Solid-State Colloidal CuInS₂ Quantum Dot Solar

Cells enabled by Bulk Heterojunctions

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Figure S1. The UPS spectra (excitation of 21.21eV) of CIS and TiO₂ used for the calculation of the Fermi level showing the cut-off region of samples biased at -5V (a) and the valence band onset (b, c). (d) Tauc plot of nanocrystalline TiO₂ film (90T, 500nm).

Films of CIS 90C, CIS 130C and CIS 170C were built up on FTO through the LbL process (6L, approx. 180nm) using 2%vol formic acid in methanol as discussed in the experimental section. TiO₂ samples were made from the 90T recipe on FTO also as discussed in the experimental section. The Fermi level was obtained by extrapolating the x-intercept of the sharp cut-off region in biased samples (-10V and -5V) excited by 21.21eV (HeI). The Fermi level was calculated by

$$E_F = E_{intercept} - 21.21 - V_{bias}$$

The average of the results from the two bias-voltages was taken. The valence band edge was calculated by taking the onset in unbiased samples and subtracting this from the obtained E_F . The conduction band edge was obtained by adding the bandgap calculated from the Tauc plot onset to the valence band edge.

Table S1. Device performance of various sizes of CIS, thicknesses and Zn content on flat-TiO2 (90T).

CIS	Zn la	yers	V _{oc}	J _{sc}	FF	PCE	$R_{s}(k\Omega)$	$R_{sh}(k\Omega)$
90°C	1.0	6	0.50±0.02	0.011±0.005	$0.29{\pm}0.02$	0.002 ± 0.0005	30.29±2.56	2259.5±477
130°C	1.0	6	$0.55{\pm}0.03$	0.077 ± 0.02	0.25 ± 0.02	0.011 ± 0.003	24.20±3.39	225.8±10.88
170°C	1.0	6	$0.59{\pm}0.05$	0.91±0.19	0.27 ± 0.03	0.15 ± 0.04	1.72 ± 0.54	25.65±13.5
170°C	1.0	12	$0.60{\pm}0.04$	0.93±0.12	0.32 ± 0.04	0.19 ± 0.02	1.41 ± 0.244	35.33±13.9
170°C	1.0	18	0.61 ± 0.01	1.08 ± 0.08	0.33 ± 0.01	0.22 ± 0.01	1.08 ± 0.04	25.97±2.17
170°C	0.3	6	$0.63{\pm}0.04$	1.26±0.36	0.31 ± 0.09	0.23 ± 0.05	1.53±0.72	18.16±86.5
170°C	0.3	12	$0.62{\pm}0.05$	1.39 ± 0.27	0.30 ± 0.06	0.29 ± 0.09	1.35±0.67	24.42±6.79
170°C	0.3	18	0.60 ± 0.01	1.67 ± 0.06	0.33 ± 0.01	0.33 ± 0.02	0.514 ± 0.07	18.91±0.38
170°C	0.1	6	0.63 ± 0.01	1.81 ± 0.55	0.26 ± 0.01	0.30 ± 0.09	1.74±0.64	22.3±7.29



Figure S2. $1/C^2$ vs voltage plot of CIS-flat TiO₂ devices, values for the V_{bi}, N and W_d were calculated using Mott-Schottky analysis.

The carrier concentration, N, was calculated using the Mott Schottky equation:

$$N = -\frac{2}{q\varepsilon_r\varepsilon_o A^2} \left(\frac{dC^{-2}}{dV}\right)^{-1}$$

where q is the elementary charge (1.602 x 10^{-19} C), ε_0 is the permittivity of free space (8.54 x 10^{-12} C V⁻¹ m⁻¹), ε_r is the relative permittivity (5.5^[1]), A is the device area (3.14 x 10^{-6} m²) and d(C⁻²)/dV is the slope of the linear region shown in FigS2. The V_{bi} is taken from the x-intercept of this extrapolation. We find that N = 2 x 10^{16} cm⁻³ and V_{bi} = 0.57 V.

With N and V_{bi} , we can calculate the depletion width W using:

$$W = \sqrt{\frac{2\varepsilon_r \varepsilon_o V_{bi}}{qN}}$$

We calculated a depletion width of 125nm at $V_{applied} = 0$.



Figure S3. Absorption coefficient of formic acid-treated CIS films. The absorption (from transmission and reflection) of films with three thicknesses d (by SEM cross-section) was taken. The average absorption coefficient α was obtained by $\alpha = A/d$.



Figure S4. The reduction of Zn during post-synthetic treatment leads to a dampening of the quantized features (a), a more redshifted emission (b) and a lower photoluminescence quantum yield (c). In dropcasted films, particles with reduced Zn have better interparticle coupling as seen in the faster PL decay probed at wavelengths lower than the PL peak.

Table S2. The reduction in zinc post-synthetically shows marked reductions in Zn and a corresponding increase in indium. Cu, Zn, In, and S contents were probed through EDX on dropcasted Zn-treated particles. The relative amounts were normalized to achieve a sum of 4.

Ref	0.3 Zn	0.1 Zn
0.47	0.45	0.44
0.44	0.35	0.30
0.97	1.03	1.08
2.12	2.18	2.18
	Ref 0.47 0.44 0.97 2.12	Ref0.3 Zn0.470.450.440.350.971.032.122.18



Figure S5. The reduction of zinc leads to higher mobilities. Mobilities were obtained through FET measurements according to [2]. ^aThe value for CIS 1.0 Zn agrees with the previous reported mobility for this material as in [2]. The (400nm-filtered) J_{sc} of CIS 0.3 Zn devices with thickness (red) fitted with 6.5% IQE and and 10% optical loss, compared with CIS 1.0 Zn devices (black) with 4.5% IQE and 10% optical loss fittings.



Figure S6. (a) Different number of layers of CIS deposited on FTO (left) and 90T (right) showing that thickness increases with increasing layers and that no infiltration occurs for 90T-

TiO₂. (b) Similar absorber thicknesses of CIS 1.0 Zn as deposited on FTO (black), CIS 1.0 Zn as deposited on 90T (blue), CIS 0.3 Zn as deposited on 90T (red).



Figure S7. (a) Secondary ion mass spectra of CIS on flat TiO_2 focusing on the first few moments of ion bombardment showing the differences in ionization probabilities as metal ratios are different from that obtained from EDX. The x-axis has been retained on the time scale as each layer will have different sputter rates. (b) Infiltration of 6 layers of CIS in porous-TiO2 (850nm) is deep. At 6 layers, no overlayer is formed.



Figure S8. IV characteristics of CIS 0.3 Zn in flat and porous TiO2 showing the increase in current due to CIS is more than 5-fold.



Figure S9. Percent absorption of full devices made from flat (blue) and porous (red) TiO₂.



Figure S10. (Top) Devices made from CIS 1.0 Zn on TiO_2 blocking layer without a Spiro spacer, from CIS 1.0 Zn on 90T without a Spiro spacer and from CIS 1.0 Zn on 90T with a Spiro spacer have similar performance. (Bottom) SEM images of CIS devices without Spiro.



Figure S11. (a) The thickness of the porous TiO2 network can be controlled by changing the dilution of the F52C solution: 1 : 3 vol. F52C with ethanol, 175nm; 1 : 1 vol., 500 nm; 1 : 0.3 vol., 850nm; 1 : 0.15 vol., 1200nm; undiluted, 1700nm. When films become thicker, the film is more prone to delamination and cracking (b).



Figure S12. CIS 1.0 Zn and CIS 0.3 Zn similarly infiltrate the porous TiO_2 resulting in comparable overlayer formation. CIS 0.1 Zn does not infiltrate the porous material and rests on top of the structure. This is seen in porous TiO_2 (500nm) with 12 layers of material (left) and porous TiO_2 (850nm) with 6 layers of material (right).

Zn	layers	TiO ₂	V _{oc}	J _{sc}	FF	PCE	R _s	R_{sh}
1.0	6	f-TiO ₂	0.59±0.05	0.91±0.19	0.27±0.03	0.15±0.04	1.72±0.54	25.65±13.5
1.0	6	p-500	0.60 ± 0.03	2.18±0.46	0.50 ± 0.06	0.65±0.18	0.31±0.14	41.53±18.9
0.33	6	f-TiO ₂	0.63±0.04	1.26±0.36	0.31±0.09	0.23±0.05	1.53±0.72	18.16±86.5
0.33	6	p-500	0.65 ± 0.02	2.66 ± 0.09	0.52 ± 0.03	0.87 ± 0.07	0.43 ± 0.16	35.51±8.9
0.33	12	p-850	0.67 ± 0.02	3.83 ± 0.52	0.39±0.01	1.01 ± 0.15	0.98 ± 0.07	13.14±1.39
0.1	6	f-TiO ₂	0.63±0.01	1.81±0.55	0.26±0.01	0.30±0.09	1.74±0.64	22.3±7.29
0.1	6	p-500	0.67 ± 0.03	1.82 ± 0.53	0.36±0.03	0.44±0.13	2.97 ± 0.68	22.5 ± 7.40

Table S3. Device performance of CIS with different Zn content on various TiO_2 substrates (f- TiO_2 , flat TiO_2 ; p-xxx, porous TiO_2 xxx nm thick).



Figure S13. Transient photocurrent (a) and transient photovoltage (b) of flat and porous devices at select bias light intensities. Porous devices have longer J_{sc} decay and V_{oc} decay and are single exponential and do not have long-lived trapped features (25-70ms range). The Voc decay time is taken from the short time scales (0-10ms). Extracted carrier lifetime (c) and excess charge carrier density (d) of flat and porous devices have completely different dependence on V_{oc} . Calculated Urbach energies are shown.



Figure S14. Raman-photoluminescence spectra of CIS films, untreated and treated, on glass, flat TiO_2 and porous TiO_2 showing a decrease in PL when placed with TiO_2 .

Calculation of diode ideality factor and power law dependence of photocurrent with intensity:

The diode ideality factor was calculated from the intensity Φ dependent V_{OC} plot using the Shockley relation:

$$V_{OC} = \frac{n_{id}kT}{q}ln(\Phi) + C$$

where the symbols have their usual meanings. The ideality factor n_{id} was calculated from the slope of the Intensity dependent V_{OC} plot at the room temperature.

The relation between photocurrent and the incident light intensity is given by,

$$T_{ph} \propto \Phi^{\alpha}$$

For an ideal generation-limited solar cell, the power component α should be 1.

Calculation of recombination rate:

The recombination rate R was calculated with the relation:

$$R = \frac{\Delta n}{\tau}$$

where Δn is the excess carrier concentration calculated from the transient techniques and τ is the recombination decay time calculated from fitting TPV curve using the relation:

$$\Delta V_{OC}(t) = \sum_{k=1}^{x} A_k \left\{ exp\left(\frac{-t}{\tau_k}\right) \right\}$$

where A_k is a weighting parameter. For flat devices we find that x = 2 and for porous devices, x = 1. We took the lifetime as the short time scales of the decay curve.

The generalised recombination rate (R) is related to the excess carrier concentration (Δn) with the following equation,

$$R \propto K_1(\Delta n) + K_2(\Delta n)^2 + K_3(\Delta n)^3$$

where K_1 , K_2 and K_3 stand for the recombination rate constant for the trap induced (first order b=1), radiative (second order b=2) and Auger recombination (third order b=3) respectively.

Urbach tail energy relation is taken from Foertig et al^[3]:

The exponential distribution of the trap states is given as,

$$N(E) = N_0 exp\left(\frac{-|E - E_B|}{E_U}\right)$$

where N_0 is the effective density of states, E_B is the band edge and EU is the Urbach tail energy.

It can be calculated using Shockley equation ideality factor (n_n) for charge carrier density given by,

$$n = n_0 exp^{(n)} \left(\frac{qV_{OC}}{\eta_n kT}\right)$$

The relation between E_U and n_n is given by,

$$E_U = \frac{n_n \kappa I}{2}$$

The ideality factors are related with the equation,

$$\frac{1}{n_R} = \frac{1}{n_n} + \frac{1}{n_\tau}$$

where n_{τ} is given by the equation,

$$\tau = \tau_0 \exp\left(\frac{-qV_{OC}}{\eta_\tau kT}\right)$$

and $n_R \approx n_{id.}$

The recombination order λ +1 is defined by

$$\lambda + 1 = \frac{1n_n}{n_\tau} + 1$$

These values are summarized in Table S4.

The V_{OC} decay curves were fitted with exponential decay to find the recombination time. The TPC curve was integrated to get the charge generated (ΔQ) in the devices due to the laser pulse. The capacitance (C) was calculated from the C= $\Delta Q/\Delta V_{OC}$ relation. The total charge carrier was calculated from the integration of C vs V_{OC} plot. Charge carrier density was calculated by dividing the total charge carriers with the device volume.

	flat	porous	
n _r	34.7	1.8	
n _n	6.7	2.3	
λ +1	1.2	2.3	
n _R	5.6	1.0	
b	1.2	2.2	
n _{id}	2.1 to 3.8	1 to 1.5	
E _{u, eqe}	141	80	
E _{U, nn}	83.4	28.2	

Table S4. Comparison of various ideality factors, power law exponents and Urbach energy calculations for flat and porous devices.

- R. Miranti, C. Krause, J. Parisi, H. Borchert, Mater. Res. Express 2015, 2, 066401. [1]
- [2]
- D. So, G. Konstantatos, *Chem. Mater.*, **2015**, 27, 8424–8432. A. Foertig, J. Rauh, V. Dyakonov, C. Deibel, *Phys. Rev. B* **2012**, *86*, 115302. [3]