# Supporting Information

## A vacuum assisted solution processing for highly efficient Sb<sub>2</sub>S<sub>3</sub> solar

#### cells

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### **Experimental section**

### Chemicals

Antimony(III) chloride (SbCl<sub>3</sub>, AR) was purchased from aladdin, thiourea (TU, AR), Titanium isopropoxide (TIPT), Lithium bis(trifluoromethylsulfonyl) imide (Li-TFSI), 4tert-butylpyridine (tBP) and chlorobenzene were purchased from J&K., ethylene glycol monomethyl ether (HOCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>, AR) were purchased from Sinopharm, Spiro-OMeTAD (99.8%) was purchased from YOUXUAN TECH., Ltd. All chemicals were used as received without further purification.

#### Synthesis of Sb-TU complex precursor solution

Solutions for spin coating were synthesized by a typical procedure as we reported previously. The preparation of pure Sb-TU complex precursor solution was accomplished by mixing 4.0 mmol of SbCl<sub>3</sub> and 12 mmol of thiourea (TU) in a 10 mL vial, and 5 mL of ethylene glycol monomethyl ether (2-ME) was used as the solvent. Then, the mixed solution was stirred at room temperature for one day prior to use. Similar to above synthetic process, K<sup>+</sup> doping of Sb<sub>2</sub>S<sub>3</sub> layer was prepared using KOH as the source of potassium. The doping amount (x at%) of K<sup>+</sup> was controlled according to the molar concentration of KOH and SbCl<sub>3</sub>. Firstly, (4-x) mmol of SbCl<sub>3</sub> and 12 mmol of thiourea (TU) was dissolved in a 10 mL vial with a constant stirring of 30 min. Afterward, x mmol of KOH was added into above mixed solution. After stirring for one day, the K<sup>+</sup> doping of Sb-TU complex precursor solution was synthesized for further use.

## Preparation of TiO<sub>2</sub> Nanorods

The cleaned FTO-coated glass (YOUXUAN TECH) washed by deionized water, ethanol and acetone were used as substrates. The compact TiO<sub>2</sub> layer was deposited onto cleaned FTO by spin-coating a mixture solution of 350  $\mu$ L titanium isopropoxide, 5 mL ethanol, and 50  $\mu$ L HCl (12 mol L<sup>-1</sup>) method at 3000 rpm for 30 s, followed by annealing at 500 °C for 60 min in air to remove the organic part. Next, the TiO<sub>2</sub> nanorods were grown on the TiO<sub>2</sub> blocking layer using a hydrothermal synthesis method. Briefly, 20 mL of 37% hydrochloric acid, 20 mL of deionized water and 0.2 mL of titanium (IV) isopropoxide (TTIP) were mixed in a stainless steel autoclave with Teflon liner of 50 mL capacity. After stirring for about 10 min, FTO-coated  $TiO_2$  blocking layer were placed into above mixed solutions and the autoclave was heated at 150 °C for 3 h. Then, the autoclave was cooled naturally to room temperature. Finally, the films were taken out from autoclave washed several times with water and ethanol and annealing in air at temperature of 500 °C for 1h to further used.

#### **Device** Fabrication

The typical structure of solar cells in this study can be described as Au/HTM/Sb<sub>2</sub>S<sub>3</sub>/TiO<sub>2</sub>-nanorod array/TiO<sub>2</sub>-bl/FTO. To prepare Sb<sub>2</sub>S<sub>3</sub> thin films, the complex solution obtained in the experimental section was spin-coating on the TiO<sub>2</sub> NRAs at a speed of 4000 rpm for 60 s, followed by pretreatment in vacuum drying oven at 125 °C for 1 min to remove the solvent. For comparison purpose, another Sb<sub>2</sub>S<sub>3</sub> thin film was dried at 150 °C in air for 1.5 min. After cooling down to room temperature, the precursor film was annealing at 270 °C for 10 min in N<sub>2</sub> prior to solar cell fabrication. After that, the hole transporting material (HTM) spiro-OMeTAD was spin-coated on Sb<sub>2</sub>S<sub>3</sub>/TiO<sub>2</sub>-nanorod/TiO<sub>2</sub>-bl/FTO substrate at a speed of 3000 rpm for 30 s and heated on a hot plate at 100 °C for 5 min in air. The spiro-OMeTAD solution was prepared by mixing 36.6 mg of spiro-OMeTAD, 14.5  $\mu$ L of 4-tert-butylpyridine (tBP), and 9.5  $\mu$ L of a 520 mg·mL<sup>-1</sup> lithium bis(trifluoromethanesulfonyl) imide (Li-TFSI) together in acetonitrile in 1 mL of chlorobenzene. Finally, the Au counter electrode was deposited by a thermal evaporator under pressure of 5.0×10<sup>-4</sup> Pa. The active area of the device was defined at 0.12 cm<sup>2</sup>

#### Characterization

Samples were characterized by powder X-ray diffraction (XRD) on a Bruker Advance D8 diffractometer equipped with Cu K $\alpha$  radiation ( $\lambda$  = 1.5416 Å). The optical characteristics of the films were measured with a UV-visible spectrophotometer (SOLID 3700) from 300 nm to 900 nm. The surface and cross sections morphologies of the samples were examined by SEM (FE-SEM siron 200). X-ray photoelectron spectroscopy (XPS) was conducted on a Thermo ESCALAB 250Xi systems with an Al K $\alpha$  monochromatized source and a multi-detection analyzer under a 10<sup>-8</sup> Torr was Finally, the J-V curves were recorded using a Keithley 2400 apparatus under solarsimulated AM 1.5 sunlight (100 mW/cm<sup>2</sup>). The external quantum efficiency (EQE, Model SPIEQ200) was measured using a single source illumination system (halogen lamp) combined with a monochromator. Electrochemical impedance spectroscopy (EIS) measurements were performed using Zahner Mess Systeme PP211 electrochemical workstation at a bias potential of -0.65 V in dark with the frequency ranging from 100Hz to 1MHz. The Fourier transform infrared spectra (FTIR) of the thin films were measured by Nicolet 8700 to obtain the information on composition of our samples recorded at ambient temperature at the resolution of 4 cm<sup>-1</sup> and scanning with the spectrum scope of 600-4000 cm<sup>-1</sup>.



Figure S1. (a-b) SEM image of the surface morphology of CP-Sb<sub>2</sub>S<sub>3</sub> film preannealed at 150 °C for 5min and 10min, respectively; (c) XRD patterns of CP-Sb<sub>2</sub>S<sub>3</sub> films preannealed at 150 °C for 5min and 10min; (d) Photocurrent density-voltage (J-V) characteristics of CP-Sb<sub>2</sub>S<sub>3</sub> based solar cells preannealed at 150 °C for 5 min (PCE=1.76%) and 10 min (PCE=2.55%).



Figure S2. (a) Thermal gravimetric analysis (TGA) of the Sb-TU complex precursor solution; (b) Photocurrent density-voltage (J-V) characteristics of CP-Sb<sub>2</sub>S<sub>3</sub> and VASP-Sb<sub>2</sub>S<sub>3</sub> based solar cells preannealed at 125 °C and 150 °C, respectively; (c-e) SEM images of the surface morphologies of CP-Sb<sub>2</sub>S<sub>3</sub> with pre-annealing at 100 °C, 135 °C and 175 °C for 1.5 min.

To find out whether there is an abrupt change of the mixture solvent, we conduct thermogravimetric analysis (TGA) of the precursor solution. The first significant weight loss of molecular precursor occurs at ~84 °C, and the second on is at around 200 °C. In this case, we conclude that there is no abrupt change in the boiling point change at 125 °C or 150 °C. Regarding the viscosity, it is reasonable that the viscosity would increase along with the evaporation. Actually, if we take a short interval of the preannealing temperature, the morphological change is not that abrupt. For instance, the SEM images of films fabricated with preannealing temperature at 100 °C, 125 °C, 135 °C 150 °C and 175 °C displays a gradual morphological change.



Figure S3. SEM images of the cross-section of the  $TiO_2$ -nanorods grown on (a) 1h, (b) 2h, (c) 3h, (d) 4h and (e) 5h, the average lengths of the nanorods are 70, 90, 135, 180, and 210 nm, respectively.



Figure S4. SEM images of the surface morphology of the  $Sb_2S_3/TiO_2$ -nanorods grown with (a) 1h, (b) 2h, (c) 3h, (d) 4h and (e) 5h; the corresponding SEM images of the cross-section of the  $Sb_2S_3/TiO_2$ -nanorods grown on (f) 1h, (g) 2h, (h) 3h, (i) 4h and (j) 5h.



Figure S5. Photocurrent density-voltage (J-V) characteristics of VASP-Sb $_2S_3$  based solar cells annealed at 270 °C in vacuum condition.

We conduct high temperature (270 °C) annealing in vacuum condition. As shown in Figure S5, a power conversion efficiency of 3.17% is obtained ( $V_{oc}$ =0.628V,  $J_{sc}$ =9.81mA cm<sup>-2</sup>, FF=51.3%), which is much lower than that of film annealed in N<sub>2</sub> atmosphere. Thus, it can be concluded that the high temperature (270 °C) annealing condition conducted in vacuum condition is inferior to that conducted in N<sub>2</sub>.



Figure S6. Bode phase plots of  $CP-Sb_2S_3$  and  $VASP-Sb_2S_3$  based solar cells measured at 0.65 V in the dark.

Table S1. Photovoltaic parameters of short-circuit current density (J <sub>sc</sub> ), open-circuit
voltage ( $V_{OC}$ ), Fill Factor ( <i>FF</i> ), and power conversion efficiency ( $\eta$ ) depending on
growth time of TiO <sub>2</sub> nanorods, the corresponding lengths are70, 90, 135, 180, and
210 nm, respectively.

Growth time	$V_{OC}$ (V)	J <sub>sc</sub> (mA cm⁻²)	FF (%)	η (%)
1h	0.640	15.90	60.0	6.14
2h	0.635	16.24	60.2	6.14
3h	0.671	16.69	56.9	6.37
4h	0.662	15.94	59.4	6.22
5h	0.645	15.34	56.8	5.54