Electronic Supplementary Information

Two Dimensional Graphene/SnS$_2$ Hybrids with Superior Rate Capability for Lithium ion Storage

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Experimental details:

**Material Synthesis:** Graphene oxide (GO) was synthesized from natural graphite (300 μm, Qingdao Graphite Company) by a modified Hummers method [1]. Graphene supported SnO$_2$ nanoparticles (G-SnO$_2$) were prepared by a controllable hydrolyzation process of tin salts in a GO containing ethylene glycol (EG)-water solution. In a typical experiment, as-synthesized graphene oxide (50 mg) was firstly suspended in a 100 mL of mixture of EG and water (10 mL of water contained) that was hosted in a round-bottom flask, and then ultrasonically treated for 1 h, forming a brown dispersion. Then 0.5 g of SnCl$_2$·2H$_2$O (dissolved in 10 mL of EG) was added to the obtained GO solution. After magnetic stirring for 20 min, the solution was heated to 120 °C and refluxed for 2 h with constant stirring under atmospheric pressure. After filtration and desiccation, the resultant black solid product was placed in a horizontal quartz tubular reactor, and heated to 500 °C at 10 °C min$^{-1}$ in Ar (99.999 %) atmosphere with a flow rate of 200 sccm. To improve the crystallinity of SnO$_2$ in G-SnO$_2$, the product was firstly annealed at 500 °C for 2 h in Ar atmosphere. Subsequently, gas mixture of H$_2$S and Ar (Volume ratio: 1:19) were introduced in turn with a flow rate of 200 sccm when the furnace was cooled down to 300 °C, and kept these conditions for 2 hours. Finally the system was cooled down to room temperature in Ar atmosphere. To investigate the effect of the pre-annealing treatment and flow rate of H$_2$S/Ar gas on the morphologies of SnS$_2$, the
same process was used except adjusting the corresponding parameters. For comparison, bare SnS$_2$ was prepared by the same procedure but without the presence of GO in the first step.

**Material Characterization:** X-ray diffraction (XRD) with Cu K$_\alpha$ radiation (Rigaku D/max-2500B2+/PCX system) was used to determine the phase composition and the crystallinity. The morphology and microstructure of the samples were investigated by FE-SEM (Hitachi S4800), FE-TEM (FEI Tecnai G2 20 ST), and TGA (Perkin Elmer, Diamond TG) measurements. Nitrogen sorption isotherms and BET surface area were measured at 77 K with a ASAP 2020 physisorption analyzer (USA). The Raman spectra were obtained on a Renishaw Micro-Raman Spectroscopy System with excitation from an argon ion laser (514 nm). Fourier-trans-form infrared (FT-IR) spectra were recorded by a Perkin-Elmer Spectrum One FTIR Spectrometer.

Electrochemical cycling tests were performed with coin-type half-cells (2032 size). The working electrode was made from the G-SnS$_2$ active material, super P carbon black, and a polyvinylidene fluoride (PVDF) binder in a weight ratio of 80:10:10 on a copper foil. The mass of the active material in each half-cell is about 2-3 mg. The electrolyte was 1M LiPF$_6$ with 1:1 ethylene carbonate: diethylene carbonate (EC: DEC), and the counter and reference electrodes were made from lithium foil. The cycle-life of the cells was tested at different rates within a fixed voltage window of 1.3 V-5 mV. The rate capability was evaluated by varying the discharge rate from 100 mA g$^{-1}$ to 6400 mA g$^{-1}$. Cyclic voltammetry was performed to examine the cathodic reaction (reduction) and the anodic reaction (oxidation) in the voltage range of 2.5-0 V (versus Li/Li$^+$), at a sweep rate of 0.1 mV s$^{-1}$. 

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Figure S1. FT-IR spectra for graphene oxide (GO), graphene supported SnO$_2$ nanoparticles (G-SnO$_2$) and graphene supported SnS$_2$ nanoplates (G-SnS$_2$).

Figure S1 shows FT-IR spectra of graphene oxide (GO), graphene supported SnO$_2$ nanoparticles (G-SnO$_2$) and graphene supported SnS$_2$ nanoplates (G-SnS$_2$). The two bands of GO appearing at 1050 cm$^{-1}$ and 1720 cm$^{-1}$ are due to the epoxide and carboxyl functional moieties, respectively. This result clearly reveals that functional groups are introduced into carbon frameworks upon oxidation. However, in case of G-SnO$_2$, epoxide and carboxylate functional groups almost disappear, indicating that GO has been reduced by the solution process. The broad band around 670 cm$^{-1}$ is associated with the anti-symmetric O-Sn-O stretching mode, clarifying that SnO$_2$ particles exist within the graphene-based matrices. After the heat treatment in H$_2$S/Ar, disappearing of the broad band around 670 cm$^{-1}$ confirmed the totally conversion of SnO$_2$ nanoparticles to SnS$_2$ nanoplates.
Figure S2. Energy-dispersive X-ray (EDX) spectrum of G-SnS$_2$. 
Figure S3. Comparison of XRD patterns of (a) G-SnS₂, (b) G-SnO₂-SnS₂ (sample collected during the second step), (c) Annealed G-SnO₂, (d) Unannealed G-SnO₂, and (e) GO.
Figure S4. TEM images of (a, b) unannealed G-SnO₂, and (c, d) annealed G-SnO₂.

Figure S5. TEM images of G-SnS₂-SnO₂ (samples collected after heat treatment in H₂S/Ar for 1 hour)
Figure S6. Cyclic voltammograms for G-SnS$_2$-S electrode, cycled between 0.05V and 2.5V at a scan rate of 0.01mV/s.

Figure S6 shows the Cyclic Voltammograms (CV) for the first ten cycles at a scan rate of 0.01mVs$^{-1}$ in the potential window of 0.05V-2.5V. Specifically, several reduction peaks are observed in the first cathodic scan. Two broader peaks were present at about 1.25 V and 1.1 V in the first potential sweeping process. The cathodic peak at 1.25 V, observed during the first sweep, was assigned to the decomposition of the SnS$_2$ into metallic tin and Li$_2$S, and the formation of solid electrolyte interface (SEI), which should be responsible for the first irreversible capacity loss. The third dominant peak between 0.6 and 0 V is known to arise from the formation of Li$_x$Sn alloys. The additional peaks at ~1.6 and ~1.9V were attributed to the lithium intercalation of the SnS$_2$ layers without phase decomposition, which were also partly responsible for the high initial discharge capacities.
**Figure S7.** Thermal analysis (by TGA and DTA) of as-prepared G-SnS$_2$-M hybrids. The SnS$_2$ content estimated from the thermal analysis was ca. 95.0 wt % (Note: SnS$_2$ had been oxidized into SnO$_2$). The analysis was taken in air using a heating rate of 10°C min$^{-1}$. The weight loss from room temperature to 200°C was due to the removal of physisorbed and chemisorbed water.
Figure S8. Nitrogen adsorption-desorption isotherms and pore-size distribution of as-prepared G-SnS$_2$-L (a, b), G-SnS$_2$-M (c, d) and G-SnS$_2$-S (e, f), respectively.

Table S1. Size distribution of SnS$_2$ nanoplates of three typical G-SnS$_2$ samples obtained at different Experimental conditions.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Experimental conditions</th>
<th>Size distribution of SnS$_2$ nanoplates</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Pre-annealing treatment of G-SnO$_2$</td>
</tr>
<tr>
<td>G-SnS$_2$-S</td>
<td>with</td>
<td>400sccm</td>
</tr>
<tr>
<td>G-SnS$_2$-M</td>
<td>with</td>
<td>200sccm</td>
</tr>
<tr>
<td>G-SnS$_2$-L</td>
<td>without</td>
<td>200sccm</td>
</tr>
</tbody>
</table>
Table S2. BET surface area, BJH adsorption cumulative volume of pores, and BJH adsorption average pore width of as-prepared G-SnS$_2$ samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>BET surface area m$^2$ g$^{-1}$</th>
<th>BJH adsorption cumulative volume of pores cm$^3$ g$^{-1}$</th>
<th>BJH adsorption average pore width nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>G-SnS$_2$-S</td>
<td>35.3</td>
<td>0.060</td>
<td>6.1</td>
</tr>
<tr>
<td>G-SnS$_2$-M</td>
<td>47.2</td>
<td>0.259</td>
<td>18.6</td>
</tr>
<tr>
<td>G-SnS$_2$-L</td>
<td>84.1</td>
<td>0.562</td>
<td>22.5</td>
</tr>
</tbody>
</table>

The isotherm for G-SnS$_2$-L and G-SnS$_2$-M is characteristic of a type IV with a type H3 hysteresis loop, revealing that the material is composed of aggregates (loose assemblages) of sheet-like particles forming slit-like pores. Meanwhile, the isotherm for G-SnS$_2$-S with a Type H4 loops feature can be attributed to adsorption-desorption in narrow slit-like pores, which is in corresponding with our microscopy findings.

Supporting references