Supporting Information

Solid-state nanocrystalline solar cells with antimony sulfide

absorber deposited by in-situ solid-gas reaction

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Deposition of Sb₂S₃ on TiO₂ film: TiO₂ porous film was deposited by doctor-blading a TiO₂ paste on a FTO glass substrate pre-coated with ~ 60 nm thick TiO₂ blocking layer. The TiO₂ paste was prepared by mixing TiO₂ power (Degussa P25), α -terpineol (C₁₀H₈O, 96%, Sigma Aldrich), ethanol, ethylcellulose (Sigma Aldrich). The TiO₂ film was annealed at 450°C for 30 min. For the deposition of Sb₂S₃, sequential deposition method was employed as follows: SbCl₃ alcoholic solution with various concentrations was coated on the TiO₂ film by spin-coating at 1000 r.p.m. for 5 s and 3,000 r.p.m. for 30 s, and followed by loading on an enclosed glass container (10 L in volume), where a 200 ml beaker containing a mixed aqueous solution (150 ml) of 20 wt.% sodium sulfide $(Na_2S \cdot 9H_2O)$ and 10 wt.% dilute sulfuric acid (H_2SO_4) , was placed in advance for generating H_2S gas. After 3~5 minutes, the film was taken out, washed by deionized water and then ethanol to remove the resulting by-product. The as-prepared Sb₂S₃ is amorphous state, and further crystallization was proceeded by thermal annealing at 300 °C for 30 minutes in a tube furnace under a H₂S flow with a flow rate of 100 ml/min.. It should be noted that all the processes were performed at room temperature under a fume hood. For comparison, conventional CBD method was employed for the deposition of Sb₂S₃ on TiO₂ film, as described by S. Messina *et al.* Briefly, TiO₂ films were placed in the CBD bath at 10°C for 2 h, which contained SbCl₃ and Na₂S₂O₃ dissolved in deionized water. The amorphous Sb₂S₃ was further annealed for crystallization at a temperature of 300°C for 30 min under a high purity Ar flow.

Device fabrication: P3HT (Rieke Metals) as the hole transport material was spin-coated from the solution (15 mg/mL in 1,2-dichlorobenzene) onto the Sb₂S₃-coated TiO₂ films with 2500 rpm for 60 s, and followed by spin coating of a poly(3-4-ethylenedioxythiophene) doped with poly(4-stylenesulfonate) (PEDOT:PSS; Baytron AI4083) diluted by methanol at 2000 rpm for 30 s. After the depositions, the resulting TiO₂/Sb₂S₃/P3HT/PEDOT:PSS films were then annealed at 90°C for 30 min in a vacuum oven. The back contact was finished by thermal evaporation of gold as a counter electrode; the evaporation was performed with a metal mask under a pressure of 5×10^{-5} Torr, giving an active area of 16 mm² for each device.

Film characterization: The morphologies of the Sb_2S_3 -coated TiO_2 film were investigated by a field-emission scanning electron microscope (JSM-7500, Japan). The photographs of the Sb_2S_3 -coated TiO_2 film were recorded by an optical microscope (Olympus MX40, Japan), and the absorption spectra were measured using a UV-Vis spectrometer (Shimadzu UV-2600). The XRD

patterns were recorded with a Bruker D8 Discover diffractometer in Bragg–Brentano mode, using Cu K α radiation (1.540598 Å) and a Ni β -filter, from 2 θ =10°–60° at a scan rate of 2° min-1, step width of 0.02° and a source slit width of 1 mm. X-ray photoelectron spectroscopy (XPS) were performed on the Thermo Scientific ESCA Lab 250Xi using 200 W monochromated Al K α radiation, and 500 μ m X-ray spot was used for XPS analysis. The base pressure in the analysis chamber was about 3×10⁻¹⁰ mbar. Typically the hydrocarbon C1s line at 284.8 eV from adventitious carbon is used for energy referencing.

Device characterization: Current-voltage characteristics of the devices were recorded by applying an external potential bias to the cell while recording the generated photocurrent with a Keithley model 2400 digital source meter. The light source was a 300 W collimated xenon lamp (Newport) calibrated with the light intensity to 100 mW\$cm⁻² under AM 1.5G solar light conditions by a certified silicon solar cell. The J–V curve was recorded by the reverse scans with a rate of 200 mV s⁻¹. The incident photon-to-current conversion efficiency (IPCE) for solar cells was performed using a commercial setup (PV-25 DYE, JASCO). A 300 W Xenon lamp was employed as a light source for the generation of a monochromatic beam. EQE spectra were recorded using monochromatic light without white light bias. Calibrations were performed with a standard silicon photodiode. IPCE is defined by IPCE(λ) = $hcJ_{sc}/e\phi\lambda$, where h is Planck's constant, c is the speed of light in a vacuum, e is the electronic charge, λ is the wavelength in meters (m), J_{sc} is the short-circuit photocurrent density (A m⁻²), and ϕ is the incident radiation flux (W m⁻²).



Figure S1 Absorption spectra of the Sb_2S_3 -coated TiO_2 films through sequential deposition method (a), and direct conversion without the H_2S treatment (b).









Elements	Weight percentage	Atom percentage
C K	3.12	9.52
O K	22.87	52.41
S K	7.08	8.09
Ti K	24.08	18.43
Sn L	10.54	3.25
Sb L	19.58	5.90
Pt M	12.73	2.39
Total	100.00	

Figure S2 Cross sectional SEM images of Sb_2S_3 -coated TiO₂ film, corresponding element distribution maps and of Sb, S, Ti and O, and contents of relevant elements, the Sb_2S_3 -coated TiO₂ film starting with 16 mg/ml SbCl₃ solution.



Figure S3 Absorption spectra of the as-deposited Sb_2S_3 on TiO_2 films using CBD method with and without the H_2S treatment before (a) and after (b) the thermal annealing.



Figure S4 XPS Cl 2p spectrum of Sb_2S_3 film obtained from the sequential deposition starting with $SbCl_3$ precursor (16 mg/ml).