# Supporting Information
*to*
# Solution-phase Deposition of SnS Thin Films via Thermo-reducing $SnS_2$

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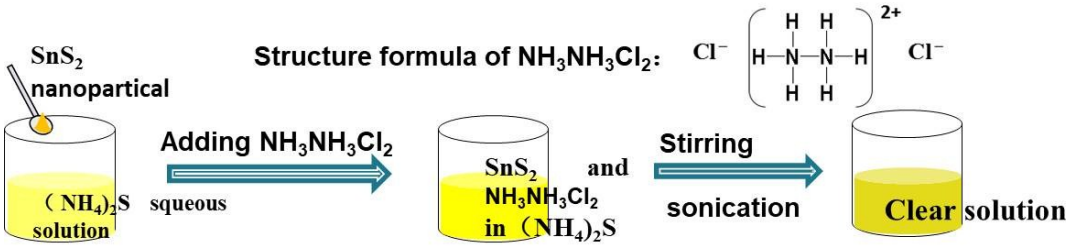
**Detail Experiment**

**Preparation of $SnS_2$ Nanocrystal and dimeric thiostannate(IV) complex ($[Sn_2S_6]^{4-}$)**

**Aqueous Solution**: Amorphous $SnS_2$ nanoparticles were prepared by dissolving $SnCl_4 \cdot 5H_2O$ (Aldrich, 99.99+%) in 0.5 M HCl and bubbled with nitrogen and subsequently $H_2S$ (99.5%, should be handled with care and appropriate safety precautions.). Nano-crystals were then dried by three times decantation of ethanol and subsequently two times with diethyl ether, which was evaporated under a flow of nitrogen gas. The 0.3426 g of $SnS_2$ nano-particles were dissolved in Milli-Q-water and two drops of $(NH_4)_2S$ aqueous solution, resulting in a volume of 3.4 mL dimeric thiostannate(IV) complex $[Sn_2S_6]^{4-}$ aqueous Solution with a concentration of 0.18 M.

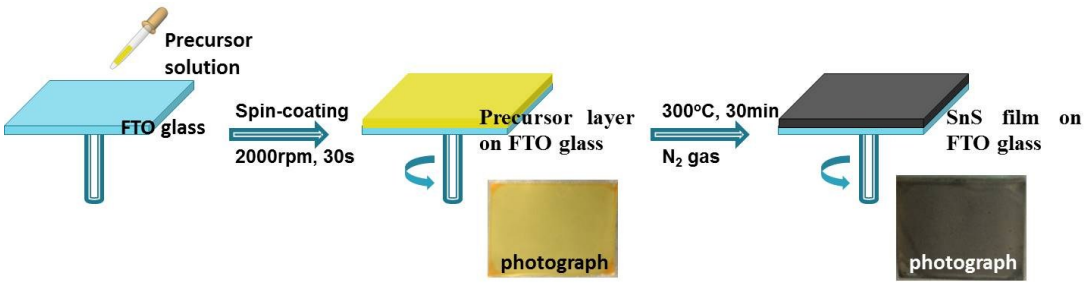
**Preparation of precursor solution:** A precursor solution was prepared by combining a small molecular reducing agent of HDC (Strem, 99.9+%) and dimeric thiostannate(IV)

complex $[Sn_2S_6]^{4-}$ in $(NH_4)_2S$ aqueous solution by molar ratio of $[Sn_2S_6]^{4-}$:HDC as 1:2 (as showing in the schematic graph). The mixing solution was stirring for 2h to make a clear solution.




**Scheme S1**. Preparing process of precursor solution.

**Deposition of SnS films:** F-doped tin oxide (FTO) transparent conducting substrates were cut and cleaned by sequential 30 min sonication in ethanol, acetone, and deionized water, followed by drying under $N_2$ stream and oxygen plasma treatment for 10 min. The precursor solution was spin-coating deposited on FTO substrates with 2000 rpm for 30s following thermos-reducing annealing procedure 300 °C for 30 mins under $N_2$ stream (as showing in the schematic graph)




**Scheme S2**. Preparing process of SnS nano-plate thin films.

**Preparation of $SnS_2$ seed layer:** Seed layers were prepared by spin coating (2000 rpm) a precursor solution of the dimeric thiostannate(IV) complex $[Sn_2S_6]^{4-}$ aqueous Solution with a concentration of 0.18 M. And then, a curing step was carried out by annealing at 200 °C for 10 mins under $N_2$ stream.

**Preparation of solar cells:** Firstly, a planar $TiO_2$ layer was deposited on glass/FTO substrates by spin coating (5000 rpm) of a precursor solution (containing 70 µL titanium isopropoxide, 55 µL ethanolamine and 1 mL 2-methoxyethanol) and calcination for 1 h at 450 °C in ambient conditions. Next, a $SnS_2$ seed layer and SnS films were deposited as demonstrated above. And then, a polymeric p-type materials of P3HT (17.25 mg in chlorobenzene) was spin coated (2000rpm) with a 30 s waiting time before spinning. Finally, an Ag layer (150 nm) was deposited on hybrid films by thermal evaporation as an electrode.

**Characterizations:** The nanostructures were examined with advanced techniques, such as the energy dispersive analysis of X-rays (EDX, JEOL) attached with transmission electron microscopy (TEM, FEI Talos), Field emission scanning electron microscope (FESEM, ZEISSMERLIN Compact), X-ray diffractometry (XRD, Rigaku Ultima IV) with Cu KR1 radiation (λ = 0.1541 nm), X-ray photoelectron spectropscopy (XPS, Thermo

Scientific) and UV-vis spectrophotometry (Hitachi 3900) in the wavelength range 350-1200 nm under normal light. Electrochemical properties were examined using cyclic-voltammetry on the potentiostat/galvanostat/potentiometer (Epsilon-EC). During measurement, the potential amplitude of A.C. was fixed to 10 mV, meanwhile its frequency region was varied from 0.01 Hz to 100 kHz. In this study, platinum spiral wire and Ag/AgCl electrodes were used as the counter and the reference, respectively.

**Additional Figures**

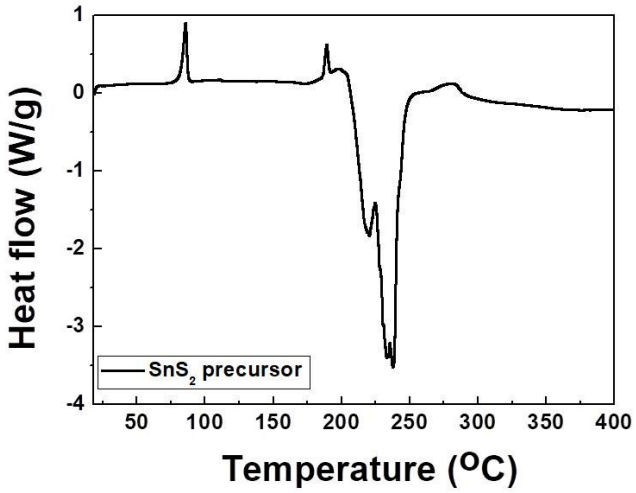



**Figure S1**. DSC test of precursor film for tracing annealing temperature of thermo-reducing process.

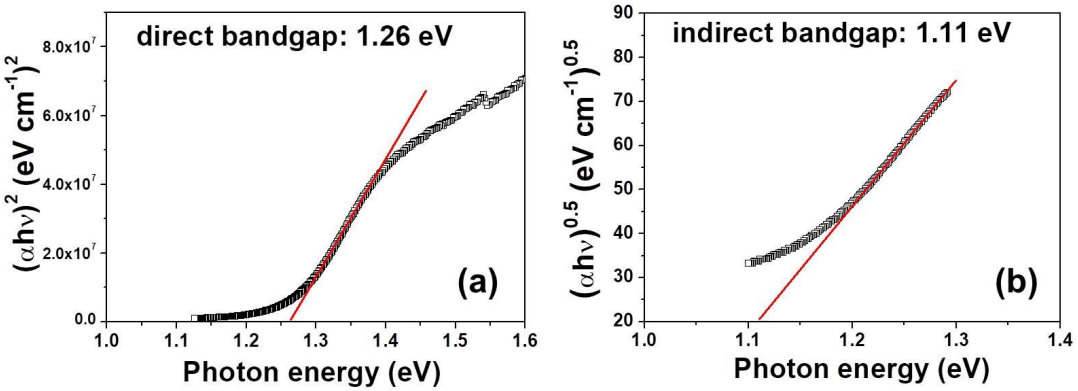



**Figure S2**. Tauc plots to determine the direct (a) and indirect (b) band gaps of SnS nano-plates film.

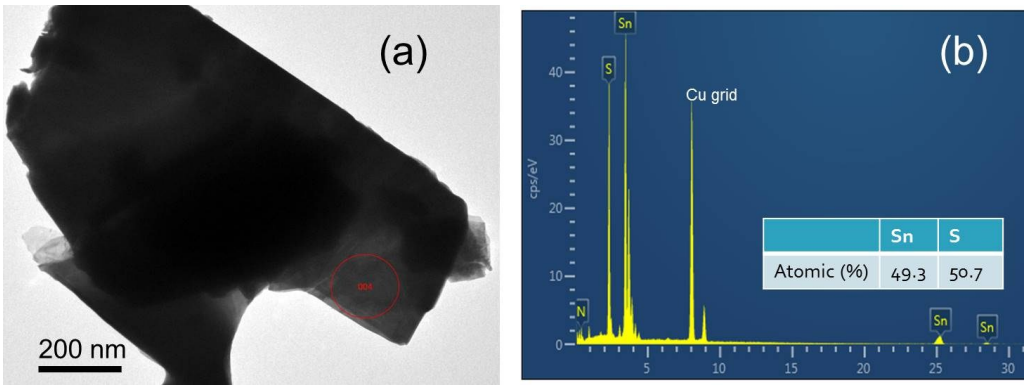



**Figure S3**. (a) TEM image and (b) EDX analysis (position at red circuit in TEM image) of SnS nano-plate.

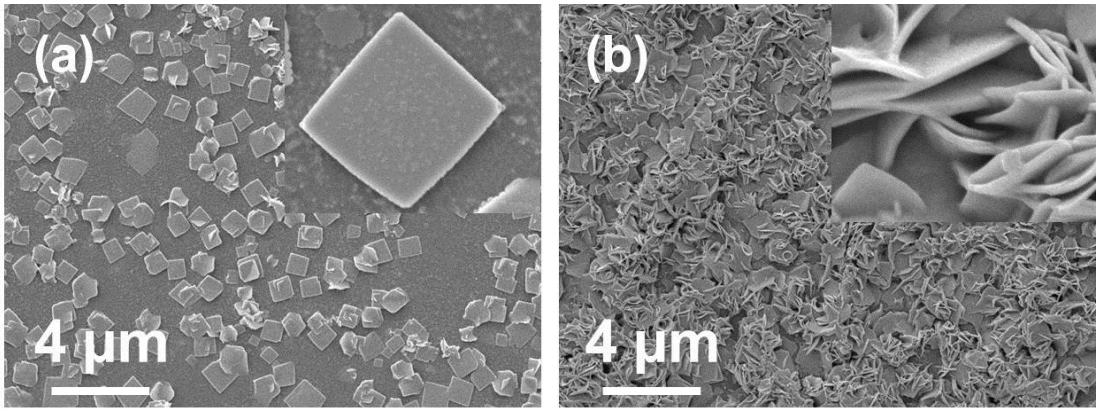



**Figure S4**. FESEM images of SnS nano-plate films deposited (a) without and (b) with seed layer (inserts is high magnification images).

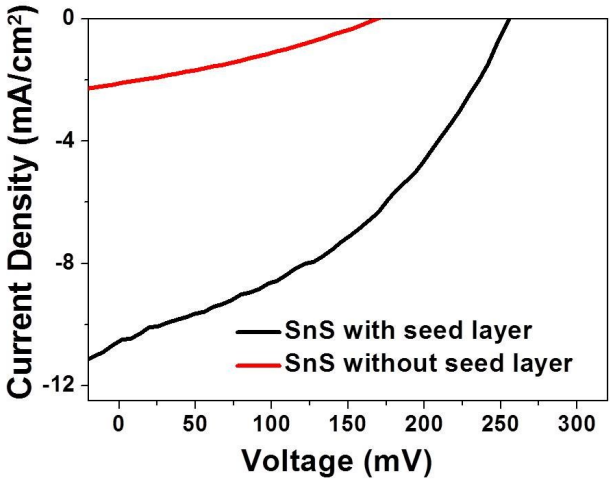



**Figure S5**. J-V curves of hybrid solar cells prepared without (red line, PCE=0.15%) and with (black line, PCE=1.05%) seed layer under 100 mW/cm$^2$ illumination.

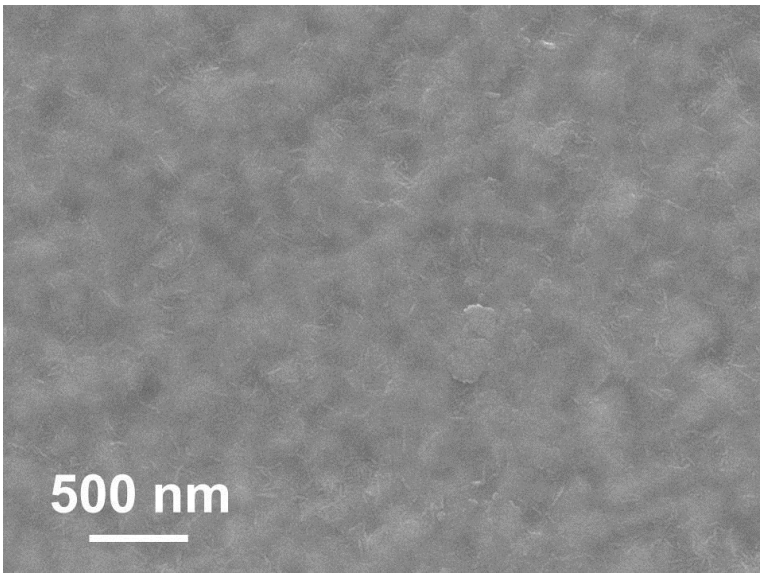
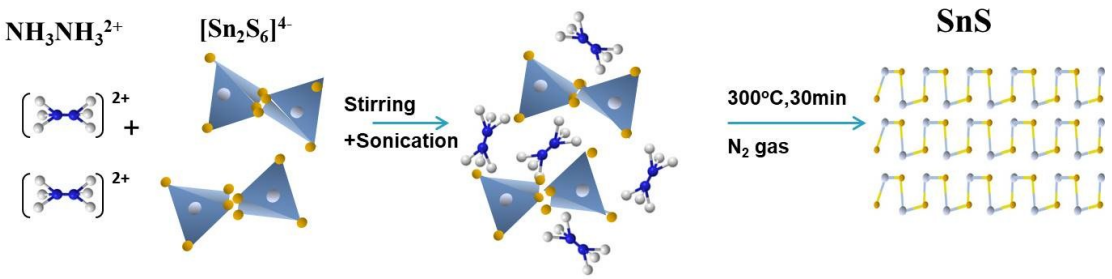



**Figure S6**. FESEM image of $SnS_2$ seed layer.

**Additional Scheme**




chemical formula：

$$Sn_2S_6^{4-} + NH_3NH_3^{2+} + S^{2-} + 6NH_4^{+} + 2Cl^{-} \xrightarrow{\Delta} 5H_2S\uparrow + N_2\uparrow + 6NH_3\uparrow + 2HCl\uparrow + 2SnS$$

**Scheme S3**. Schematic graph of mechanism and probable chemical formula for depositing SnS thin films by thermo-reducing process.