

Supporting Information

High Efficiency Solution-Processed CZTSSe Thin Film Solar Cells Prepared from Binary and Ternary Nanoparticles

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General

All metal salts and reagents were used as received from commercial sources. Whatman[®] Puradisc[™] 25 GD 1.0 μm GMF-150 filter media with polypropylene housing were used to filter the nanoparticle dispersions.

Materials. Sources and purities of metal salts and other reagents were as follows: CuCl (anhydrous, 99.999%) from Alfa Aesar; CuCl₂ (anhydrous, \geq 99.995%) from Aldrich; SnCl₄ (anhydrous, 98%) from Alfa Aesar; ZnCl₂ (\geq 98%) from EMD Millipore; trioctylphosphine oxide (TOPO; \geq 90%) from Strem Chemicals; oleylamine (\geq 40%) from TCI America; and selenium shots (amorphous, 1-3 mm, 99.999% metal basis) from Alfa Aesar.

Procedures Used for Device Preparation and Analysis

Devices were prepared by coating inks onto Mo-sputtered SLG substrates, annealing the resulting film, and depositing CdS, insulating ZnO (i-ZnO), indium tin oxide (ITO), silver grids, and indium electrodes according to the procedures given below. Analytical measurements (e.g., XRD, XAS, I-V analysis, and EQE) were obtained as described below and were used to characterize annealed films and finished devices.

Mo-Sputtered SLG Substrates. Mo-sputtered SLG substrates were purchased from Thin Film Devices, Inc. (Anaheim, CA) with a 750 nm layer of Mo on Pilkington Optifloat[™] Clear 3.2 mm glass (Pilkington North America, Inc., Toledo, Ohio).

Indium Electrodes. The CZTS/Se, CdS, i-ZnO, and ITO layers around the devices were removed by scribing. Indium electrodes were then applied onto the Mo substrates by using a solder tip at temperatures between 150 and 310 °C, typically 210 °C.

IV Analysis. Current (I) versus voltage (V) measurements were performed on the samples using two Agilent 5281B precision medium-power SMUs in a E5270B mainframe in a four-point probe configuration. Samples were illuminated with an Oriel 81150 solar simulator under 1 sun AM 1.5G. Active-area efficiencies were determined by subtracting the area shaded by silver lines from the total area of the device.

XAS Analysis. XANES spectroscopy at the Cu, Zn and Sn K-edges was carried out at the Advanced Photon Source at the Argonne National Laboratory. Data were collected in fluorescence geometry at beamline 5BMD, DND-CAT. Thin-film samples were presented to the incident X-ray beam as made. An Oxford spectroscopy-grade ion chamber was used to determine the X-ray incident intensity (I_0). The I_0 detector was filled with 570 Torr of N₂ and 20 Torr of Ar. The fluorescence detector was a Lytle Cell filled with Xe installed perpendicular to the beam propagation direction. Data were collected from 8,879 eV to 9,954 eV for the Cu edge. The high final energy was used in order to capture a portion of the Zn edge in the same data set, allowing edge step ratio determination as an estimate of the Cu:Zn ratio in the film. The Zn edge data were collected over the range 9,557 eV to 10,404 eV. Sn edge data covered the range of 29,000 eV to 29,750 eV. The data energy scales were calibrated based on data from metal reference foils collected prior to sample data collection. A second order background was subtracted and the spectra were normalized. Data from several Cu, Zn and Sn sulfide, selenide, and oxide standards (Cu₂ZnSnS₄, Cu₂ZnSnSe₄, Cu₂SnS₃, CuS, Cu₂S, CuSe, Cu₂Se, CuO, Cu₂O, ZnS, ZnSe, ZnO, SnS, SnSe, SnO and SnO₂) were obtained under the same conditions. Non-linear least squares fitting of a linear combination of the appropriate standards to the spectra obtained from the samples yielded the phase distribution for each element.

hot into the copper solution, resulting immediately in a dark brown, turbid mixture. The mixture was stirred for 5 min at 280 °C and then removed from the heat and cooled rapidly.

Synthesis of Coated copper tin sulfide (CTS) Nanoparticles. A solution of CuCl (3.96 g, 40 mmol), SnCl₄ (5.21 g, 20 mmol), and TOPO (46.4 g, 120 mmol) in 150 mL of oleylamine was heated at 260 °C under a nitrogen atmosphere with continuous mechanical stirring for 30 min, resulting in a transparent orange solution. Next, sulfur (1.92 g, 60 mmol) was dissolved in 30 mL of oleylamine by heating to 120 °C with mechanical stirring. The sulfur solution was injected hot into the copper-tin solution, resulting immediately in a dark brown, turbid mixture. The reaction mixture was stirred at 260 °C for 3 min and then cooled down in tap water for 1 min, and then in ice-water until it reached thermal equilibrium with the ice-water bath.

Synthesis of Coated SnS Nanoparticles. A solution of SnCl₄ (10.42 g, 40 mmol) and TOPO (46.4 g, 120 mmol) in 150 mL of oleylamine was heated at 220 °C under a nitrogen atmosphere with continuous magnetic stirring for 30 min, resulting in a transparent yellow solution. Next, sulfur (1.536 g, 48 mmol) was dissolved in 30 mL of oleylamine by heating to 120 °C with mechanical stirring. The sulfur solution was injected hot into the tin solution, resulting immediately in a black, turbid mixture. The reaction mixture was maintained at 220 °C for 5 min and then cooled down in tap water for 1 min, and then in ice-water until it reached thermal equilibrium with the ice-water bath.

Synthesis of Coated ZnS Nanoparticles. A solution of ZnCl₂ (5.72 g, 42 mmol) and trioctylphosphine oxide (48.7 g, 126.4 mmol) in 150 mL of oleylamine was heated at 170 °C under a nitrogen atmosphere with continuous magnetic stirring for 1 h, resulting in a transparent orange solution. Next, sulfur (1.613 g, 50.4 mmol) was dissolved in 30 mL of oleylamine by heating to 120 °C with mechanical stirring. The sulfur solution was injected hot into the zinc solution. The reaction mixture was heated to 320 °C, maintaining this temperature for 75 min, and then cooled in the air for 3 min, then in tap water for 1 min, and then in ice-water until it reached thermal equilibrium with the ice-water bath.

(Figure S4a). XRD analysis (Figure S4b) suggested the co-existence of several phases of SnS with potentially a small amount of SnS₂ present. XAS analysis suggested that there is also a small amount of SnO₂ present as an impurity.

ZnS. The ZnS sphalerite structure was determined by XRD (Figure S5). The particles were close to spherical in shape with 10 nm diameter.

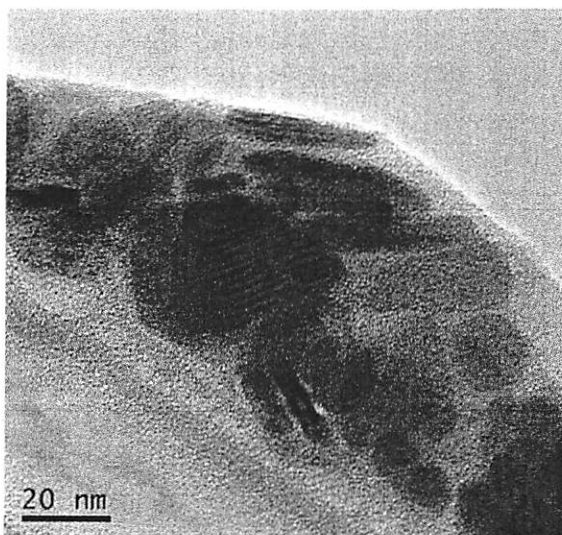


Figure S1a. TEM image of the synthesized CuS nanoparticles.

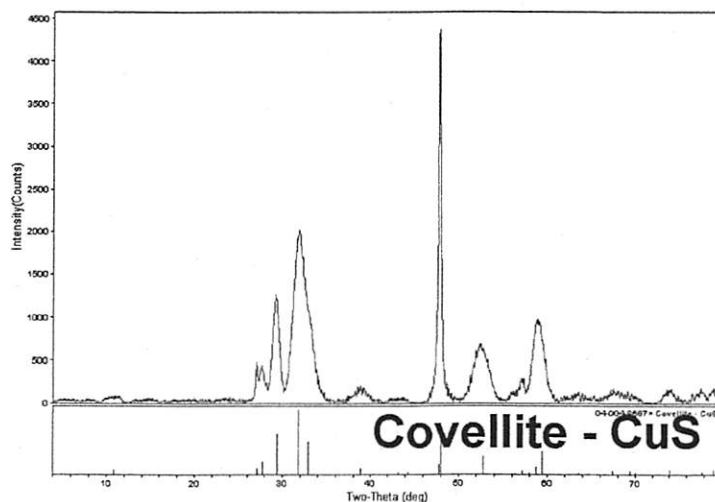


Figure S1b. XRD pattern of the synthesized CuS nanoparticles.

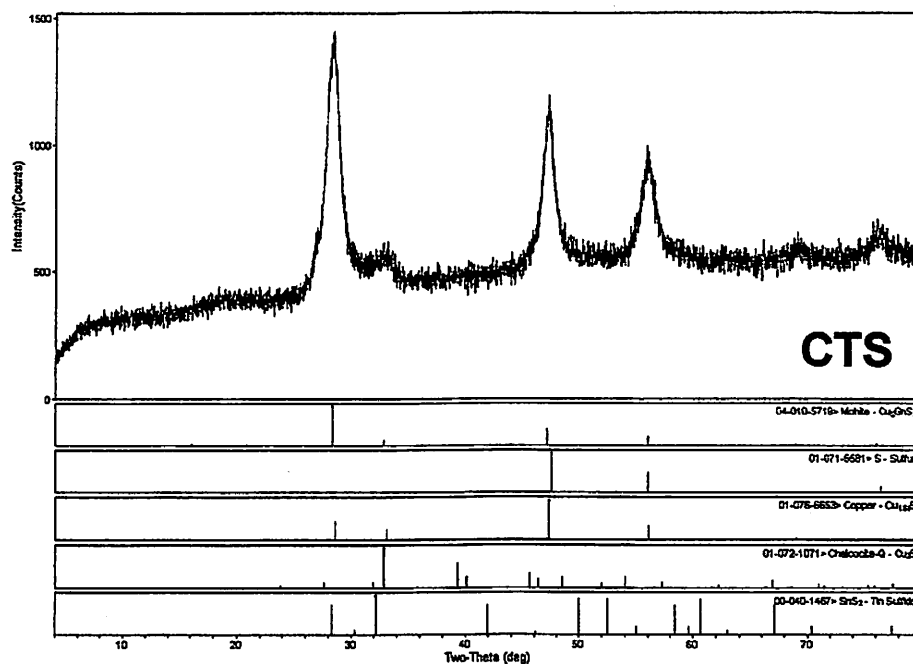


Figure S3a. XRD pattern of the synthesized CTS nanoparticles.

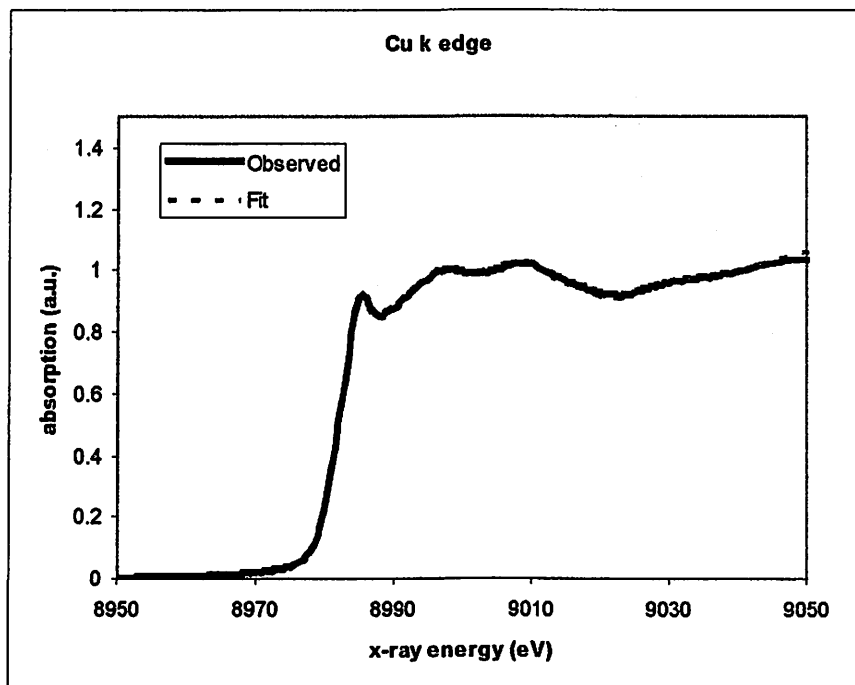


Figure S3b. Cu k edge XANES data of the synthesized CTS nanoparticles.

Control of Metal Ratios in CZTSSe Films

As described below, the Cu/Zn ratio in CZTSSe films was controlled by varying the CTS/ZnS ratio in the precursor ink.

CTS, ZnS, and SnS nanoparticles were prepared as described above and separately dispersed with probe sonication in hexanethiol (200 mg of nanoparticles per mL of hexanethiol). Each of the three dispersions was individually passed through a 1 micron syringe filter. Then the three dispersions were mixed with the volume ratios given in Table S1 to provide Inks 1 - 4.

Table S1. Precursor Ink Recipes for Inks 1 - 4

Ink	CTS/ZnS (vol/vol)	CTS	ZnS	SnS
1	1.6	0.752	0.47	0.078
2	1.75	0.7611	0.4349	0.104
3	1.9	0.7666	0.4034	0.13
4	2.05	0.7689	0.3751	0.156

Following 10 min of sonication to aid mixing, a portion of each ink was applied to a Mo-coated glass substrate by spin coating with a ramp rate of 1000 rpm and spinning speed of 3000 rpm for 20 sec. The samples were then soft-baked on a hot plate at 150 °C for 2 min and then at 300 °C for 2 min. The deposition, spin-coating, and soft-baking procedures were repeated 7 additional times to yield 8-layer coatings. Next, the coated substrates were annealed at 560 °C for 20 min according to the above general procedure with ~150 mg of elemental selenium and ~40 mg of Sn in separate small ceramic boats. Figure S6 shows that Cu/Zn ratio in annealed CZTSSe films, as determined by ICP-AES, increased linearly with the volume ratio of CTS/ZnS in the corresponding inks. The XRD patterns of the samples are shown in Figures S7a through Figure S7d and indicate that CZTSSe was the major crystalline phase of all four films.

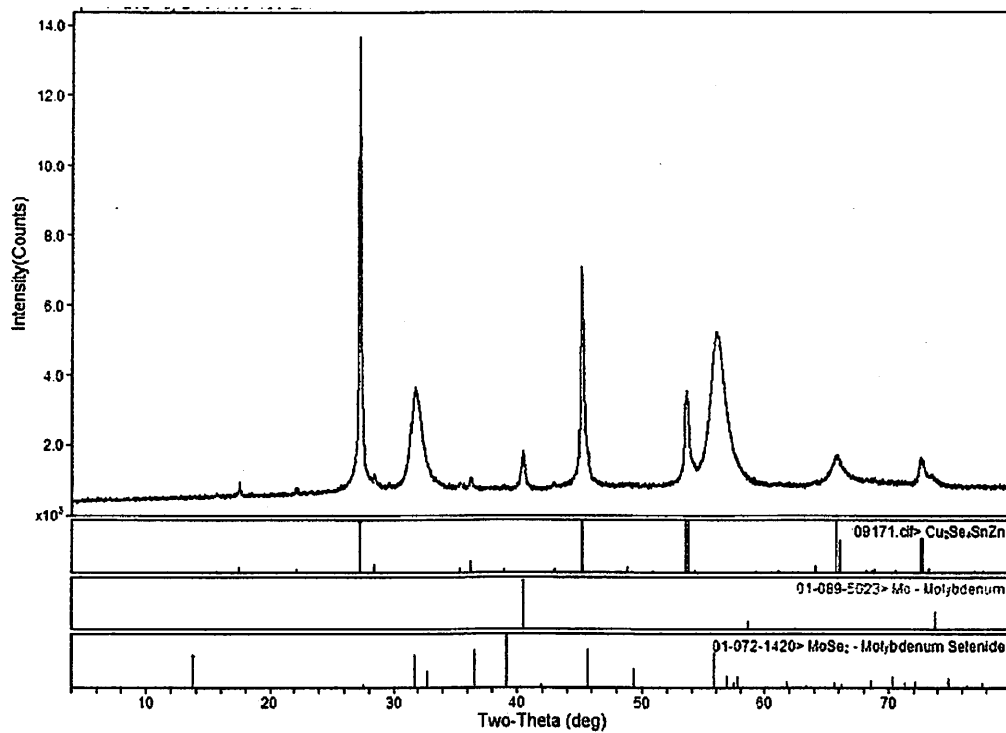


Figure S7b. XRD pattern of the annealed film derived from Ink 2 of Table S1.

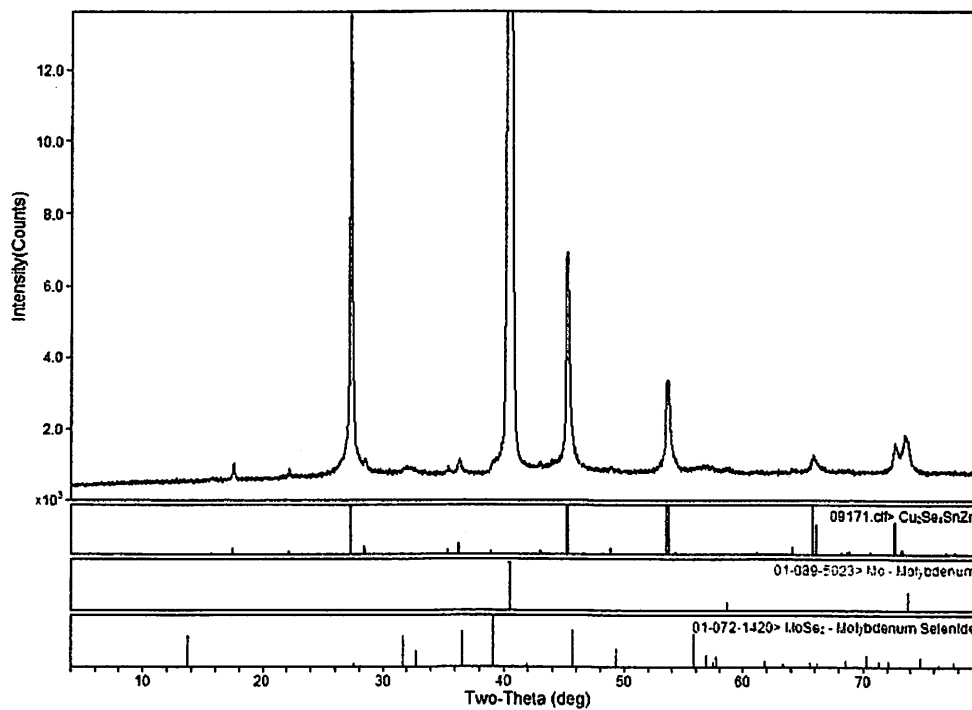


Figure S7c. XRD pattern of the annealed film derived from Ink 3 of Table S1.

was annealed at 560 °C for 20 min, according to the above general procedure, with ~50 mg of elemental selenium and ~40 mg of Sn in separate small ceramic boats. The XRD pattern of the resulting CZTSSe film is shown in Figure S8.

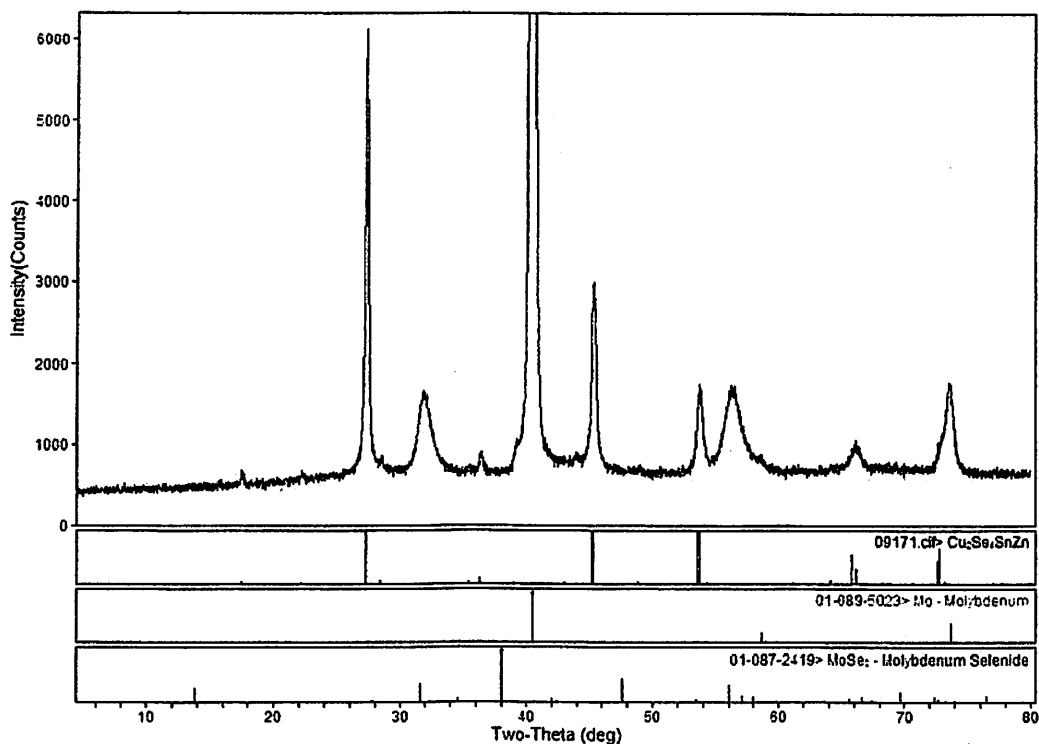


Figure S8. XRD pattern of a CZTSSe film formed from binary nanoparticles.

Device Fabrication and Measurements

8.5% Total-Area Efficiency Device (Figures 2). CTS, ZnS, and SnS nanoparticles were prepared as described above and then separately dispersed by probe sonication in hexanethiol (200 mg of nanoparticles per mL of hexanethiol). Next, each of the three dispersions was individually passed through a 1 micron syringe filter. The CZTS precursor ink was made by mixing the three dispersions at 11.0% (by volume) SnS dispersion, 30.7% (by volume) ZnS dispersion, and 58.3% (by volume) CTS dispersion, followed by bath sonication for 20 min. A portion of the precursor ink was deposited and spin-coated onto a molybdenum-coated glass substrate with a ramp rate of 1000 rpm

dispersions at 5.87% (by volume) SnS dispersion, 24.64% (by volume) ZnS dispersion, and 69.49% (by volume) CTS dispersion. Following 20 min of bath sonication, the inks were applied to Mo-coated glass substrates by spin coating with a ramp rate of 1000 rpm and spinning speed of 3000 rpm for 20 sec. The samples were soft-baked on a hot plate at 175 °C for 2 min and then at 300 °C for 2 min. The deposition, spin-coating, and soft-baking procedures were repeated 5 additional times to yield 6-layer coatings.

Next, the coated substrates were annealed at 520 °C for 30 min, according to the above general procedure, with ~200 mg of elemental selenium in a small ceramic boat. The annealed samples were then etched with 0.5 M KCN solution at 50 °C for 1 min and then with 1 M HCl solution at room temperature for 1 min. Thorough rinsing with deionized water was performed after each etching step. Next, CdS deposition was carried out as described above. Following deposition of i-ZnO, ITO, Ag grids, and indium electrodes, IV measurements were obtained.

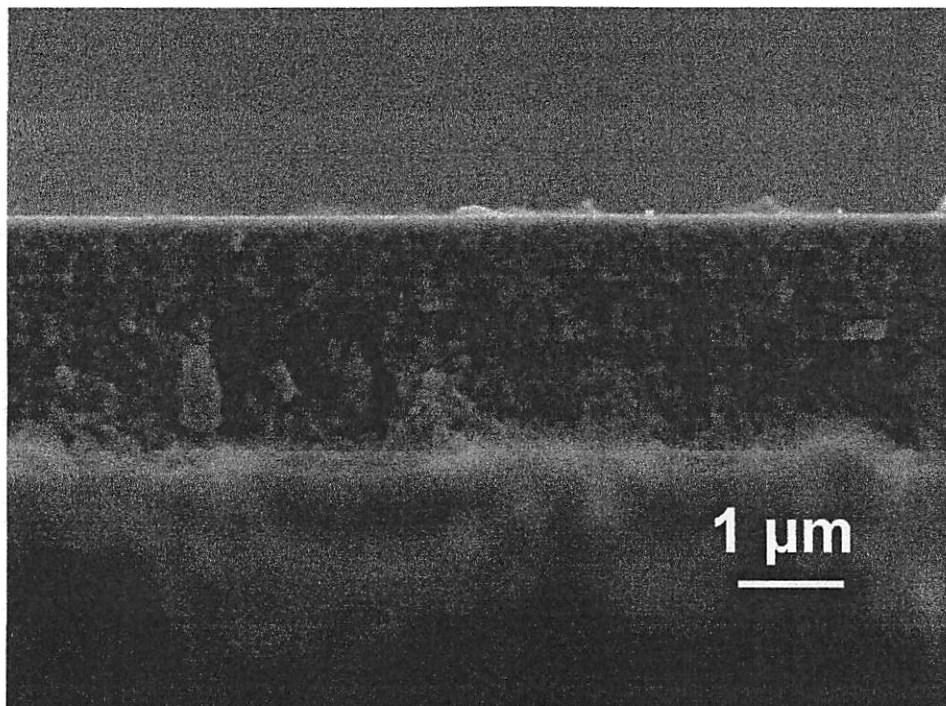


Figure S9. Cross-sectional SEM image of a soft-baked precursor film, analogous to that used to prepare the 8.5% efficiency device of Figure 2.

- (1) Redinger, A.; Hoenes, K.; Fontane, X.; Izquierdo-Roca, V.; Saucedo, E.; Valle, N.; Perez-Rodriguez, A.; Siebentritt, S. *Appl. Phys. Lett.* **2011**, *98*, 101907.
- (2) Jiang, C.; Lee, J.-S.; Talapin, D. V. *J. Am. Chem. Soc.* **2012**, *134*, 5010-5013.
- (3) Grossberg, M.; Krustok, J.; Raudoja, J.; Timmo, K.; Altosaar, M.; Raadik, T. *Thin Solid Films* **2011**, *519*, 7403-7406.