**Supplementary Information**

# Highly Efficient Inorganic-Organic Heterojunction Solar Cells Based on SnS-sensitized Spherical $TiO_2$ Electrodes

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## Experimental Details

**Synthesis of spherical $TiO_2$ powders and films**

Preparation of spherical $TiO_2$ was performed in the presence of hexadecylamine (HDA), as structure-directing agent, via a sol-gel method, followed by a solvothermal treatment. The solution composition of HDA: $H_2O$: KCl: ethanol: TTIP (molar ratio) was varied, in the range of $0.33:3:5.5\times10^{-3}$:236.5:1.0. The detailed process is described in the reference.[1]

**Synthesis of nanocrystalline $TiO_2$ powders**

Nanocrystalline $TiO_2$ particles were synthesized by hydrothermal methods.[2] Briefly, titanium alkoxide solution (TTIP (titanium iso-propoxide): acetic acid=1:1 (molar ratio)) was poured into deionized water under vigorous stirring at room temperature. After peptization, the resultant mixture was treated in a titanium autoclave at 250 °C for 12 h. Finally, the resultant colloidal solution was concentrated and centrifuged to produce a white precipitate of $TiO_2$ particle.

**Preparation of ordered mesoporous $TiO_2$ films**

Well-ordered mesoporous $TiO_2$ films were prepared via a supramolecular-templated route and a subsequent layer-by-layer deposition.[3] Triblock copolymer Pluronic F127 was used as structure-directing agent. The precursor solution was composed of TTIP: AcAc: HCl: $H_2O$/ethanol: F127. Then, the solution was deposited on FTO glass by spin coating. The films were sintered to remove organic solvent and to improve the nanocrystallinity of the mesoporous $TiO_2$. The thickness of the well ordered $TiO_2$ films was *ca.* 5 μm.

**Fabrication of $TiO_2$ electrodes**

To prepare the electrodes, parts of the conductive layer on the FTO glass were first etched using zinc powder and hydrochloric acid. Then, the FTO was washed and sonicated in ethanol and acetone. A dense $TiO_2$ layer was spin coated on the conductive layer using $TiO_2$ organic sol and sintered at 450 °C for 2 h.[4] $TiO_2$ powder were dispersed in the solution of terpineol and ethyl cellulose to form viscous paste. Then, the paste was coated on the pre-patterned FTO glass using a doctor-blade method. The films were sintered at 500 °C for 30 min in air. Next, the films were soaked in 40 mM $TiCl_4$ at 70 °C for 30 min, and then sintered again at 500 °C for 30 min in air. The thickness of the films was controlled to be *ca.* 8 μm.

**SnS deposition**

SnS-sensitized $TiO_2$ films were prepared by a modified chemical bath deposition (CBD).[5] Considering the wetting properties of $TiO_2$ films, we adjusted the solvent of the CBD solution, from pure water to a mixed solution of ethanol and deionized water. The SnS CBD solution was composed of 1.13g $SnCl_2$ dissolved in 5 mL acetone, 8 mL of 98% triethanolamine, 8 mL thioacetamide, and 6 mL 25%-28% ammonia solution. The total volume of the solution was adjusted to 100 mL using a mixed solution of ethanol and deionized water (v/v, 2:8). For the SnS deposition, the $TiO_2$ films were placed in the CBD solution at 75 °C for varying times.

**Solar cell fabrication**

Poly(3-hexylthiophene) (P3HT, Sigma Aldrich, 15 mg/mL in chlorobenzene) was spin coated on $TiO_2$-SnS films at 2500 rpm for 60 s and dried on a hot plate at 110 °C for 10 min. Then, a poly (3-4-ethylenedioxythiophene) doped with poly (4-stylenesulfonate) (PEDOT: PSS, Sigma Aldrich) was spin coated twice on $TiO_2$-SnS-P3HT films at 2500 rpm for 60 s, and then dried at 110 °C for 10 min. Silver paste was coated on the top of a $TiO_2$-SnS-P3HT-PEDOT: PSS film using a doctor-blade method and dried at 100 °C for 10 min. To completely remove the solvent, the devices were annealed at 90 °C for 2 h in a vacuum oven. The active area of the devices was 0.12 $cm^2$. A mask made of black tape, with an area of 0.04 $cm^2$, was used to define the illumination area of the devices.

**Characterization.**

The phase compositions of $TiO_2$ and SnS were determined using X-ray diffraction analysis (XRD, D/MAX-2400) with Cu Kα radiation (γ=0.154 nm). Microstructures of spherical $TiO_2$ films were studied using field-emission scanning electron microscopy (FE-SEM S-4800, Hitachi). An automatic adsorption apparatus (Belsorp 18-plus) was used to analyze the surface areas of $TiO_2$ films by Brunauer-Emmett-Teller (BET) method. The UV-Vis reflection spectra were measured using a spectrophotometer (JASCO V-570). Current-voltage curves of HSCs were obtained at ambient conditions by applying an external bias to the cells and measuring the generated photocurrent under white light irradiation using a digital source meter (Keithley 2601) and a solar simulator (100 mW/$cm^2$, PEC-L15). Photon flux was determined using a power meter (Nova, Ophir Optronics Ltd.) and a calibration cell (BS-520, s/n 019, Bunkoh-Keiki Co., Ltd.). The electron lifetime ($\tau$) and charge extraction measurement were performed using the SLIM-PCV (PSL-100, EKO) with stepped laser beam. The Fermi level potential of SnS/$TiO_2$ and $TiO_2$ films were analyzed using an impedance spectrum analyzer (Zahner IM6e) along with the Mott-Schottky equation,[6] i.e.

$$\frac{1}{C^2} = \left(\frac{2}{e\varepsilon\varepsilon_0 N_D}\right)\left(E - E_F - \frac{kT}{e}\right)$$

where $C$ represents the capacitance of the space charge region, $\varepsilon_0$ the vacuum permittivity, $\varepsilon$ the dielectric constant of the $TiO_2$ layer, $e$ the electron charge, $E$ the applied potential, $E_F$ the Fermi level potential, $k$ the Boltzmann constant, $T$ the absolute temperature, and $N_D$ the donor density. The temperature term is generally small and can be neglected. In this work, measurements were performed by applying a sinusoidal potential perturbation with a small

amplitude (10 mV), superimposed on a fixed dc potential, varying within appropriate potential windows from -0.6 to 0 V (vs. Ag/AgCl) in PBS buffer solution (10 mM $Na_2HPO_4/KH_2PO_4$; 2 mM $K_3PO4$; 137 mM NaCl; 2.7 mM KCl, pH 7.4-7.6; Shanghai Sangon Biological Engineering Technology & Service Co., Ltd.). The $TiO_2$ films used for this analysis had a film thickness of *ca.* 6 μm.

## References

[1] Y. B. Cheng, D. H. Chen, L. Cao, F. Z. Huang, P. Imperia and R. A. Caruso, *J Am. Chem. Soc.* 2010, **132**, 4438.
[2] S. Ito, T. N. Murakami, P. Comte, P. Liska, C. Grätzel, M. K. Nazeeruddin and M. Grätzel, *Thin Solid Films*, 2008, **516**, 4613.
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[4] S. Q. Zhang, H. Yu, H. J. Zhao, G. Will and P. R. Liu, *Electrochim Acta* 2009, **54**, 1319.
[5] H. Gong, Y. Wang, B. H. Fan and G. X. Hu, *J Phys. Chem. C* 2010, **114**, 3256.
[6] F. Fabregat-Santiago, G. Garcia-Belmonte, J. Bisquert, P. Bogdanoff and A. Zaban, *J Electrochem Soc*, 2003, **150**, E293.

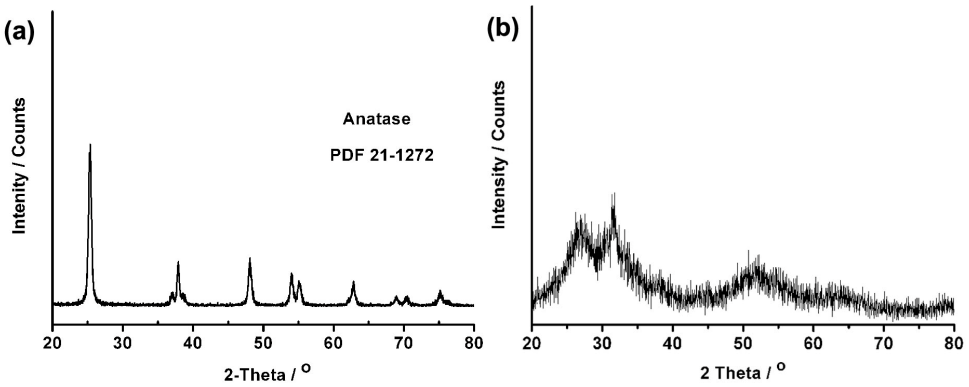


**Figure S1.** XRD patterns of $TiO_2$ powder (a) and SnS (b) deposited in chemical bath at 80 °C for 3 h.

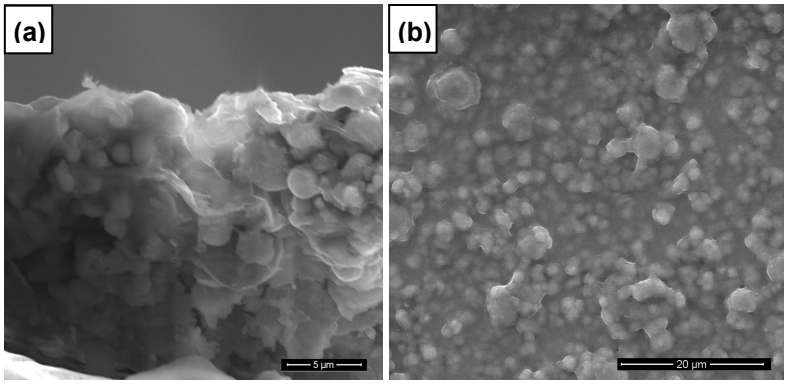


**Figure S2**. SEM images of the cross section of SnS-HSCs (a) and plane section of $TiO_2$-SnS-P3HT (b).

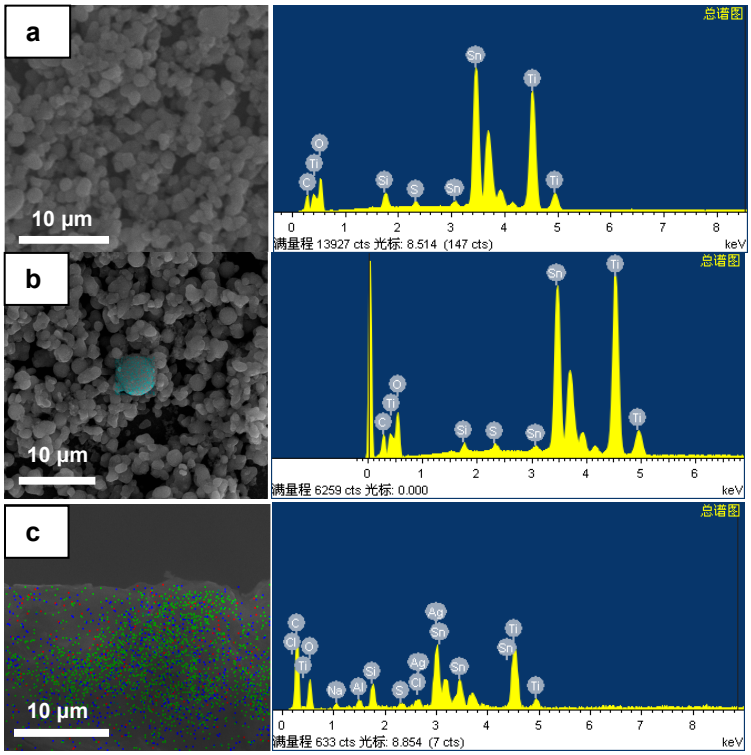


**Figure S3**. EDX spectra. (a) SnS-$TiO_2$ film; (b) SnS-sensitized a single $TiO_2$ sphere; (c) Cross-section of $TiO_2$-SnS-P3HT-Ag HSCs, Ti (red), Sn (bule), S (green).

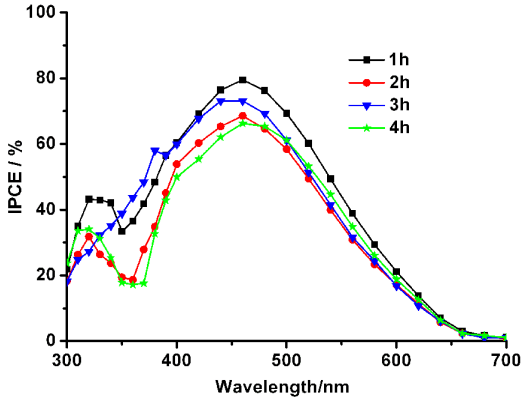


**Figure S4.** IPCE spectra of SnS-HSCs varying with CBD time.

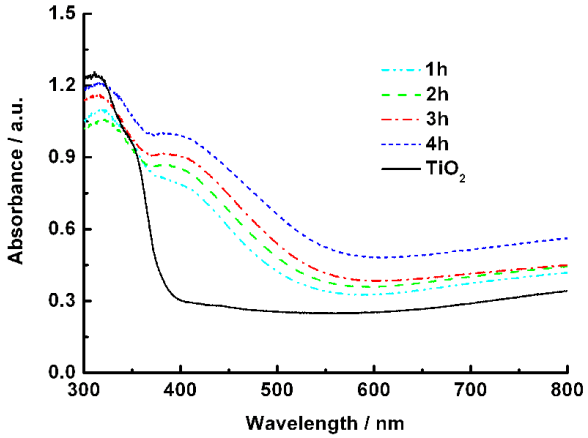


**Figure S5.** UV-Vis absorption spectra of SnS-$TiO_2$ films with varying SnS CBD time.

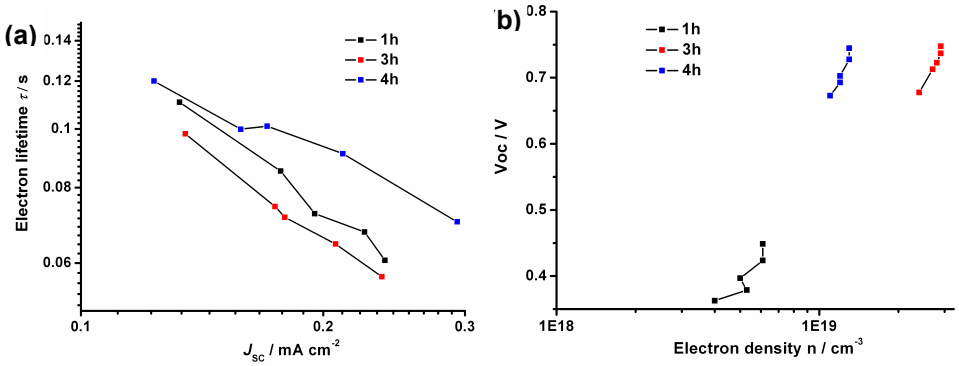


**Figure S6**. (a) $J_{SC}$ dependent τ; (b) electron density n dependent $V_{OC}$ of SnS-HSCs with varying SnS CBD time.

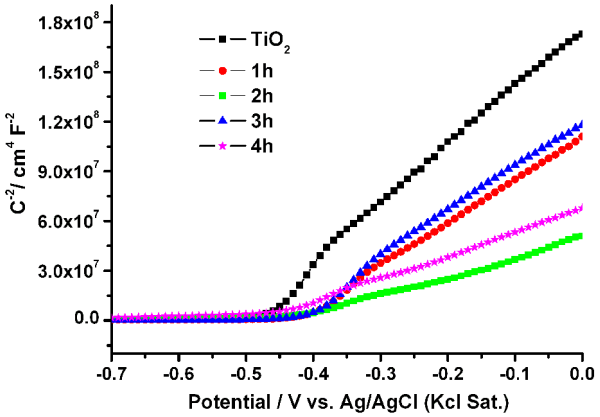


**Figure S7.** Mott-Schottky curves of $TiO_2$ and $TiO_2$-SnS films. The thickness of $TiO_2$ films were *ca*. 6 μm.

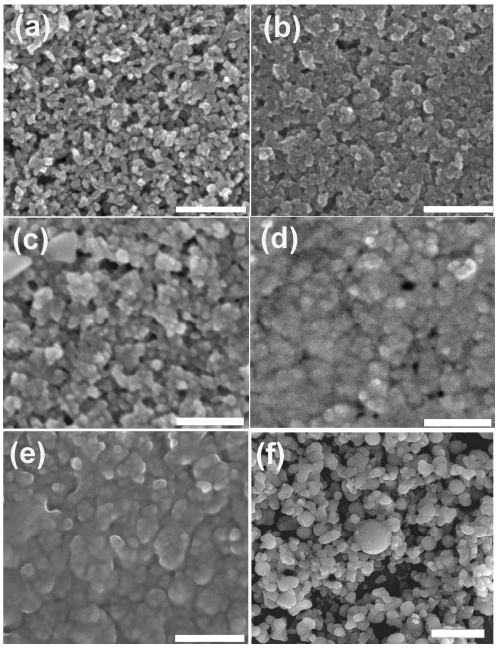


**Figure S8.** SEM images of SnS-sensitized nc-$TiO_2$ films varying with CBD time. (a) 0h; (b) 1h; (c) 2h; (d) 3h; (e) 4h, scale bar 200 nm; (f) SnS-sensitized spherical $TiO_2$ films with the CBD time 3h, scale bar 10 μm.