Electronic Supplementary Information to:

A direct solution deposition approach to CdTe thin films

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Materials:

Te powder (30 mesh, 99.997%), ethylenediamine (≥99.5%), 1-propanethiol (99%), ethanethiol (97%), 1-hexanethiol (95%), and FTO-coated glass (Pilkington TEC 15, ~13 Ω/sq) were obtained from Sigma Aldrich and used without purification. Handling of all chemicals was done in a nitrogen filled glove box.

$CdCl_2$, (ultra-dry, 99.996%) was obtained from Alfa Aesar and handled in a nitrogen filled glove box.

Copper pellets (99.999%) and gold shot (99.99%) were obtained from Kurt J. Lesker Company.

Additional Experimental Details:

Glass Preparation and CdS Deposition

Spin coating is done preferably on FTO-coated glass due to its high thermal and chemical stability. As Fig. 3 of the main article demonstrates, the decreased thermal stability of ITO can result in significant diffusion of In into the film. The FTO-coated glass is cleaned on receipt by sonication in ultra-pure water (18.3 MΩ).

CdS is deposited via a modified water-based chemical bath deposition from our previous reports. Briefly, 22 mL of 0.015 M $CdSO_4$, 28 mL of 30% NH_4OH, and 150 mL of ultrapure water are added to a beaker while the cleaned FTO-glass is briefly soaked in ultrapure water. The precursor mixture is poured into a 500 mL jacketed beaker (previously heated to 65 °C) and the FTO-coated glass is then immersed by suspending above a gently turning stir bar (~60 rpm) using a hemostat. After one minute, 5.5 mL of a 0.75 M thiourea solution are poured into the beaker and the reaction proceeds for 40 minutes. At the 10, 20, and 30 minute marks an additional 5.5 mL of 0.75 M thiourea solution are added to achieve a thicker CdS of about 150-200 nm, similar to other reports.[1]

After 40 minutes, the sample is removed and rinsed with ultra-pure water and results in a thickness of ~200 nm. After CdS deposition, the films are annealed in air in a convection oven at 120 °C for 5 minutes to remove trace water. The films are brought into the glove box and typically are annealed on a hot plate for 10 minutes at 400 °C prior to applying the CdTe coatings. As a result of this annealing the CdS films typically transition from yellow-orange to more orange in color and show some increased resistance to dissolution in the thiol-diamine mixture.

Solution formulation

To formulate a precursor solution, a $CdCl_2$ and elemental Te are dissolved at concentrations of 0.15-0.22 M simultaneously in ethylenediamine (en) and 1-propanethiol (pt). The solubility of Te is the limiting

factor on the concentration, with full dissolution at 0.22 M Te being attained with overnight stirring (approx. 14-16 hours). The presence of co-dissolved $CdCl_2$ has not shown any effect on the maximum concentration of Te that can be dissolved. However, the ratio between the solvents does exhibit an effect on the amount of Te that can be dissolved. A ratio of 2:1 (en:pt) seems to have the highest solubility at up to ~0.22 M, whereas 3:1 dissolves well up to ~0.20 M, with decreasing concentrations attained at higher ratios. Our best films are achieved by using en:pt of 2:1 or 3:1 and concentrations of 0.20 to 0.22 M, as this minimizes the number of coatings needed and results in a denser film. We have also observed that larger ratios (en:pt > 3:1) form large Te crystallites upon film drying, such that a rough non-uniform surface is achieved. Other thiols such as ethanethiol or hexanethiol have also been used with limited success. Ethanethiol would be desirable as it is more volatile that pt, but we have had some difficulty getting this solution to uniformly wet the FTO-glass and produce uniform coatings. However, we have found that the wetting abilities of the solvents seems to have some dependence on the vendor from which they are sourced.

The solution formulation may also be modified to achieve an alternative Cu-doping strategy to thermal evaporation of Cu and diffusion into the film. In this modification, trace Cu is dissolved into the precursor solution directly. For this purpose, we initially targeted 5 ppm CuCl in the solution compared with the concentration of $CdCl_2$. As $CdCl_2$ is dissolved most often at 0.2 M, this requires a solution that is 1E-6 M CuCl. This is accomplished by successive dilution. First, 0.4 mmol (39.6 mg) of CuCl is dissolved in 4 mL of a 3:1 en-pt volumetric mixture, resulting in a 0.1 M solution. Thirty µL of this solution is then diluted in 5.970 mL of 3:1 en-pt resulting in a 0.0005 M solution. One can then calculate how much of this solution to add to the $CdCl_2$-Te precursor solution to achieve the 5 ppm target. For a 13 mL 0.2 M $CdCl_2$-Te precursor solution, this requires adding 26 µL of the CuCl solution. Note that the addition of 26 µL changes the final concentration of the solution slightly and could be adjusted by initially using 12.974 mL of en-pt in formulating the $CdCl_2$-Te solution, though the difference in final concentration is not large. This doping strategy was used to prepare the films shown in Fig. 2, but this has not shown to have noticeable effect on either device performance or growth properties, likely because control of film impurities (S, Cl, C) and CdS consumption are much more significant factors.

Spin coating

If coating directly on FTO-coated glass, it is necessary to clean the glass several times with ethylenediamine and lint-free, clean room wipes to modify the surface properties to enable uniform wetting of the surface with the precursor solution. This may also help when CdS has been previously deposited. To achieve uniform coatings, it is important to apply enough precursor solution to cover the entire glass (about 350-400 µL). A two-step coating program was used in which the glass spins at 500 rpm for 5 s, followed by rapid ramping to 1100 rpm for 40 seconds. At this point the film is mostly dry and is directly placed on a pre-heated hot plate at 500 °C. After 90 s it is removed from heat and placed on two thin Al foil fins so the sample is suspended in the nitrogen for gradual, uniform cooling to avoid thermal stress to the glass and film. After about 2 minutes the sample can be placed on an Al block for final cooling to room temperature. Adequate cooling between coatings is important for reproducible coatings.

Sensitivity to process variables

Some of the key process variables are solution concentration, spin coater speed (rpm), annealing temperature, and annealing temperature. We have found it advantageous to use a solution as

concentrated as possible, which is difficult to obtain higher than 0.20-0.22 M for the diamine-monothiol system. Fewer coatings are needed and grain density is improved at higher concentrations. The spin coating speed was optimized with the desire to have as thick a coating as possible each time, subject to the constraint that with increased thickness the film becomes subject to cracking as it dries. In this study, 1100 rpm was used most typically. An annealing temperature of 500 °C was used which resulted in the best incorporation of Te into the film. The XRD of a film on ITO-glass whose coatings were annealed at 350 °C is shown in Fig. S1, as well as the result after annealing the final film at 500 °C. We observe increased Te compared with the film shown in the publication when coatings were annealed at 500 °C (Fig. 1) and notice that a post-bake for 5 minutes at 500 °C eliminates the Te signal (Fig. S1). We believe this to be due to improved Te incorporation, but can also be due to volatilization of residual Te, which melts ca. 451 °C.
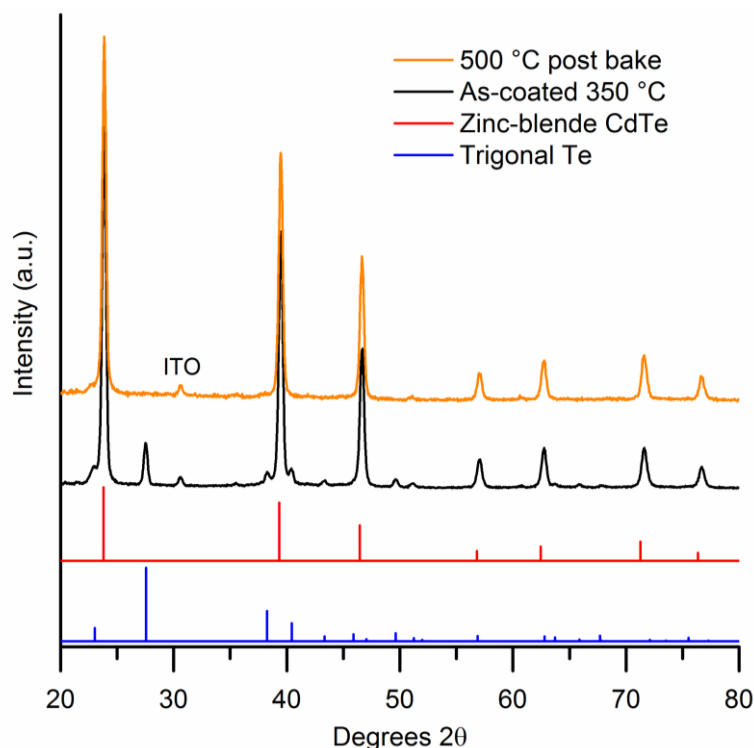

Fig. S1. XRD of a film coated on ITO-glass at room temperature and then annealed at 350 °C showing increased Te content compared to films annealed at 500 °C (Fig 1). Note that when the film is then annealed for an additional 5 minutes at 500 °C the Te signal disappears.

The temperature at which the film is annealed in a sealed glass ampoule is also important. Temperatures between 500-620 °C have been investigated, though our best device was obtained at a temperature of 550 °C. A significant observation is that by 620 °C, CdTe begins to have an appreciable vapor pressure such that on cooling, we see the condensation of large CdTe grains scattered on the surface of the original film. This can be seen both in plan view (Fig. S2a) and from a cross section (Fig. S2b). This is not surprising as this is nearing temperatures used for close space sublimation. The phase of these grains has been confirmed to be CdTe from XRD and SEM-EDS (data not shown).
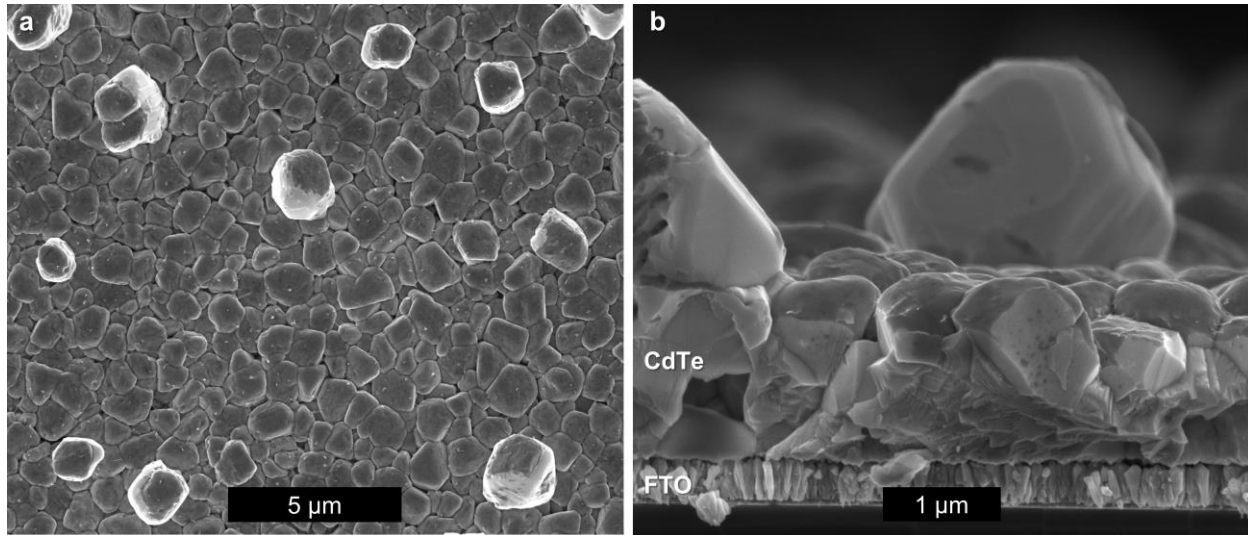
Fig. S2. SEM image of (a) plan view and (b) cross section of a film annealed at 620 °C in an ampoule for 30 mins. Large grains of CdTe condense on cooling as a result of the appreciable vapor pressure of CdTe.
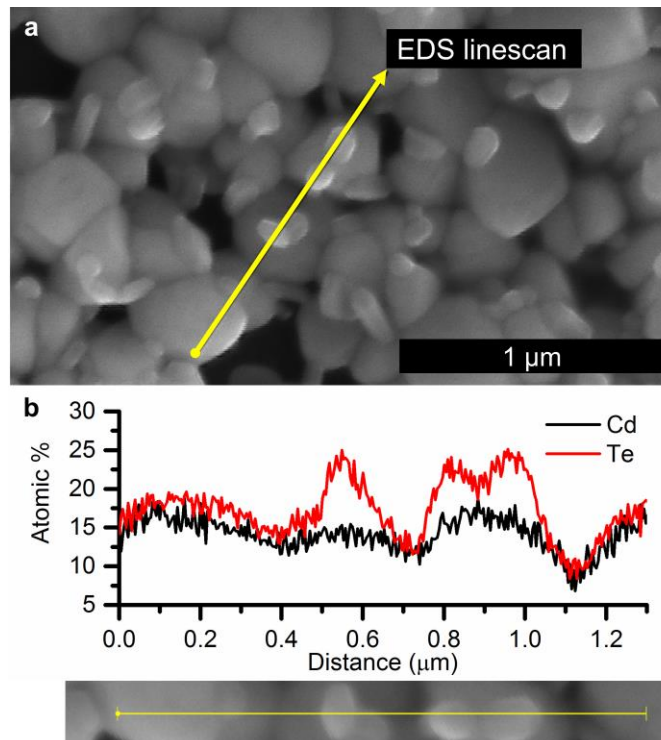
Additional Characterization:

Fig. S3. (a) Plan view SEM image of an as-coated film with characteristic small grains on surface of film. (b) SEM-EDS line scan results. The at% of Te and Cd track each other well in the large grains as expected for the CdTe phase. In contrast, the small grains are observed to be unincorporated Te or highly Te-rich phases.
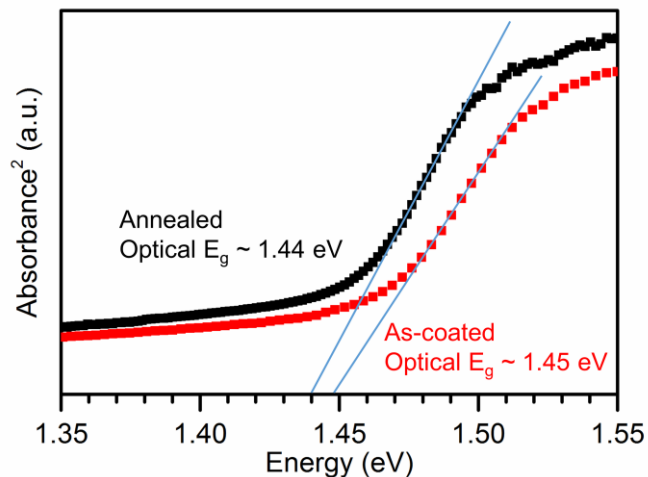
Fig. S4. Tauc plot using UV-Vis spectroscopy absorbance data for the as-coated and annealed films. Optical band gaps of about 1.45 eV (as-coated) and 1.45 eV (annealed) are estimated from the data. The slight decrease after annealing may be related to the slight reduction in sulfur content.
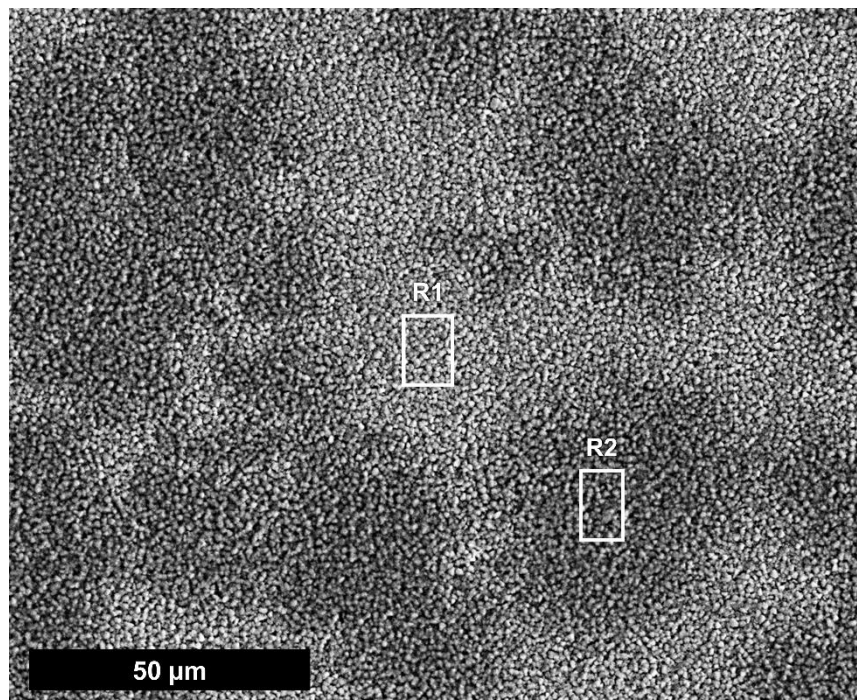

Fig. S5. Low magnification SEM image of an as-coated film showing regions of lighter (R1) and darker (R2) contrast. When SEM-EDS is performed on each region, we find that R1 has decreased Cl content compared to R2. For the film shown, R1 has a Cl/Cd ratio of 0.035 (as obtained from the atomic percentages). For R2, it is 0.19. The Cl/Cd ratio for the entire region combined is 0.12.
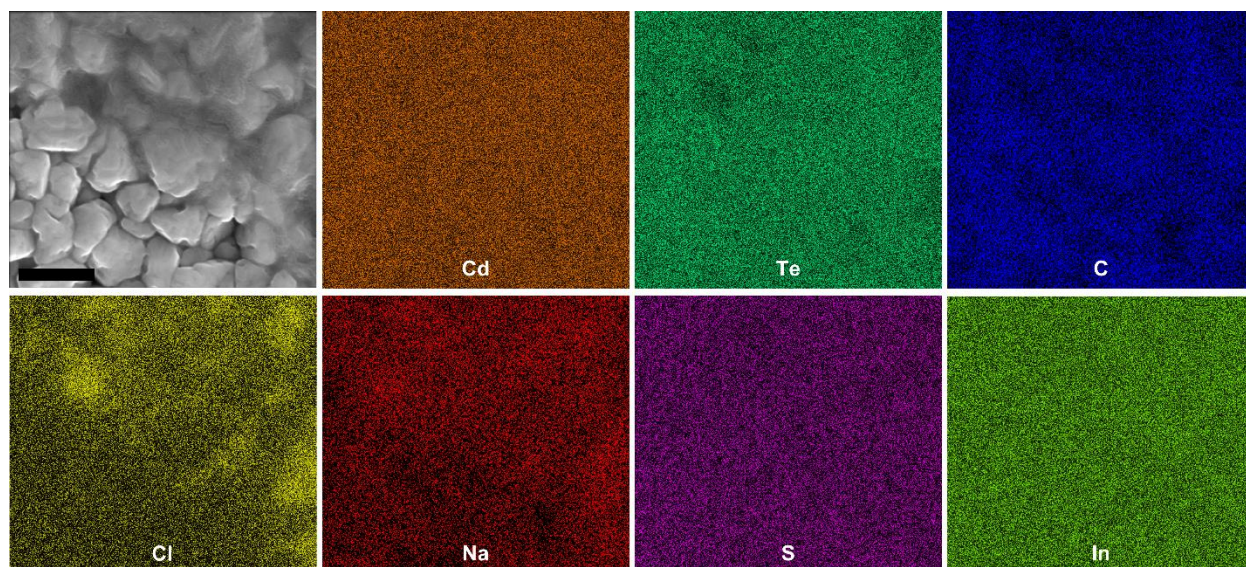
Fig. S6. SEM-EDS map at boundary of light and dark regions of an as-coated film on ITO-coated soda lime glass with no CdS layer. Where Cl is high, Te is lower, indicating a likely Cd-Cl or Cd-Cl-Te phase in those regions. Na is also slightly higher where Cl is high, suggesting Na may be preferentially diffused from the glass toward the Cl. Elements C, S, and In appear to be fairly well distributed throughout the film.
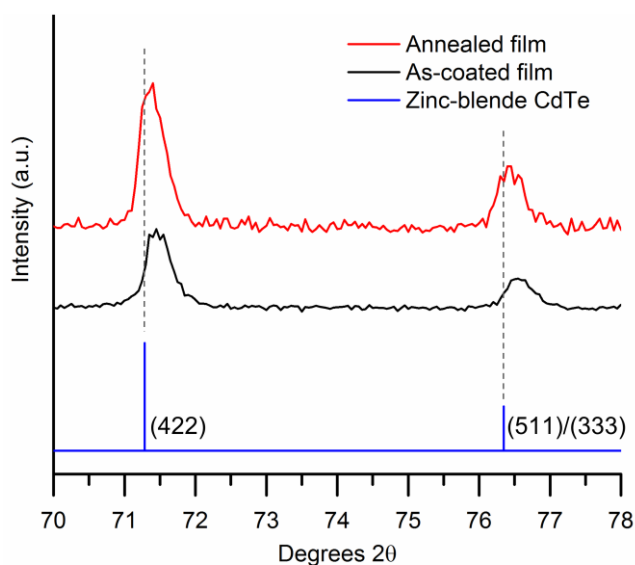

Fig. S7. Detailed view of XRD showing shifting of peaks indicative of S incorporation in the film. The peak positions of the (422) peak are estimated to be 71.48 and 71.40 deg. 2θ for the as-coated and annealed films, respectively. For the (511)/(333) peak they are estimated to be 76.57 and 76.45 deg. 2θ. Using the published peak positions for zinc-blende CdS and CdTe (ICSD coll. codes 81925 and 161692) and assuming linear shifting with S incorporation, the shifting observed in these peaks corresponds to an average Te/S of 0.02 (as-coated) and 0.01 (annealed), in good agreement with the EDS data reported in Table 1.
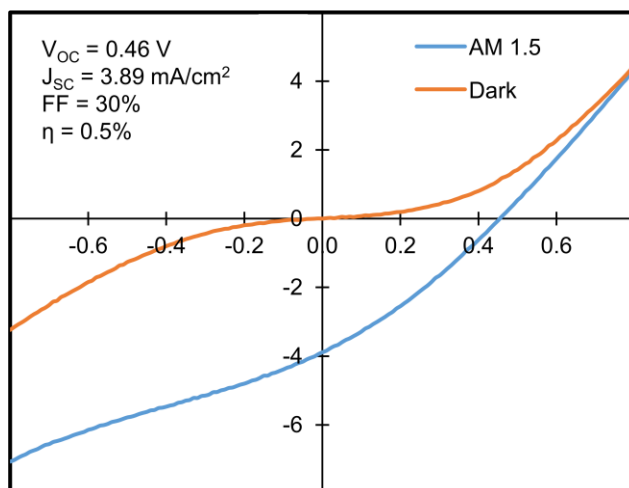
Fig. S8. J-V response of a finished CdTe cell based on a standard FTO-CdS-CdTe-Cu/Au architecture. The device area was estimated by image analysis at ~0.065 cm². Significant performance variability can exist across a sample.
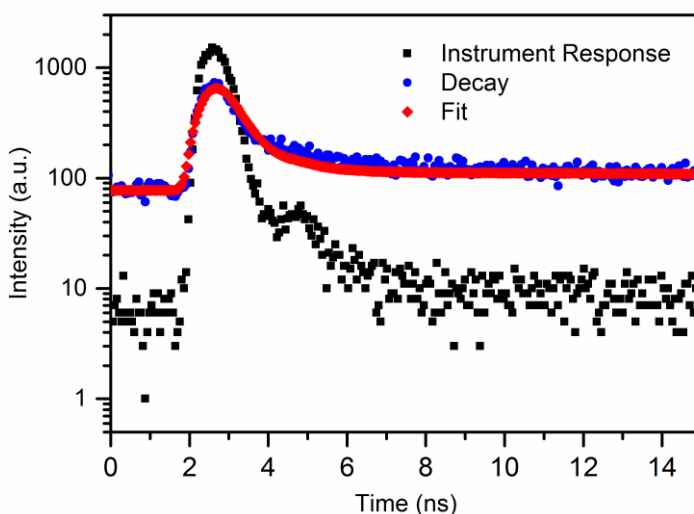

Fig. S9. Time-resolved photoluminescence of the completed devices. The response was fit to a biexponential decay of the form $I(t) = C_1 e^{-t/\tau_1} + C_2 e^{-t/\tau_2}$ yielding τ_1=465 ps, τ_2=75.7 ns, C_1 = 0.038, and C_2=7.3 x 10^{-4}. The reasonable τ_1 lifetime suggests that front surface recombination is not expected to be the fundamental limit to the low V_{OC} observed for the device reported herein. While the grains reported herein are large compared with other solution processed routes, they are somewhat smaller than those found in champion devices. This is expected to lead to comparatively higher surface recombination rates at grain boundaries and result in lower lifetimes. The defects from chlorine and potentially sulfur may also be leading to higher recombination rates and low lifetimes.
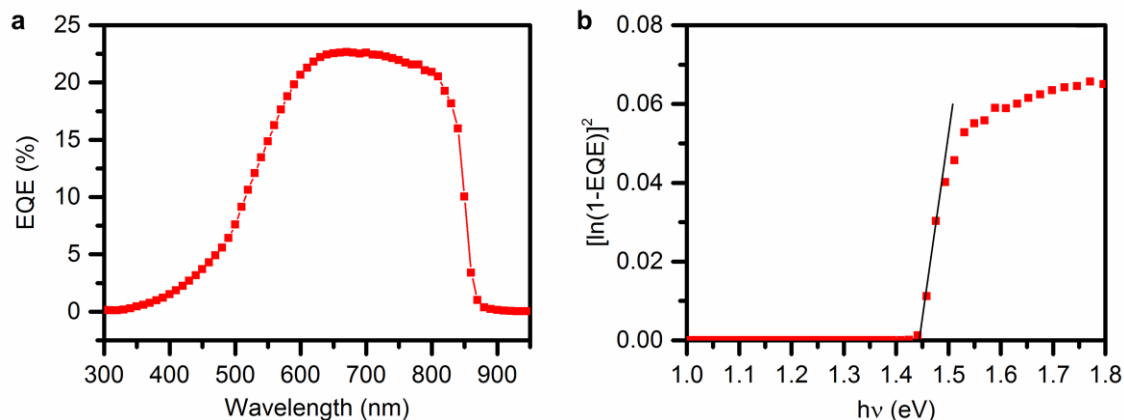
Fig. S10. (a) External quantum efficiency (EQE) measurements of a similarly processed device to the one shown in Fig. S8 with η = 0.3%, V_{OC} = 0.26, J_{SC} = 4.7 mA/cm^2, and FF = 27.2%. The integrated EQE yields a J_{SC} of 4.98 mA/cm^2 in reasonable agreement with the J-V analysis. (b) Band gap measurement by plotting $[\ln(1\text{-}EQE)]^2$ against hv yields a band gap of about 1.44 eV in good agreement with the UV-Vis analysis (Fig. S4).
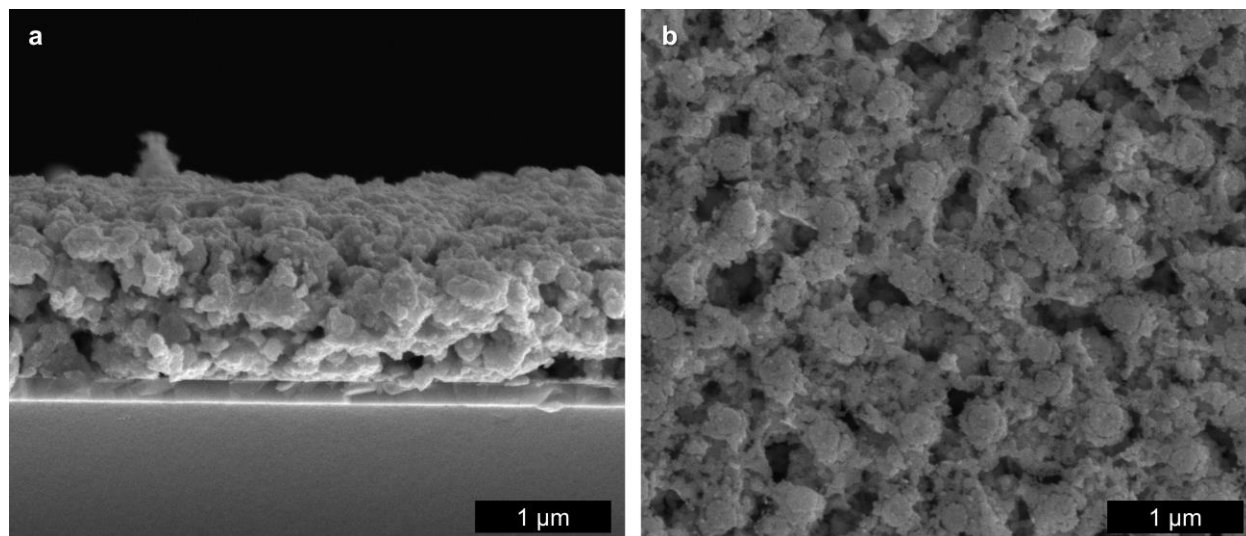

Fig. S11. SEM images of films produced using Cd(CH$_3$CO$_2$)$_2$ (cadmium acetate) in place of CdCl$_2$. No dense, large grain growth is observed from either (a) the fractured cross section or (b) the plan view of the film. Similar morphologies are seen when 90% of the CdCl$_2$ is substituted as well.

Characterization details

X-ray diffraction

XRD was done using a Rigaku SmartLab with a Cu K$_\alpha$ (λ = 1.5406 Å) source operating at 40kV/44mA. Data was collected using a step size of 0.05 degrees at a scan speed of ~1.4 degrees/min.

Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS)

SEM images were collected using an FEI Nova NanoSEM at an accelerating voltage of 5 kV, 3.0 spot size, and working distance of ~2-3 mm using the TLD (through-the-lens detector). EDS measurements were performed using an FEI Quanta 3D at 20kV with an Oxford INCA Xstream-2 silicon drift detector with Xmax80 window and analyzed using Aztec software.

Scanning transmission electron microscopy energy dispersive spectroscopy (STEM-EDS)

STEM-EDS was obtained using a 200 kV probe-corrected, dedicated scanning transmission electron microscope (STEM, Hitachi HD 2700C), used at the Center for Functional Nanomaterials at Brookhaven National Lab.

UV-Vis Spectroscopy

UV-Vis spectroscopy was performed in transmission mode using a PerkinElmer Lambda 950.

Solar simulator and J-V analysis

Device performance was obtained from current-voltage (J-V) measurements completed using an Oriel Sol3A solar simulator (Model No. 94023A) filtered to AM 1.5 G and calibrated to 1000 W/m^2 with an Oriel 91150V silicon reference cell. Four-point probe contacting was employed for the measurements.

Time-resolved photoluminescence (TRPL)

TRPL was performed using a 637nm diode laser (pulse width <1 ns, 1MHz) and an InGaAs photomultiplier tube (Hamamatsu H10330A-45). These are coupled with a Horiba Jobin Yvon Fluorolog-3. The instrument response function was measured at 260 ps.

External quantum efficiency (EQE) analysis

External quantum efficiency (EQE) measurements were performed with an AC lock-in amplifier using a chopper frequency of 162 Hz with a preamplifier to aid in signal processing; EQE calibration was performed with reference UV-enhanced Si (Newport, Model 818-UV-L) and Ge (Newport, Model 818-IR-L) diodes.

Reference

1   D. H. Rose, F. S. Hasoon, R. G. Dhere, D. S. Albin, R. M. Ribelin, X. S. Li, Y. Mahathongdy, T. A. Gessert and P. Sheldon, *Prog. Photovoltaics Res. Appl.*, 1999, **7**, 331–340.