

Electronic Supporting Information (ESI)

Copper deficient Zn–Cu–In–Se quantum dot sensitized solar cells for high efficiency

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Table S1 The nominal reactant ratio and chemical compositions of ZCISe QDs obtained from ICP-AES.

Nominal reactant molar ratio				Chemical composition	Measured molar
Cu	In	Se	Zn	determined	ratio of Cu/In
				By ICP-AES	By ICP-AES
0.5	1	3	0.4	$\text{Cu}_{0.72}\text{In}_{1.30}\text{Zn}_{0.14}\text{Se}_{2.79}$	0.55
0.7	1	3	0.4	$\text{Cu}_{1.01}\text{In}_{1.48}\text{Zn}_{0.11}\text{Se}_{3.04}$	0.68
1.0	1	3	0.4	$\text{Cu}_{1.34}\text{In}_{1.45}\text{Zn}_{0.13}\text{Se}_{3.12}$	0.92

Table S2 The values of energy level of ZCISe QDs with different Cu/In molar ratios reckoned according to the UPS and UV measurements.

Cu/In molar ratio	First E_{cutoff} (eV)	Secondary E_{cutoff} (eV)	E_g (eV)	E_F (eV)	E_V (eV)	E_C (eV)
0.5	1.42	17.44	1.67	-3.78	-5.20	-3.53
0.7	0.96	17.36	1.63	-3.86	-4.82	-3.19
1.0	1.36	17.83	1.58	-3.39	-4.75	-3.17

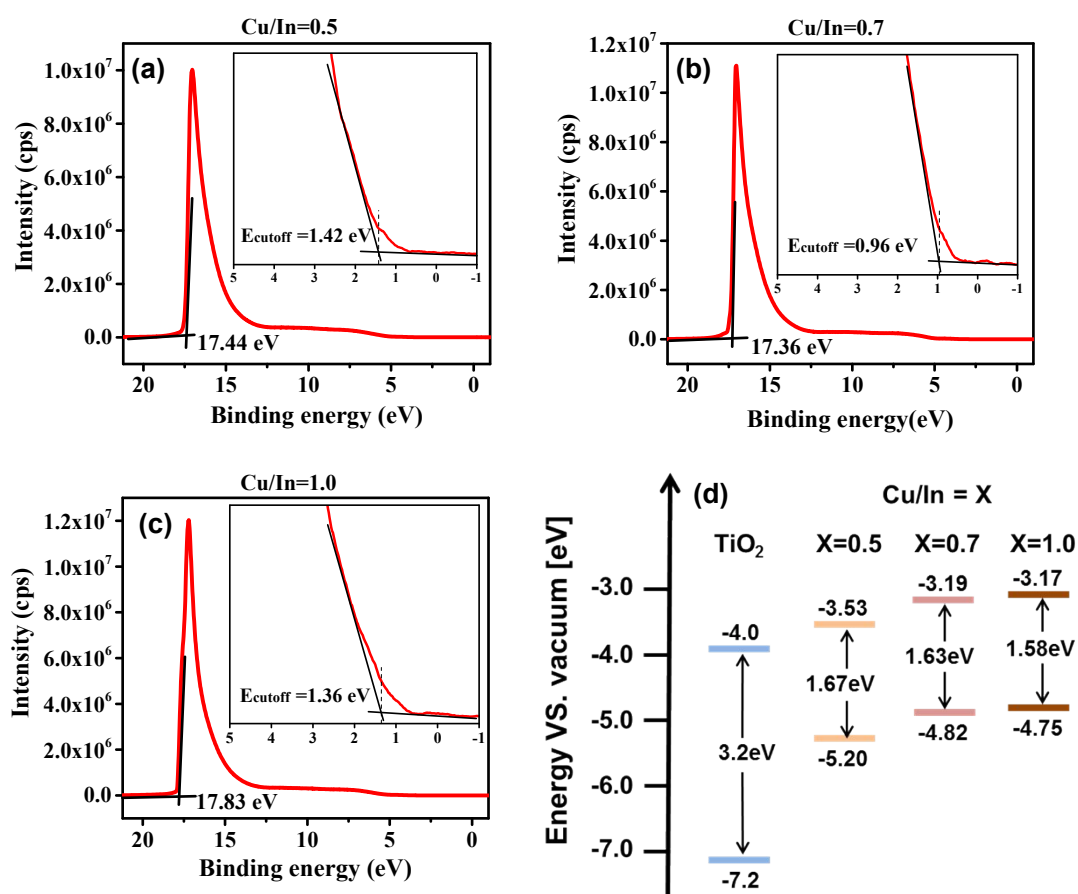


Fig. S1 The UPS spectrum of ZCISe QDs with different Cu/In molar ratios. (a) Cu/In=0.5; (b) Cu/In=0.7; (c) Cu/In=1.0; (d) Obtained energy level diagram of TiO₂ and corresponding ZCISe QDs.

Table S3 Individual photovoltaic parameters of ZCISe based QDSCs with different Cu/In molar ratios under the illumination of 1 full sun intensity (AM 1.5G, 100mW/cm²).

Cu/In molar ratio	J_{sc} (mA·cm ⁻²)	V_{oc} (V)	FF	PCE (%)
0.5	23.89	0.606	0.574	8.31
	23.88	0.612	0.570	8.32
	23.91	0.607	0.570	8.28
	23.88	0.609	0.570	8.30
	23.82	0.613	0.568	8.29
Average	23.87±0.03	0.609±0.003	0.570±0.002	8.30±0.016
0.6	25.24	0.600	0.582	8.81
	25.18	0.602	0.580	8.79
	25.20	0.590	0.579	8.61
	25.21	0.597	0.582	8.76
	25.17	0.596	0.585	8.78
Average	25.20±0.03	0.597±0.004	0.581±0.002	8.75±0.08
0.7	25.88	0.603	0.602	9.39
	26.01	0.597	0.592	9.21
	25.93	0.604	0.595	9.32
	25.98	0.602	0.590	9.23
	25.82	0.602	0.594	9.23
Average	25.92±0.08	0.602±0.003	0.595±0.004	9.28±0.08
0.8	25.51	0.605	0.582	8.98
	25.62	0.601	0.587	9.04
	25.56	0.597	0.592	9.03
	25.54	0.592	0.591	8.94
	25.58	0.600	0.590	9.06
Average	25.56±0.04	0.600±0.005	0.588±0.004	8.98±0.05
1.0	24.82	0.595	0.573	8.47
	24.77	0.594	0.575	8.46
	24.65	0.595	0.571	8.40
	24.80	0.594	0.573	8.44
	24.86	0.594	0.570	8.42
Average	24.78±0.08	0.594±0.001	0.572±0.002	8.44±0.028
0.7/MC-Ti	25.80	0.746	0.638	12.28
	25.83	0.738	0.650	12.39
	26.08	0.741	0.639	12.35
	25.97	0.752	0.644	12.57
	25.95	0.749	0.641	12.46
Average	25.93±0.11	0.745±0.006	0.642±0.005	12.41±0.11

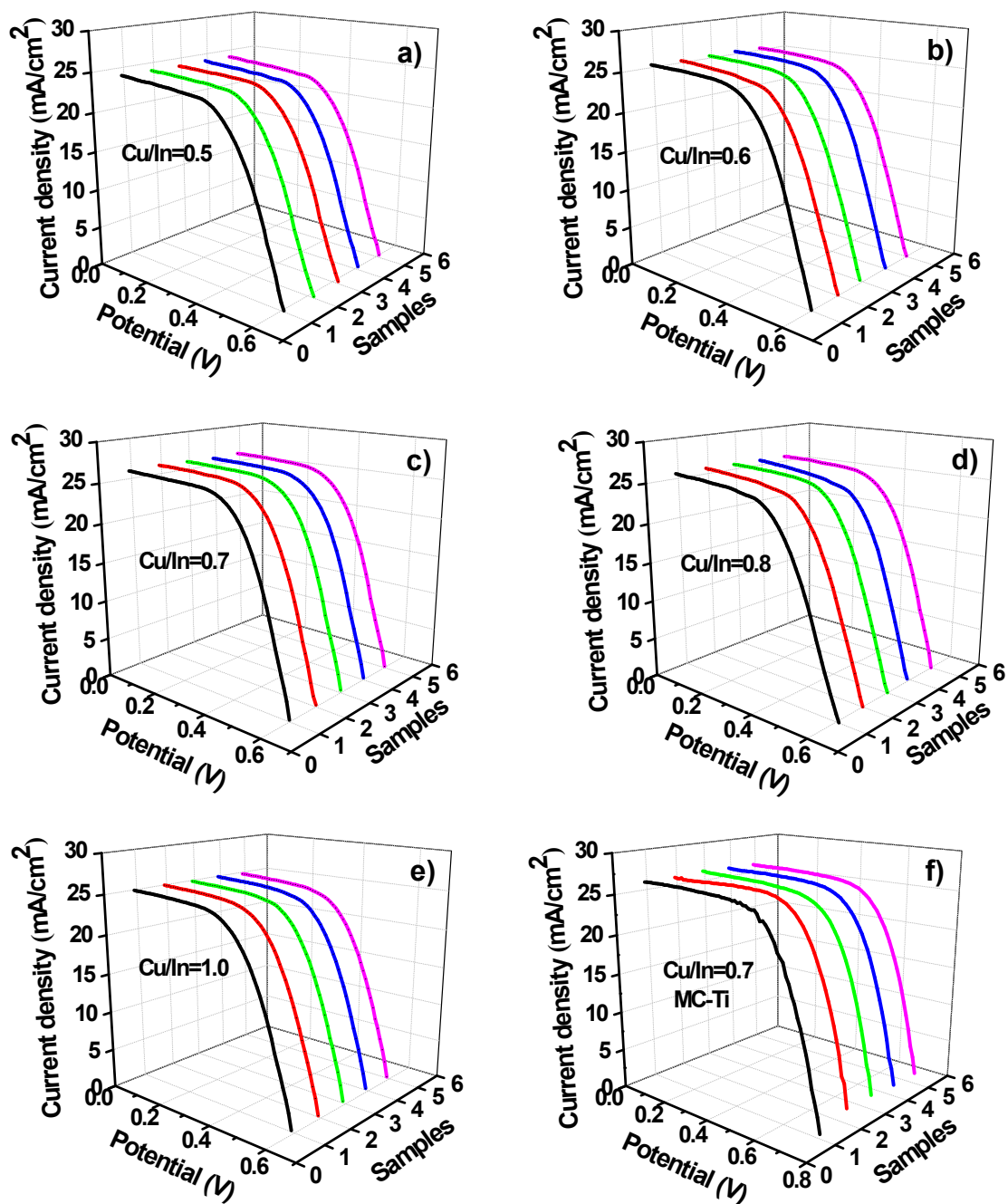


Fig. S2 Individual $J-V$ curves of ZCInSe based QDSCs with different Cu/In molar ratios under the illumination of 1 full sun intensity (AM 1.5G, 100 mW/cm²). (a) Cu/In=0.5, (b) Cu/In=0.6, (c) Cu/In=0.7, (d) Cu/In=0.8, (e) Cu/In=1.0, (f) Cu/In=0.7 with MC-Ti as counter electrode.

Table S4 Impedance parameters under the forward bias of -0.6 V: series resistance R_s , counter electrode charge transfer resistance R_{CE} , recombination resistance R_{rec} , chemical capacitance C_μ , and electron lifetime τ_n ($\tau_n = R_{rec} \cdot C_\mu$).

Cu/In molar ratio	R_s $\Omega \cdot \text{cm}^2$	R_{CE} $\Omega \cdot \text{cm}^2$	R_{rec} $\Omega \cdot \text{cm}^2$	C_μ $\text{mF} \cdot \text{cm}^2$	τ_n ms
0.5	8.558	2.93	301.4	5.54	1669
0.7	10.75	6.14	318.0	5.70	1812
1.0	12.94	4.91	244.7	5.86	1434

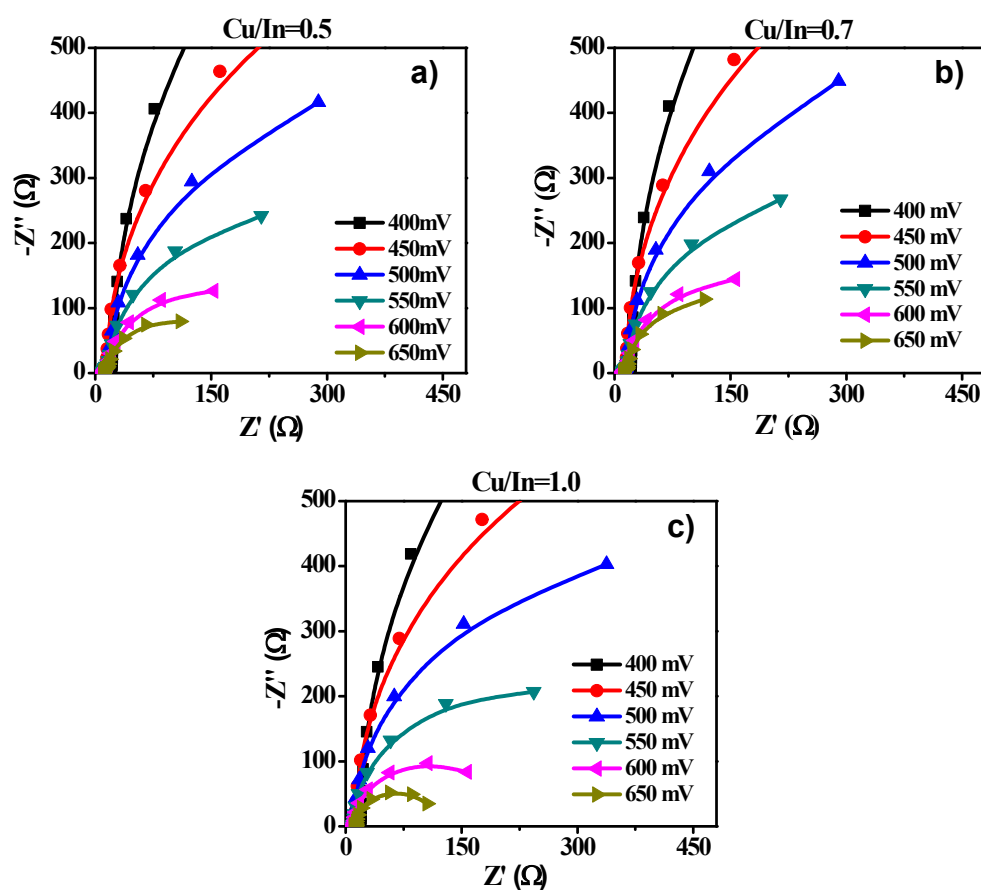


Fig. S3 Nyquist curves under different bias voltages for ZCISE QDSCs with different Cu/In molar ratios (0.5, 0.7, and 1.0).