

Electronic Supplementary Information (ESI)
for
SnX (X = S, Se) thin films as cost-effective and highly efficient
counter electrodes for dye-sensitized solar cells

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Experimental Details

Materials. SnSe (99.999%) and SnS (99.5%) powders were purchased from Alfa Aesar. 1,2-ethylenediamine was purchased from Sinopharm Chemical Reagent (Shanghai, China), 1,2-ethanedithiol was purchased from J&K Chemical (Beijing, China). All of the reagents were used without further purification.

Preparation of CEs. SnSe (0.35 M), and SnS (0.35 M) precursor inks were prepared by dissolving the as-bought bulk powders into a solution composed of 10:1 vol/vol ethylenediamine and ethanedithiol in a N₂-filled glove box with stirring and heating at 75°C for 24 h. SnSe and SnS CEs were prepared by either drop-casting or spin-coating the dissolved precursor inks onto a fluorine-doped tin oxide (FTO) glass substrate, followed by a mild annealing treatment at 350°C under flowing nitrogen for 30 min. The prepared SnS and SnSe CEs are stored under inert atmosphere before use to avoid the possible oxidation in air.

Fabrication of DSCs. TiO₂ mesoporous films (18 μm thick) composed of a transparent

(12 μm) and superimposed light-scattering layer (6 μm) were prepared according as previously reported.¹ Dye-sensitized photoelectrodes were prepared by soaking the TiO_2 films in a 0.3 mM Na-Ru(4,1'-bis(5-hexylthiophen-2-yl)-2,2'-bipyridine)(4-carboxylic-acid-4'-carboxylate-2,2'-bip-yridine) (thiocyanate)₂ (C101 dye, which was kindly provided by Prof. Peng Wang) solution in acetonitrile overnight at room temperature. The electrolyte used for DSCs contained 0.03 M I_2 , 0.06 M LiI, 0.5 M *tert*-butylpyridine, 0.6 M 1-butyl-3-methylimidazolium iodide, and 0.1 M guanidinium thiocyanate in anhydrous acetonitrile. The sandwich-type solar cells were fabricated by placing the CEs on a sensitized TiO_2 photoanode using a thermal adhesive film (Surlyn, 60 μm , Dupont). The electrolyte solution was then injected by vacuum backfilling followed by a sealing procedure with a Surlyn film and a cover glass under heat. The active surface area of the mask-covered solar cells was measured to be 0.25 cm^2 .

Characterizations. Fourier transform infrared spectroscopy (FT-IR) was performed on a Nicolet 8700 FTIR spectrometer (USA). X-ray diffraction (XRD) data were obtained on an X-ray diffraction analysis instrument with Cu $\text{K}\alpha$ irradiation ($\lambda = 0.154 \text{ nm}$) (TTR-III, Rigaku Corp., Japan). Surface morphology of the films was observed by field emission scanning electron microscopy (FESEM, FEI, Quanta 200FEG). Energy dispersive X-ray spectroscopy (EDS) was measured on an energy dispersive spectrometer equipped on the SEM equipment. Cyclic voltammetry (CV) measurement was carried out in a three-electrode system with a scan rate of 20 mV s^{-1} using a nitrogen-purged electrolyte contains 0.1 M LiClO_4 , 10 mM LiI, and 1 mM I_2 in acetonitrile, a Pt mesh used as the counter electrode and an Ag/Ag^+ electrode serving as the reference electrode. Electrochemical impedance spectroscopy (EIS) was carried out on a symmetrical dummy cell at an applied bias of 0 V the modulation frequency ranging from 0.1 Hz to 500 kHz, with a 5 mV ac amplitude. Dummy cells were fabricated by sandwiching two identical electrodes with the same redox electrolyte as used in the solar cells filled in-between. Tafel polarization curves were measured on the dummy cells with a scan rate of 50 mV s^{-1} .

¹. The geometric surface area of the symmetrical cells was 0.56 cm². The BET specific surface area of the films was measured with a nitrogen adsorption-desorption apparatus (Tristar 3020, Micromeritics). All the electrochemical measurements were conducted on an electrochemical workstation (Autolab 302N, Metrohm, Switzerland). *J-V* characteristics of the solar cells were derived with a Keithley 2420 digital source meter (Keithley, USA) under a 450W xenon lamp (Oriel Sol3A Solar Simulator 94043, Newport Stratford Inc., USA).

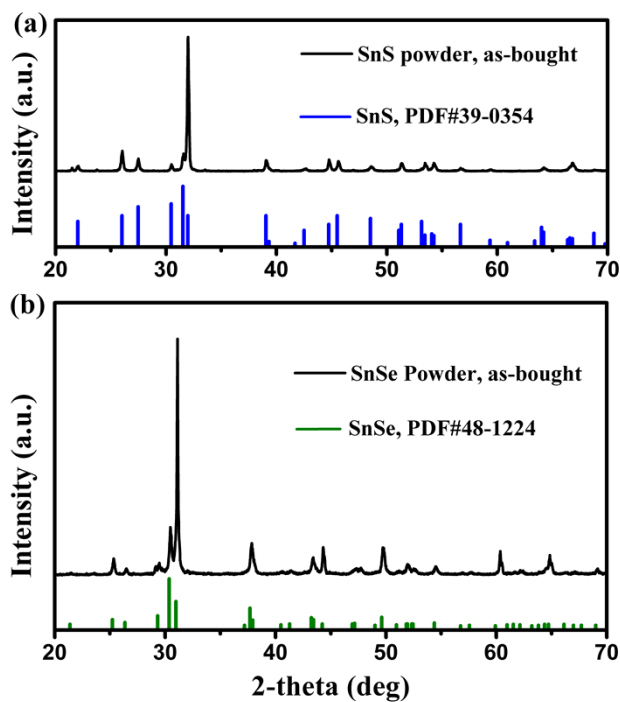


Figure S1. XRD patterns of the commercial as-bought SnS and SnSe powders.

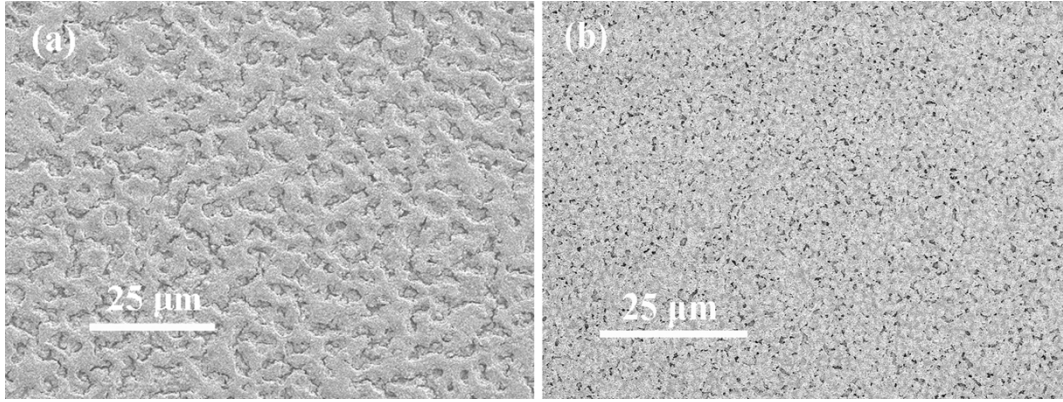


Figure S2. Top-view SEM images of (a) SnS and (b) SnSe thin films.

Table S1 Photovoltaic performance of the DSCs with different CEs along with the fitted parameters extracted from impedance spectroscopy of the symmetric cells.^a

CE	V_{oc}/mV	$J_{sc}/mA\ cm^{-2}$	FF	PCE/%	$R_s/\Omega cm^2$	$R_{ct}/\Omega cm^2$	$Z_N/\Omega cm^2$
Pt	761±2	16.30±0.05	0.72±0.01	8.93±0.09	11.83±0.11	0.73±0.01	0.41±0.02
SnS (spin-coated)	761±3	16.06±0.08	0.72±0.01	8.80±0.11	13.71±0.13	0.72±0.01	0.40±0.02
SnS (drop-cast)	762±2	16.54±0.12	0.73±0.01	9.20±0.12	13.00±0.21	0.33±0.01	0.35±0.01
SnSe (spin-coated)	761±3	16.24±0.10	0.72±0.01	8.90±0.10	12.16±0.14	0.73±0.01	0.41±0.01
SnSe (drop-cast)	763±1	16.55±0.06	0.74±0.01	9.34±0.11	12.50±0.22	0.25±0.01	0.33±0.02

^aThe data shown are the average values obtained from 4 devices with standard deviation.

Table S2 Comparison of the photovoltaic device performance measured with representative photoanodes from different batches assembled with a SnSe (or SnS) (drop-cast) counter electrode.

Sample	V_{oc}/mV	J_{sc}/mA	FF	PCE/%	Sample	V_{oc}/mV	J_{sc}/mA	FF	PCE/%
SnSe	V	cm^{-2}			SnS		cm^{-2}		
1	763	16.53	0.74	9.33	1	762	16.52	0.73	9.19
2	762	16.55	0.73	9.21	2	762	16.41	0.72	9.00
3	762	16.45	0.73	9.15	3	761	16.45	0.72	9.01

4	762	16.50	0.73	9.18	4	761	16.31	0.73	9.06
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- 1 L. H. Hu, S. Y. Dai, J. Weng, S. F. Xiao, Y. F. Sui, Y. Huang, S. H. Chen, F. T. Kong, X. Pan, L. Y. Liang and K. J. Wang, *J. Phys. Chem. B*, 2007, **111**, 358-362.