Supporting Information

Experimental Section

Materials: All reagents including $SnCl_2 \cdot 2H_2O$, $Na_2S_2O_3 \cdot 5H_2O$, sulfur powders, hexadecyl trimethyl ammonium bromide (CTAB), tartaric acid, sodium hydroxide and ethanol were analytical grade and were used without any further purification. The fluorine-doped tin oxide (FTO) conductive glasses were cleaned ultrasonically with diluted hydrochloric acid, ethanol, acetone, and deionized water and then dried with an electric hair dryer.

Synthesis: In a typical procedure of synthesizing SnS_2 hollow microspheres, 0.1115 g $SnCl_2 \cdot 2H_2O$, 0.248 g $Na_2S_2O_3 \cdot 5H_2O$, 0.064 g sulfur powders and 0.0364 g CTAB were dissolved in a mixture composed of 19 mL 0.1 mol/L sodium tartrate - tartaric acid buffer solution (pH = 3) and 5 mL ethanol at room temperature with a 30 mL Teflon-lined autoclave. Afterward, a piece of FTO glass (2.5 cm × 1 cm) was placed with an angle against the wall of the Teflon-liner with the conducting side facing down. The hydrothermal synthesis was conducted at 200 °C for 12 h in an electric oven. When the reaction was finished, the autoclave was cooled down to room temperature naturally. Finally, the FTO glass was taken out, washed thoroughly with distilled water, carbon disulfide and ethanol for several times and dried in vacuum oven at 60 °C for 6 h for further characterization. For preparation of SnS_2 3D nanoflake-based hollow microspheres, we added 0.223 g $SnCl_2 \cdot 2H_2O$, 1.24 g $Na_2S_2O_3 \cdot 5H_2O$, 0.16 g sulfur powders into the reaction system and other reaction conditions used are the same to the above synthesizing process.

Characterization: The prepared products were characterized by X-ray diffractometer (XRD, D8 ADVANCE), field emission scanning electron microscopy (FE-SEM, JSM-6330F), transmission electron-microscopy (TEM, JEM2010-HR), respectively. The surface area of the product was calculated from nitrogen adsorption/desorption isotherms at 77 K which were conducted on an ASAP 2020 V3.03 H instrument. Before measurement, all samples were kept at 100 °C for 5 h under the flowing nitrogen.

Electrochemical Performance: The 2032 coin-type cells were assembled in an argon-filled glove box using pure lithium as the counter electrode, 1M $LiClO_4$ [ethylene carbonate (EC): dimethylcarbonate (DMC) 1:1 in volume] as the electrolyte, and a microporous membrane (Celguard 2400, USA) as the separator. Charge–discharge cycles of the cells were measured over potential ranging from 0.001 V to 1.2 V at a current density of 0.1 C (1 C = 645 $mAh \cdot g^{-1}$). The working electrodes were prepared by coating the slurry consisted of 80 wt% active materials which were directly scraping from the FTO glass, 10 wt% acetylene black, and 10 wt% polyvinylidene fluoride (PVDF) dissolved in N-methyl pyrrolidinone (NMP) on copper foil. The electrodes were dried at 120 °C for 12 h in vacuum and then pressed under 10 MPa.

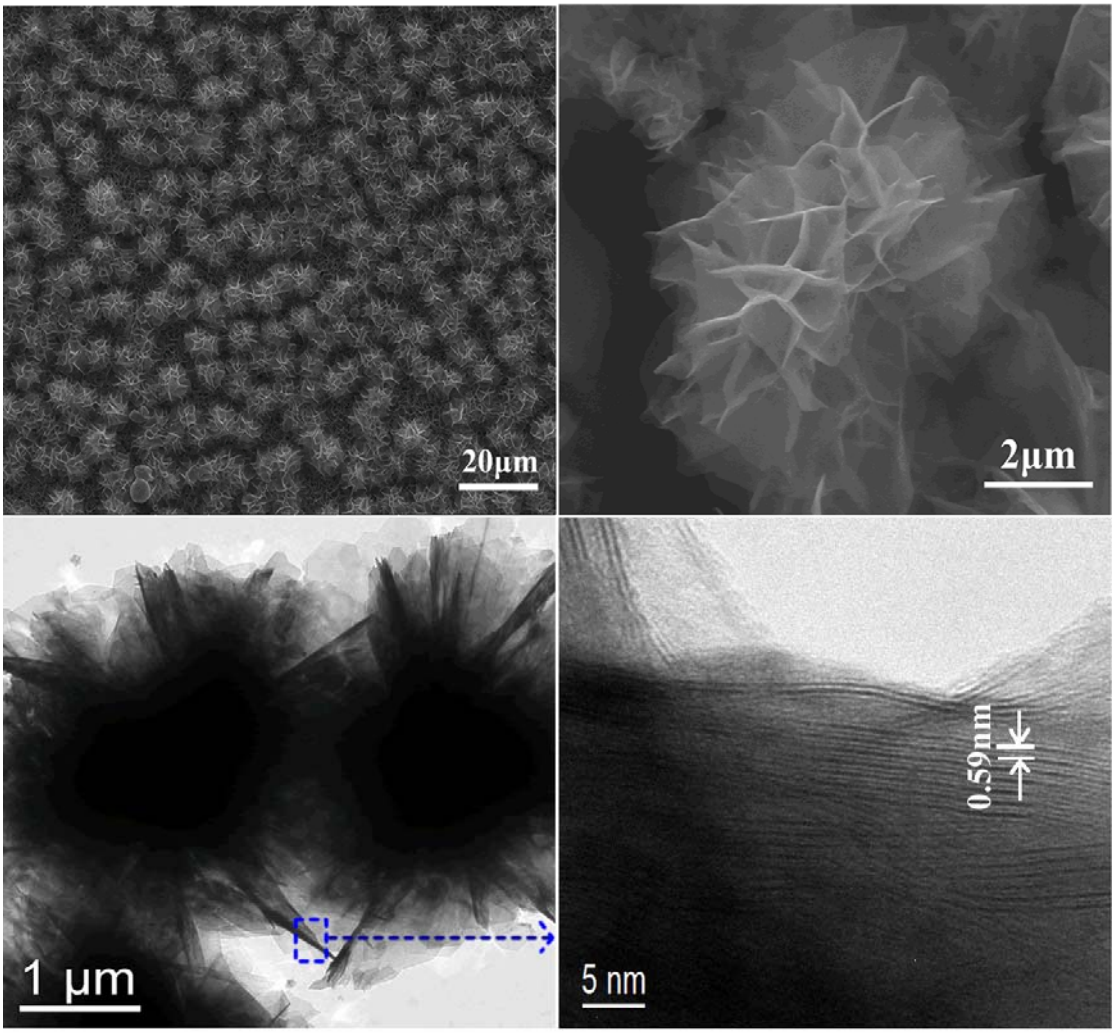

Fig. S1 (a, b) SEM, (c) TEM and (d) HRTEM of SnS_2 flower-like structures synthesized without adding CTAB.

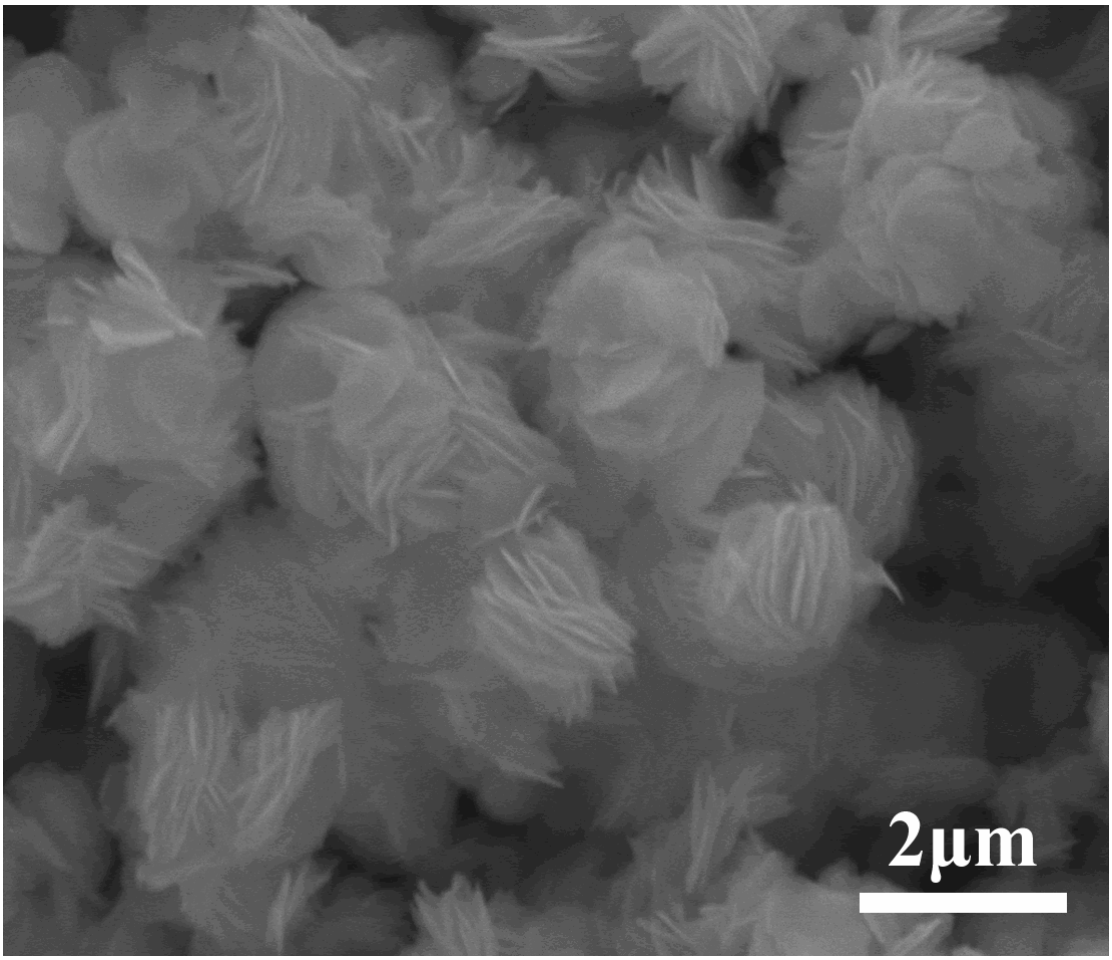

Fig. S2 SEM image of the SnS_2 multilayer-nanoflakes synthesized without adding FTO glass.

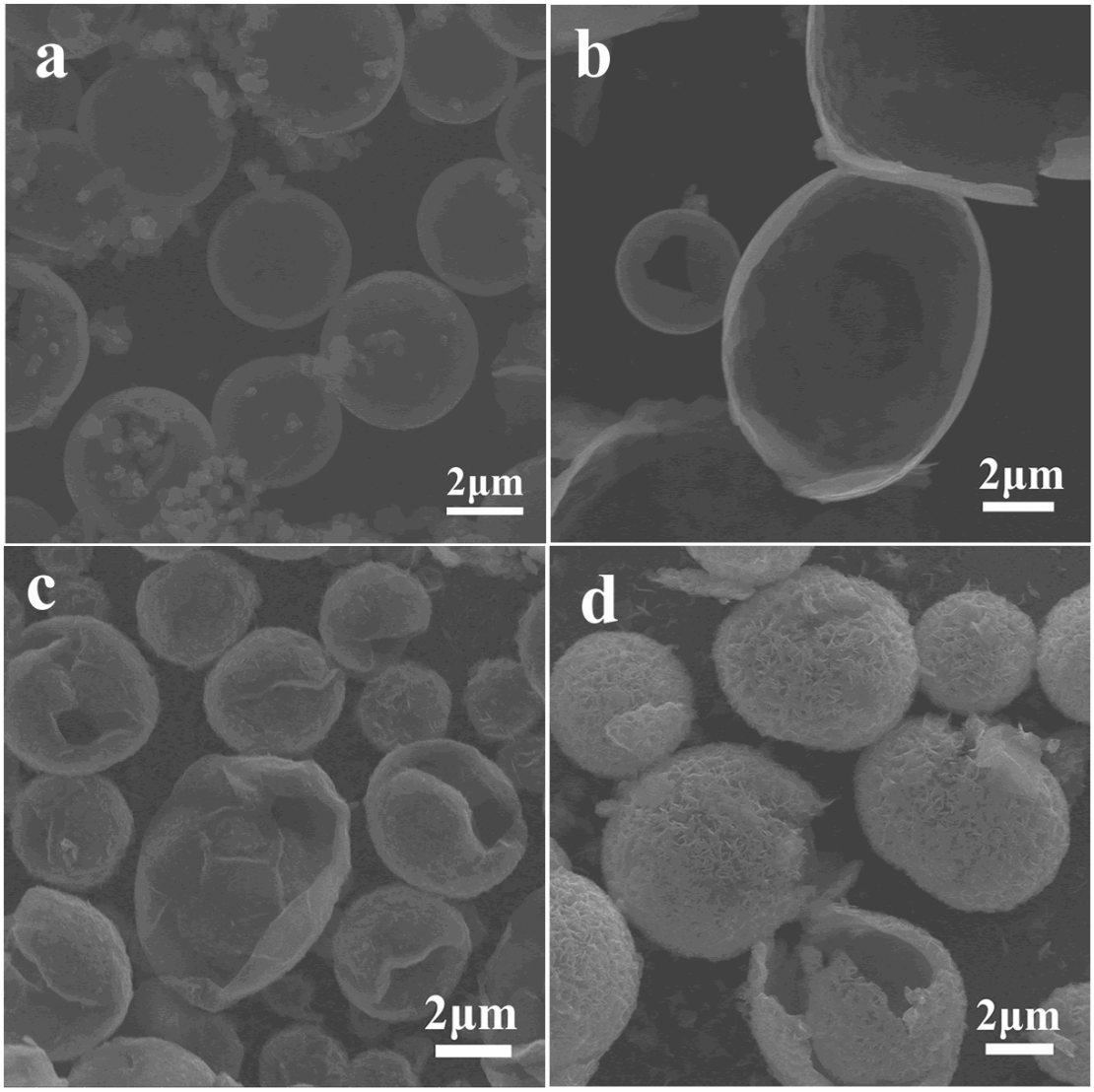

Fig. S3 SEM images of the SnS_2 3D nanoflake-based hollow microspheres synthesized with different reaction temperatures. (a) 140 °C, (b) 160 °C, (c) 180 °C and (d) 220 °C.

The surface area of these SnS_2 hollow microspheres were determined by nitrogen adsorption and desorption measurement at 77 K, as is shown in Fig. S4. The specific surface area for SnS_2 3D nanoflake-based hollow microspheres calculated by the Brunauer-Emmett-Teller (BET) method is 35.5 $m^2 g^{-1}$, which is much larger than that of SnS_2 hollow microspheres 17.0 $m^2 g^{-1}$.

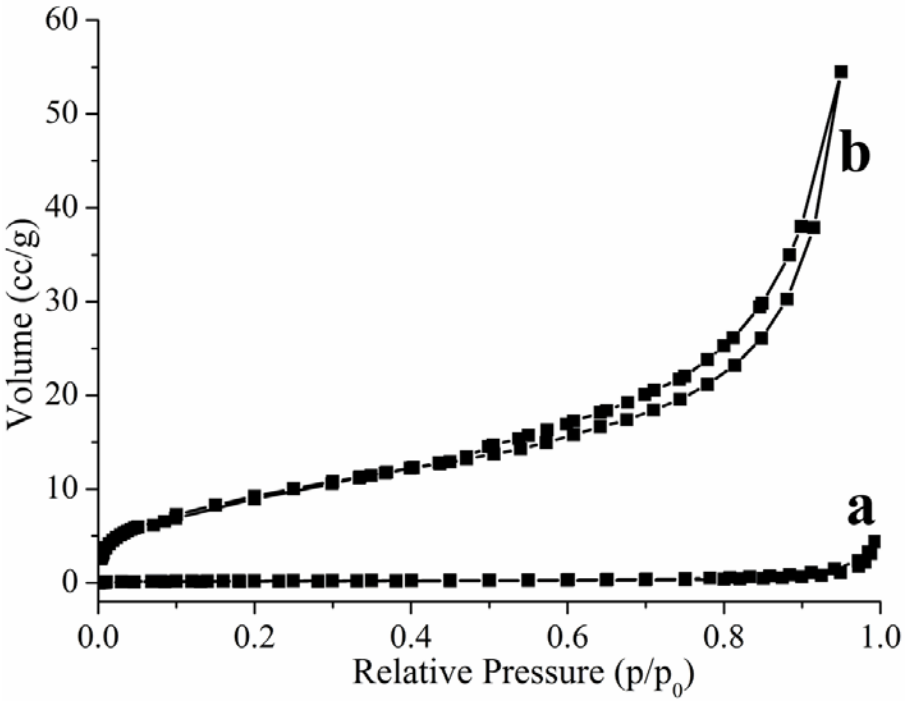

Fig. S4 Nitrogen adsorption–desorption isotherms of the (a) SnS_2 hollow microspheres and (b) SnS_2 3D nanoflake-based hollow microspheres.