Electronic Supplementary Information

Solution-Deposited Pure Selenide CIGSe Solar Cells from Elemental Cu, In, Ga, and Se†

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Table S1. Data of hydrazine and 1,2-ethylenediamine.

Solvent	Boiling point (°C)	Melting point (°C)	Vapor pressure (kPa)	Surface tension (mN/m)
Hydrazine	113.5	1.4	1.92	66.67
1,2-ethylenediamine	117.26	11.3	1.43	40.77

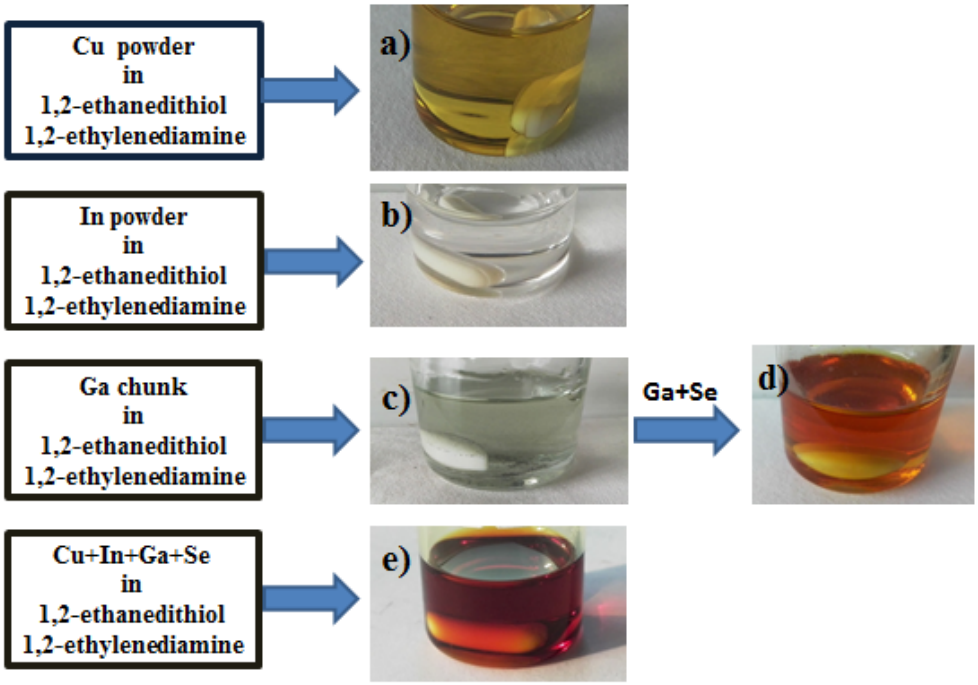

Fig. S1 Photographs of (a) elemental Cu solution; (b) elemental In solution; (c) elemental Ga solution; (d) elemental Ga and Se solution; (e) elemental Cu, In, Ga and Se solution.

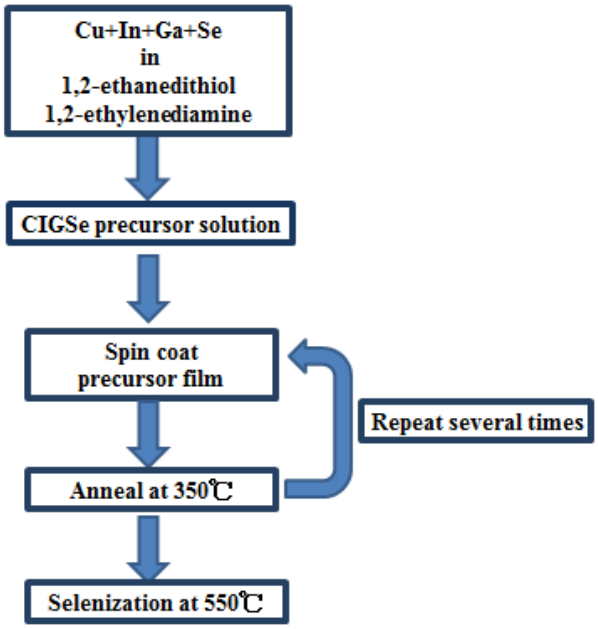

Fig. S2 Schematic diagram of the solution preparation and film deposition process of the CIGSe absorber layers.

Table S2. Chemical composition of the as-prepared and selenized CIGSe thin film.

	Cu	In	Ga	Se
As-prepared film	13.9	12.6	5.2	25.2
Selenized film	14.98	13.87	5.6	52.4

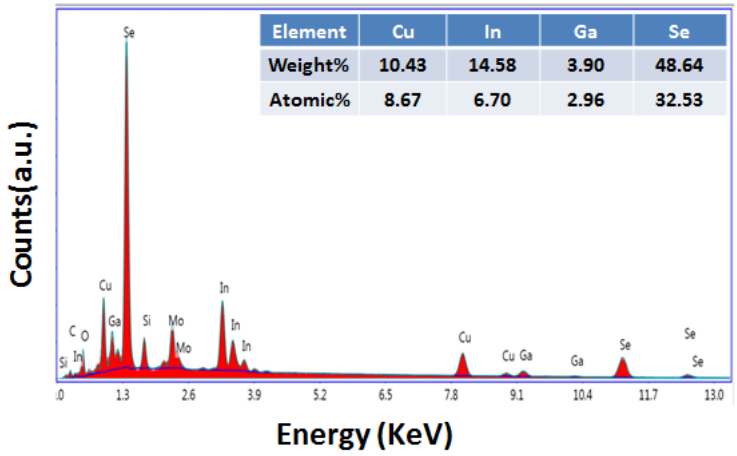

Fig. S3 EDS spectra of the fine-grained bottom layer.

Table S3. Detail photovoltaic parameters for 9 solar cell devices.

	PCE (%)	**V_{oc} (mV)**	**J_{sc} (mA/cm²)**	**FF (%)**
1	9.50	528	26.64	67.48
2	9.00	531	25.01	67.94
3	8.70	524	24.58	67.72
4	8.67	524	24.69	66.96
5	8.66	521	24.60	67.55
6	8.40	521	25.07	64.55
8	8.30	523	25.10	63.74
9	7.94	520	24.77	61.63
average	**8.65**	**524**	**25.06**	**65.95**

Experimental Section

Formation of CIGSe Precursor Solution: First, Cu (0.0699 g, 1.10 mmol), In (0.0960 g, 0.83 mmol), Ga (0.0250 g, 0.35 mmol), Se (0.18125 g, 2.29 mmol), 5 mL of 1,2-ethylenediamine and 0.5 mL of 1,2-ethanedithiol were mixed added into a argon filled round bottom flask. Then the solution was stirred at 60 ^{o}C for several hours until all substance dissolved. The solution stays stable for weeks in a closed environment.

Fabrication CIGSe thin film and CIGSe device: First, 600 nm Mo forming the back contact of the device sputtered on a (20×20×1.0 mm^3) soda-lime glass. Then the prepared CIGSe precursor was spin-coated at 3000 rmp for 30 s onto the molybdenum-coated glass. The film was then immediately dried at 350 ^{o}C on a preheated hot plate for 1 min. Then repeated the spin-coating/sintering step for several times until the thickness of the film reached 1~2 μm. The CIGSe absorber film was deposited in an argon-filled glove-box with water and oxygen levels maintained below 1 ppm. Next, the as-deposed CIGSe thin film was selenized in a graphite box containing 0.3 g of Se at 550 °C for 20 min in the tubular furnace. And next 70 nm CdS layer was deposited using a chemical bath approach for 12 min. Followed about 50 nm ZnO and 280 nm ITO were sputtered onto the glass/ Mo/CIGSe/CdS device. Finally, on the top of the device about 1~2 μm Al grid electrode was made though thermal evaporation. At last the conventional glass/Mo/CIGSe/CdS/ZnO/ITO/Al device was completed. The CIGSe device was made without antireflection layer. Each device, with an active area of 0.19 cm^2, was separated from neighboring devices by mechanical scribing.

Characterization: Thermogravimetric analysis (TGA) scans were performed using the TG/DTA 6200 thermogravimetric analyzer, SII, Inc, in the nitrogen atmosphere up to 800 ^{o}C. X-ray data were collected using a Philips X' PertPro with Cu Kα radiation. And SEM of the samples' were taken by using field emission scanning electron microscope of JSM-5600LV at 20 KV. The composition of film was characterized by scanning electronic microscope (SEM) equipped with an Energy Dispersive X-Ray Spectroscopy (EDX, Nano SEM 45050/EDX). J-V curve was measurement using a Keithley 2400 source meter under the standard AM1.5 illumination (100 $mW \cdot cm^{-2}$). The external quantum efficiency (EQE) spectrum was measured by a Zolix SCS100QE system.