Electronic Supplementary Material (ESI) for Materials Advances.

Supporting Information

to

Deposition and Facile Control over Morphology of Phase-pure SnS Thin Films using Spin-coating Route

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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 nanocrystals 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). The nanocrystals were dried by three times decantation of ethanol and subsequently two times with diethyl ether, which was evaporated under a flow of nitrogen gas. The SnS_2 nanocrystals of 0.3426 g 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: For spin-coating, precursor solutions with different reducing agents of Hydrazine hydrate (Strem, 99.9+%), Hydrazine monohydrochloride (Strem, 99.9+%) and Hydrazine dihydrochloride (Strem, 99.9+%) were prepared by combining a small molecular reducing agent and dimeric thiostannate(IV) complex $[Sn_2S_6]^{4-}$ in $(NH_4)_2S$ aqueous solution by molar ratio of $[Sn_2S_6]^{4-}$: reducing agent as 1:2. Finally, the mixing solutions were stirring for 2h to make clear solutions.

Deposition of SnS films: The conducting and transparent substrates of F-doped tin oxide (FTO) 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 3000 rpm for 30s following thermo-reducing annealing procedure 300 °C for 30 mins under N_2 stream.

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) and Field emission scanning electron microscope (FESEM, ZEISSMERLIN Compact), X-ray diffractometry (XRD, Rigaku Ultima IV) with Cu KR1 radiation (λ = 0.1541 nm) and UV-vis spectrophotometry (Hitachi 3900) in the wavelength range 350-1200 nm under normal light. A RENISHAW inVia confocal Raman spectrometer was used to measure the spectra of the samples at 532 nm, 50 mW laser, with the instrument spectrum ranging from 10 cm^{-1} to 9000 cm^{-1}. The materials for TEM measurement were scratched from substrates, and dispersed in ethanol. Electrochemical properties were examined using cyclic-voltammetry on the potentiostat/galvanostat/potentiometer (Epsilon-EC). In this study, platinum spiral wire and Ag/AgCl electrodes were used as the counter and the reference, respectively.

Additional Figures

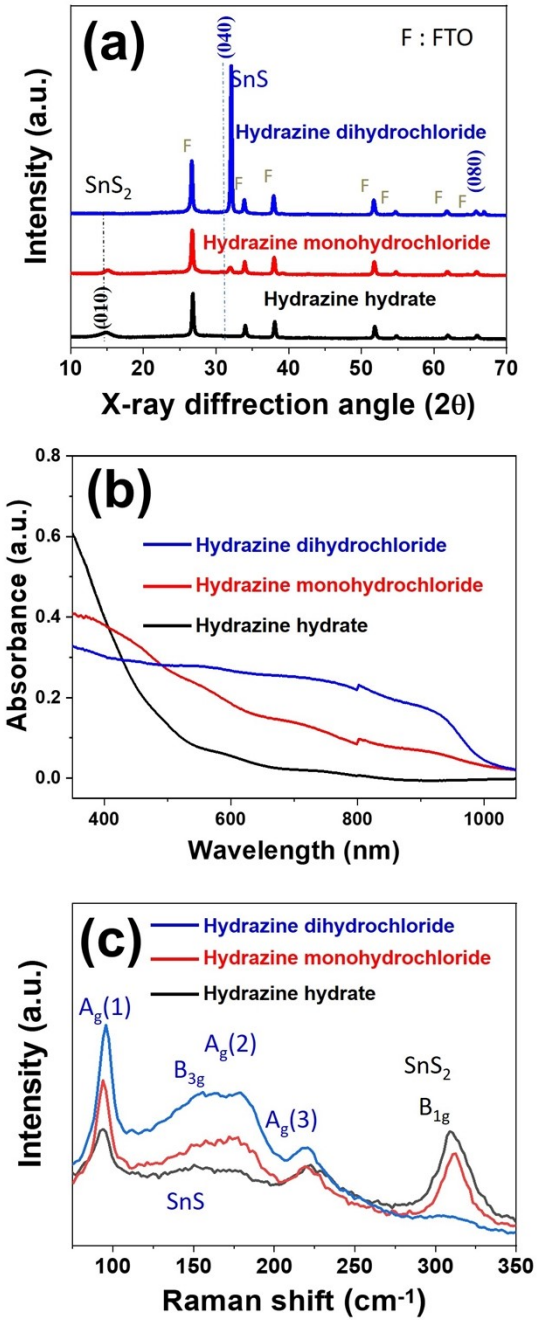

Figure S1. (a) XRD pattern, (b) UV-bis spectrum and (c) Raman shift spectrum of spin-coating deposited films after sequential thermo-reducing process with HH, HMC and HDC.

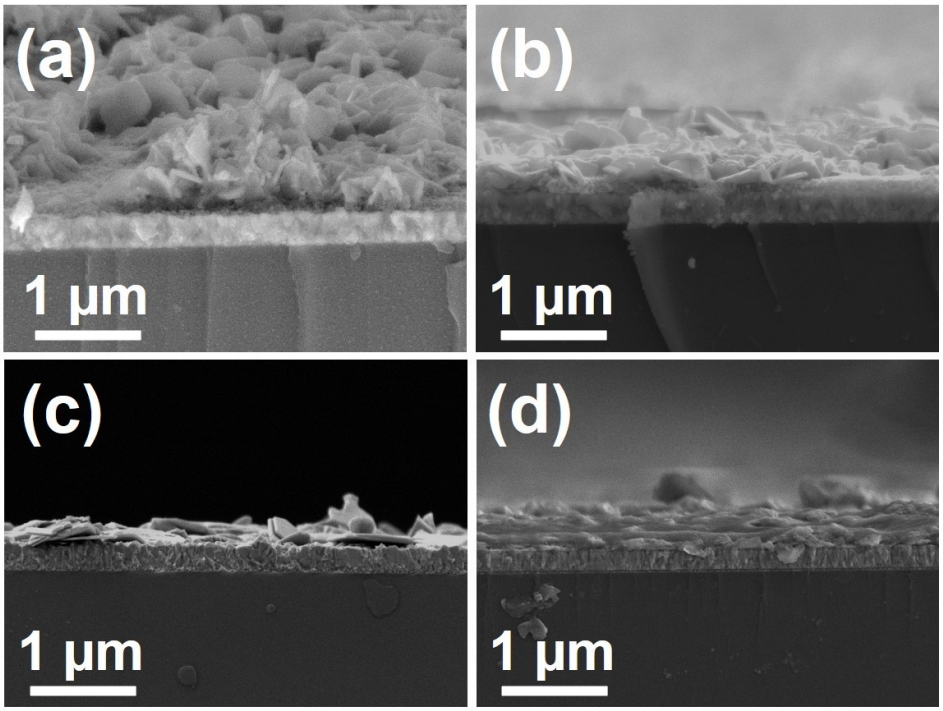

Figure S2. FESEM Cross-section views of SnS films on FTO with temperature ramping rate of 5 ℃/min (a, e), 10 ℃/min (b, f), 30 ℃/min (c, g) and 60 ℃/min (d, h).

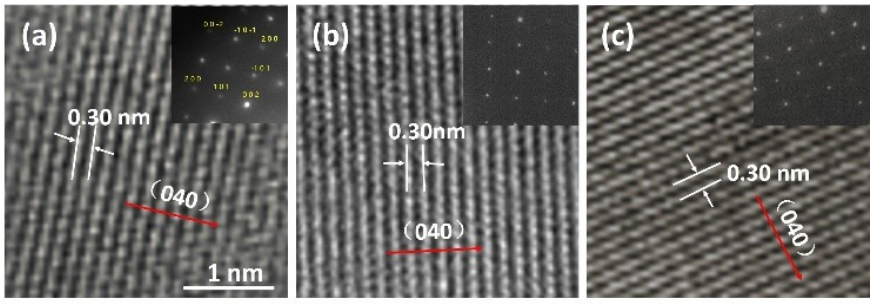

Figure S3. HRTEM images of (a) 5 ℃/min, (b) 10 ℃/min and (c) 60 ℃/min (SAED patterns of SnS nanocrystals were shown as an inset).

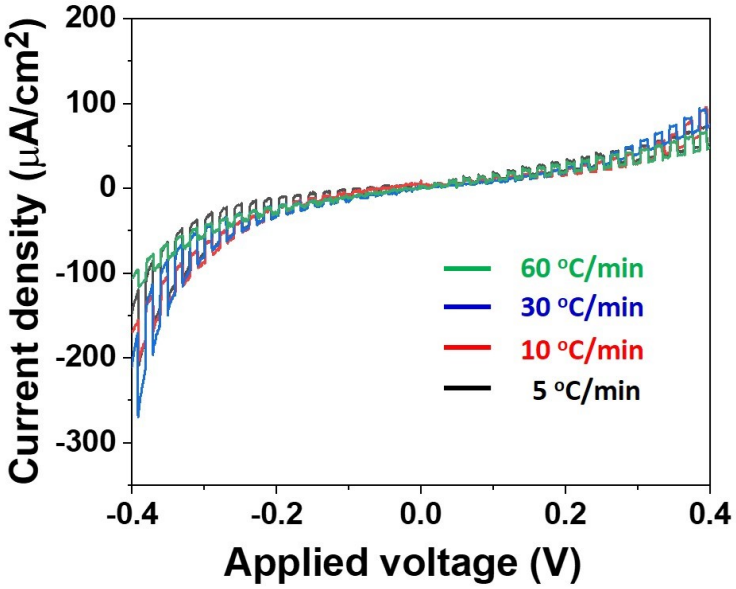

Figure S4. Cyclic voltammogram of p-type SnS films at 2 mV s^{-1} with chopped simulated 1 Sun illumination every 10 s in contact with 0.1 M $Eu(NO_3)_3$(aq).

Additional Table

	Reducing with HH	Reducing with HMC	Reducing with HDC
Sn (Atomic %)	38.5	43.2	51.6
S (Atomic %)	61.5	56.8	48.4

Table S1. EDX analysis of spin-coating deposited films after sequential thermo-reducing process with HH, HMC and HDC.

	5 °C/min	10 °C/min	30 °C/min	60 °C/min
Sn (Atomic %)	49.4	49.2	50.3	50.1
S (Atomic %)	50.6	50.8	49.7	49.9

Table S2. EDX analysis of SnS films with temperature ramping rate of 5 ℃/min (a, e), 10 ℃/min (b, f), 30 ℃/min (c, g) and 60 ℃/min (d, h).