Supporting Information

A Fast Chemical Approach towards Sb₂S₃ Film with Large Grain Size for

High-Performance Planar Heterojunction Solar Cells

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Chemicals

Antimony(III) oxide (Sb₂O₃,AR), ethanol(CH₃CH₂OH, AR), carbon disulfide (CS₂,AR) and *n*-butylamine (CH₃(CH₂)₃NH₂, AR) were purchased from Sinopharm, Spiro-OMeTAD (99.8%) was purchased from Yingkou Youxuan Trade Co., Ltd. Lithium bis(trifluoromethylsulfonyl) imide (Li-TFSI), 4-tert-butylpyridine (tBP) and chlorobenzene were purchased from J&K. All chemicals were used as received without further purification.

Synthesis of Sb-complex

1.0 mmol of Sb_2O_3 was loaded into a 10 mL vial containing 2.0 mL of ethanol and 1.5 mL of carbon disulfide (25 mmol) with magnetic stirring at room temperature, then 2.0mL n-butylamine (20 mmol) was dropped slowly to the vial and the solution continue to stir at least 30 min for obtaining a homogenous solution. Afterwards, 2 mL above solution was diluted with 1 mL ethanol to form Sb-complex.

Device Fabrication

The typical structure of solar cells in this study can be described as Au/HTM/Sb₂S₃/bl-TiO₂/FTOe. The compact TiO₂ layer was deposited onto cleaned FTO by spin-coating a mixture solution of 350 µL titanium isopropoxide, 5 mL ethanol, and 50 μ L HCl (12 mol L⁻¹) method at 3000 rpm for 30 s, followed by annealing at 500 °C for 60 min in air to remove the organic part. Sb₂S₃ thin films, as an absorber layer, were prepared by two kind of method in this work. For Sb_2S_3 (FCA) thin films, Sb-complex solution was spin-coating at a speed of 8000 rpm for 30 s, followed by annealing on a hot plate in N₂-purged glove box at 200 °C for 1 min and 300 °C for 2 min. For Sb₂S₃ (CBD) thin films, about 200 nm thickness precursor Sb₂S₃ thin films were prepared by traditional CBD method¹ at 5 °C for 2 h. The asdeposited thin films were annealed at 300°C for 10min in N₂ prior to solar cell fabrication. The hole transporting material (HTM) spiro-OMeTAD was spin-coated on Sb₂S₃/bl-TiO₂/FTO substrate at a speed of 3000 rpm for 60 s and heated on a hot plate at 100 °C for 30 min in air. The spiro-OMeTAD solution was prepared by mixing 73.2 mg of spiro-OMeTAD, 28.8 µL of 4-tert-butylpyridine (tBP), and 18.8 μ L of a 520 mg mL⁻¹ 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^{-4} Pa. The active area of the device was defined at 0.12 cm^2 .

Materials and device performance characterization

The surface and cross-section morphologies of the Sb_2S_3 thin films were characterized by field emission SEM (FE-SEM siron 200). Thermogravimetric analysis (TGA) was recorded on a TGA Q5000 instrument under nitrogen atmosphere at a heating rate of 10 °C/min. The crystallinity and preferred orientations of samples

were investigated by X-ray diffraction (XRD) using a Bruker Advance D8 diffractometer equipped with graphite-monochromatized Cu K (radiation (λ =1.5406 Â). UV-vis spectroscopy was characterized by an UV-vis-NIR 3600 spectrometer. Finally, Sb₂S₃ based solar devices are characterized using the oriel AAA solar simulator under standard AM1.5 illumination (100 mW·cm⁻²) and the external quantum efficiency (EQE, Model SPIEQ200) was measured using a single source with a monochromator. illumination system (halogen lamp) combined Electrochemical impedance spectroscopy measurements were performed using Zahner Mess Systeme PP211 electrochemical workstation at a bias potential of -0.6 V in dark with the frequency ranging from 1Hz to 4 MHz. The Fourier transform infrared spectra (FTIR) of the solution is measured by Nicolet 8700 to obtain the information on structural changes during the reaction process of precursor solution recorded at ambient temperature at the resolution of 4 cm⁻¹ and scanning with the spectrum scope of $400-4000 \text{ cm}^{-1}$.

1. S. Messina, M. T. S. Nair, P. K. Nair, *Thin Solid Films* 2007, 515, 5777.



Figure S1 FTIR spectrum of the product from reaction between CS_2 and n-butylamine (black), and the reaction between Sb_2O_3 , CS_2 and n-butylamine (red).



Figure S2 (a, b) Large-view SEM images of Sb₂S₃ film fabricated by FCA method.



Figure S3 SEM image of the cross section of the device based on FCA-prepared $\mathrm{Sb}_2\mathrm{S}_3$.



Figure S4 Large-view SEM image of Sb₂S₃ film fabricated by CBD method.



Figure S5 SEM image of the cross section of the device based on CBD-prepared $\mathrm{Sb}_2\mathrm{S}_3$.



Figure S6 UV-vis absorption spectrum of Sb_2S_3 film fabricated by FCA, the absorption spectrum of TiO₂ compact blocking layer is also attached for reference.



Figure S7 Current density-voltage curves of the devices with Sb_2S_3 film fabricated by FCA and CBD methods under darkness.