Supporting Information

Porous Copper Zinc Tin Sulfide Thin Film as Photocathode for Double Junction Photoelectrochemical Solar Cell

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Experimental

Preparation of porous CZTS thin film

The porous CZTS thin film was synthesized by a solvothermal approach. In a typical experiment, Copper chloride dehydrate ($CuCl_2·2H_2O$, 0.1135g), Zinc chloride dehydrate ($ZnCl_2$, 0.0625g), Stannous chloride dehydrate ($SnCl_2·2H_2O$, 0.0845g) and Thiourea (CH_4N_2S, Tu, 0.2235g) were dispersed in ethanol (10mL) in a beaker (The molar ratio of metal chlorides could be changed as required.). The precursor was added to a teflon-lined stainless steel autoclave with a capacity of 30 mL. A piece of Molybdenum (Mo) foil was put aslant in the autoclave, after cleaned in HF solution, ultrapure water and ethanol. Then the autoclave was maintained at 200℃ for 6h. After cooling to room temperature, the superjacent film on the Mo foil was porous CZTS thin film. Washed with ethanol and water for several times, the films were annealed at 500℃ for 30min under S vapor.

Fabrication of solar cells

Porous TiO_2 photoanode, N719 dye, I^-/I_3^- electrolyte and Pt serosity are all bought from WuHan Geao Instruments Science & Technology Co., Ltd. SEM of TiO_2 photoanode is shown in figure S4. The TiO_2 thin film has a thickness of 12μm. And the area of the TiO_2 thin film is 5mm*5mm. I^-/I_3^- electrolyte contains DMPⅡ(0.3M), LiI (0.5M), I_2 (0.05M),4-TBP (0.5M) in 3-Methoxypropionitrile.

Some dye was dissolved dispersed in ethanol to form a solution (5×10^{-4}mol/L). The TiO_2 photoanode was heated up to 80℃ and dropped into the solution for 24h to prepare the dye sensitized TiO_2 (DS-TiO_2) photoanode. Pt electrode was obtained by annealing the FTO glass which had been coated with the Pt serosity at 400℃ for 20min. DSSCs were assembled with a active area of about 0.25cm^2. And the DS-TiO_2/CZTS solar cell was fabricated by replacing the Pt electrode with porous CZTS thin film.

Characterizations and measurements

The crystallinities of porous CZTS thin films were analyzed by X-ray diffraction (XRD) on a Bruker AXS D8 Advance X-ray diffractometer with Cu Kα radiation (λ=1.5418Å). The morphology and structure of the as-prepared porous CZTS thin film were studied by FE-SEM (JSM-6700F) and TEM (JEM-1011, 100 kV). Transmittance and reflectance spectra of the thin films were obtained using SolarCellScan100 (Zolix). Current-voltage curves were recorded using electrochemical analyzer (CHI660C). A xenon lamp (about 100mW/cm^2) was used as light source. The cells were measured without light-shading mask.

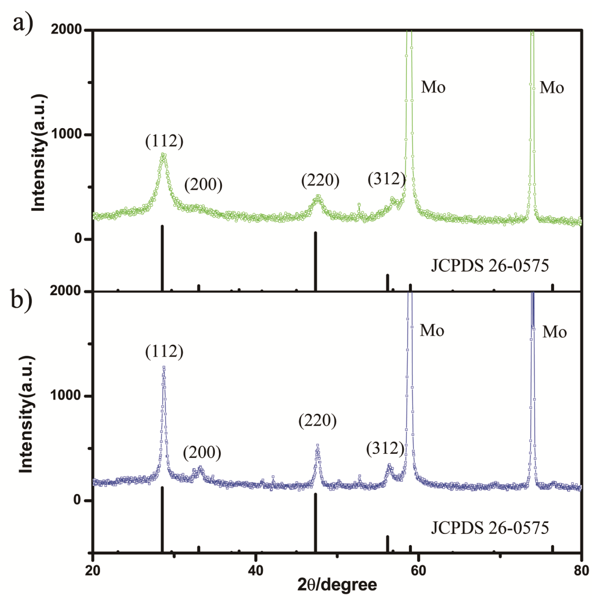

Figure S1. X-ray powder diffraction (XRD) patterns of porous CZTS film. a) sample before annealing. b) sample after annealing at 500□ for 30min. peaks at 2θ= 28.8, 33.0, 47.8, and 56.5° correspond to diffractions of the (112), (200) (220), and (312) planes of kesterite structure CZTS, respectively. No characteristic peaks in Figure S1b might be attributed to the superfluous sulfur while being annealed.

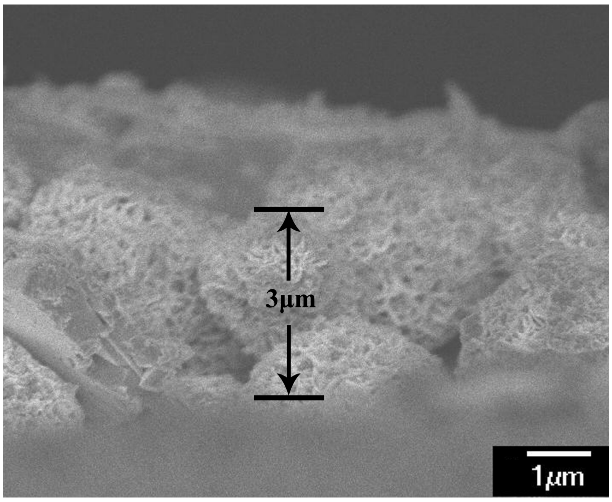

Figure S2. Cross-sectional SEM images of the porous CZTS thin film.

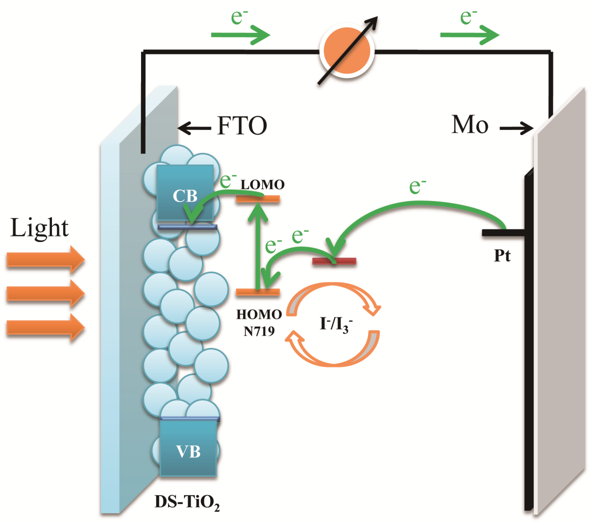

Figure S3. Scheme of the DS-TiO_2/Pt solar cell. The green arrows indicate the possible electron transfer process.

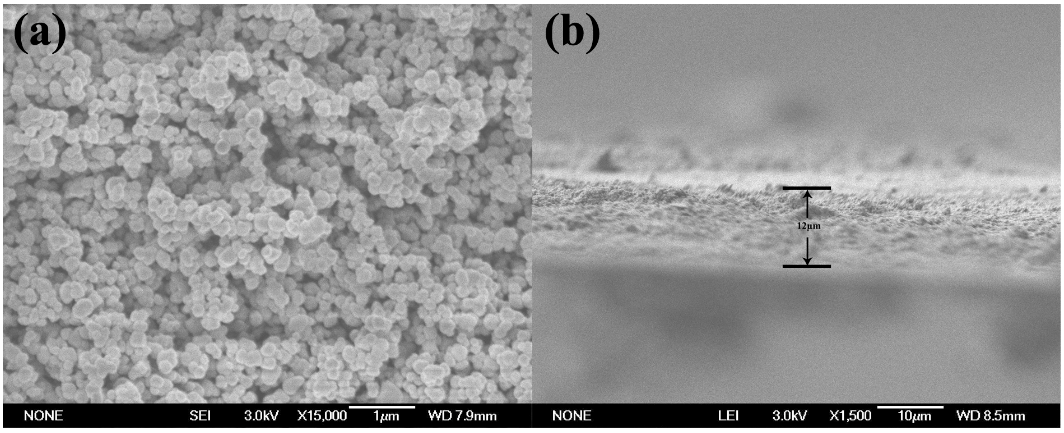

Figure S4. SEM images of porous TiO_2 thin film. (a) the top view. (b) the cross-sectional view.

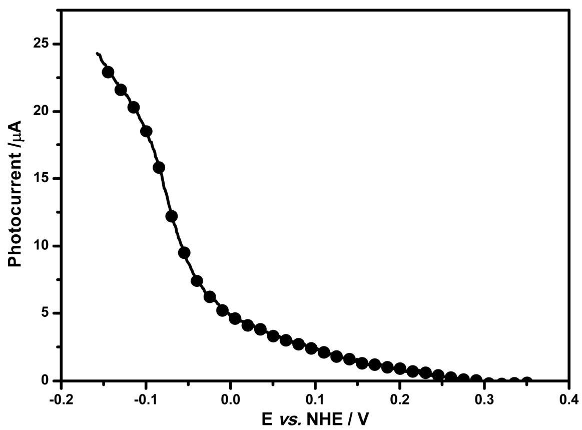

Figure S5. Photocurrent voltage plots for porous CZTS films. The curve was measured using a 3-electrode with platinum wire counter and saturated calomel electrode (SCE). 0.2M Tetrabutylammonium Perchlorate in 3-Methoxypropionitrile is used as electrolyte. The flat band potential (E_{fb}) obtained from the current-voltage curve of the photocurrent response is approximately 0.3V vs NHE, which is a little different from the E_{fb} (0.3-0.4V vs NHE) in 0.2 M $Eu(NO_3)_3$ in water (pH 2.3). (J. J. Scragg, P. J. Dale, 1, L. M. Peter, G. Zoppi, and I. Forbes *phys. stat. sol. (b)* 2008, **245**, 1772–1778.)

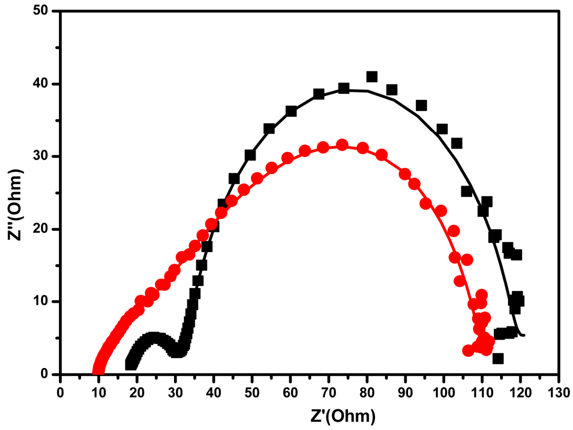

Figure S6. Nyquist plots of solar cells. black: DS-TiO_2/Pt solar cell. red: DS-TiO_2/CZTS solar cell. The lines show theoretical fits using the reported equivalent circuits.[20]