

## Supporting Information

### Ultralarge Single Crystal SnS Rectangular Nanosheets

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## Experimental Section

**Chemical:** Tin (II) chloride ( $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ; 98%, AR)(Shanghai Experiment Reagent Co., Ltd.), Sodium diethyldithiocarbamate trihydrate ( $\text{Na}(\text{Ddtc}) \cdot 3\text{H}_2\text{O}$ ; 99%) (Sinopharm Chemical Reagent Co., Ltd.), Oleylamine (OM; 80-90%, Aladdin), Oleic acid (OA; 90%, Aldrich), 1-Octadecen (ODE; 90%, Aldrich), absolute ethanol and cyclohexane were of analytical grade and used as received without further purification.

**Synthesis of  $\text{Sn}(\text{Ddtc})_2(\text{Phen})$ :** Typically, 10 mmol of  $(\text{Phen}) \cdot 3\text{H}_2\text{O}$  were dissolved in 80 mL of boiling water. Then, it was introduced into 40 mL of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  (10 mmol) aqueous solution with vigorous stirring. The color of the mixture solution was turned to yellow because of the reaction between Phen and tin ions. After 10 min, 40 mL of  $\text{Na}(\text{Ddtc}) \cdot 3\text{H}_2\text{O}$  (20 mmol) aqueous solution was added dropwisely into above yellow solution, and the color of the aqueous mixture changed to yellowish. After 3 h, the resulting yellowish precipitate was filtered, washed with distilled water, and dried in air at 70 °C.

**Synthesis of orthorhombic SnS nanosheets:** The synthesis was carried out using the oxygen-free procedure. A typical procedure is described as follows: 0.046 g of  $\text{Sn}(\text{Ddtc})_2(\text{Phen})$  was added into OM/ODE(OM:ODE=20 mmol : 20 mmol) mixture solvents in a three-necked flask (100 mL) at room temperature. Then, the slurry was heated to 120 °C to remove water and oxygen with vigorous magnetic stirring under vacuum for 20 min in a temperature-controlled electro mantle. The solution was then heated to 300 °C and was kept for 1 h under  $\text{N}_2$  atmosphere. Then it was allowed to cool down to room temperature naturally. And 40 mL of ethanol was poured into the solution, the resultant mixture was centrifugally

separated and the products were collected.

**Synthesis of hexagonal SnS<sub>2</sub> nanoplates:** The synthetic procedure was the same as that for SnS nanosheets synthesis, except that the solvent used here is a mixture of OA/OM /ODE (10 mmol : 10 mmol : 20 mmol), the amount of precursor is 0.3 g and the temperature is 280 °C.

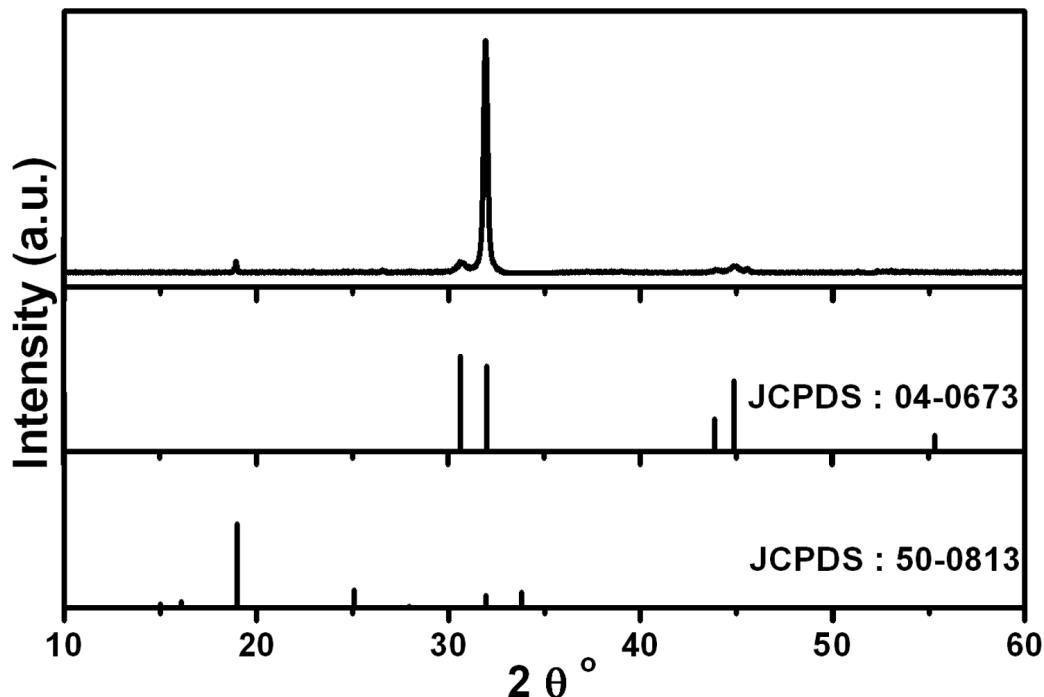


Figure S1. XRD pattern of the nanosheet electrodes after the 5th electrochemical discharge reaction. JCPDS: 04-0673 and JCPDS: 50-0813 were recorded for Sn and P<sub>2</sub>S<sub>5</sub>, respectively.

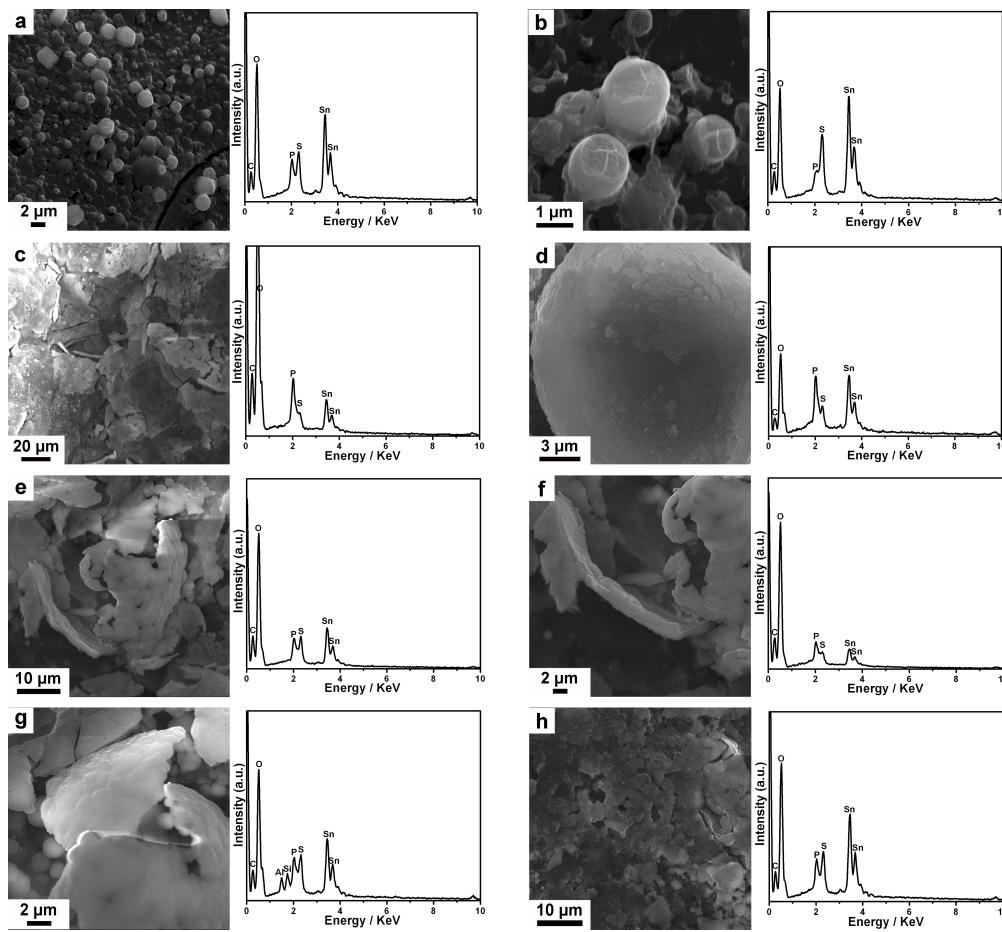


Figure S2. SEM images and corresponding EDS spectra from the different areas of SnS nanosheet electrodes after the 5th electrochemical discharge reaction.