Electronic Supplementary Information

Modulation of Sulfur Partial Pressure in Sulfurization to Significantly Improve Photoelectrochemical Performance over Cu_2ZnSnS_4 Photocathode

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Experimental:

CZTS photocathodes were prepared by electrodepositing metal precursors and sulfurizing with sulfur powder. Fluorine doped Tin Oxide (FTO) substrate was cleaned ultrasonically in distilled water, ethanol, acetone, ethanol for 30 minutes respectively and dried under flowing nitrogen. The Cu, Sn, and Zn precursors were deposited on FTO sequentially in three electrode cells with Pt wire counter electrode and Ag/AgCl reference electrode at normal temperature without stirring. All chemicals were analytical reagent grade (purchased from Sinopharm Chemical Reagent Co. Ltd., China) except for special statements. Electrodeposition parameters of Cu-Sn-Zn metal stacks were 0.02 M $CuSO_4$ in 0.5 M sodium citrate (Tianjin Guangfu Fine Chemical Research Institute, China), 0.05 M $SnCl_2$ in 0.05 M NaOH, 0.04 M $ZnSO_4$ in 0.5 M sodium citrate, electrodepositing amount of 0.5 C, 0.3 C, 0.3 C and applied 1.1 V, 1.2 V, 1.3 V vs. Ag/AgCl reference electrode, respectively. Corundum ark containing metal precursor coated on FTO and 0.1 g sulfur powder (Alfa Aesar, 99.9995%) was inserted into a quartz tube filled with 0.6 bar Ar gas. The thin film sample was heated with a rate of 10 ℃/min up to 550 ℃ and maintained for 1 h, and then cooled naturally. Pre-alloying sample synthesized by alloying at 320 ℃ for 30 min before the further sulfurization.

Characterizations:

XRD (D8 Advanced X-ray diffractometer), Raman spectroscope (XploRA PLUS), Ultraviolet-Visible-Infrared (UV-Vis-IR) spectrophotometer (UV-3600), Field Emission Scanning Electron Microscope (S4800) equipped with Energy Dispersive Spectrometer (Genesis XM2) were used to characterize the samples. Photoelectrochemical (PEC) measurements of as-prepared samples were carried out in three-electrode mode under irradiation of AM 1.5G (100 mW/cm^2) using Pt wire counter electrode and Ag/AgCl reference electrode in 0.2 M $Eu(NO_3)_3$ aqueous solution. An electrochemical station (CHI 660e) was utilized to measure photocurrent density. Incident Photon to Current Efficiency was obtained by using 300 W Xenon lamp (CEL-HXF300), Electrochemical station (CHI 660e), Monochromator (7ISW151) and Spectroradiometer (AvaSolar-1) applied bias of -0.5 V vs. Ag/AgCl reference electrode.

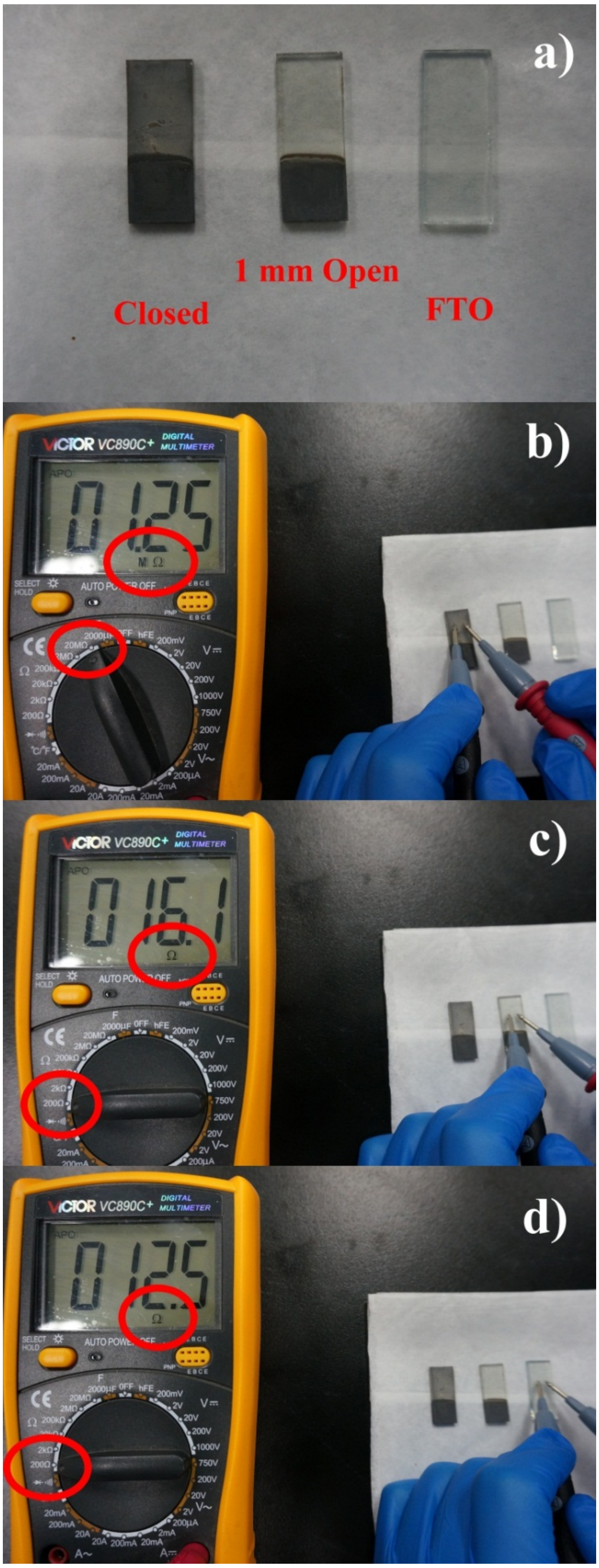

Fig. S1 The resistance of the bared electric part.

The resistance of the bared electric part increases to ~ MΩ after sulfurizing in closed system.

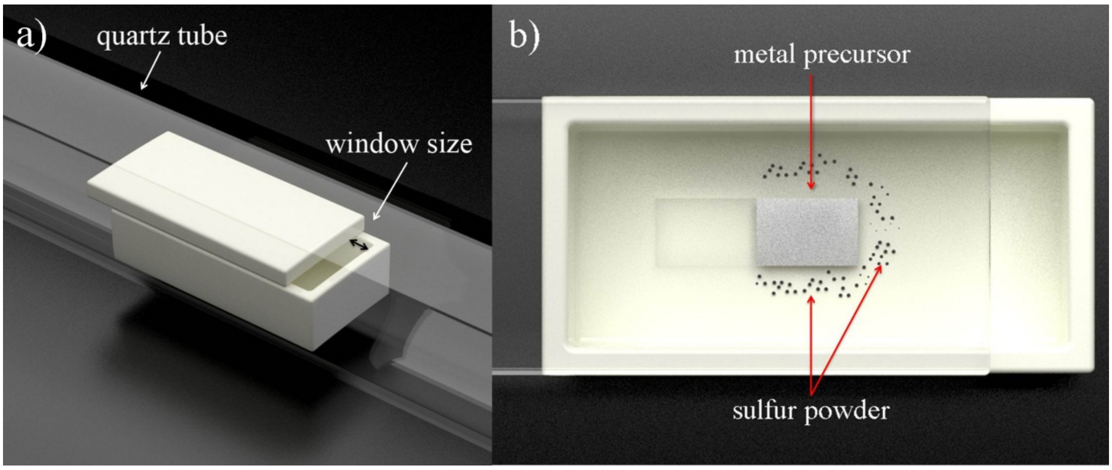

Fig. S2 (a) The experimental device for synthesizing CZTS photocathode. (b) The vertical view of device.

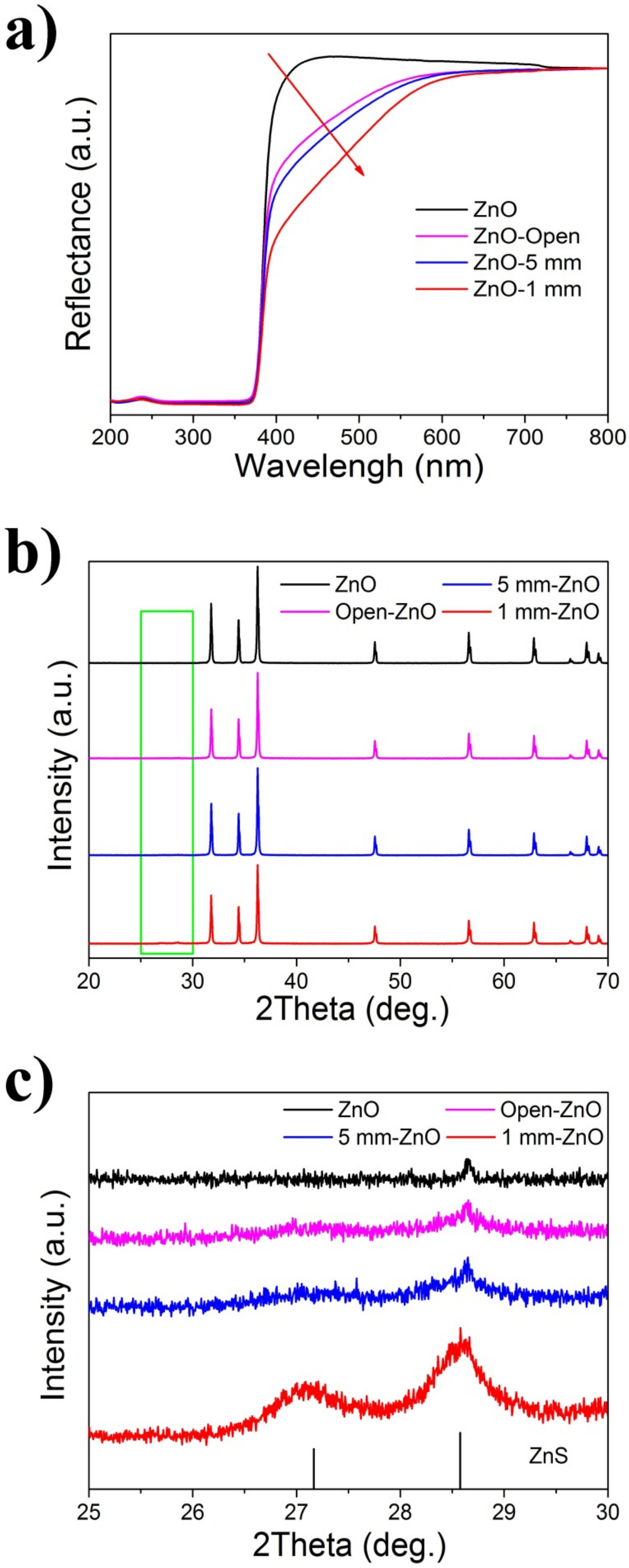

Fig. S3 a) Reflectance spectra, b), c) XRD pattern of ZnO processed with different condition.

Commercial ZnO (purchased from Sinopharm Chemical Reagent Co. Ltd., China) was put into the corundum ark and sulfurized under the same condition as CZTS photocathodes.

Firstly, we measured the UV-visible Reflectance Spectra of ZnO processed under different condition. As shown in Fig. S3a, the reflectance intensities reduce sequentially with the decreases of window sizes at the wavelength ranged from 400 to 600 nm. The larger S pressure causes the easier penetration of S into ZnO, which leads to the decrease of reflectance intensities. Secondly, XRD measurement was utilized to further confirming the variation of S pressure. No obvious differences can be found in Fig. S3b; however, after enlarging the green area in Fig. S3b, two XRD peaks corresponding to ZnS appear and the intensity increase with the reducing of window sizes during sulfurization processes as shown in Fig. S3c. The larger S pressure causes the more amounts of ZnS. In conclusion, the S pressure can be modulated by adjusting the window size.

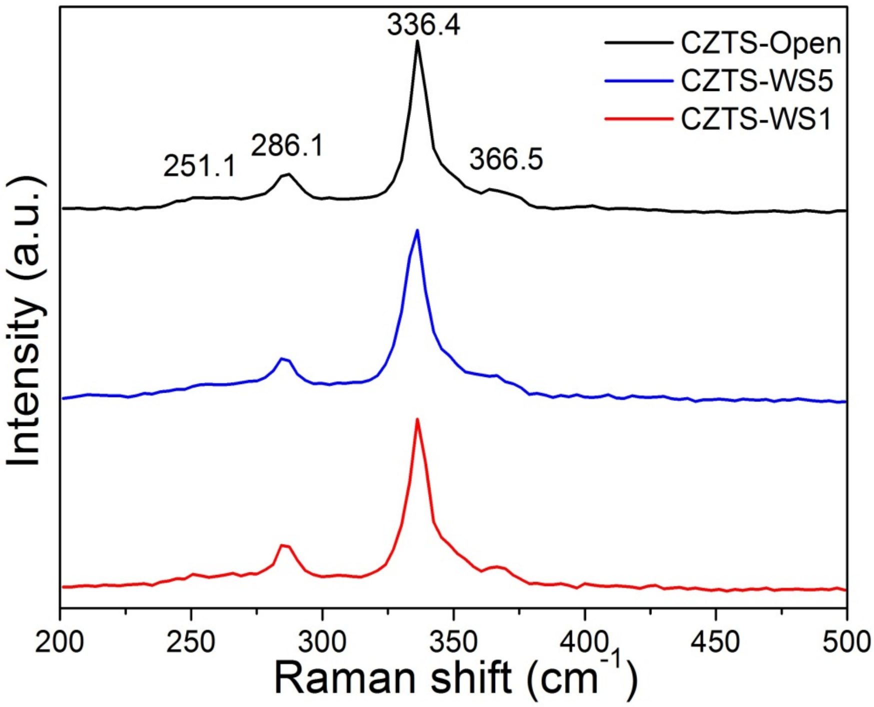

Fig. S4 Raman spectra of CZTS photocathode were fabricated by different window size.

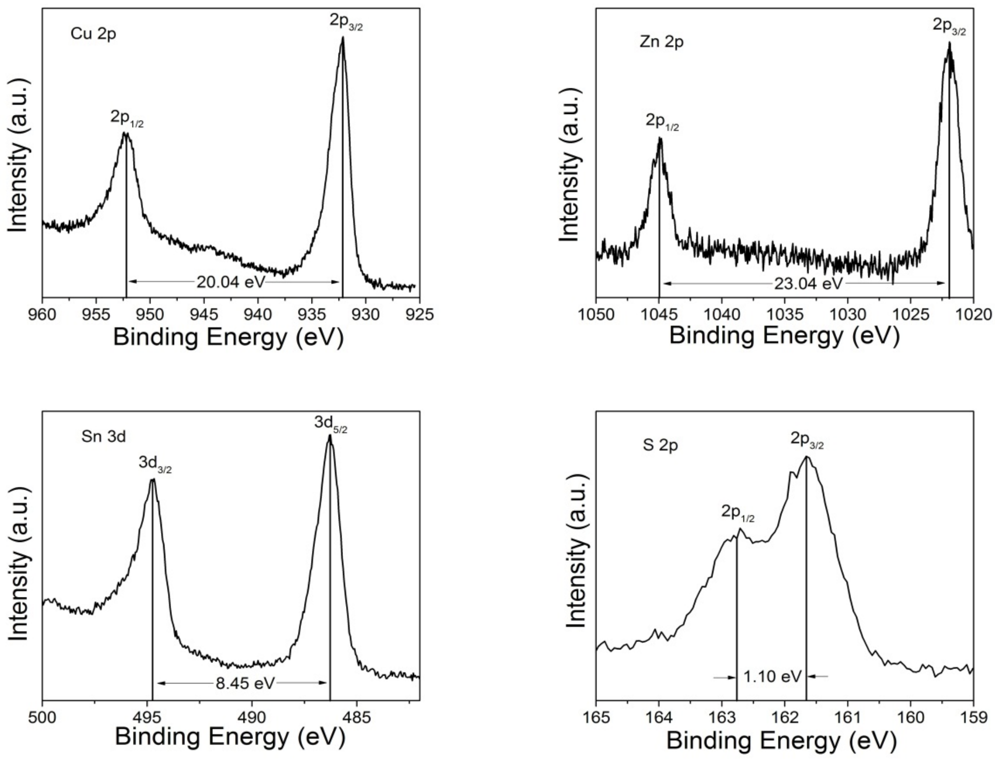

Fig. S5 XPS spectra of CZTS-WS1.

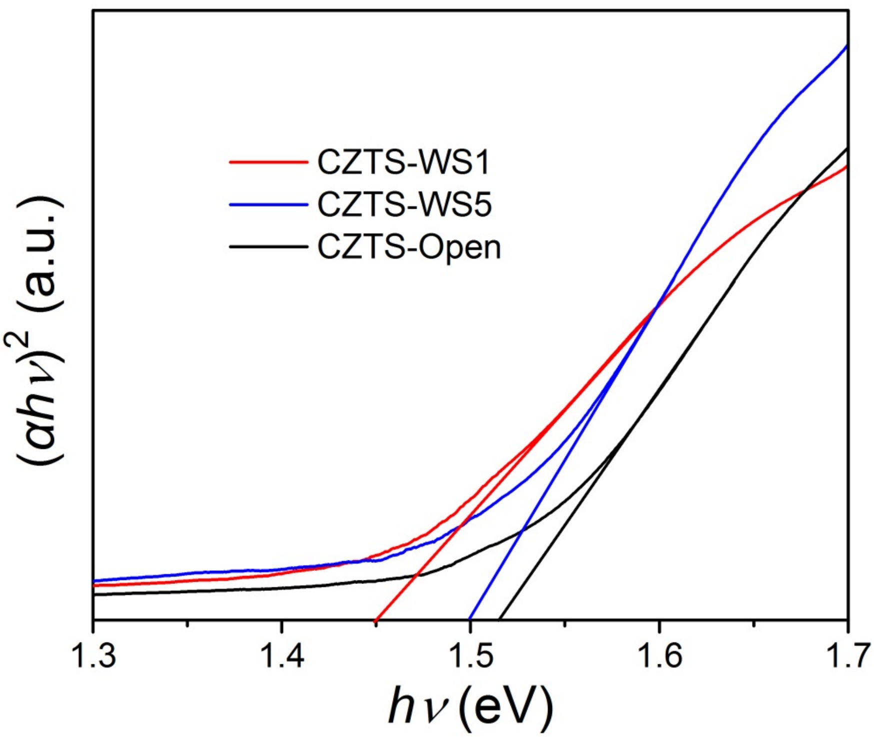

Fig. S6 The band gaps of CZTS photocathodes were deduced from absorption spectra.