss stages at about 725 and 864 K. The first on near 725 K could be ascribed to the oxidization of SnS_x, and the second one could be attributed to the combustion of graphene sheets, which were associated with two exothermic peaks in the differential scanning calorimetry (DSC) curve. The final production of TGA was SnO_2 with a weight ratio of 74.7%. Because of the weight loss during the oxidization tin sulfide, the mass ratio of SnS_x in composites could be roughly calculated to be about 80%.

References

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