Supporting Information

Sulfur-terminated Tin Oxide for Durable, Highly Reversible Storage of Large-Capacity

Lithium

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Experimental section

1. Materials preparation

To prepare SnO_2 , 5 mmol $SnCl_4 \cdot 5H_2O$, 0.5 mL HCl (12 M) and 25 mmol urea were dissolved in 75 mL DI water to obtain a clear solution, which was placed in a 100 mL Teflonlined stainless-steel autoclave and reacted at 180 °C for 24 h. The precipitates were centrifuged, washed several times with ethanol and water, and dried at 70 °C for 12 h. To prepare SnO_{2-x} -S (or SnO_{2-x} -S^h), the above procedure was followed except its solution contained an additional 10 (or 75) mmol thiourea.

To prepare SnO_{2-x} -S-rGO, the above procedure was again followed except its solution contained not only an additional 10 mmol thiourea but also a certain amount of GO. Here, GO was prepared by a modified Hummers method, and the obtained GO was dispersed in DI water at the concentration of 3 mg mL⁻¹ until further use. Likewise, SnO₂-rGO was prepared with addition of rGO but not thiourea.

To estimate the contribution of rGO in overall capacity of SnO₂-*x*-S-rGO, GO solution, 0.5 mL HCl (12 M), 25 mmol urea and 10 mmol thiourea were dissolved in 75 mL DI water to obtain a clear solution, which was placed in a 100 mL Teflon-lined stainless-steel autoclave and reacted at 180 °C for 24 h.

2. Preliminary experiment on sulfur stability

5 mg Li_2S and 5 mg Li_2SO_4 were added to 5 mL electrolyte (see Electrochemical cells) in a recirculating argon glovebox and stored for one month, which did not cause any dissolution.

3. Material characterization

X-ray diffraction (XRD) was conducted using a D2 Bruker X-ray diffractometer with Cu K α radiation ($\lambda = 1.5418$ Å) at a scanning rate of 2° min⁻¹ in the 2 θ range of 5–80°. Ultravioletvisible (UV-vis) absorption spectroscopy in the wavelength range of 250–800 nm was measured using a Hitachi UV-4100 spectrophotometer. X-ray photoelectron spectroscopy (XPS) was obtained in an Axis Ultra spectrometer (Kratos Analytical) using Al K α radiation (hv = 1486.7 eV). Before each run of data collection, the radiation energy was calibrated using the 284.8 eV peak of adventitious carbon. Transmission electron microscopy (TEM) was performed in a JEM-2100F microscope (JOEL) with the ability to collect elemental information in HAADF-STEM mode. Additional HAADF-STEM and EELS were performed using a JEM ARM200CF TEM. The mass content of combustible rGO in a composite was measured by thermogravimetric analysis in a Q600SDT TGA (Thermal Analysis) in air at a heating rate of 10 °C min⁻¹ in the temperature range of room temperature to 700 °C. Raman spectra were collected by a DXRxi Micro Raman imaging spectrometer (Thermal Fisher) using an excitation laser with a wavelength of 532 nm.

Post-electrochemical-testing characterization was done with special precaution to minimize atmospheric oxidation and contamination. For XPS, the electrode sample collected from a coin cell was loaded into an inert gas (Ar) injection rod inside a recirculating Ar glove box, then transferred into the high vacuum (~ 10^{-9} Pa) test chamber of XPS without exposure to air. The said coin cell was previously tested to a certain potential under 0.02 A g⁻¹, before being opened in the glove box to avail its content. For TEM, the collected electrode content was similarly obtained from a coin cell tested to a certain potential (typically 0.01 V or 3 V in the first discharge/charge cycle) inside a glove box and immersed in dimethyl carbonate (DMC). While still inside the glove box, it was next grounded by mortar-pestle into a powder-DMC slurry. The slurry was dipped onto a carbon-membrane-coated Cu-screen TEM sample holder to obtain the TEM sample, which was placed in a sealed container until TEM examination.

4. Electrochemical measurement

A slurry consisting of 80 mg active materials (SnO₂, SnO_{2-x}-S, SnO₂-rGO, or SnO_{2-x}-S-rGO), 10 mg acetylene black and 0.5mL 20 mg mL⁻¹ polyvinylidene difluoride (PVDF) as solid content was uniformly coated onto a copper foil by the doctor-blade method. The coated foil was dried at 70 °C overnight, then cut into Φ 14 mm circular disks as anode. Lithium foil (China

Energy Lithium) was used as the counter and reference electrode, and a glass fiber mat (Whatman) was used as the separator. The electrolyte used was 1 M LiPF₆ in ethyl carbonate (EC) and diethyl carbonate (DEC) (w/w = 50:50) with 10.0 % fluoroethylene carbonate (FEC) and 1.0 % vinylene carbonate (VC). Coin cells containing the above were assembled in a recirculating argon glovebox, which kept the moisture below 0.1 ppm and oxygen content below 1 ppm. Similar reference cells containing rGO instead of an active material as anode were also prepared.

Electrochemical tests in the cyclic and rate-testing modes were performed in a LAND-CT2001C test system in the potential window of 0.01–3 V vs. Li/Li⁺. Additional electro-impedance spectroscopy (EIS), current-voltage (I–V) curves and cyclic voltammetry (CV) of the assembled coin cells were conducted using a CH1760E electrochemical workstation (Chenhua, Shanghai). The EIS range was from 0.1 Hz to 100 kHz with an excitation amplitude of 5 mV at open circuit voltage (OCV), the range of I–V curve was from –0.03 to 0.03 V at a scanning rate of 0.1 mV s⁻¹, and the range of CV curves was 0.01 to 3 V vs. Li/Li⁺ at a scanning rate of 0.3 mV s⁻¹.



Figure S1. Physical characterizations of SnO₂, SnO_{2-x}-S and SnO_{2-x}-S-rGO. (a) XRD and (b) BET of SnO₂, SnO_{2-x}-S and SnO_{2-x}-S-rGO. To aid readability, the BET data (V_{abs}) of SnO_{2-x}-S was translated upward by 50 units and that of SnO_{2-x}-S-rGO by 90 units. (c) TEM image of SnO_{2-x}-S. (d–e) TEM images and (f) selected area electron diffraction (SAED) pattern of SnO₂. (g) TEM image and (h) SAED pattern of SnO_{2-x}-S-rGO. (i) TEM image and (j) SAED pattern of SnO_{2-x}-S-rGO. TG analysis of (k) SnO₂-rGO and (l) SnO_{2-x}-S-rGO.



Figure S2. UV-vis results of SnO₂, SnO_{2-x}-S and SnO_{2-x}-S^h and XRD of SnO_{2-x}-S^h. (a) UV-Vis spectra and powders (inset) of SnO₂, SnO_{2-x}-S and SnO_{2-x}-S^h, the last one having more thiourea addition during synthesis. (b) XRD pattern of SnO_{2-x}-S^h.



Figure S3. Spectral information of SnO_2 , SnO_{2-x} -S and SnO_{2-x} -S^h. (a) Raman spectra of SnO_2 , SnO_{2-x} -S and SnO_{2-x} -S^h (SnS_2 , SnS and SnO samples are all from commercially available sources and measured without further purification). (b) FT-IR spectra of SnO_2 and SnO_{2-x} . In (a), peaks at 210 and 150 cm⁻¹ may correspond to the 220 and 150 cm⁻¹ peaks in the phonon density of SnO_2 (https://www.materialsproject.org/materials/mp-856/), and they may have appeared in violation of the standard Raman selection rule for the bulk crystal because of the unusual surface termination on the nanocrystals, which is expected to be more distinct on SnO_{2-x} -S^h.



Sn: 57.12/118.6=0.482 O: 39.68/15.999= 2.480 S: 3.19/32.06= 0.100 Sn:S= 4.82:1

Figure S4. The confirmation of sulfur content according to the TEM-EDS.



Figure S5. XRD pattern and digital image of SnO₂ synthesized as followed: SnCl₄·5H₂O, HCl, urea, and thiourea were dissolved in DI water to obtain a clear solution, which was placed in a 100 mL Teflon-lined stainless-steel autoclave and reacted at 120 °C for 24 h, suggesting two-step process in SnO_{2-x}-S (SnO₂ generation and edged sulfurization).



Figure S6. Sn 3d XPS spectrum of SnO₂ and SnO_{2-x}-S.



Figure S7. Electrical conductivity test of SnO_2 , SnO_{2-x} -S and SnO_{2-x} -S-rGO. (a-c) Room-temperature *I-V* characteristics of compressed pellets of SnO_2 , SnO_{2-x} -S and SnO_{2-x} -S-rGO showing Ohmic behavior.



Figure S8. XPS surveys of (a) SnO₂, (b) SnO_{2-x}-S, (c) SnO_{2-x}-S^h, and (d) SnO_{2-x}-S-rGO. (e) S 2*p* spectrum.



Figure S9. Nyquist plots of AC impedance of SnO_2 , SnO_{2-x} -S and SnO_{2-x} -S-rGO electrodes; scanned from 0.01 to 10^5 Hz with excitation amplitude of 5 mV.



Figure S10. Galvanostatic charge/discharge curves of (a) SnO₂, (b) SnO_{2-x}-S, (c) SnO₂-rGO and (d) SnO_{2-x}-S-rGO electrodes showing the 1st, 2nd, 5th, 10th, 20th, 50th and 100th cycle, respectively.



Figure S11. Galvanostatic intermittent titration technique (GITT) for SnO_{2-x}-S and SnO₂. GITT curves of (a) SnO₂-_x-S and (b) SnO₂ electrodes at the 2^{nd} cycles. (c) A single titration profile of SnO_{2-x}-S electrode during the 2^{nd} charge cycle (current density: 30 mA g⁻¹; Current pulse time: 0.5 h; Relaxation time: 2 h). (d) Variation of voltage against $\tau^{1/2}$ to show the linear fit. Li⁺ diffusion coefficients calculated by the GITT during charge cycling of (e) SnO_{2-x}-S and (f) SnO₂. The Li⁺ chemical diffusion coefficients determined through Fick's second law: $D_{Li}^{+} = \frac{4}{\pi\tau} \left(\frac{nV}{A}\right)^2 \left(\frac{\Delta Es}{\Delta E\tau}\right)^2$, where *n*, *V*, and *A* are the mole of active material, molar volume of active material,

geometric area of the electrode, respectively, and E_s and E_τ are defined in (c).



Figure S12. CV curve of SnO₂-rGO. First five CV cycles of SnO₂-rGO starting at 3 V running clockwise across the potential window of 0.01-3.0 V (*vs.* Li/Li⁺) at the scan rate of 0.3 mV s⁻¹.



Figure S13. Electrochemical cell performances of rGO. (a) First 100 cycle performance of rGO anode at current density of 0.1 A g^{-1} between 0.01–3 V (*vs.* Li/Li⁺). (b) Galvanostatic charge/discharge curves of rGO electrode showing the 1st, 2nd, 5th, 10th, 20th, 50th, and 100th cycle. (c) Long-term cyclic performance of rGO anode; at current density of 2 A g^{-1} except for first 50 cycles.



Figure S14. SnO_{2-x}-S-rGO's charge capacity up to 800 cycles divided into contribution from alloying reactions and conversion/redox reactions.



Figure S15. (a) SAED pattern and (b) Sn 3*d* XPS of SnO_{2-x}-S-rGO electrodes after charging to 3 V at the end of 1^{st} cycle.



Figure S16. Post-electrochemical-testing TEM characterization of SnO_2 , SnO_{2-x} -S SnO_{2-x} -S-rGO after discharge to 0.01 V in 1st cycle. TEM images of (a–b) SnO_{2-x} -S-rGO, (d–e) SnO_{2-x} -S and (g–i) SnO_2 electrodes. High angle annular dark field scanning transmission electron microscopy (HAADF-STEM) image and elemental mapping show uniform distribution of S and Sn in (c) SnO_{2-x} -S-rGO and (f) SnO_{2-x} -S. Note: lattice spacing values of 0.232 nm, 0.244 nm and 0.274 nm shown in various insets match the ones in $Li_{22}Sn_5$ (822), LiSn (111) and $Li_{22}Sn_5$ (640), respectively. However, the above assignments are not unique and other possibilities also exist.



Figure S17. The particle size confirmation of discharging product of SnO_{2-x} -S by dark field and bright field images. (a) TEM images of SnO_{2-x} -S electrodes after discharge to 0.01 V in 1st cycle showing nanoparticles of various sizes. (b–c) Comparison between dark field and bright field images of one region of nanoparticle cluster. HAADF-STEM image and obtained in a JEM ARM200CF TEM in the Institute of Physics, Chinese Academy of Sciences.



Figure S18. Post-electrochemical-testing TEM characterization of SnO_{2-x} -S after charging to 3 V in 30th cycle. (a) HRTEM and (b) LRTEM images of SnO_{2-x} -S. (c) High angle annular dark field scanning transmission electron microscopy (HAADF-STEM) image and elemental mapping.



Figure S19. Post-electrochemical-testing TEM characterization of SnO_{2-x} -S-rGO after charging to 3 V in 30th cycle. (a) HRTEM and (b) LRTEM images of SnO_{2-x} -S-rGO. (c) High angle annular dark field scanning transmission electron microscopy (HAADF-STEM) image and elemental mapping.



Figure S20. Post-electrochemical-testing TEM characterization of SnO_{2-x} -S after discharging to 0.01 V in 30th cycle. (a) HRTEM and (b) LRTEM images of SnO_{2-x} -S. (c) High angle annular dark field scanning transmission electron microscopy (HAADF-STEM) image and elemental mapping.

Figure S21. Post-electrochemical-testing TEM characterization of SnO_{2-x} -S-rGO after discharging to 0.01 V in 30th cycle. (a) HRTEM and (b) LRTEM images of SnO_{2-x} -S-rGO. (c) High angle annular dark field scanning transmission electron microscopy (HAADF-STEM) image and elemental mapping.

Figure S22. HAADF-STEM image and its elemental mapping of SnO_{2-x}-S after charging to 3 V in 1st cycle.

Figure S23. S distribution in discharging product of SnO_{2-x} -S^h by STEM-EELS. (a) HAADF-STEM image of SnO_{2-x} -S^h electrode discharged to 0.01 V. One nanocrystal surrounded by amorphous region is marked by blue circle. (b) EELS (electron energy loss) distribution along a line scan (marked by arrowed red line). (c) Integrated energy loss over the entire energy range of 100 eV to 300 eV of (b) along the line scan. (d) EELS averaged over the amorphous "shell" region marked by green rectangles in (a–c). HAADF-STEM image and EELS obtained in a JEM ARM200CF TEM in the Institute of Physics, Chinese Academy of Sciences.

Figure S24. HAADF-STEM image and its elemental mapping of SnO₂ after charging to 3 V in 1st cycle.