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$_4$·5H$_2$O, 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 Teflon-lined 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, SnO$_2$-rGO was prepared with addition of rGO but not thiourea.

To estimate the contribution of rGO in overall capacity of SnO$_{2-x}$-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$_2$S and 5 mg Li$_2$SO$_4$ 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 Kα radiation ($\lambda = 1.5418$ Å) at a scanning rate of 2° min$^{-1}$ in the 2θ range of 5–80°. Ultraviolet-visible (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 Kα radiation \( (hν = 1486.7 \text{ eV}) \). 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 (\( \sim 10^{-9} \text{ Pa} \)) 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 \( (\text{SnO}_2, \text{SnO}_2_{\alpha-x} \text{-S, SnO}_2 \text{-rGO, or SnO}_2_{\alpha-x} \text{-S-rGO}) \), 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 \( \Phi 14 \) 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 LiPF$_6$ 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 SnO$_2$, SnO$_{2-x}$-S and SnO$_{2-x}$-S-rGO. (a) XRD and (b) BET of SnO$_2$, 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 SnO$_2$. (g) TEM image and (h) SAED pattern of SnO$_2$-rGO. (i) TEM image and (j) SAED pattern of SnO$_{2-x}$-S-rGO. TG analysis of (k) SnO$_2$-rGO and (l) SnO$_{2-x}$-S-rGO.
Figure S2. UV-vis results of SnO$_2$, 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 SnO$_2$, 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 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$_h$. 


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

<table>
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Atom ratio:
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 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 SnO₂₅-S (SnO₂ generation and edged sulfurization).
Figure S6. Sn 3d XPS spectrum of SnO2 and SnO2-x-S.

Figure S7. Electrical conductivity test of SnO2, SnO2-x-S and SnO2-x-S-rGO. (a-c) Room-temperature $I-V$ characteristics of compressed pellets of SnO2, SnO2-x-S and SnO2-x-S-rGO showing Ohmic behavior.
Figure S8. XPS surveys of (a) SnO$_2$, (b) SnO$_{2-x}$-S, (c) SnO$_{2-x}$-S$^h$, and (d) SnO$_{2-x}$-S-rGO. (e) S 2p 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) SnO$_2$, (b) SnO$_{2-x}$-S, (c) SnO$_2$-rGO and (d) SnO$_{2-x}$-S-rGO electrodes showing the 1$^{st}$, 2$^{nd}$, 5$^{th}$, 10$^{th}$, 20$^{th}$, 50$^{th}$ and 100$^{th}$ cycle, respectively.
Figure S11. Galvanostatic intermittent titration technique (GITT) for SnO$_2$-S and SnO$_2$. GITT curves of (a) SnO$_2$-S and (b) SnO$_2$ electrodes at the 2$^{nd}$ cycles. (c) A single titration profile of SnO$_2$-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$_2$-S and (f) SnO$_2$. The Li$^+$ chemical diffusion coefficients determined through Fick's second law:

$$D_{Li^+} = \frac{4nV_s}{\pi\tau A} \left(\frac{\Delta E_s}{\Delta E \tau}\right)^2$$

where $n$, $V$, and $A$ are the moles of active material, molar volume of active material, geometric area of the electrode, respectively, and $E_s$ and $E$ 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 3d 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 1$^{\text{st}}$ 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 1$^\text{st}$ 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 30$^{\text{th}}$ 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 30$^{th}$ 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$_{2}$-S after discharging to 0.01 V in 30$^{th}$ cycle. (a) HRTEM and (b) LRTEM images of SnO$_{2}$-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 30$^{th}$ 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 1$^{\text{st}}$ cycle.
Figure S23. S distribution in discharging product of SnO$_{2-x}$-S$^3$ by STEM-EELS. (a) HAADF-STEM image of SnO$_{2-x}$-S$^3$ 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 SnO$_2$ after charging to 3 V in 1$^{st}$ cycle.