Supporting Information

Formation mechanism of ZnS impurities and their effect on photoelectrochemical properties on a Cu₂ZnSnS₄ photocathode

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Fig. S1 SEM-EDS elemental maps of Sample r-1.2 and r-0.6.



Fig. S2 (a) Visible and (b) UV Raman spectra of CZTS without sulfur annealing with Zn/Sn precursor ratio of 1.2 prepared with different reaction time (10 min, 30min and 120min) in the mixture solution.



Fig. S3 An energy band diagram of CZTS in aqueous solution.



Fig. S4 Cross-sectional SEM images of the as-annealed CZTS thin films prepared with different Zn/Sn precursor ratios.

Table S1 Chemical composition of the as-annealed CZTS thin films prepared with different reaction time in the mixture solution measured by EDS.

Reaction time	Chemical compositon of CZTS after annealing					
(minutes)	Zn/Sn=0.6			Zn/Sn=1.2		
	Cu/Zn+Sn	Zn/Sn	S/metal	Cu/Zn+Sn	Zn/Sn	S/metal
10	0.67	1.67	1.11	0.65	1.90	1.12
30	0.85	1.10	0.97	0.79	1.81	1.12
120	0.87	1.07	1.07	0.77	1.80	1.08