

## Supporting Information

### Solution-Processed Sulfur Depleted Cu(In, Ga)Se<sub>2</sub> Solar Cells Synthesized from a Monoamine-Dithiol Solvent Mixture

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#### 1. Cation precursors preparation

##### Chemicals

Copper (I) selenide (Cu<sub>2</sub>Se, 99.95%, Aldrich), copper (II) acetate (Cu(OAc)<sub>2</sub>, 99.99%, Aldrich), copper (II) acetylacetonate (Cu(acac)<sub>2</sub>, 99.9%, Aldrich), copper (I) chloride (CuCl, 99.99%, Aldrich), indium (III) selenide (In<sub>2</sub>Se<sub>3</sub>, Aldrich), indium (III) acetate (In(OAc)<sub>3</sub>, 99.99%, Aldrich), indium (III) acetylacetonate (In(acac)<sub>3</sub>, 99.99%, Aldrich), indium (III) chloride (InCl<sub>3</sub>, 99.999%, Aldrich), gallium (III) acetylacetonate (Ga(acac)<sub>3</sub>, 99.99%, Aldrich), gallium (III) chloride (GaCl<sub>3</sub>, 99.99%, Aldrich), gallium(III) iodide (GaI<sub>3</sub>, 99.99%, Aldrich), hexylamine (99%, Aldrich), 1,2-ethanedithiol (98%, Aldrich), and selenium powder (99.99%, Aldrich).

##### Solutions

Both monoamine-monothiol and monoamine-dithiol mixtures can be used to dissolve a variety of metal cation sources. As shown in Figure 1a, 0.2 mmol of GaI<sub>3</sub>, Ga(acac)<sub>3</sub>, GaCl<sub>3</sub>, Cu(OAc)<sub>2</sub>, Cu(acac)<sub>2</sub>, CuCl, In(OAc)<sub>3</sub>, In(acac)<sub>3</sub>, InCl<sub>3</sub>, 0.4 mmol of Cu<sub>2</sub>Se, and ~0.1 mmol of In<sub>2</sub>Se<sub>3</sub> were dissolved in 2 mL solvent mixture of monoamine-dithiol (HA-EDT, vol/vol = 10:1) respectively (Figure S1 a). All the metal salts except metal chalcogenides can easily dissolve in a monoamine-monothiol mixture (HA-PT, vol/vol = 4:1) as well (Figure 1b). 0.2 mmol of GaI<sub>3</sub>, Ga(acac)<sub>3</sub>, GaCl<sub>3</sub>, Cu(OAc)<sub>2</sub>, CuCl, Cu(acac)<sub>2</sub>, In(OAc)<sub>3</sub>, In(acac)<sub>3</sub>, InCl<sub>3</sub> were dissolved in 2 mL HA-PT solvent mixture (vol/vol = 4:1) respectively. The dissolution

process was performed in a N<sub>2</sub> glovebox with oxygen and moisture levels less than 0.1 ppm at room temperature.

Table S1. Solubility limits of metal salts and metal selenides in monoamine-dithiol (HA-EDT, vol/vol = 10:1) mixture and monoamine-monothiol mixture (HA-PT, vol/vol = 4:1) (20-25 °C, 1 atm)

	HA-EDT (vol/vol = 10:1)	HA-PT (vol/vol = 4:1)
GaI <sub>3</sub>	0.48 M	0.62 M
Ga(acac) <sub>3</sub>	0.51 M	0.37 M
GaCl <sub>3</sub>	0.71 M	0.83 M
Cu(OAc) <sub>2</sub>	0.16 M	0.77 M
Cu(acac) <sub>2</sub>	0.18 M	0.67 M
CuCl	1.00 M	0.50 M
Cu <sub>2</sub> Se	0.50 M	-
In <sub>2</sub> Se <sub>3</sub>	~ 0.05 M	-
In(OAc) <sub>3</sub>	0.37 M	0.09 M
In(acac) <sub>3</sub>	0.50 M	0.10 M
InCl <sub>3</sub>	0.61 M	0.42 M

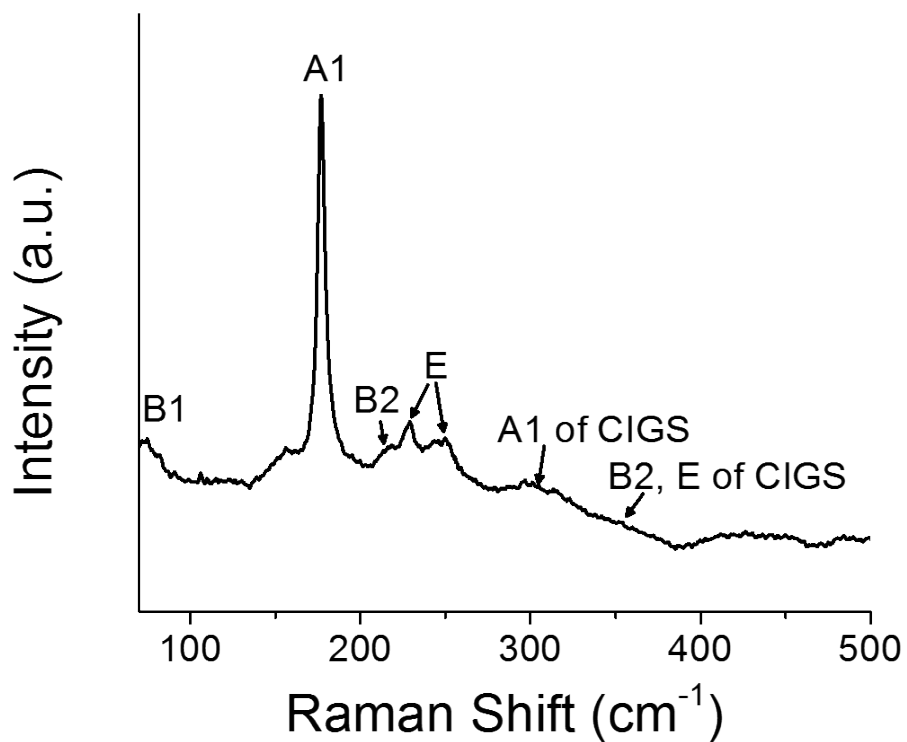


Figure S1. Raman spectrum of a selenized CIGSSe film. The film was fabricated by selenizing the CIGS nanoparticle film as described in our previous work.<sup>[41]</sup>

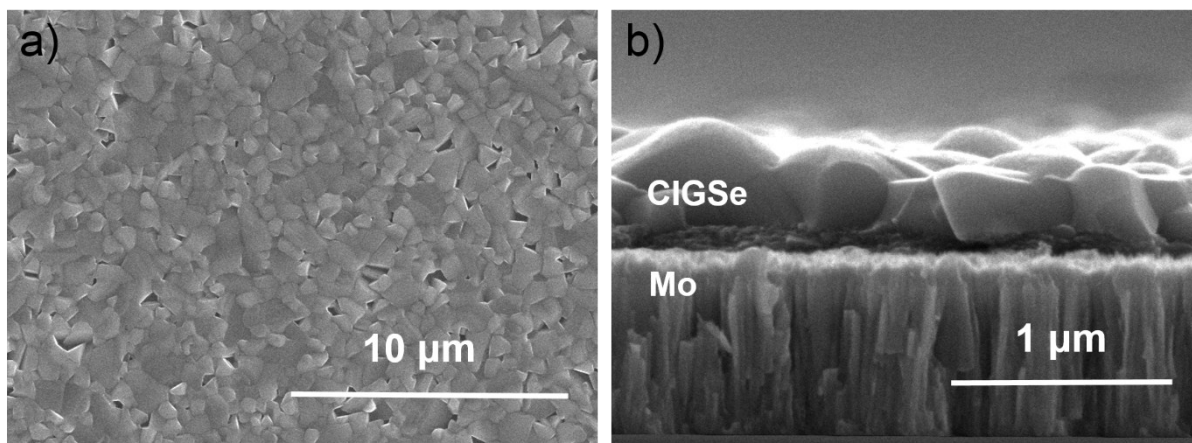


Figure S2. a) Top-view SEM image, and b) cross-section SEM image of the ultrathin CIGSe/Mo/glass thin film after selenization

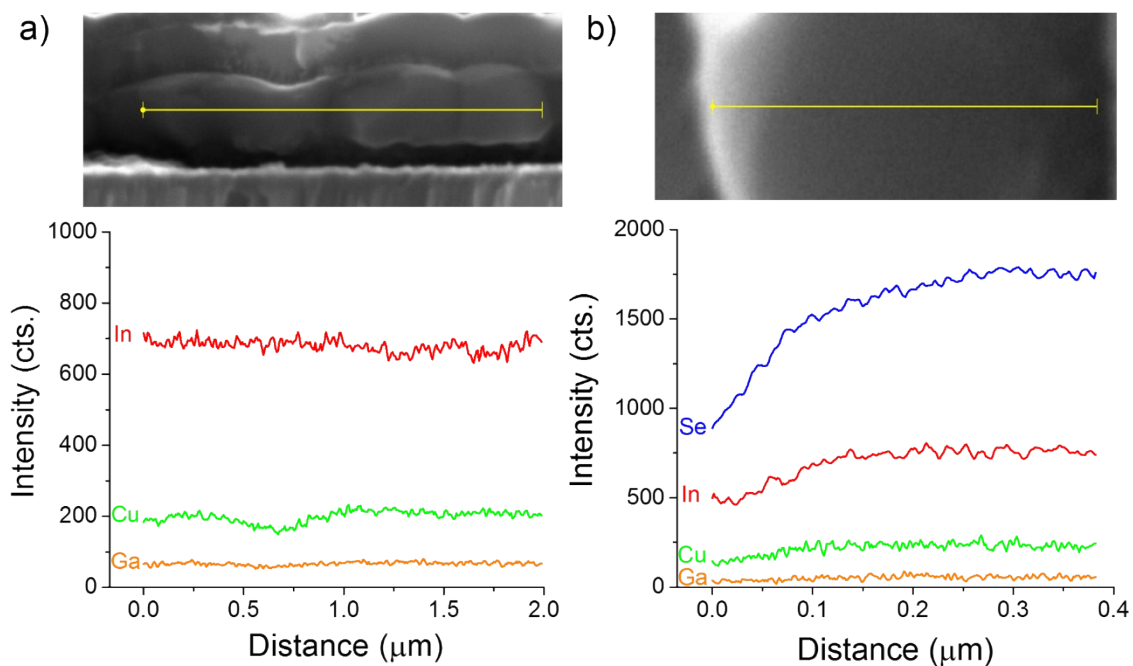


Figure S3. a) Horizontal and b) vertical (from top to the bottom (Mo) side) EDX line scans of the ultrathin CIGSe solar cell

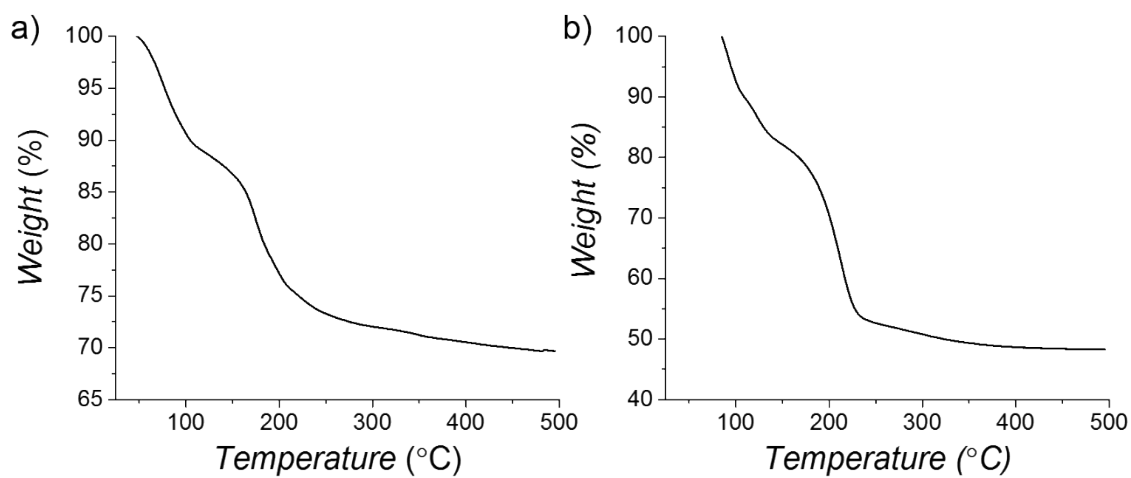


Figure S4. Thermogravimetric analysis (TGA) of room temperature dried a) Cu<sub>2</sub>Se precursor and b) CIGSe precursor. (10 °C/min ramp rate, helium atmosphere)

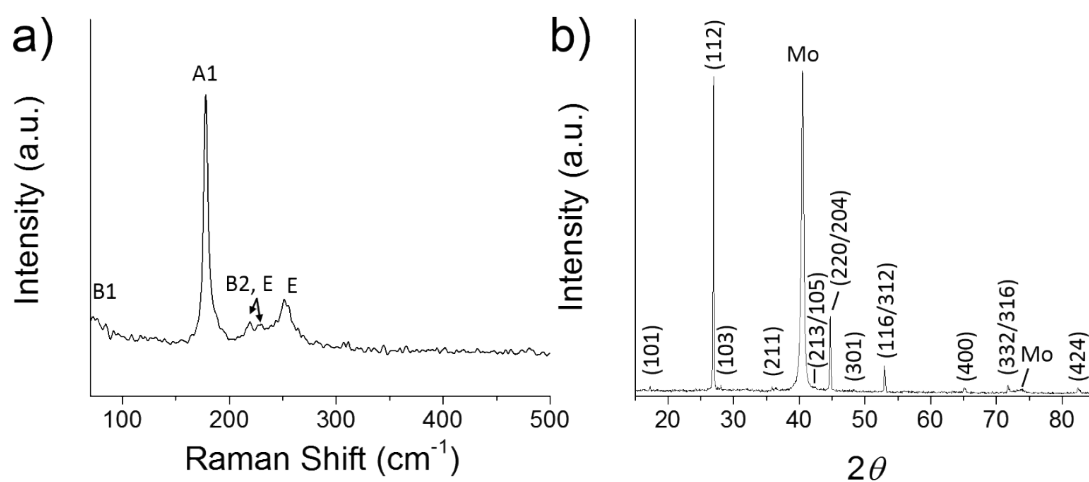


Figure S5. a) Raman spectrum and b) XRD diffraction pattern of the modified CIGSe/Mo/glass film after selenization. Absence of shoulder at 150-160  $\text{cm}^{-1}$  in Raman and the peak at  $25.9^\circ$  in PXRD indicates substantial reduction in OVC.

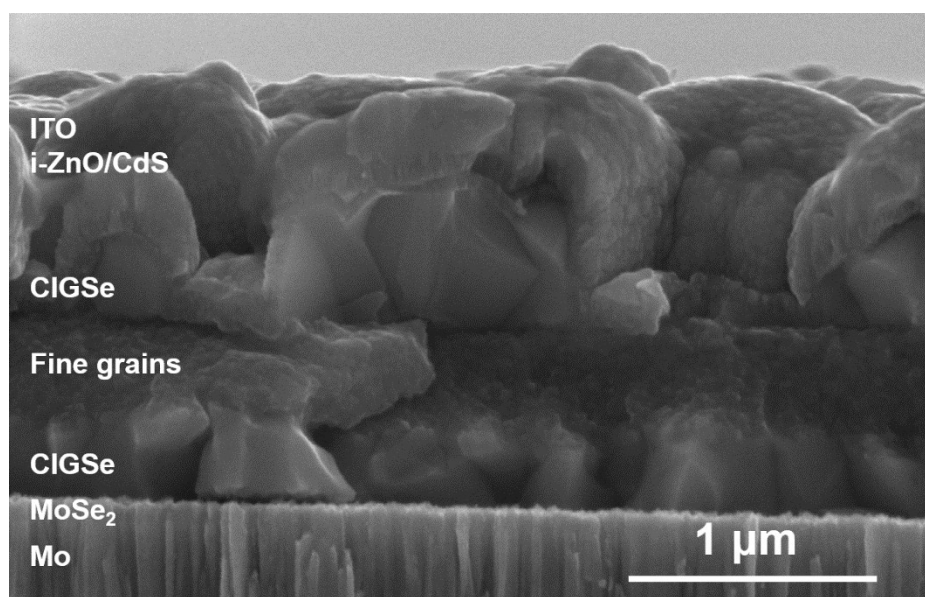


Figure S6. Cross-sectional SEM image of a typical sandwich-structured CIGSe solar cell.

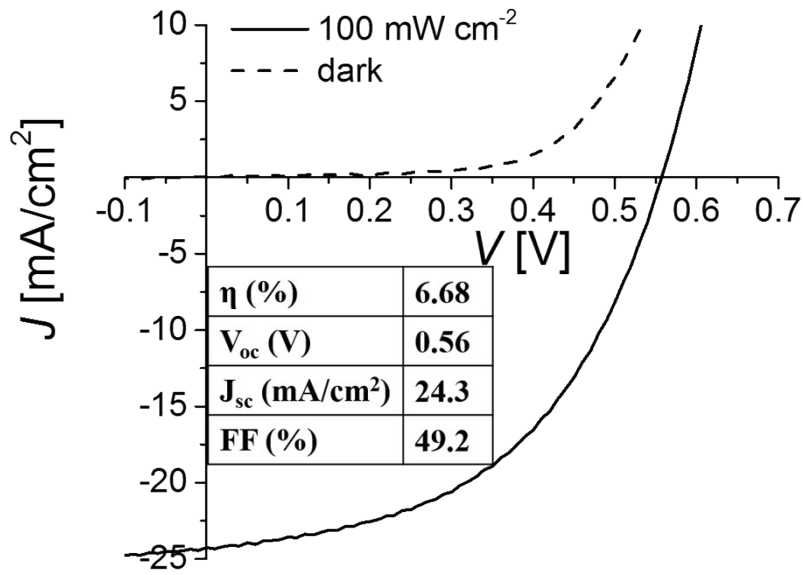


Figure S7.  $J$ - $V$  curves and performance parameters for the sandwich-structured CIGSe solar cell without antireflective layer (AM 1.5G illumination; 100mW cm<sup>-2</sup>; 0.47 cm<sup>2</sup> total device area including Ni/Al grid-covered area).

Table S2. Photovoltaic parameters of 4 ultrathin CIGSe solar cells.

Cell	$\eta$ (%)	$V_{oc}$ (mV)	FF (%)	$J_{sc}$ (mA/cm <sup>2</sup> )
1	10.30	540	59	32.7
2	9.67	550	61	28.7
3	9.68	540	63	28.3
4	9.86	560	64	27.7
AVG	9.88	548	62	29.4

Table S3. Photovoltaic parameters of 3 modified CIGSe solar cells.

Cell	$\eta$ (%)	$V_{oc}$ (mV)	$FF$ (%)	$J_{sc}$ (mA/cm <sup>2</sup> )
1	11.10	540	64.6	31.9
2	12.1	560	66.1	32.7
3	12.20	560	65.4	33.3
AVG	11.8	553	65.4	32.6

Table S4. Composition of the as prepared selenized CIGSe film from different cation precursors

Different types of cation precursors	Atomic ratio	
	[Cu]/([In]+[Ga])	[Ga]/([In]+[Ga])
CuCl, InCl <sub>3</sub> , Ga(acac) <sub>3</sub>	0.98	0.07
CuCl, InCl <sub>3</sub> , Ga(acac) <sub>3</sub> <sup>a</sup>	0.99	0.04
CuCl, InCl <sub>3</sub> , GaCl <sub>3</sub>	1.24	0.05
CuCl, InCl <sub>3</sub> , GaI <sub>3</sub>	1.18	0.13
CuCl, In(acac) <sub>3</sub> , Ga(acac) <sub>3</sub>	1.02	0.06
Cu(acac) <sub>2</sub> , InCl <sub>3</sub> , Ga(acac) <sub>3</sub>	1.06	0.08
Cu(acac) <sub>2</sub> , In(acac) <sub>3</sub> , Ga(acac) <sub>3</sub>	0.94	0.29
Cu <sub>2</sub> Se, In(OAc) <sub>3</sub> , Ga(acac) <sub>3</sub>	0.93	0.30

<sup>a</sup> Atomic ratio of cation precursors is [Cu]:[In]:[Ga] = 0.92:0.5:0.5 in the precursor solution. For all other precursor solutions, [Cu]:[In]:[Ga] = 0.92:0.7:0.3.

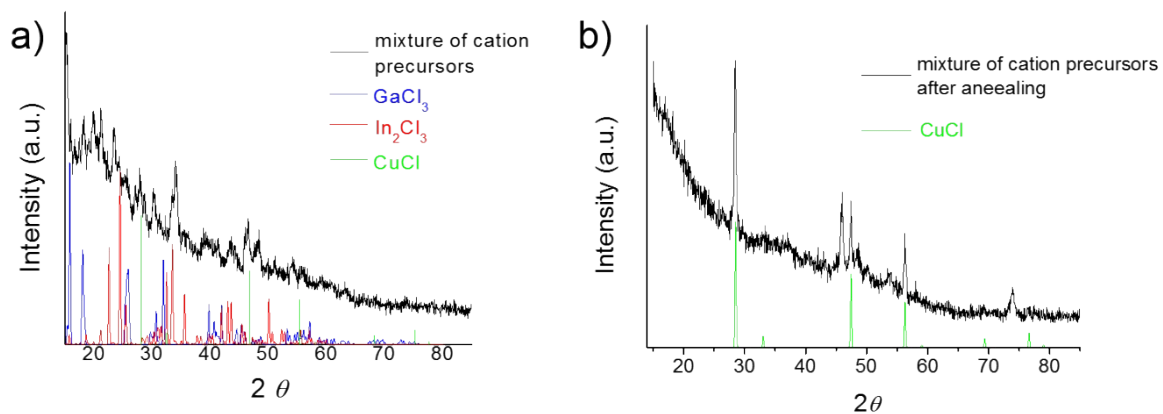


Figure S8. XRD diffraction patterns of the  $\text{CuCl}$ ,  $\text{InCl}_3$ ,  $\text{Ga}(\text{acac})_3$  precursors films on Mo-coated glass by drop casting a) at room temperature; b) after annealing at  $250^\circ\text{C}$  for 5min