Supporting Information for

Facile, relative green, inexpensive synthetic approach toward large-scale SnS$_2$ nanoplates for high-performance lithium-ion batteries

Yaping Du, Zongyou Yin, Xianhong Rui, Zhiyuan Zeng, Xue-Jun Wu, Juqing Liu, Yuanyuan Zhu, Jixin Zhu, Xiao Huang, Qingyu Yan and Hua Zhang*

Experimental Section:

Synthesis of SnS$_2$ Nanoplates: Typically, 1 mmol of SnCl$_4$·5H$_2$O aqueous solution was added into a mixture containing 10 mmol OA, 5 mmol OM and 20 mmol ODE in a three necked flask at room temperature. The slurry was heated to 140 °C to remove water and oxygen for 30 min, and an optically transparent solution was obtained. After the solution was quickly heated to 280 °C, 1 mmol of S powder dispersed in 5 mmol of OM was injected into the solution at 280 °C under an argon atmosphere. The resultant mixture was kept at 280 °C for 1 h to give a slightly turbid solution. Then, an excess amount of ethanol and acetone was poured into the solution at room temperature. The resultant mixture was centrifugally separated and the products were collected. The precipitated nanocrystals were washed several times with ethanol and then dried in air at 75 °C overnight. The yields of all the obtained nanocrystals were around 80%. The prepared nanocrystals could be redispersed in various nonpolar organic solvents, such as toluene.

Characterization: Powder X-ray diffraction (PXRD) patterns of the dried powders were recorded on Bruker D8 diffractometer (German) with a slit of 1/2° at a scanning rate of 2° min$^{-1}$, using Cu Kα radiation ($\lambda = 1.5406$ Å). The lattice parameters were calculated with the least-squares method. Samples for transmission electron microscopy (TEM) characterization were prepared by drying a drop of nanocrystal dispersion in toluene on amorphous carbon-coated copper grids. High-resolution TEM (HRTEM) images were obtained with a JEOL 2100F (Japan) operated at 200 kV. Samples for field emission scanning electron microscopy (FESEM, JSM-7600) coupled with energy dispersive X-ray spectroscopy (EDS) analysis were prepared by drying a drop of nanocrystal dispersion in toluene on silicon substrate. Room-temperature Raman spectra were measured with a WITec CRM200 confocal Raman microscopy system with the excitation line of
488 nm and an air cooling charge coupled device (CCD) as the detector (WITec Instruments Corp, Germany). The Raman band of a silicon wafer at 520 cm$^{-1}$ was used as the reference to calibrate the spectrometer. The photoluminescence spectrum of SnS$_2$ nanoplates was obtained on a Shimadzu/RF-5301PC fluorescence spectrometer (Japan) at room temperature. The UV-vis absorption spectrum of the nanocrystals was obtained on a Shimadzu/UV-1800 UV-vis spectrometer (Japan). X-ray photoelectron spectroscopy was performed on a Kratos AXIS Ultra photoelectron spectrometer using Al KR radiation (1486.71 eV). The Fourier Transform Infrared (FTIR) absorption spectra of the nanocrystals were carried on Perkin Elmer/Spectrum GX FTIR Spectrometer (USA). The thermal gravimetric analysis (TGA, Q500, USA) was carried out in the temperature of 25 to 900 °C at a heating rate of 10 K min$^{-1}$ in air.

*Electrochemical Properties of SnS$_2$ Nanoplates Used as Electrodes in Lithium-ion Batteries:* The prepared SnS$_2$ nanoplates were annealed in Ar:H$_2$ (80%:20%, volume) for 5 min at 700 °C before it was used for the lithium-ion battery. 80 wt% SnS$_2$, 10 wt% P3-SWCNT and 10 wt% polyvinylidene fluoride (PVDF) binder were mixed in the 1-methyl-2-pyrrolidinone (NMP) solvent. The obtained slurry was coated onto Cu foil disk to form working electrode, which was then dried in vacuum at 50 °C for 12 h to remove the solvent. Electrochemical measurements were carried out on the CR2032 coin-type cells with lithium metal as the counter/reference electrode, CELGARD 2400 membrane as the separator, and a solution of 1M LiPF$_6$ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 by volume) as the electrolyte. The coin cells were assembled in an Ar-filled glove box with concentration of moisture and oxygen below 1.0 ppm. The charge-discharge tests were performed in a NEWARE battery tester at a voltage range of 0.005-3.0 V. Cyclic voltammetry (0.005-3V, 0.3 mVs$^{-1}$) was performed using an electrochemical workstation (CHI 660C, USA).
Fig. S1. (a) Raman and (b) EDS spectrum of SnS$_2$ nanoplates.

Fig. S2. FTIR spectra of oleic acid, oleylamine and SnS$_2$ nanoplates dispersed in toluene.
Fig. S3. $^1$H NMR (CDCl$_3$) spectra of (1) SnS$_2$ nanoplates, (2) OM and (3) OA, which were recorded on Varian Mercury 400 MHz spectrometers with the number of transmit of 64. TMS (tetramethylsilane) was used as internal standard reference. The chemical shift, $\delta$ 5.34(2H, br), is consistent with those for oleic acid and oleylamine, indicating the presence of oleylamine and oleic acid ligands in the SnS$_2$ nanoplates.
Fig. S4. XPS spectra of (a) Sn 3d and (b) S 2p signals recorded for SnS₂ nanoplates. The obtained binding energy was calibrated using C1s as the reference at 284.8 eV.

Fig. S5. Schematic illustration of lithiation process of SnS₂ nanoplates.
Fig. S6. XRD pattern (a) and TEM image (b) of SnS$_2$ nanoplates after annealed in Ar:H$_2$ (80%:20%, volume) at 700 °C, which were then used for the lithium-ion battery experiments, demonstrate the same hexagonal phase and nanoplate morphology is retained.
**Fig. S7.** TEM-EDS elemental mapping revealing the presence of C, Sn and S in the annealed SnS$_2$ nanoplates.
**Fig. S8.** Raman spectrum showing the presence of C in annealed SnS$_2$ nanoplates.

**Fig. S9.** TGA profile of C@SnS$_2$ nanoplates heated in air from room temperature to 900 °C.
**Fig. S10.** Nyquist plots of SnS$_2$ nanoplates before and after annealing process. The plots are obtained by applying a sine wave with amplitude of 10.0 mV in the frequency range 100 kHz–0.01 Hz. In the impedance spectroscopy, the high frequency activity in both plots is attributed to the charge transfer phenomenon, while the low frequency region of the plots is ascribed to the mass transfer process. The Nyquist plots for SnS$_2$ nanoplates before and after annealing process are different in diameters of the semicircles, and thereby the associated impedance values. This indicates the impedance in annealed SnS$_2$ nanoplates is reduced after thermal treatment.
**Fig. S11.** 1.62 g of SnS₂ nanoplates have been synthesized.