

# Supporting Information for

## Over 6% Efficient Cu(In,Ga)Se<sub>2</sub> Solar Cell

## Screen-Printed from Oxides on FTO

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## EXPERIMENTAL DETAILS

### Materials

In the current study, the following reagents were purchased and used as received: copper oxide nanopowder ( $\text{CuO}$ ,  $\geq 99\%$ , 30–50 nm, Alfa Aesar), indium oxide nanopowder ( $\text{In}_2\text{O}_3$ , 99.9%,  $< 100$  nm, Sigma-Aldrich), gallium oxide ( $\text{Ga}_2\text{O}_3$ , 99.999%,  $\approx 325$  mesh powder, Alfa Aesar), di(propylene glycol) methyl ether, (DPM,  $\geq 99\%$ , Sigma-Aldrich), oleic acid (OA, 90%, Sigma-Aldrich), terpeneol (Sigma-Aldrich), ethyl cellulose (EC, 48% ethoxyl, Sigma-Aldrich), selenium shots (Se, amorphous, 99.999%, 2–6 mm, Alfa Aesar), potassium cyanide (KCN,  $\geq 98.0\%$ , Sigma-Aldrich), thiourea ( $\text{CS}(\text{NH}_2)_2$ ,  $\geq 99.0\%$ , Sigma-Aldrich), cadmium acetate ( $\text{Cd}(\text{ac})_2$ , 99.995%, Sigma-Aldrich), ammonium hydroxide aqueous solution (28–30%, Acros Organics). Ultrapure water was produced by Milli-Q Advantage A10 system (Millipore) with resistivity of 18.2 M $\Omega$ .cm. Acetone ( $\geq 99.5\%$ ), isopropanol ( $\geq 99.8\%$ ), and ethanol ( $\geq 99.8\%$ ) were purchased from Honeywell.

### Oxide ink formulation

For the precursor ink 1.684 g of  $\text{CuO}$ , 2.572 g of  $\text{In}_2\text{O}_3$ , 0.744 g of  $\text{Ga}_2\text{O}_3$  [ $\text{Cu}:(\text{In} + \text{Ga}) = 0.8:1.0$ ;  $\text{In}:\text{Ga} = 0.7:0.3$ ], 50 g of DPM, and 2 g of OA were first subjected to wet bead milling at 5000 rpm for 30 min using a Dyno Mill (WAB). Then, the oxide mixture was separated from DPM and OA by centrifugation at 1000 rpm for 30 min follow by 5000 rpm for 30 min, and the resultant wet paste was stored in a vial. A 5% solution of EC in terpeneol was prepared by the dissolution of the appropriate amount of EC in terpeneol at 70 °C under stirring. To prepare an ink with 50% weight content of the oxides, the appropriate amount of oxide wet paste was added to the 5% EC solution in terpeneol. The ink was mixed first with a spatula and then let stir on magnetic stirring plate, at room temperature, overnight.

### Oxide ink properties

The contact angle of oxide ink on fluorine-doped tin oxide (FTO) substrate was measured to be  $27^\circ \pm 2^\circ$ , while the surface tension was calculated to be 32.9 mN  $\text{m}^{-1}$ . Dynamic viscosity with non-Newtonian or thixotropic behavior was observed (Figure S1). Surface energy of FTO substrate was determined to be 74.39 mN  $\text{m}^{-1}$ . All measurements were performed at 22 °C.

### Scree printer parameters

A semi-automatic DX-3050D screen printer (DSTAR), equipped with a vacuum table and adjustable speed of the printing squeegee rulers, was used. The following settings were used for screen printing of photoabsorber layer: 50  $\times$  70 cm mesh size (Figure S2); 180 threads  $\text{cm}^{-1}$  mesh count; 27  $\mu\text{m}$  thread diameter; 24  $\mu\text{m}$  mesh opening; 1.3  $\mu\text{m}$  emulsion thickness (as

estimated from SEM cross-sectional observation (Figure S4)); 5 mm off-contact height;  $0.3 \text{ m s}^{-1}$  squeegee velocity; 85 shore squeegee; and  $75^\circ$  deflection angle.

### **PV devices fabrication**

A  $2.5 \times 2.5 \text{ cm}^2$  fluorine-doped tin oxide (FTO) glass substrates ( $7\Omega \square^{-1}$ , Dyesol) were consecutively cleaned by acetone, isopropanol, and  $\times 3$  with MQ water by ultrasonication at  $60^\circ\text{C}$  for 20 min. Then, the FTO substrates were rinsed by MQ water and ethanol, dried by  $\text{N}_2$  flow, and finally subjected to an oxygen plasma cleaning for 10 min.

To obtain the photoabsorber films on FTO, the oxide ink was screen printed twice using a homemade 180 mesh screen printer and dried at  $100^\circ\text{C}$  on a hot plate after both depositions for 3 min. Afterwards, the as-printed photoabsorber layers were calcined at  $400^\circ\text{C}$  for 30 min to remove residual organics (DPM, OA, EC, terpineol), and subjected to the gas transport selenization procedure.

The gas transport selenization was performed in a tubular furnace, where two film samples were placed inside a graphite box alongside with 0.3 g of elemental Se, and charged into quartz tube. Previous to selenization, the tube was flushed with 5%  $\text{H}_2/\text{Ar}$  mixture at 100 sccm during 1 h. Then, under 5%  $\text{H}_2/\text{Ar}$  flow, the furnace was heated to  $550^\circ\text{C}$  at  $50^\circ\text{C min}^{-1}$ , held at this temperature for 30 min, and then immediately opened to ensure rapid cooling. During cooling, the gas flow inside the quartz tube was switched to Ar.

The as-prepared film samples were etched by 5% aqueous KCN solution at room temperature for 30 s. To deposit  $\approx 70 \text{ nm}$  CdS buffer layer, the chemical bath deposition technique was employed. A water bath was heated to  $60^\circ\text{C}$  and the deposition solution was prepared: 85 mL of MQ water, 15 mL of ammonium hydroxide, 0.13 g of cadmium acetate dissolved in 15 mL of MQ water, and 1.33 g of thiourea dissolved in 15 mL of MQ water. The film samples were then placed in the deposition solution and let react for 7 min while mixing the solution for 10 s at the beginning of each minute by moving the sample up and down.

The window layers were deposited by sputtering at 160 W and 20 sccm of Ar flow. An intrinsic zinc oxide (i-ZnO) resistive layer was first deposited during 4 min, followed by sputtering of Al-doped zinc oxide (ZnO:Al) transparent conducting window layer for 14 min. This sputtering procedure provides ca. 50 nm and 200 nm thick i-ZnO and ZnO:Al layers, respectively.

To finalize the PV devices, one edge of the devices were scratched with a scalpel to reach the back FTO contact, which was then filled-up with a thin layer of indium metal welded to ensure a good contact with the probes for  $J-V$  curve measurements.

## **CHARACTERIZATION**

### **Oxide ink characterization**

The contact angle, surface tension and surface energy were measured at 22 °C using drop shape analysis–contact angle (DSA–CA) method with DSA3 software (KRÜSS). The drop volume was 10  $\mu\text{L}$ . Water and diiodomethane were employed to determine surface energy of the FTO substrate. For viscosity analysis a Physica MCR 300 Modular Compact Rheometer was used at room temperature and at shear rates between 0 and 500  $\text{s}^{-1}$ .

### **Optical Microscopy**

The screen printed ink patterns and their quality were assessed by optical microscopy using Eclipse LV100 ND microscope (Nikon) with  $\times 10$  ocular lens and  $\times 5$  and  $\times 100$  objective lenses.

### **X-ray Diffraction**

The phase composition of the fabricated films was determined using X-ray diffraction (XRD). The data were collected using an X'Pert PRO diffractometer (PANalytical) with Ni-filtered  $\text{Cu K}\alpha$  radiation and a PIXcel detector. The XRD patterns were matched to International Centre for Diffraction Data (ICDD) PDF-4 database using the HighScore software package (PANalytical).

### **Raman Spectroscopy**

To inspect the local structure of the CIGSe photoabsorber layers, Raman spectroscopy measurements were performed on an alpha300 R confocal Raman microscope (WITec) using a 532 nm Nd:YAG laser for excitation. The laser beam with power of 2 mW was focused on the film sample by a  $\times 50$  lens (Zeiss). Afterwards, Raman spectra were collected with a 600 and 1800 groove  $\text{mm}^{-1}$  grating using 100 acquisitions with a 2 s acquisition time.

### **Electron Microscopy**

The morphology of the photoabsorber layers and PV devices were analyzed by scanning electron microscopy (SEM) using Quanta 650 FEG ESEM and Helios NanoLab 450S DualBeam microscopes (FEI), fitted with the spectrometers for energy-dispersive X-ray spectroscopy (EDX).

The focused ion beam (FIB) method was used to prepare the lamella for cross-sectional investigation. To investigate fine microstructure and the chemical composition of the FTO/CIGSe/CdS/i-ZnO/ZnO:Al PV devices, high-angle annular dark-field scanning transmission electron microscopy (HAADF–STEM), selected area electron diffraction (SAED), and EDX in STEM mode (STEM–EDX) were performed using JEM-ARM200F cold

FEG probe and image aberration-corrected microscope (JEOL), operated at 200 kV and equipped with large angle CENTURIO EDX detector and QUANTUM GIF.

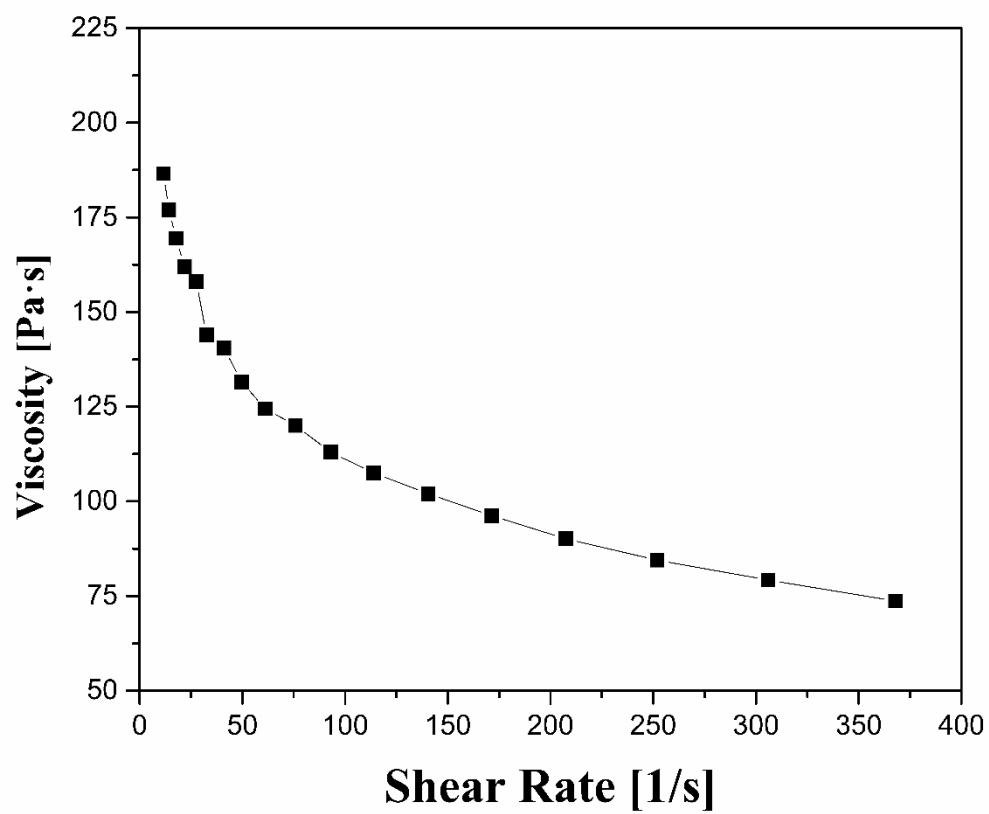
### **Optical Properties**

The optical band gap of Cu(In,Ga)Se<sub>2</sub> photoabsorber layer was determined using absorption UV–Vis–NIR spectroscopy. Room temperature data were collected using a LAMBDA 950 UV/Vis/NIR spectrophotometer (PerkinElmer) equipped with 60 mm integrating sphere and InGaAs detector.

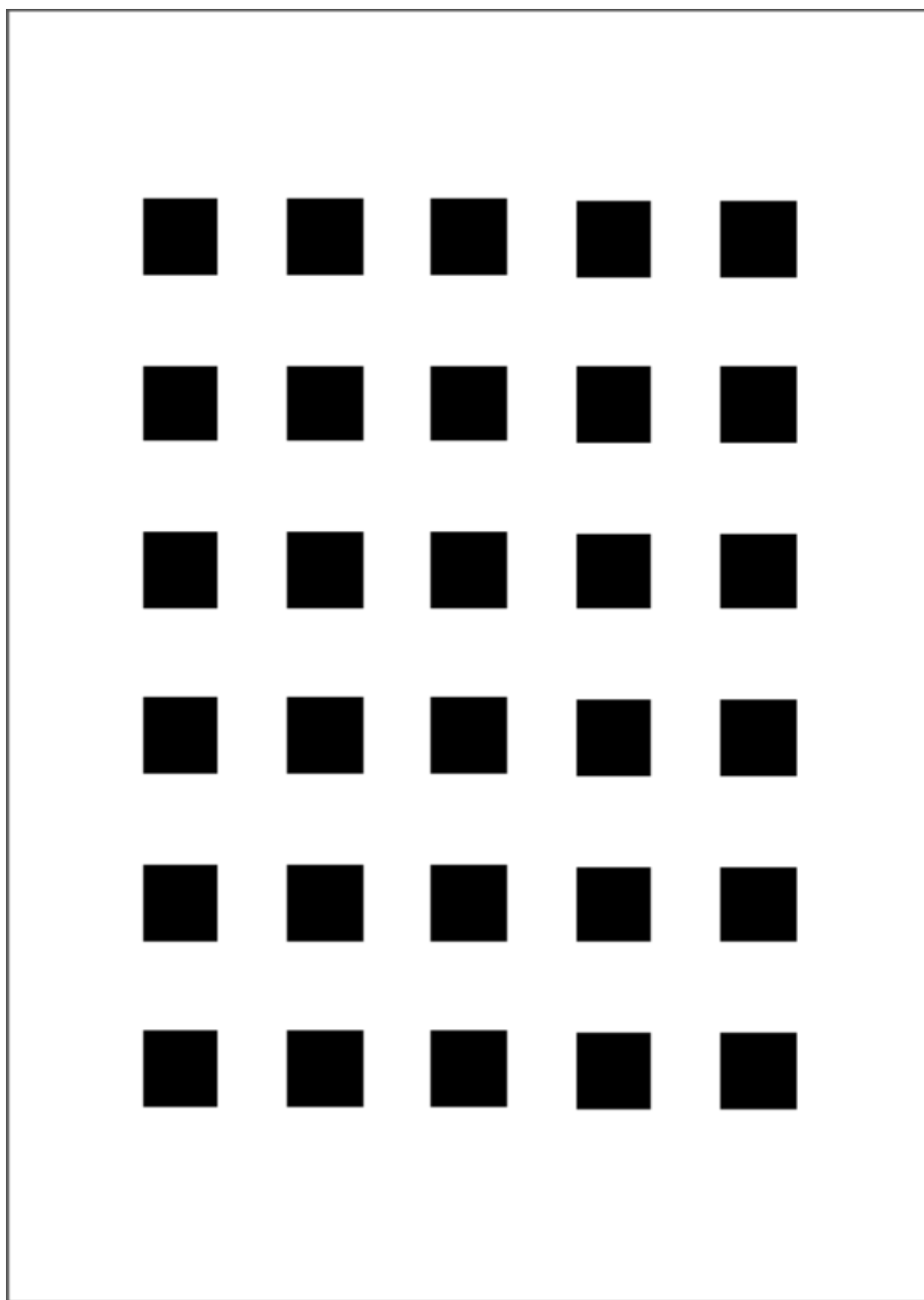
### ***J–V* characterization**

Current density-voltage (*J–V*) curves of the PV devices were measured with a Oriel Sol3A Class AAA Solar Simulator (Newport), with illumination source maintained at 100 mW cm<sup>–2</sup> while using an AM 1.5 filter. Prior to all measurements, the confirmation of total illumination irradiance was conducted using a silicon reference cell, verifying an irradiance of 0.994 or 1.010 for different measurements, which is consistent with the 1 Sun ± 2% error for irradiance measured at the plane of solar cell according to the Standard Testing Conditions. The as-fabricated CIGSe solar cells were masked and only an active area of 0.28 cm<sup>2</sup> was illuminated and measured using two probe system, introducing top contact on active area cell (ZnO:Al top-layer) and indium welded back contact.

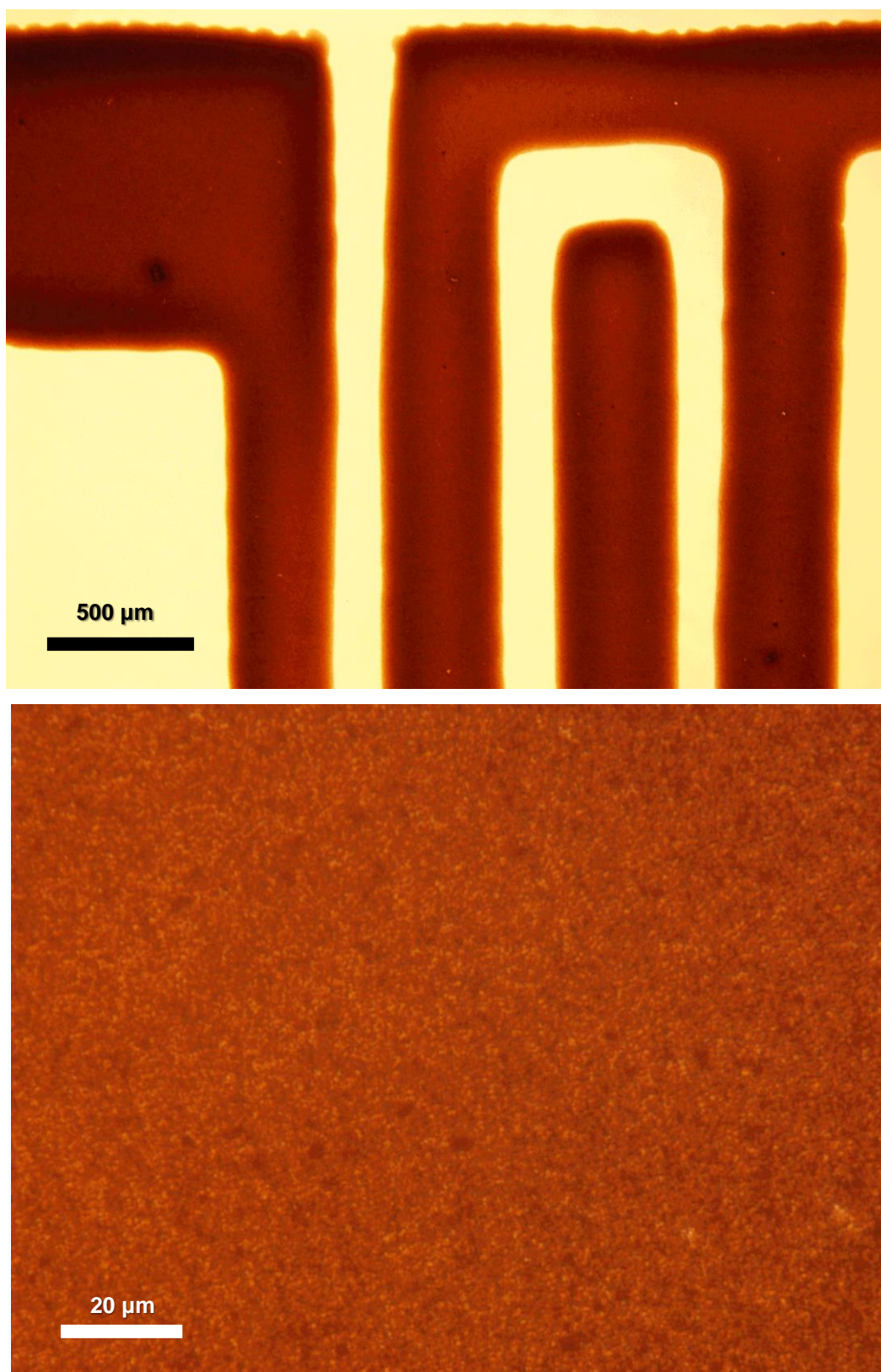
## FIGURES



**Figure S1.** Dynamic viscosity of the as-formulated oxide ink suggesting a non-Newtonian or thixotropic characteristic behavior of the ink.

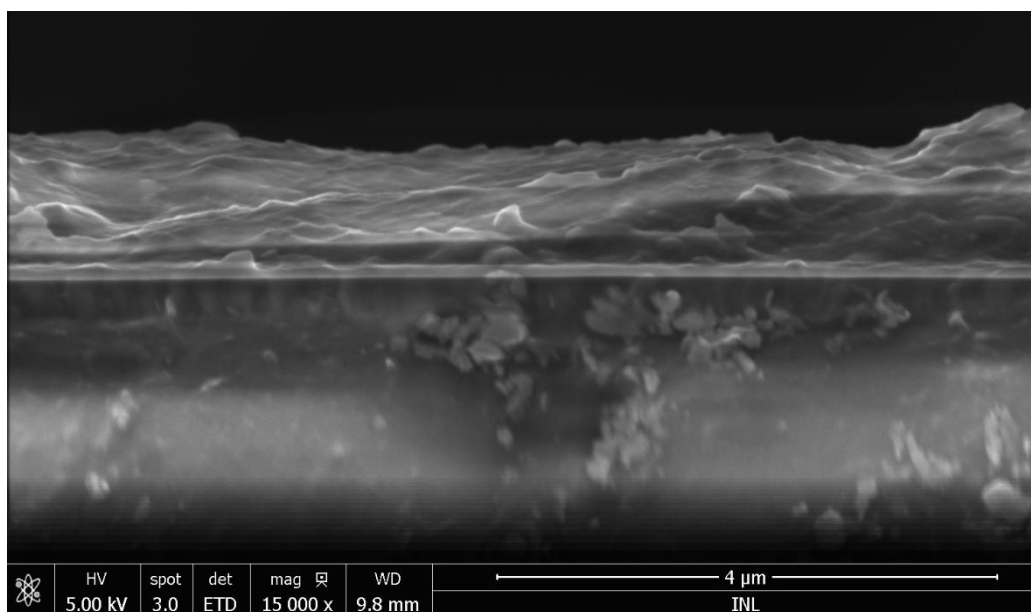


**Figure S2.** Layout of mesh size ( $50 \times 70 \text{ cm}^2$ ) with imprinted photolith of square dimensions ( $4 \times 4 \text{ cm}^2$ ) used to screen print oxides' ink for deriving CIGS photoabsorber layer.

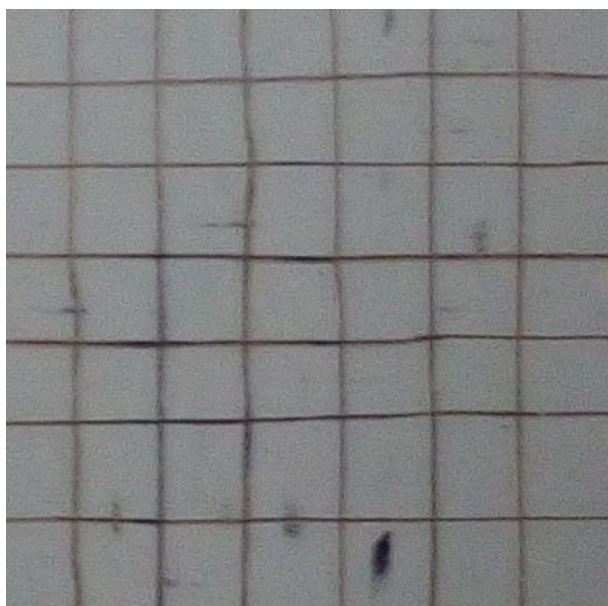


**Figure S3.** Low magnification optical microscopy image (top) of the screen printed oxide ink confirming well-defined printed pattern, together with the high magnification optical microscopy image (bottom) evidencing good dispersion of oxide particles.

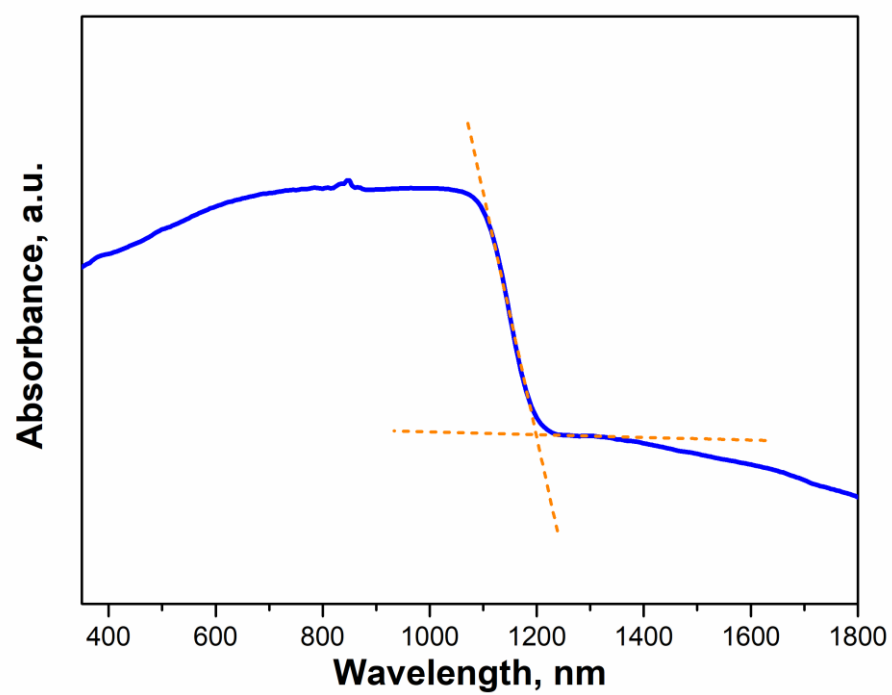




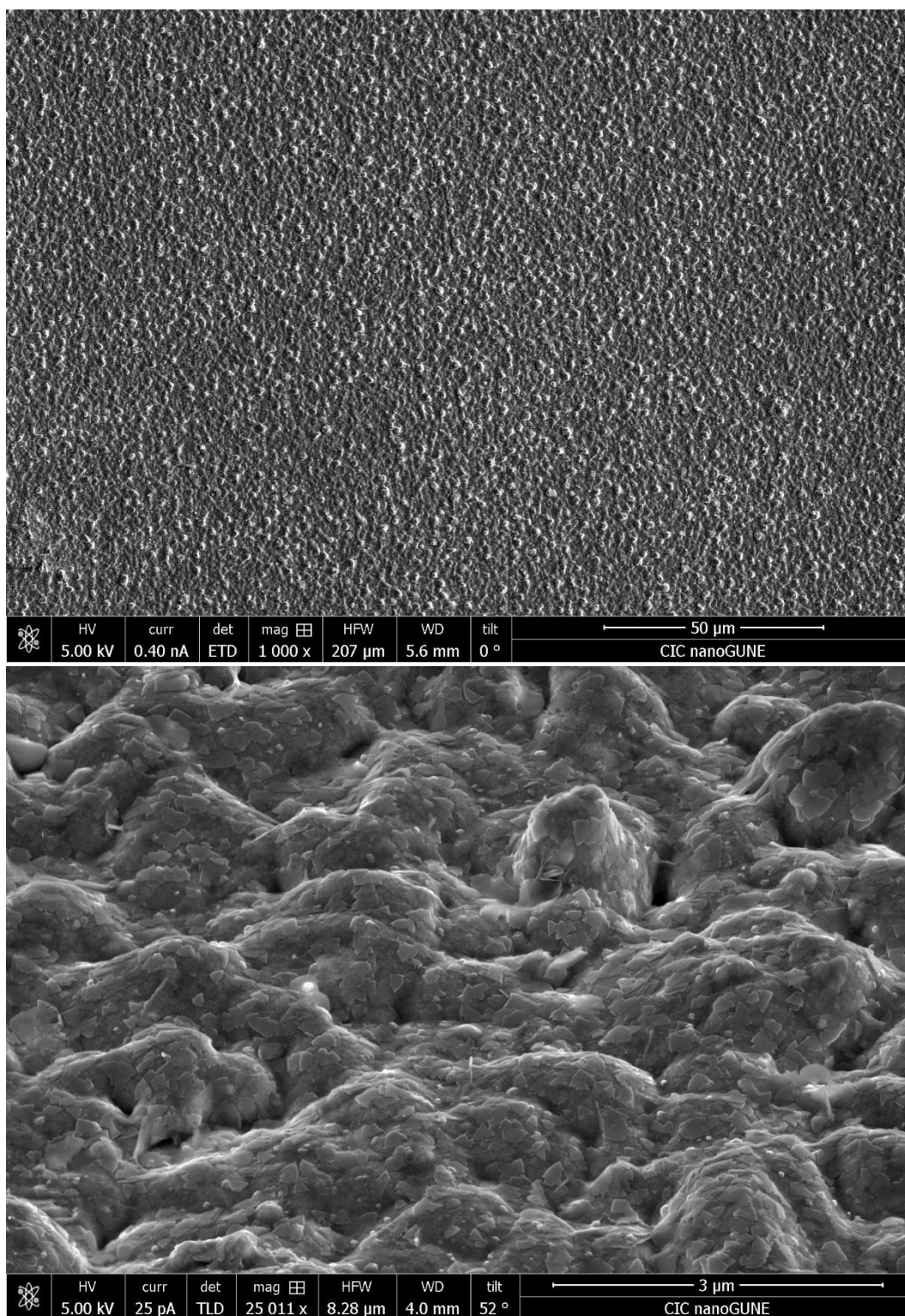
**Figure S4.** Cross-sectional SEM image of one screen printed layer of the as-formulated oxides' ink, indicating the emulsion thickness of approximately 1.3 μm.



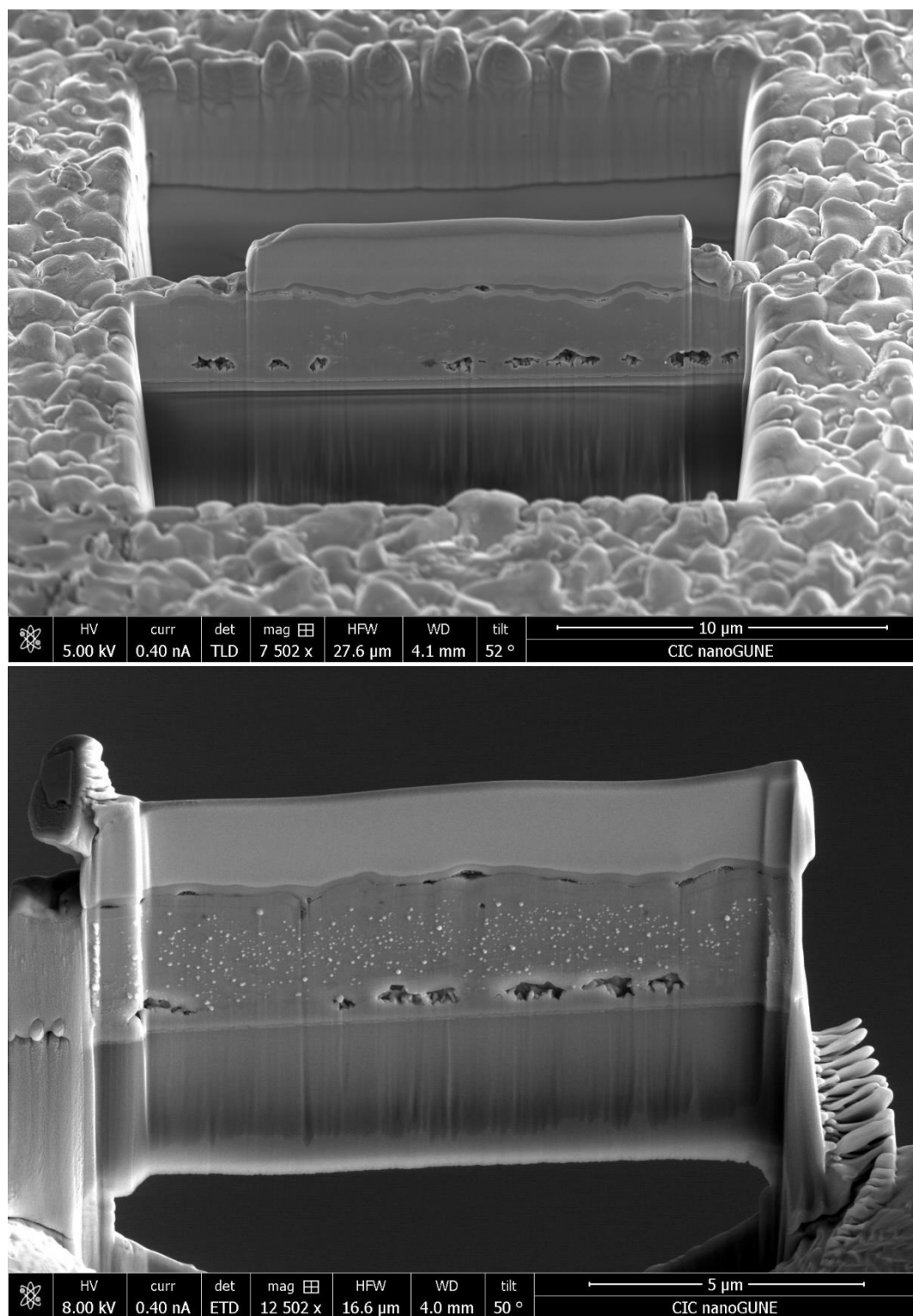
**Figure S5.** Image of the cross-cut area from photoabsorber layer after adhesion test (Standard D3359 – 09 measurement). The adhesion of photoabsorber to FTO substrate was classified to be 4B, since less than 5% of photoabsorber area was removed on six parallel cuts.



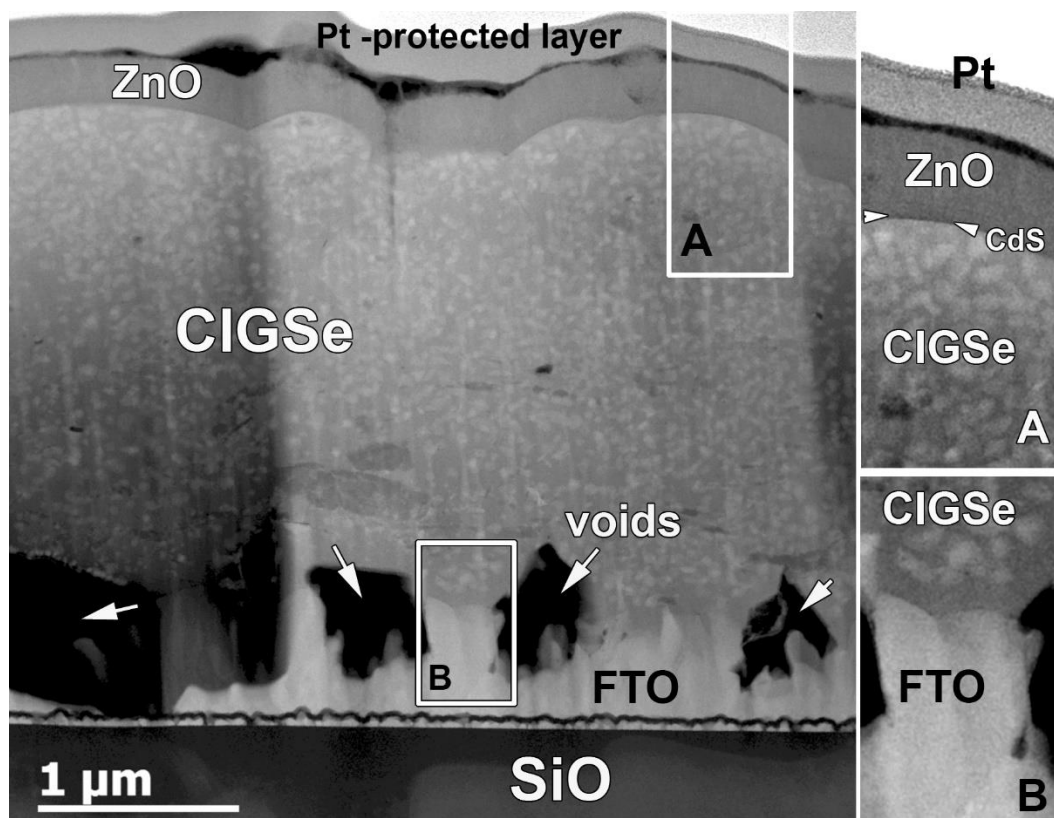
**Figure S6.** UV–Vis–NIR absorption spectrum of the representative CIGSe thin-film.



**Figure S7.** Low (top) and high (bottom) magnification SEM images of the top surface of the representative FTO/CIGSe/CdS/i-ZnO/ZnO:Al PV devices.

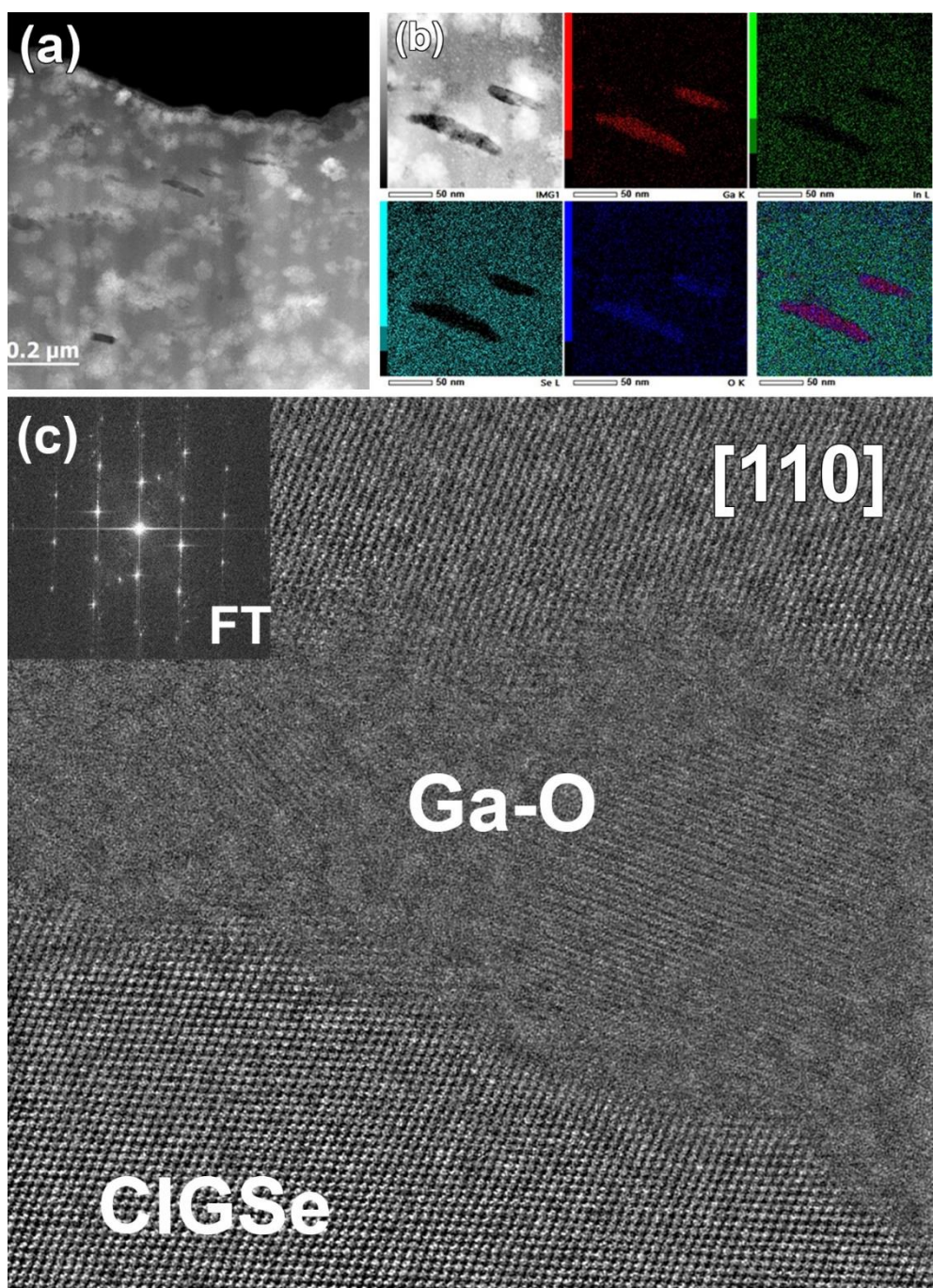


**Figure S8.** SEM images showing the FIB preparation of the lamella of the representative FTO/CIGSe/CdS/i-ZnO/ZnO:Al solar cell device.

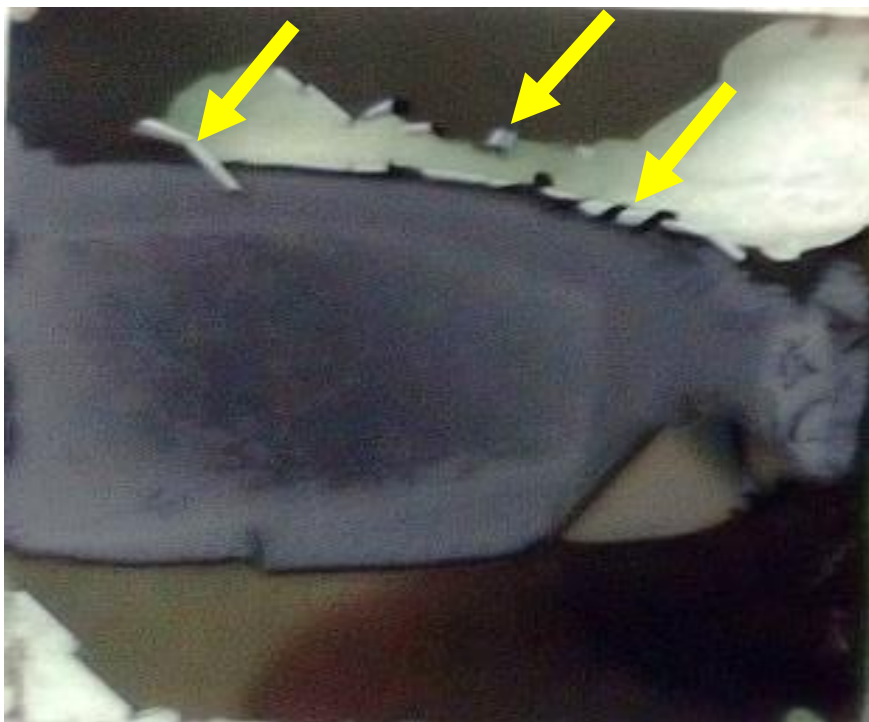


**Figure S9.** STEM image showing layers structure of the representative FTO/CIGSe/CdS/i-ZnO/ZnO:Al solar cell device.





**Figure S10.** (a) Cross-sectional low-magnification HAADF-STEM image of FTO/CIGSe/CdS/i-ZnO/ZnO:Al PV device, showing inclusions of unreacted Ga-O phase. (b) Enlargement of the inclusions, together with the simultaneously collected EDX maps of Ga, In, Se, O elements and their mixture, confirming the existence of Ga-O inclusions within the CIGSe layer. (c) [110] high-resolution transmission electron microscopy (HRTEM) image of the CIGSe from Figure S10b, showing the presence of partially crystalline Ga-O phase.



**Figure S11.** Photograph of CIGSe photoabsorber layer deposited on top of the typical molybdenum/soda-lime glass back contact. Strong peeling of the photoabsorber and back contact molybdenum layers is clearly observed after selenization.



## TABLES

**Table S1.** Precursors, deposition technique, selenization, device structure and the efficiency of the selected high performance CIGSe solar cells reported in the literature.

Precursors	Deposition technique	Selenization	Device	Efficiency	Reference in the MS
<b>Cu and In oxide NPs and Ga oxide mesh size</b>	Screen printing	Burn-off at 400 °C for 30 min → Selenization under 5% H <sub>2</sub> /Ar at 550 °C for 30 min (graphite box)	FTO/Cu(In,Ga)Se <sub>2</sub> /CdS/i-ZnO/ZnO:Al	6.1%	Current study
<b>Cu and In oxide NPs</b>	Screen printing	Burn-off at 400 °C for 1 h → Reduction under 5% H <sub>2</sub> /Ar at 500 °C for 1h → Sulfurization under Ar at 500 °C → Selenization under Ar at 550 °C for 45 min (graphite box)	Mo/CuIn(S,Se) <sub>2</sub> /CdS/i-ZnO/ZnO:Al	2.21%	12
<b>Cu and In oxide NPs</b>	Screen printing	Burn-off at 400 °C for 1 h → Reduction under 5% H <sub>2</sub> /Ar at 500 °C for 1 h → Selenization under Ar at 550 °C (graphite box)	Mo/CuInSe <sub>2</sub> /CdS/i-ZnO/ZnO:Al	2.4%	10
<b>Cu, In, and Ga oxide NPs</b>	Doctor blade	Reduction under H <sub>2</sub> /N <sub>2</sub> at 500–550 °C → Selenization under H <sub>2</sub> Se/N <sub>2</sub> at 420–450 °C	Mo/Cu(In,Ga)Se <sub>2</sub> /CdS/ZnO	13.6%	8
<b>CuInS<sub>2</sub> NPs</b>	Doctor blade	Hotplate thermal treatment at 150 °C and at 250 °C for 10 min	FTO/TiO <sub>2</sub> /In <sub>2</sub> S <sub>3</sub> /Zn-doped CuInS <sub>2</sub> /C	7.24%	25
<b>Cu, In, and Ga metallic NPs</b>	Doctor blade	Selenization under N <sub>2</sub> at 570 °C for 1 h (20 mbar)	Mo/Cu(In,Ga)Se <sub>2</sub> /CdS/i-ZnO/ZnO:Al	8.1%	5
<b>Cu(In,Ga)S<sub>2</sub> NPs</b>	Spin coating	Annealing under N <sub>2</sub> → Selenization under N <sub>2</sub> (graphite box)	Mo/CuInGa(S,Se) <sub>2</sub> /CdS/i-ZnO/ITO	13.8%	6
<b>Cu(In,Ga)Se<sub>2</sub> NPs</b>	Doctor blade	Dry on hotplate at 350 °C → Selenization under Ar at 500 °C for 20 min	Mo/Cu(In,Ga)(S,Se) <sub>2</sub> /CdS/i-ZnO/ITO	15.0%	26
<b>CuInSe<sub>2</sub> powder</b>	Screen printing	Annealing under N <sub>2</sub> at 600 °C for 15 min (rapid thermal annealing)	Mo/CuInSe <sub>2</sub> /In <sub>2</sub> S <sub>3</sub> /TiO <sub>2</sub> /FTO	0.65%	19
<b>Cu<sub>2</sub>S, In<sub>2</sub>S<sub>3</sub>, Ga, Se</b>	Spray deposition	Selenization under N <sub>2</sub> (53 kPa) for 50 min at ramping of 35 °C/min (graphite box)	Mo/Cu(In,Ga)Se <sub>2</sub> /CdS/i-ZnO/ZnO:Al	9.8%	30
<b>Metal chlorides, thiourea, and DMSO</b>	Spin coating	Annealed on hotplate at 250 °C for 2 min (inside glove box) → Selenization under Ar at 540 °C for 20 min	Mo/CuIn(S,Se) <sub>2</sub> /CdS/i-ZnO/ITO	13.0%	27

<b>Metal nitrates</b>	Doctor blade	Dry on hotplate under N <sub>2</sub> at 140 °C for 3–4 min and after heated until 200 °C → Selenization under N <sub>2</sub> at 600 °C for 7 min	Mo/Cu(In,Ga)Se <sub>2</sub> /CdS/ i-ZnO/ZnO:Al	13.3%	28
<b>Metal chlorides, thiourea, and DMSO</b>	Spin coating	Annealed on hotplate at 250 °C for 2 min (inside glove box) → Selenization under Ar at 540 °C for 20 min	Mo/ Cu(In,Ga)(S,Se) <sub>2</sub> /CdS/ i-ZnO/ITO	14.7%	27
<b>Cu<sub>2</sub>S, In<sub>2</sub>Se<sub>3</sub> (with hydrazine solution)</b>	Spin coating	Annealing on hotplate at 540 °C (inside glove box)	Mo/Cu(In,Ga)(S,Se) <sub>2</sub> /CdS/ i-ZnO/ITO	15.2%	29
<b>Cu, In, and Ga metal stacks</b>	DC sputtering	Selenization under H <sub>2</sub> Se followed by sulfurization under H <sub>2</sub> S	Mo/Cu(In,Ga)(Se,S) <sub>2</sub> / (Zn,Mg)O/Zn(O,S,OH)/ i-ZnO/ZnO:B	23.35%	4

**Table S2.** Average and standard deviation of open circuit voltage ( $V_{oc}$ ), current density ( $J_{sc}$ ), fill factor ( $FF$ ) and efficiency of ten fabricated cells.

<b>Sample</b>	<b><math>V_{oc}</math> (V)</b>	<b><math>J_{sc}</math> (mA cm<sup>-2</sup>)</b>	<b><math>FF</math></b>	<b>Efficiency (%)</b>
<b>1</b>	0.23	32.9	31.9	1.8
<b>2</b>	0.22	27.5	28.9	1.7
<b>3</b>	0.27	18.9	35.2	1.9
<b>4</b>	0.25	20.5	33.4	1.8
<b>5</b>	0.30	17.3	27.2	1.5
<b>6</b>	0.31	21.2	34.4	2.2
<b>7</b>	0.31	29.6	33.0	3.0
<b>8</b>	0.30	32.8	32.4	3.2
<b>9</b>	0.34	35.2	46.4	5.5
<b>10</b>	0.31	36.8	53.8	6.1
<b>Average</b>	0.28	27.3	35.7	2.9
<b>Standard Deviation</b>	0.04	6.9	7.8	1.6