Electronic Supplementary Information

High-density Cu–In intermetallic nanocrystal films: towards printable $CuInSe_2$ solar cells with high efficiencies

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Synthesis of Cu−In alloy nanoparticles and their characterization

Cu−In intermetallic nanoparticles were synthesized via chemical reduction method using metal chlorides as metal sources and sodium borohydride as a reducing agent.[21] First, a precursor solution was prepared by dissolving 0.747 g of copper (II) chloride and 1.536 g of indium (III) chloride in 50 mL of tetraethylene glycol (TEG). A reducing solution was prepared by dissolving 2.838 g of sodium borohydride in 50 mL of TEG. Then, the precursor solution was dropped at a rate of 1 mL min^{-1} into the reducing solution that was kept at 0 °C in an ice bath. The black particles were precipitated during mixing the solutions. On completion of reaction, the precipitates were collected from the solution by vacuum filtration, washed several times with deionized water, ethanol, and methanol, and dried in an oven at 60 °C for 6h. The entire synthesis process was carried out under ambient conditions and was found to provide high product yield over 95%. The above synthetic process was repeated for four times to obtain a sufficient amount of the powder. The resulting nanoparticles were

analyzed to determine the crystalline phase, morphology, and chemical composition with XRD, SEM, TEM, and EDS. The synthesized nanoparticles were found to consist of CuIn of 40−100 nm diameter, Cu_2In of *ca.* 15 nm diameter, and elemental In likely in an amorphous state (Fig. S1). The overall composition was in good agreement with the initial mixing ratio, *i.e.*, [Cu]/[In] = 0.80 ± 0.03.

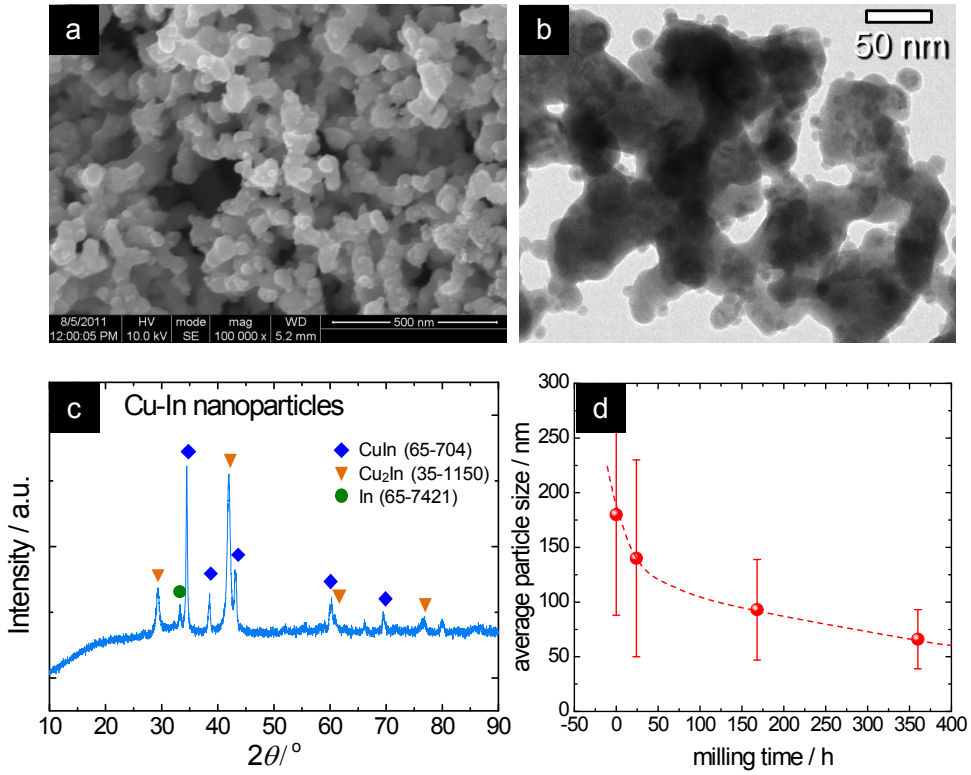

Fig. S1 (a) SEM image (b) TEM image, (c) XRD pattern of as-synthesized Cu−In intermetallic nanoparticles, and (d) average particle size of Cu−In intermetallic nanoparticles as a function of milling time. The dashed curve in (d) is for visual guidance.

Characterization of $CuInSe_2$ thin films

The crystallographic features of the $CuInSe_2$ films were characterized by X-ray diffraction (XRD; Bruker D8 Advance, Rigaku, D/max 2500) with Cu Kα radiation (λ = 1.541 Å). Raman spectra of the $CuInSe_2$ films were measured with a Renishaw inVia spectrometer equipped with a 4 mW Nd:YAG laser beam with a wavelength of 532 nm. The excitation beam was focused on a spot diameter of *ca.* 1 μm through a 50× objective microscope. Under this condition, no sample damage or thermal effects were clearly recognized. The EDS

spectra were collected from at least five randomly selected areas to make use of their mean values.

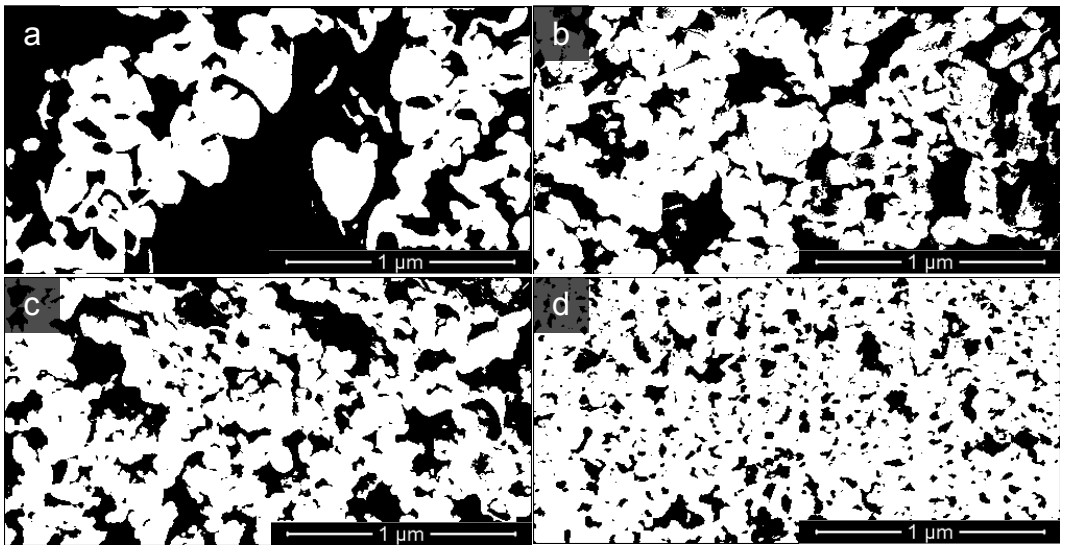

Fig. S2 Binary images of FIB-milled cross sections of the as-coated Cu−In alloy nanoparticle layers prepared without milling (a) and with milling for 24 h (b), 168 h (c), and 360 h (d), converted using the specified threshold level with an image analyzer to estimate the porosity of the nanoparticle layers. Note that the closed pores are depicted in black.

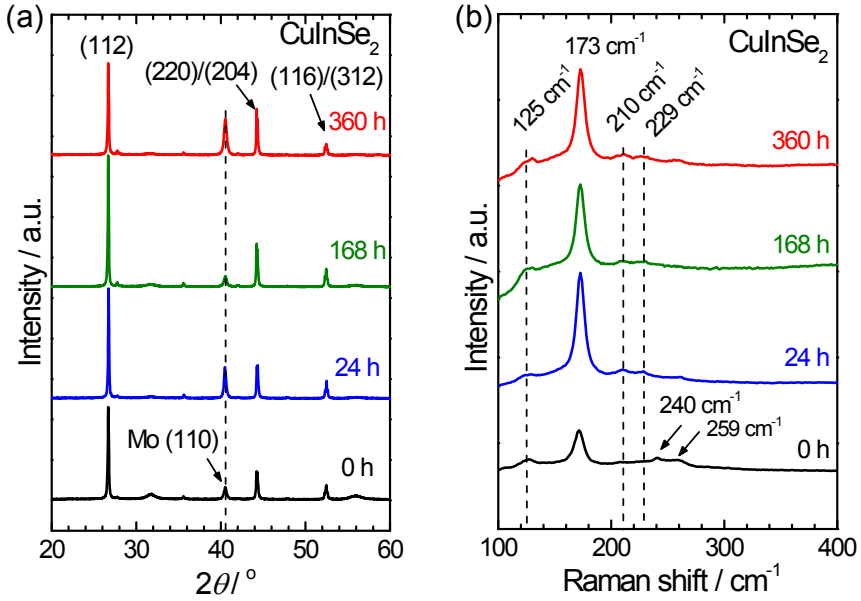

Fig. S3 XRD patterns (a) and Raman spectra (b) of $CuInSe_2$ thin films selenized at 500 °C for 30 min from Cu−In nanoparticle layers prepared with inks milled for various durations. Note that an intense peak at around 173 cm^{-1} (A_1 mode) and weak peaks at around 210 cm^{-1} and

229 cm^{-1} (B_2/E modes) are assigned to $CuInSe_2$ in chalcopyrite structure, while the weak peak at around 240 cm^{-1} corresponds to the $MoSe_2$ layer. The small peak at 259 cm^{-1} indicates that a small amount of CuSe phase remained in the sample A.

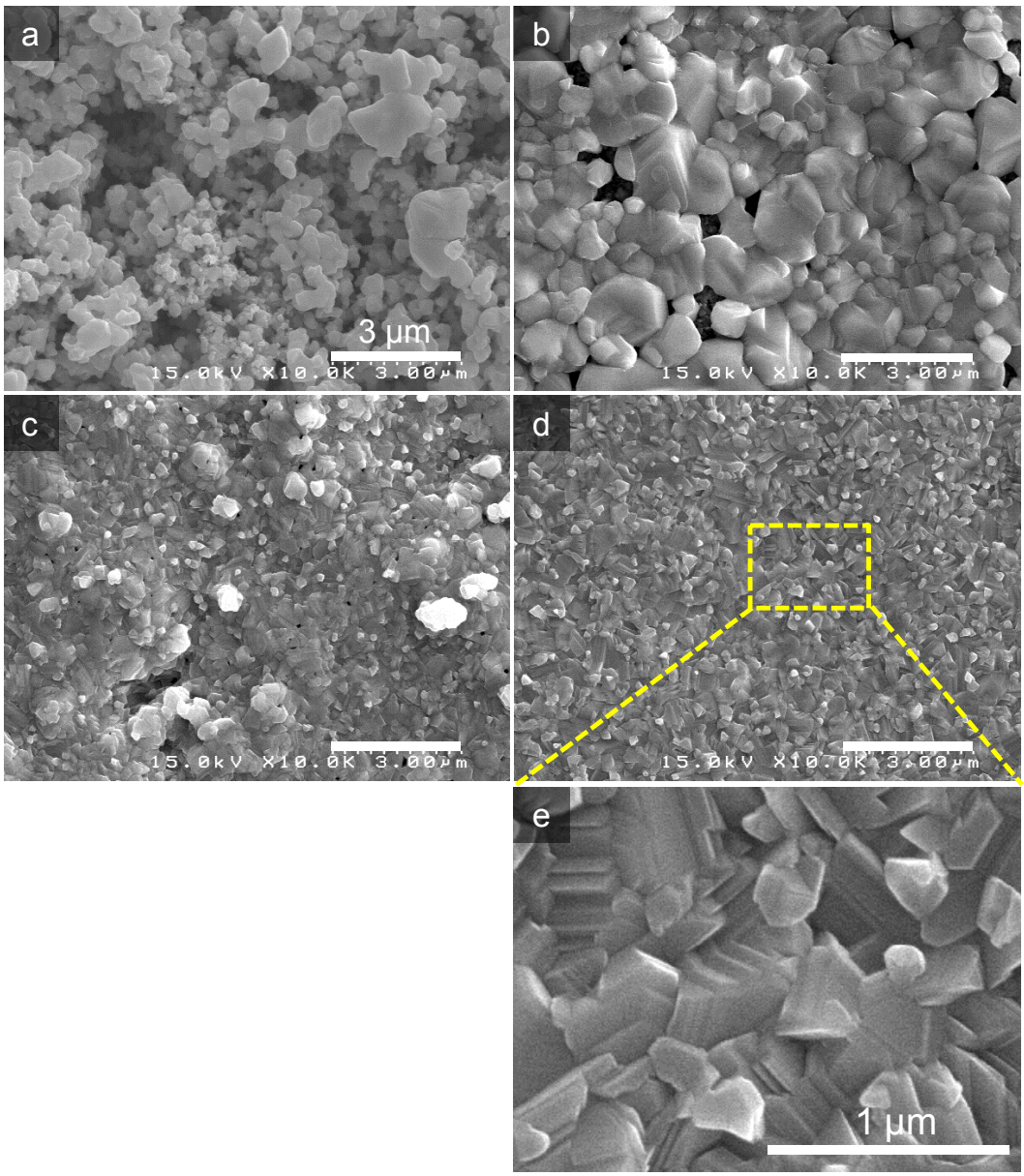

Fig. S4 Surface morphologies of the selenized films from the Cu−In alloy nanoparticles prepared without milling (a) and with milling for 24 h (b), 168 h (c), and 360 h (d) over a larger area including those shown in Fig. 3(a−d). The grain structure of Sample D (milled for 360 h) is more clearly seen in part (e).

Table S1 Compositions of $CuInSe_2$ thin films selenized at 500 °C for 30 min using Cu–In nanoparticles films prepared with milling for various times

Milling time / h	[Cu] / [In]	[Se] / ([Cu] + [In])	[O] /%
0 h	0.81 ± 0.04	1.16 ± 0.04	8.2 ± 1.1
24 h	0.82 ± 0.02	1.05 ± 0.03	5.7 ± 1.2
168 h	0.84 ± 0.02	1.00 ± 0.02	3.5 ± 1.3
360 h	0.86 ± 0.02	1.01 ± 0.02	0 ± 0

Characterization of $CuInSe_2$ solar cells

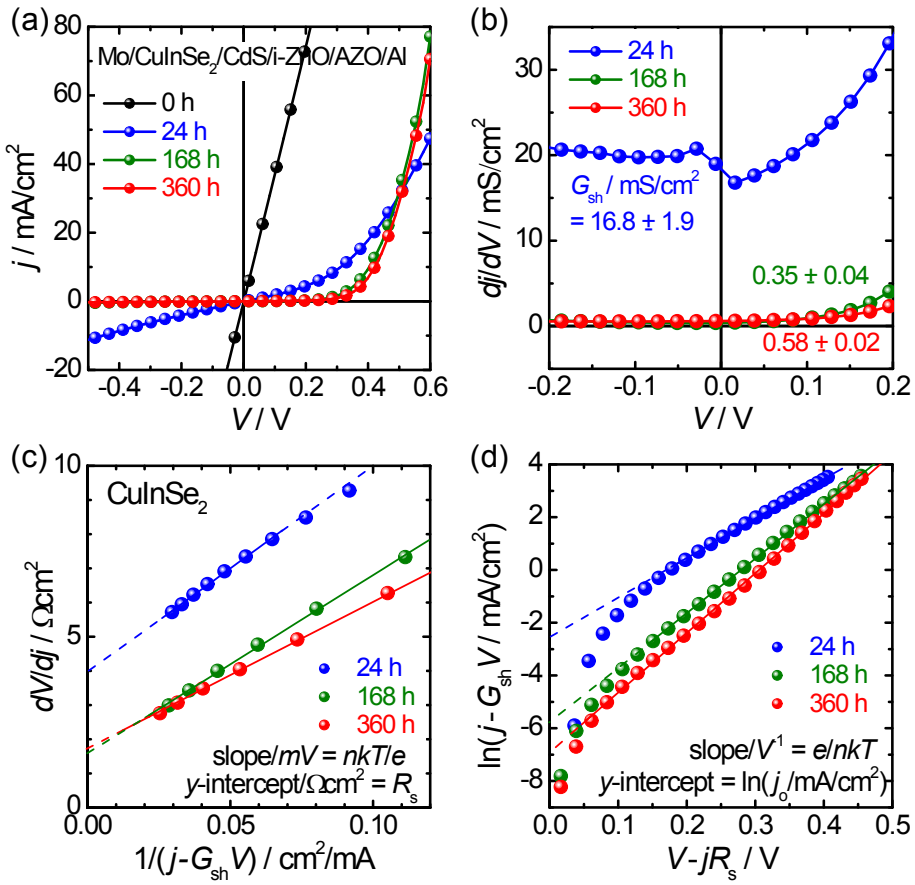

Fig. S5 A diode analysis on CISe solar cells prepared with Cu−In alloy nanocrystal inks milled for various times: (a) j–V characteristics in the dark, (b) a plot of dj/dV *vs.* V, where G_{sh} was extracted from the plateau value assuming that a linear shunt current predominates the diode current in the range of $V < 0$, (c) a plot of dV/dj *vs.* $1/(j - G_{sh}V)$, where R_s and n were evaluated from the y-intercept and the slope, respectively, in the high bias regime, and (d) a semi-logarithmic plot of $(j - G_{sh}V)$ *vs.* $V - jR_s$ for determination of n and j_0. The ideality factor, n, is determined in part (c) and (d), respectively, and both values were in good agreement, thus supporting the validity of this analysis.

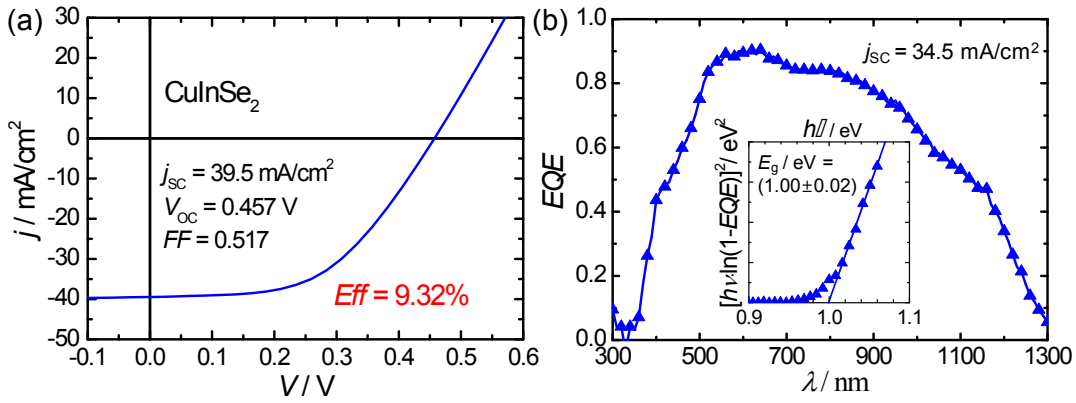

Fig. S6 Photovoltaic performance of the best-performing CISe solar cell prepared with milling for 360 h: (a) *j*−*V* characteristics under AM 1.5G illumination and (b) *EQE* spectra under a short-circuit condition.

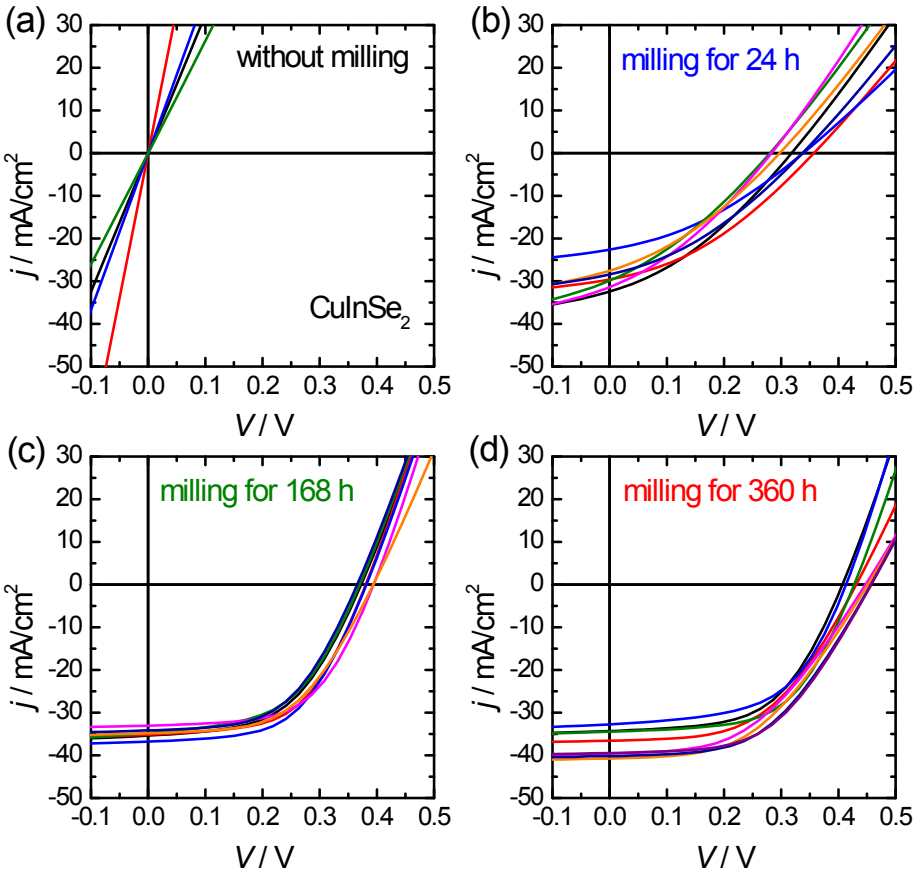

Fig. S7 *j*−*V* characteristics under AM 1.5G illumination of all the CISe devices on a substrate (3 × 4 cm^2) used to calculate the mean efficiency values, <η> for the cells prepared with Cu−In alloy nanocrystal inks milled for (a) 0 h, (b) 24 h, (c) 168 h, and (d) 360 h.

Table S2 Photovoltaic parameters of all the CISe solar cells on a substrate (3 × 4 cm^2) used to calculate the mean values for power conversion efficiencies

Milling time / h	Cell No.	V_{OC} / V	j_{SC} / mA cm^{-2}	*FF*	η / %	$\langle\eta\rangle$ / %
0 h	1	0	0	0	0	0
	2	0	0	0	0	
	3	0	0	0	0	
	4	0	0	0	0	
24 h	1	0.318	32.4	0.335	3.47	3.1 ± 0.5
	2	0.357	30.0	0.356	3.76	
	3	0.338	22.6	0.348	2.66	
	4	0.280	29.8	0.314	2.62	
	5	0.283	31.4	0.322	2.86	
	6	0.297	27.6	0.327	2.68	
	7	0.337	28.4	0.343	3.29	
168 h	1	0.372	35.4	0.520	6.85	7.1 ± 0.4
	2	0.380	35.2	0.553	7.39	
	3	0.382	36.8	0.543	7.62	
	4	0.370	34.7	0.515	6.62	
	5	0.394	33.1	0.569	7.41	
	6	0.394	34.8	0.520	7.13	
	7	0.365	34.1	0.530	6.60	
360 h	1	0.408	33.4	0.566	7.72	8.4 ± 0.7
	2	0.431	36.6	0.511	8.06	
	3	0.413	32.7	0.552	7.45	
	4	0.428	34.5	0.572	8.44	
	5	0.447	39.6	0.468	8.29	
	6	0.452	40.7	0.473	8.72	
	7	0.457	40.2	0.503	9.23	
	8	0.457	39.5	0.517	9.32	