Supplementary Information

8.2% Efficient Solution-Processed $CuInSe_2$ Solar Cell Based on Multiphase $CuInSe_2$ Nanoparticles

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Experimental details

Raw Materials: All chemicals were used as received without further purification. Ethylene glycol (EG, $C_2H_6O_2$, 99.5+%,) and polyethylene glycol 400 (PEG, $C_{2n+2}H_{4n+6}O_{n+2}$, n= 7~9, extra pure) were obtained from Junsei. Copper acetate monohydrate ($Cu(CO_2CH_3)_2 \cdot H_2O$, 98%,), indium acetate ($In(CO_2CH_3)_3$, 99.99%), selenium powder (Se, 99.99%), and polyvinylpyrrolidone (PVP, $(C_6H_9NO)_n$, M.W: 55,000) were purchased from Aldrich. Ethyl alcohol (C_2H_6O, 99.5+%) was obtained from Burdick & Jackson.

Synthesis of multiphase stoichiometric CISe Nanoparticles: In a dry microwave vessel, a 0.6 g (2.9 mmol) of $Cu(CO_2CH_3)_2 \cdot H_2O$, 1.43 g (4.9 mmol) of $In(CO_2CH_3)_3$ and 0.75 g (9.8 mmol) of elemental selenium were dissolved in 20 g of polyethylene glycol 400. The reaction mixture was irradiated with a microwave to reach a reaction temperature of 280 ^{o}C and the reaction temperature was maintained for 25 min. Upon completion of synthesis reaction, the reaction solution was cooled to room temperature and the nanoparticles were separated by centrifugation, collected, and washed three times with ethyl alcohol. Then, the resulting nanoparticles were dried under vacuum overnight at 40^{o}C to provide black powders.

Ink Preparation and Colloidal Film Deposition: For preparing the ink, multiphase CISe nano particles with the solid content of 20 wt% were added in a mixed solvent with 0.76 g of ethyl alcohol and 1.68 g of EG, and PVP was added as an organic additive to form a crack free layer. The prepared ink was mixed by a ball milling to break softly agglomerated nanoparticles and was then deposited on Mo-coated soda lime glass substrate. The resulting thin film was dried at 80 ^oC in vacuum oven. Selenization was carried out in a vacuum evaporator equipped with Knudsen-type effusion cell. The chamber was evacuated to base pressure of 5×10^{-6} torr, and the elemental Se was evaporated. The flux of Se vapor was adjusted by the effusion cell temperature and Se was effused at 180 ^oC. The samples were selenized at various temperatures from 300 to 530 ^oC for 30 min on a hot plate located in a chamber.

Solar Cell Fabrication and Device Performance Measurement: Solar cells were fabricated based on Mo/CISe/CdS/*i*-ZnO/*n*-ZnO/Al device architecture. A 60 nm thick CdS buffer layer was deposited on CISe layer by chemical bath deposition, and 50 nm thick *i*-ZnO and 500 nm thick Al-doped *n*-ZnO layer were deposited by RF magnetron sputtering on top of CdS layer. 500 nm thick Al grid electrodes were deposited as a current collector using a thermal evaporator. The active area of device was 0.44 cm^2. Device performances including the conversion efficiency and external quantum efficiency were characterized by using a class AAA solar simulator (WXS-155S-L2, WACOM, Japan) and incident photon conversion efficiency measurement unit (PV measurement, Inc., USA), respectively.

Characterization: The morphological property, crystalline phase, and composition of multiphase CISe nanoparticles were analyzed using a field emission scanning electron microscopy (FESEM, JSM-6700F, JEOL), X-ray diffraction (XRD, D/Max 2200V/PC, Rigaku), and inductively coupled plasma mass spectrometry (ICPMS, Thermo Scientific iCAP 6500), respectively. The thermal behaviors of organic additive, PVP, was monitored using a thermal gravimetric analyses (SDT2960, TA Instruments) and the surface image of CISe absorber layer was observed by an optical microscopy (LEITZ ERGO PLAN, Leica). The composition variation and phase transformation of CISe films depending on the selenization temperature were analyzed by an energy dispersive X-ray spectroscopy (EDS, Quantax 200, Bruker) and XRD measurement, respectively. The composition profile in CISe layer selenized at 530 ^{o}C under Se atmosphere was characterized using a scanning ion mass spectrometry (SIMS, IMS 7f, CAMECA).

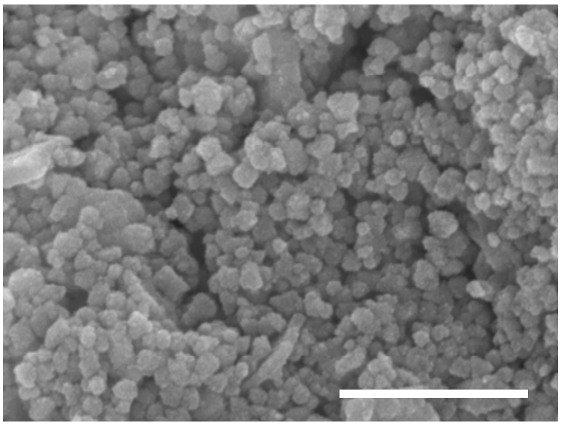

Figure S1. SEM image of as-synthesized multiphase stoichiometric CISe nanoparticles. The scale bar is 500 nm.

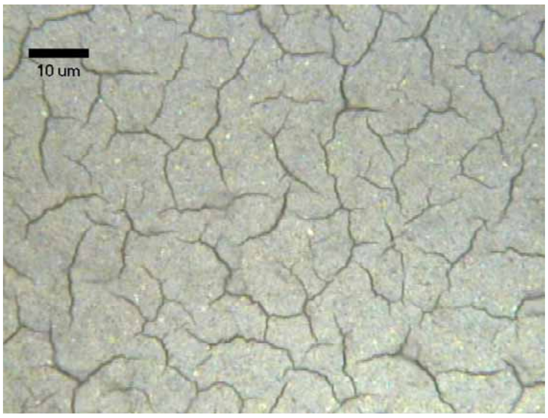

Figure S2. Top-view optical microscope (OM) image for the as-dried film prepared from the PVP-free CISe ink.

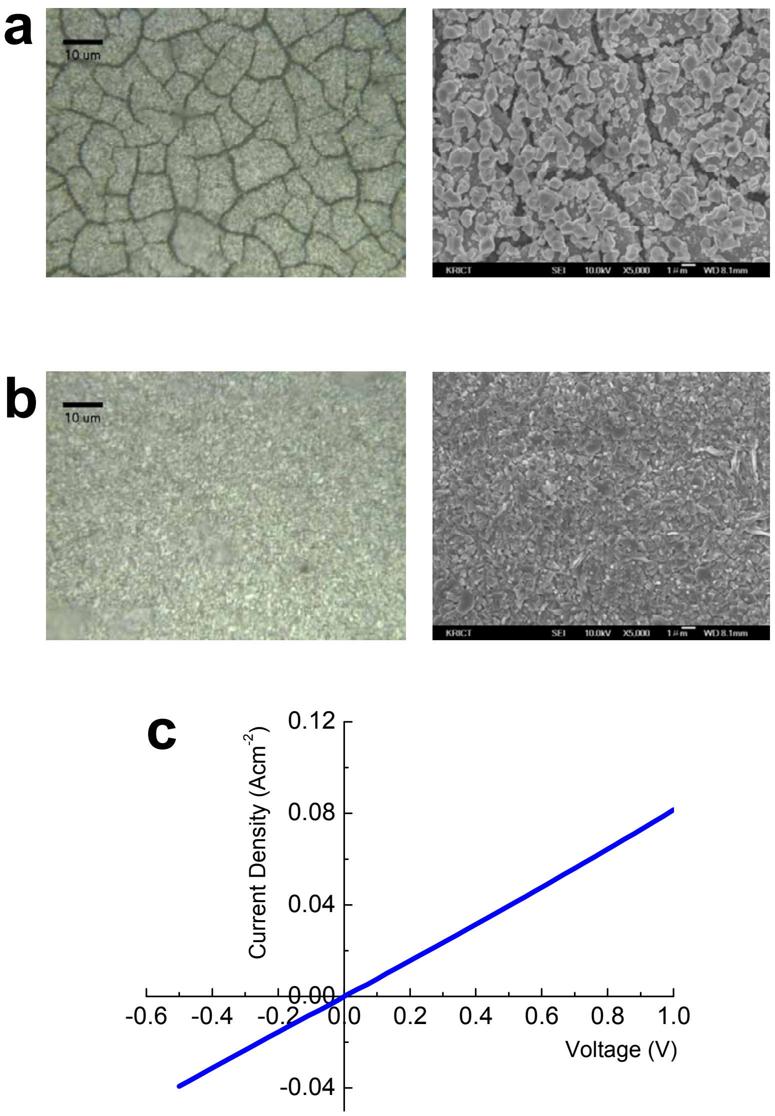

Figure S3. Top-view OM and SEM images for the CISe absorber layers prepared from (a) PVP-free CISe ink and (b) PVP-added CISe ink after selenization at 530 °C. (c) Dark *I-V* characteristic of the photovoltaic device employing CISe absorber layer prepared from PVP-free CISe ink. The CISe layers were selenized at 530 °C.

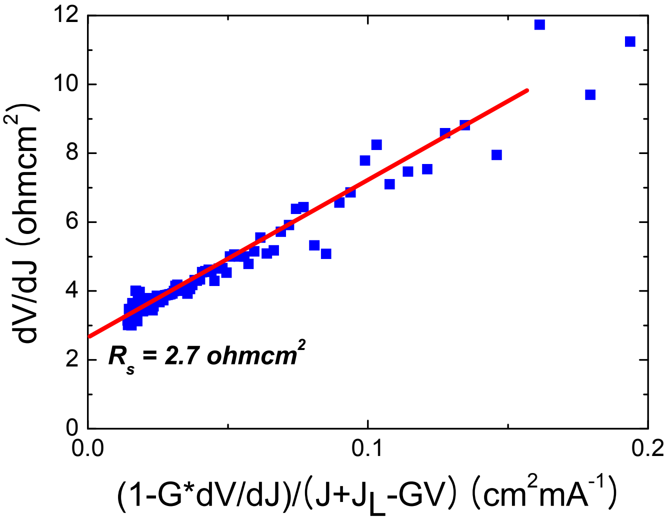

Figure S4. dV/dJ vs. (J+J$_L$)$^{-1}$ curve for calculating the series resistance of the 8.2% efficient CISe solar cell.

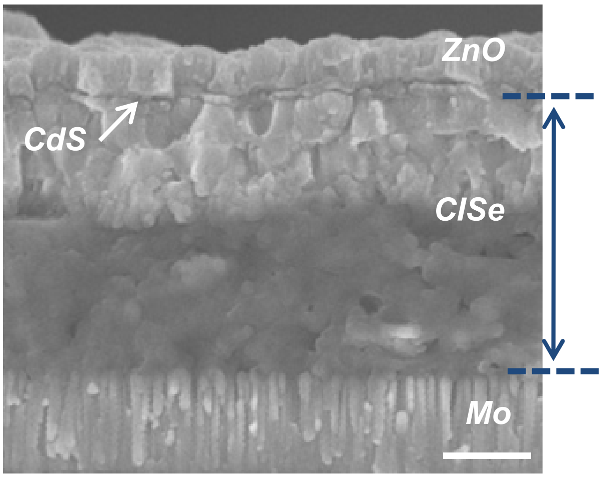

Figure S5. Cross-sectional SEM image for the 8.2% efficient CISe solar cell. The scale bar is 1 μm in SEM image.

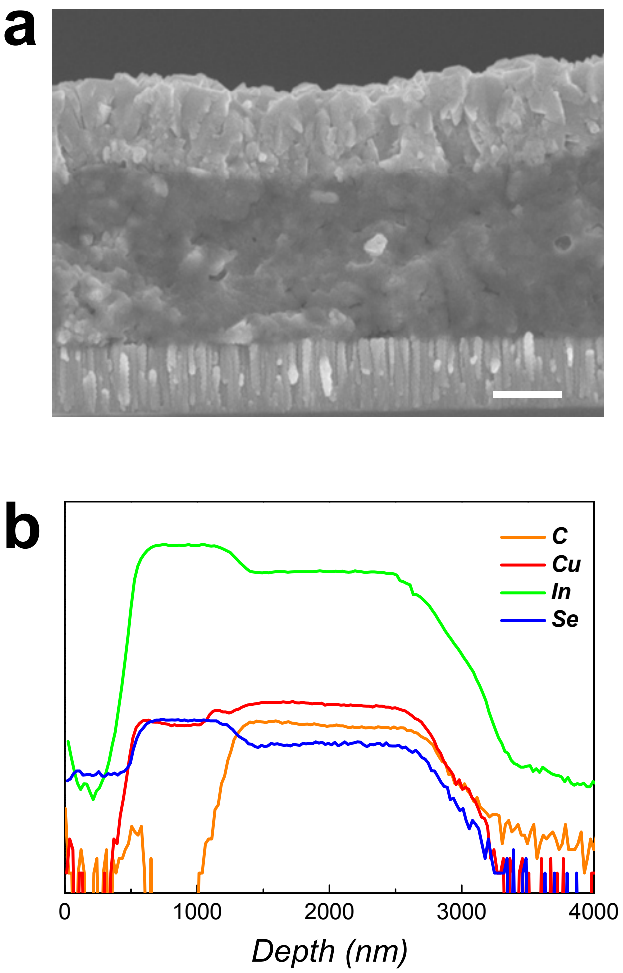

Figure S6. (a) Cross-sectional SEM image and (b) composition profile, measured by a scanning ion mass spectrometry (SIMS) analysis, for the solution-processed CISe absorber layer selenized at 530 °C. The scale bar is 1 μm in SEM image.

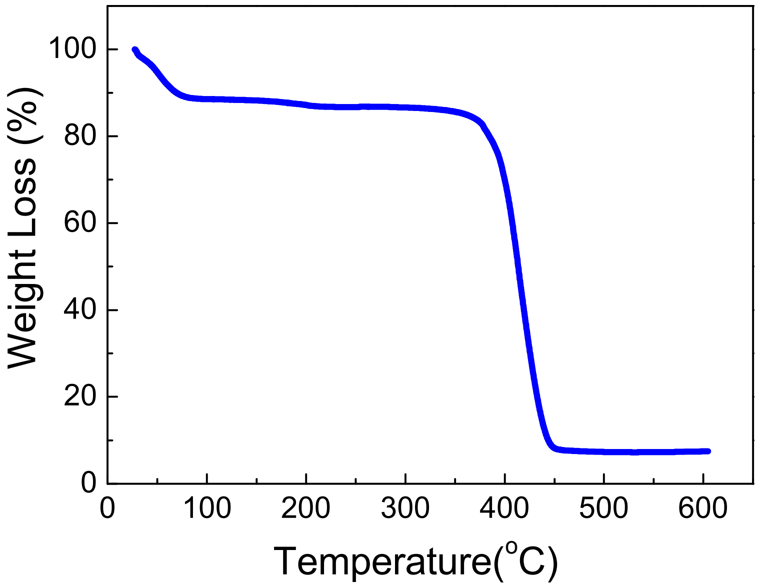

Figure S7. TGA result for PVP under an oxygen free atmosphere (nitrogen). The heating rate was 5 °C/min. The weight loss below 90 °C is due to the evaporation of absorbed water and the weight loss above 100 °C is attributed to the thermal decomposition of PVP.