#### **# Supporting Information**

## An Efficient Cu<sub>2</sub>Zn<sub>1-x</sub>In<sub>x</sub>Sn(S,Se)<sub>4</sub> Multicomponent Photocathode via One-Step Hydrothermal Approach for Thin Film Solar Cell

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Table S1: Preparative parameters for hydrothermal synthesis of the  $Cu_2Zn_{1-x}In_xSn(S,Se)_4$  thin

films.

Sr. No.	Sample	In <sup>3+</sup> ion	Composition	рН	Temperature
	Code	concentration			
		(M/mL)			
1	I <sub>1</sub>	0.00	$Cu_2ZnSn(S,Se)_4$		
2	I <sub>2</sub>	0.025	$Cu_2Zn_{0.075}In_{0.025}Sn(S,Se)_4$	$8.2\pm0.2$	$180 \pm 2^{\circ}$ C
3	I <sub>3</sub>	0.05	$Cu_2Zn_{0.05}In_{0.05}Sn(S,Se)_4$		
4	I <sub>4</sub>	0.075	$Cu_2Zn_{0.025}In_{0.075}Sn(S,Se)_4$		

**Table S2:** Compositional data for  $Cu_2Zn_{1-x}In_xSn(S,Se)_4$  thin films temperature.

Sample	Cu	Zn	In	Sn	S	Se	(Zn + In)	Си	(Cu + Zn + In + Sn)
Code							Sn	$\overline{(Zn + In + Sn)}$	(S+Se)
I <sub>1</sub>	25.4	14.4	0.0	14.2	23.5	22.5	1.11	0.84	1.24
I <sub>2</sub>	25.7	11.6	4.2	14.4	22.1	22	1.09	0.85	1.26
I <sub>3</sub>	25.9	10.4	5.6	13.8	21.5	22.8	1.15	0.86	1.25
I <sub>4</sub>	26.2	10.1	6.2	13.4	20.3	25.8	1.21	0.88	1.18

Figure S1. Plot of thickness associated with band gap energy of  $Cu_2Zn_{1-x}In_xSn(S,Se)_4$  films as a function of  $In^{3+}$  ion concentration.

The thickness of the CZITSSe films is analyzed with surface profilometer. The thickness of the CZITSSe thin films was increased from 540 to 645 nm as function of  $In^{3+}$  ion concentration. As a thickness of films increases, the band gap energy was decreased from 1.42 to 1.34 eV.



Figure S2: The cross-section SEM images of deposited CZTSSe and  $In^{3+}$  doped CZITSSe (I<sub>1</sub>-I<sub>4</sub>) thin films



# Figure S3: Correlation between $J_{sc}$ corresponding to $V_{oc}$ as a function of $In^{3+}$ ion concentration in photoelectrochemical performance.

Figure S3 (a, b) depicts the correlated data of  $Cu_2Zn_{1-x}In_xSn(S,Se)_4$  thin films respectively. As  $In^{3+}$  ion concentration increases the short circuit current and open circuit voltage increases.

