

Supporting Information

Low-Cost SnS_x Counter Electrodes for Dye-Sensitized Solar Cells †

*Xiao Chen,^{‡a} Yu Hou,^{‡a} Bo Zhang,^a Xiao Hua Yang,^{*a} and Hua Gui Yang^{*a,b}*

^a Key Laboratory for Ultrafine Materials of Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, China.

^b Centre for Clean Environment and Energy, Gold Coast Campus, Griffith University, Gold Coast, Queensland 4222, Australia.

Correspondence and requests for materials should be addressed to H.G.Y. (email: hgyang@ecust.edu.cn) or X.H.Y. (email: yangxiaohuayou@163.com).

Synthesis of SnS_x

In this section, we described the synthetic methods of SnS_x including SnS nanosheets (SnS NSs), SnS nanowires (SnS NWs) and SnS₂ nanosheets (SnS₂ NSs) separately.

SnS NSs were synthesized by a two-step method. Firstly, 6 mmol of SnCl₂ • 2H₂O (Aldrich 98 %) was dissolved in absolute ethanol (10 mL) under stirring for 15 min. Meanwhile, 30 mmol of sodium diethyldithiocarbamate (Na-DEDTC, Sigma-Aldrich, ≥99.0 %, ACS reagent) was dissolved in absolute ethanol (50 mL) under stirring for 20 min. Then, the obtained SnCl₂ ethanol solution was added dropwise into the Na-DEDTC ethanol solution under vigorous stirring for 5 min. After the above reaction, the precipitate Sn-DEDTC₂ was separated by centrifugation at 8000 rpm for 5 min, washed with absolute ethanol for several times and dried at room temperature under vacuum. Based on the synthesis of Sn-DEDTC₂, SnS NSs were prepared by thermal decompositions of the molecular precursor Sn-DEDTC₂. Firstly, 20 mL of oleylamine (Sigma-Aldrich, 70 %) was heated in 393 K under vacuum with magnetic stirring for 30 min to remove residual water and oxygen, during which the flask was purged periodically with dry nitrogen gas. Then another 5 mL of oleylamine containing 1 mmol of Sn-DEDTC₂ was injected into the above solution, and heated to 573 K for 30 min and then cooled naturally to 323 K, forming a black colored solution. By an addition of 30 mL of ethanol, the black product was centrifuged, and further purified by being dispersed in 10 mL of chloroform and was precipitated again with excess ethanol and dried at room temperature under vacuum .¹

SnS NWs were synthesized through hydrothermal reaction in a 50 mL Teflon-lined stainless steel autoclave. Typically, 2 mmol of SnCl₂ • 2H₂O (Aldrich 98 %) and 6 mmol of sodium sulphide (Aldrich 99 %) dissolved in 40 mL of ethylene glycol (Sigma-Aldrich, ≥99.0 %) were employed as starting reagents and mixed thoroughly under magnetic stirring. Then, 1 mL of acetic acid (Sigma-Aldrich, ≥99.7 %, ACS reagent) was added until the pH value was adjusted to less-than 7.0. The closed autoclave was heated to 453 K in an electric oven for 12 hours. After the reaction, black powdered product was finally obtained by centrifugation, washed with distilled water and dried in air at 333 K.

SnS₂ NSs were synthesized through hydrothermal reaction at 453 K for 12 h, by using 5 mmol of SnCl₄ • 5H₂O (Aldrich 98 %) and 20 mmol of thiourea (Aldrich 99 %) dissolved in 40 mL of 5 vol.% acetic acid in deionized water as precursors. After the hydrothermal reaction, the as-formed yellow precipitates were filtered, washed with distilled water and ethanol, and finally dried in vacuum at 333 K.²

Electrodes preparation

The procedure of preparing the TiO₂ photoanode and the SnS_x CEs were described in detail as follow. Firstly, the fluorine doped SnO₂ (FTO) conducting glass (NSG, 8 Ω/square) substrate was dipped into 40 mM TiCl₄ for 30 min at 343 K (TiCl₄ treatment). Then a 12 μm-thick layer of 20 nm-sized TiO₂ particles was loaded on the FTO by screen printer technique with an area of about 0.25 cm². After sintering at 398 K, the obtained layer was further coated with a 4 μm-thick scattering layer of 200 nm-sized TiO₂ particles (HEPTACHROMA, DHS-NanoT200) followed by sintering at 773 K. Another TiCl₄ treatment was carried followed by sintering at 773 K for 30 min. After cooling to 353 K, the photoanodes (TiO₂ films) were immersed in a 5 × 10⁻⁴ M solution of N719 dye (Solaronix SA, Switzerland) in acetonitrile/tert-butyl alcohol (V/V=1/1) for 24 h. The SnS_x coated CEs were prepared on the FTO substrate using a paste by screen printer procedure. The paste was made by mixing 0.5 g SnS_x powder with 2.03 g anhydrous terpeneol, 2.6 g ethyl celluloses in ethanol (10 wt%) and 8 mL ethanol followed by stirring and sonication, following by the contents in dispersion were concentrated by evaporator. Then the formed films were annealed at 723 K for 30 min in a nitrogen atmosphere. For comparison, the Pt-electrode was prepared by drop-casting 0.5 mM H₂PtCl₆/ethanol solution on the clean FTO conductive glass. Subsequently, the FTO glasses coated with Pt were then sintered in a tube furnace at 723 K for 30 min under ambient conditions.³

Fabrication of DSCs

DSCs were assembled together with the dye-sensitized TiO₂ electrode and the SnS_x CE by a 25 μm-thick hot-melt film (Surlyn 1702, DuPont) and sealed up by heating. The cell internal space was filled with typical liquid electrolytes using a vacuum pump. The liquid electrolyte was composed of 0.60 M 1-butyl-3-methylimidazolium iodide, 0.03 M I₂, 0.50 M 4-tert-butyl pyridine, and 0.10 M guanidinium thiocyanate with acetonitrile as the solvent. The assembled DSCs were used for the photocurrent-voltage test with an active area of 0.25 cm². For EIS measurement, the symmetrical dummy cells was assembled by two identical CEs clipping the above liquid electrolyte.⁴

Materials characterization

The morphology and structure of the samples were characterized by high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2010F, F20, 200 kV) and field emission scanning electron microscopy (FESEM, HITACHI S4800) and X-ray diffraction (XRD, Bruker D8 Advanced Diffractometer, Cu Kα radiation, 40 kV). The current-voltage tests of DSCs were performed under one sun condition using a solar light simulator (Oriel, 91160, AM 1.5 globe). The power of the simulated light was calibrated to 100 mW cm⁻² using a Newport Oriel PV reference cell system (model 91150 V). The EIS experiments was measured with dummy cells in the dark by using an electrochemical workstation (Parstat 2273, Princeton). The frequency range of EIS

experiments was from 100 mHz to 1 MHz with an AC modulation signal of 10 mV and bias DC voltage of 0.60 V. The curves were fitted by the Zview software. Cyclic voltammetry (CV) was conducted in a three-electrode system in an acetonitrile solution of 0.1 M LiClO₄, 10 mM LiI, and 1 mM I₂ at a scan rate of 20 mV s⁻¹ by using a BAS 100 B/W electrochemical analyzer. Platinum served as a CE and the Ag/Ag⁺ couple was used as a reference electrode.

References:

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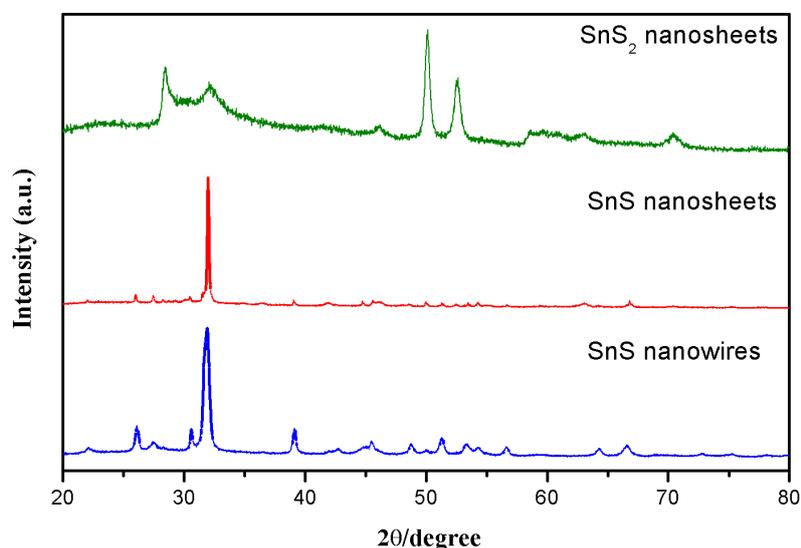


Fig. S1 XRD patterns of the synthesized SnS₂ NSs, SnS NSs and SnS NWs, respectively.