

***In situ* synthesis of SnS₂@graphene nanocomposites for rechargeable lithium batteries**

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Preparation of SnS₂@graphene nanocomposite:

Graphene oxide was prepared by a modified Hummers' method.^{1,2} In a typical synthesis of SnS₂@graphene nanocomposite, 10 mg of graphene oxide was dispersed into 25 mL deionized(DI) water by ultrasonication for 30 min, following the addition of 0.5 mL of aqueous HCl solution (35 wt.%) under stirring. After 10 min, 120 mg of tin dichloride dihydrate (SnCl₂·2H₂O, Alfa Aesar, 98 %) and 160 mg of thioacetamide (TAA) were added into the solution. After stirring, the solution was, then, transferred to a 100 mL Teflon-lined stainless steel autoclave and then heated in an electric oven at 180 °C for 6 h. A black product was harvested after centrifugation and dried at 50 °C overnight.

Characterization:

The morphology of all studied samples were investigated by using a scanning electron microscopy (SEM) Hitachi S4800 operated at 5 kV, and the nanostructures of samples were characterized by using a transmission electron microscopy (TEM) Philips FEI 200CX operated at 160 kV, high resolution transmission electron microscopy (HRTEM) JEOL 2100F with an image-side Cs-corrector operated at 200 kV, and X-ray diffractometer PANalytical X'pert Pro using Cu K α radiation ($\lambda=1.5416$ Å). Nitrogen adsorption/desorption isotherms were measured on a Quantachrome Instrument (Autosorb ASIC-2). The carbon concentration were measured using a CHN analyzer (Flash EA 1112, ThermoFinnigan). Raman spectra were obtained with a Renishaw inVia Raman microscopy system with a laser wavelength of 532 nm. X-ray photoelectron spectroscopy (XPS) analysis was performed using a Kratos Amicus XPS. Photoemission was stimulated by monochromated Mg K α radiation (12 kV) with an operating power of 180 W. Binding energies were referenced to the C1s binding energy set at 284.8 eV.

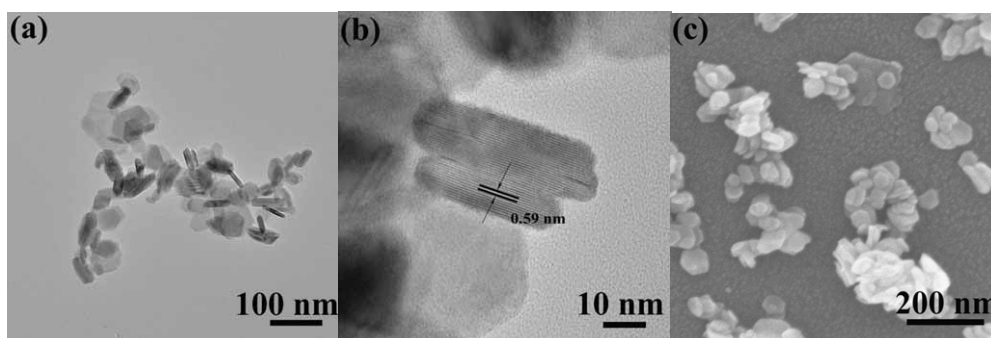


Figure S1. (a, b) TEM and (c) SEM images of SnS₂ nanotablets without graphene support.

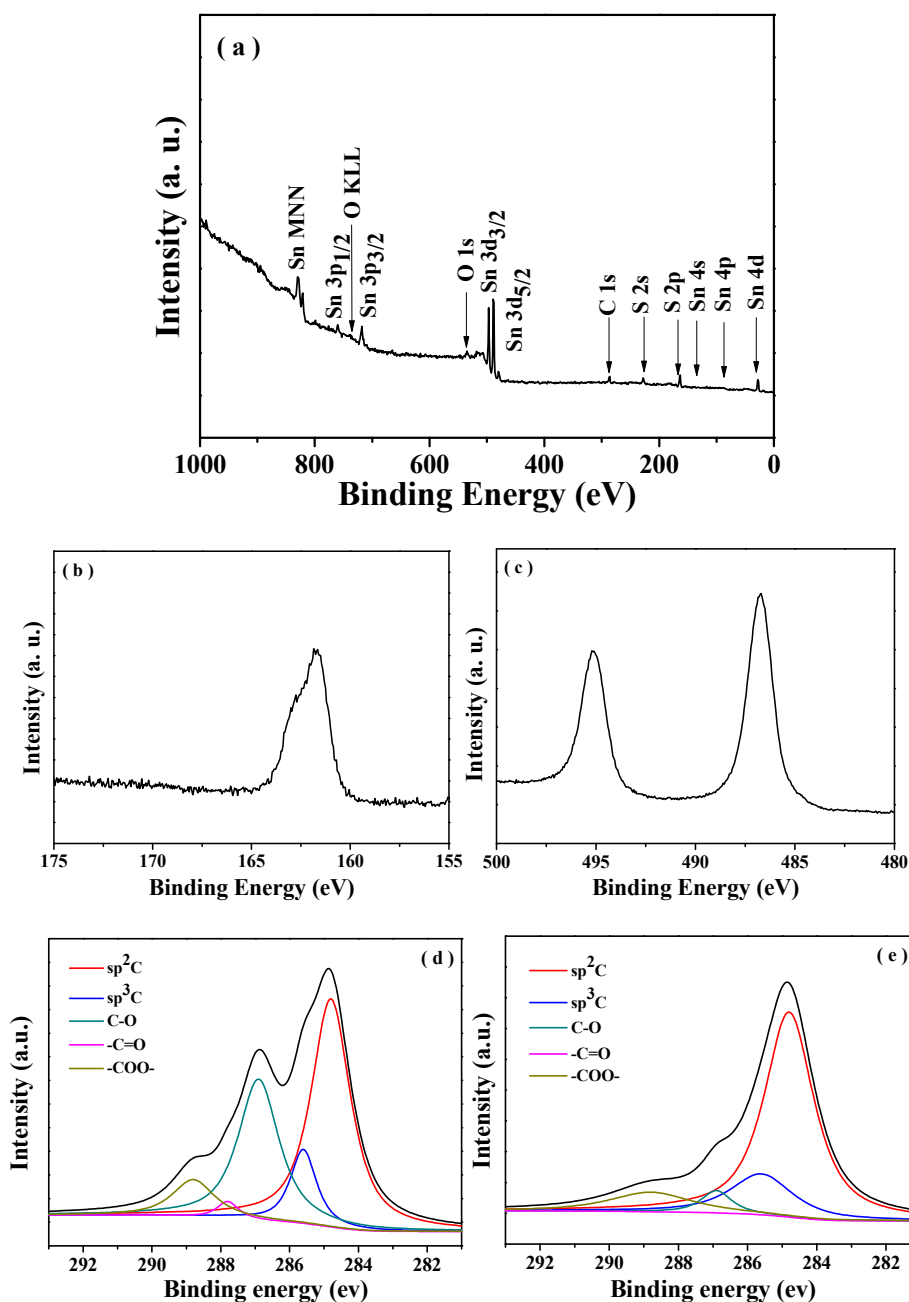


Figure S2. (a) XPS general spectrum of SnS₂@graphene nanocomposite. (b) S 2p and (c) Sn 3d XPS spectra of SnS₂@graphene nanocomposite. (d) and (e) Fit curves of C 1s spectra of GO and SnS₂@graphene nanocomposite.

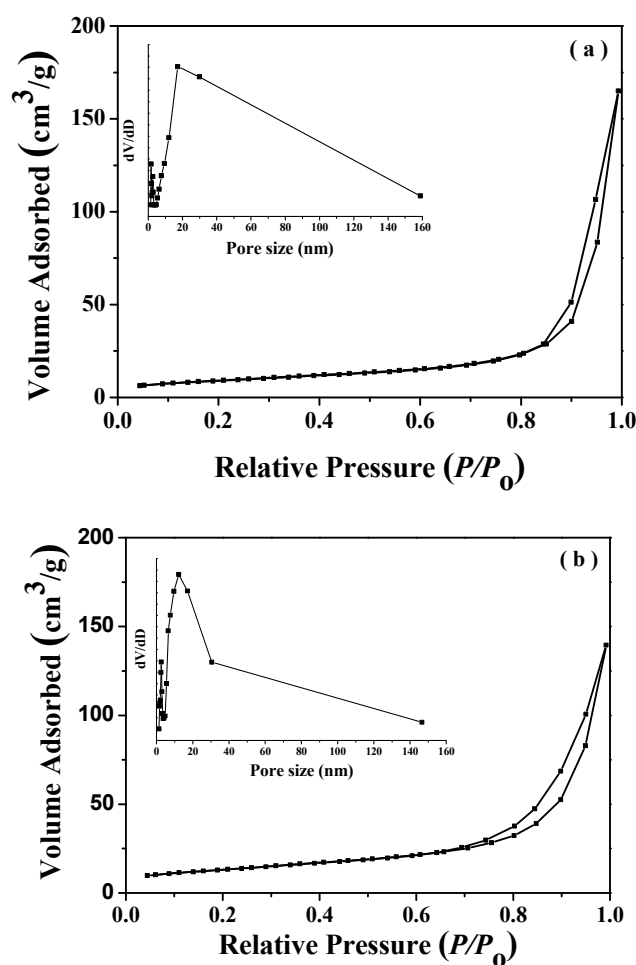


Figure S3. (a) N_2 adsorption-desorption isotherm of SnS_2 nanotablets. (b) N_2 adsorption-desorption isotherm of $SnS_2@graphene$ nanocomposite. The inset shows the pore size distribution calculated from the desorption branch.

Electrochemical Measurements:

The electrochemical measurements were carried out using Land CT2001A with lithium metal as the counter and reference electrodes at room temperature. The electrode consisted of active materials ($SnS_2@graphene$ nanocomposite), conductivity agent (acetylene black), and polymer binder (polyvinylidene difluoride, PVDF, Aldrich) by weight ratio of approximately 80:10:10. The electrolyte was 1M $LiPF_6$ in a 50:50 w/w mixture of ethylene carbonate and diethyl carbonate. Cell assembly was carried out in an Ar-filled glove box with the concentrations of vapor and oxygen below 1 ppm. The working electrode was measured at room temperature in the whole process. The cell was charged and discharged with a voltage window of 0.01-2.00 V and 0.005-1.00V. Cyclic voltammetry (0.01-2.00 V and 0.005-1.00V, $0.1\text{ mV}\cdot\text{s}^{-1}$) was performed using an electrochemical workstation (CHI660C).

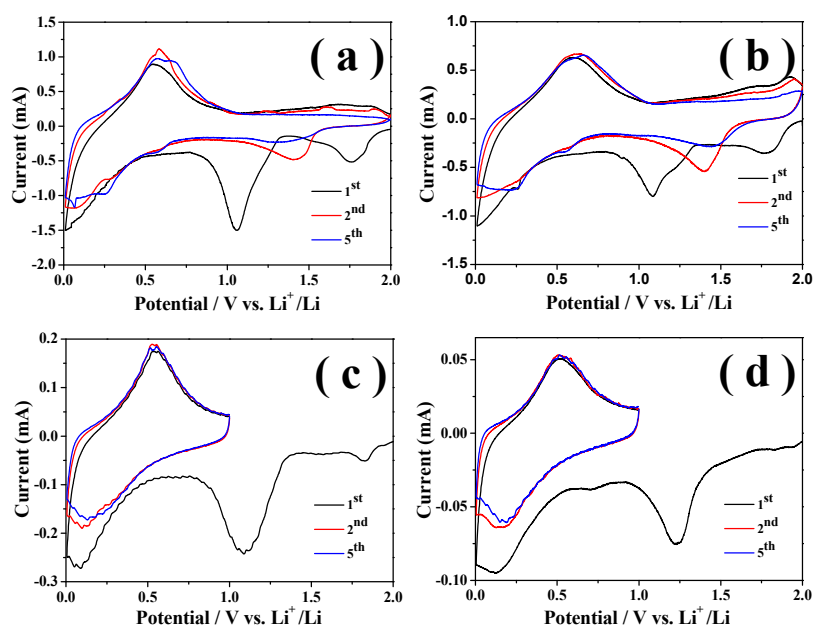


Figure S4 Cyclic voltammograms of SnS_2 (a, c) and $\text{SnS}_2/\text{graphene}$ composite (b, d) at a scanning rate of 0.1 mV/s over the voltage range from 0.01 to 2.00 V (a, b) and 0.005 to 1.00V (c, d).

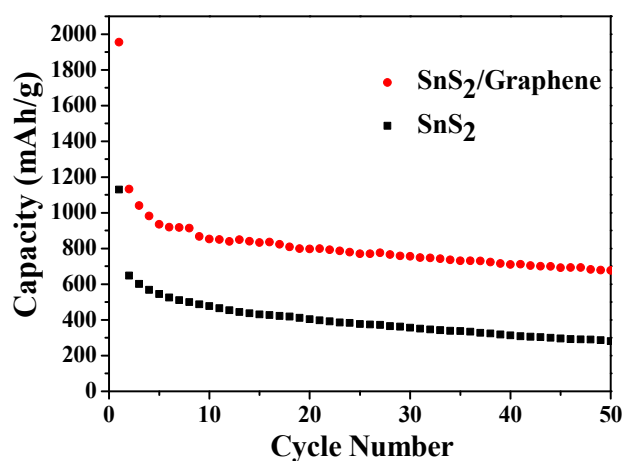


Figure S5 Discharge capacities versus cycle number for the $\text{SnS}_2/\text{graphene}$ composite and SnS_2 at a current rate of 0.5C. All charge-discharge measurements were conducted with a voltage window of 0.01- 2.00 V.

Figure S5 shows cycling performance of SnS₂@graphene nanocomposite and pure SnS₂ in the voltage window of 0.01-2.00V at a rate of 0.5C. As compared to the cycling performance in the range of 0.005-1.00V, a much higher capacity loss rate was obtained in spite of the existence of graphene.

- S1. W. S. Hummers and R. E. Offeman, *Journal of the American Chemical Society*, 1958, **80**, 1339.
- S2. Z.-S. Wu, W. Ren, L. Gao, B. Liu, C. Jiang and H.-M. Cheng, *Carbon*, 2009, **47**, 493.