

Supporting Information

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Low-Temperature Solution Processing of Mesoporous Metal–Sulfide Semiconductors as Light-Harvesting Photoanodes**

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Experimental Section

Sample and device fabrication:

Antimony triethyldithiocarbonate (antimony ethylxanthate, $\text{Sb}(\text{EX})_3$) was prepared as described previously.^[1]

$\text{Sb}(\text{EX})_3$ precursor pastes were prepared by adding a 3:1 molar ratio of hexylamine to a stirred 40 mg/mL chlorobenzene solution of antimony triethyldithiocarbonate. Doctor-blading onto cleaned glass (for transient absorption, x-ray diffraction and UV-Vis absorption studies), fluorine-doped tin oxide (FTO, Ossila) substrates (for scanning electron microscopy and x-ray photoelectron spectroscopy) or indium-doped tin oxide (device fabrication) formed an orange $\text{Sb}(\text{EX})_3$ precursor film. Films were annealed for 30 minutes on a hot plate in a nitrogen glove box to yield porous crystalline Sb_2S_3 films.

Photovoltaic devices include a thin, dense TiO_2 layer in between the ITO substrate and the Sb_2S_3 layer, which was deposited by spin coating a 7:5.5:100 by volume solution of titanium isopropoxide, ethanol amine and 2-methoxyethanol at 6000 rpm for 30 seconds, followed by annealing in atmospheric conditions for 30 minutes at 450 °C. CdS layers (20 nm) were deposited from a 100 mg/mL chlorobenzene solution of a pyridine adduct of cadmium ethylxanthate by spin coating at 6000 rpm for 30 seconds, followed by annealing at 160 °C for 30 minutes in a nitrogen glove box. CdS is a common window layer for both thin-film and hybrid photovoltaics.^[1-2] Here, we find that device performance is significantly inhibited when a CdS layer is not included in the device architecture (see Supporting Information Figure 9). Control devices in the ITO/dense TiO_2 /CdS/P3HT/PEDOT:PSS/Ag configuration (without the mesoporous Sb_2S_3 layer) also performed very poorly. It is expected that the CdS layer acts to reduce direct recombination between photogenerated holes transferred to P3HT and electrons at the TiO_2 /ITO electrode.^[2b]

Poly-3-hexylthiophene (P3HT, Merck) was spin-coated from a 25 mg/mL solution at 2500 rpm for 1 minute. Poly(3,4-ethylenedioxythiophene) poly(styrenesulphonate) (PEDOT:PSS, Ossila) containing 1% Zonyl (du Pont) by volume was spin coated before 100 nm thick Ag contacts were vacuum deposited as the top electrode to give devices with an active area of 0.045 cm².

Characterisation:

Absorption spectra were determined by subtracting the percentage transmission and reflection (as measured on a Perkin-Elmer Lambda 750 UV-vis-n-IR absorption spectrometer fitted with an integrating sphere) from unity.

For pump-probe micro to millisecond transient absorption spectroscopy, films were excited by a dye laser (Photon Technology International GL-301, sub-nanosecond pulse width) pumped by a pulsed nitrogen laser (Photon Technology International GL-3300,). A quartz halogen lamp (Bentham IL1) was passed through a monochromator and used to probe changes in the absorption characteristics of the film as a function of time after the laser excitation. The probe light was detected using home-built silicon (≤ 1000 nm) or $\text{In}_x\text{Ga}_{1-x}\text{As}$ (> 1000 nm) photodiodes. Films were kept under flowing N_2 during the measurement.

Scanning electron microscopy was performed using the In Lens detector of a LEO 1525 Field Emission Scanning Electron Microscope operating at 5 kV. Samples were sputter coated with a ~ 17 nm layer of chromium prior the measurement to improve conductivity.

X-ray diffraction was conducted with a PANalytical X'Pert Pro MRD diffractometer using Ni filtered Cu K-alpha radiation at 40 kV and 40 mA.

Current-voltage characteristics of complete cells were measured using a Keithley 2400 series source meter, under illumination from a 150 W Xenon lamp (ScienceTech SS150W solar simulator) with IR filter (Water Filter) and AM1.5 filter (ScienceTech) where relevant. Illumination for IPCE measurements was provided by a quartz halogen lamp (Bentham IL1) filtered through a monochromator.

X-ray photoelectron spectroscopy (XPS) was performed at beamline I411 at the synchrotron facility MAX-IV (Lund, Sweden).^[3] A photon energy of 758 eV was used and the photoelectrons were detected with a Scienta R4000 analyser. The binding energy of the XPS spectra was referenced versus the Fermi level at zero binding energy. The spectra are intensity calibrated using the Sb $3d_{5/2}$ peak.

Supplementary Information

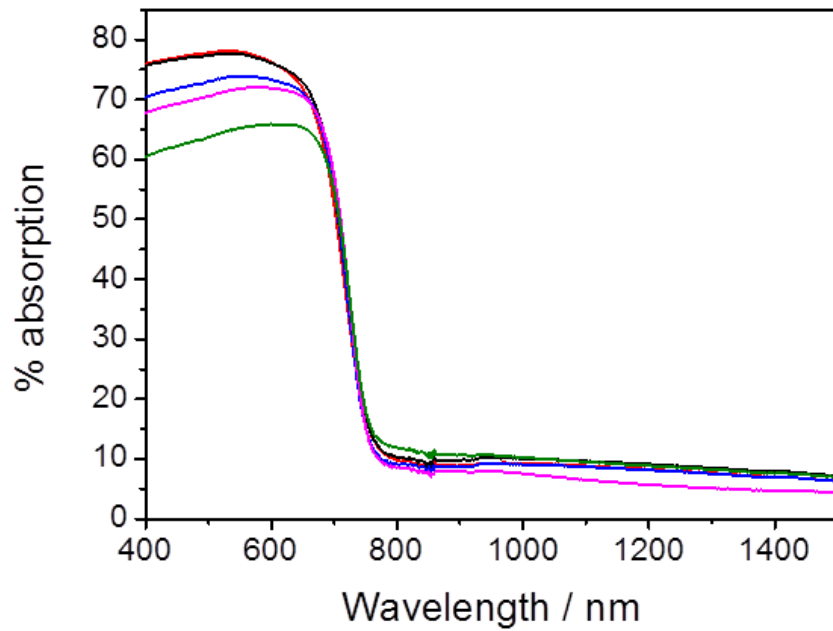


Figure 1 – Absorption spectra of Sb₂S₃ films as a function of precursor layer annealing temperature (red = 120 °C, black = 160 °C, blue = 200 °C, pink = 250 °C, green = 300 °C).

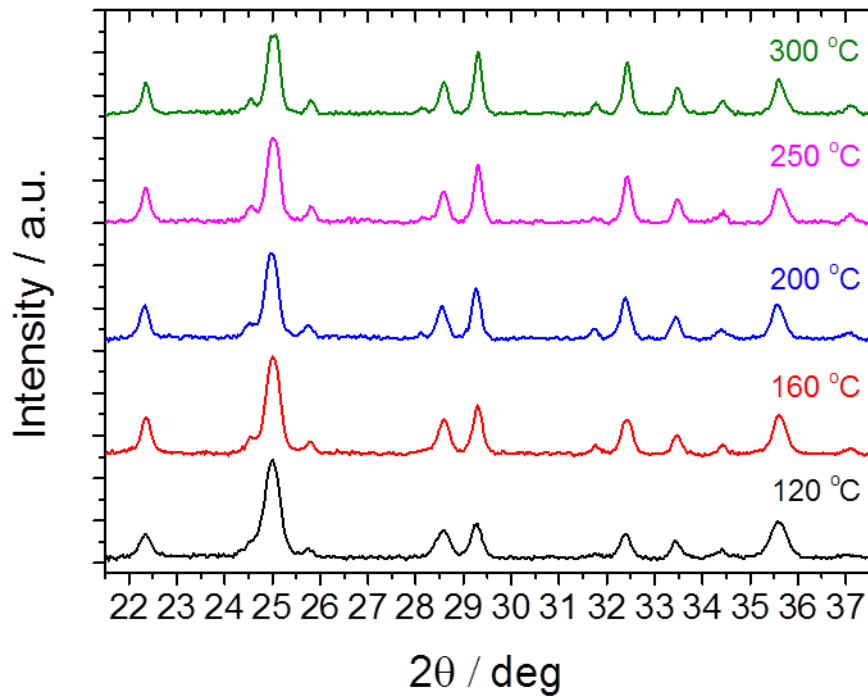


Figure 2 - / X-ray diffraction patterns of Sb₂S₃ films as a function of annealing temperature.

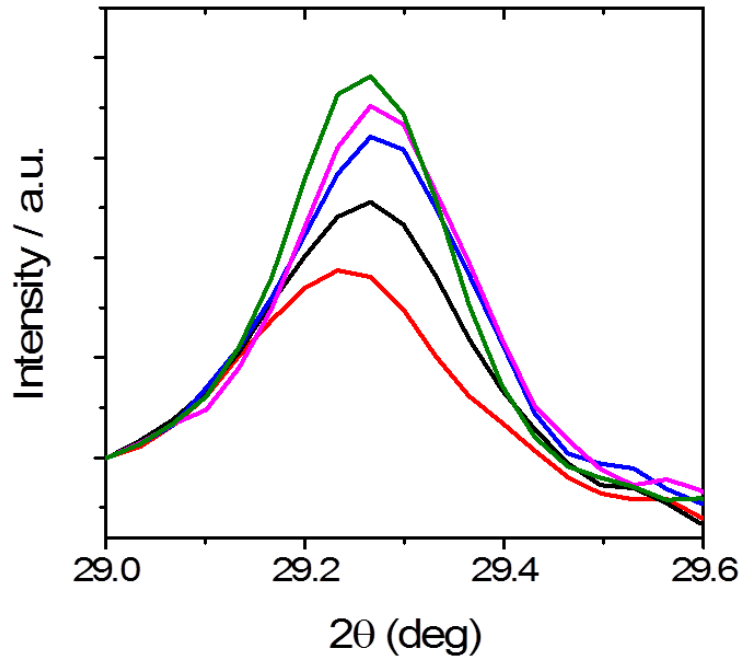


Figure 3 – Increase in full-width half-max of Sb₂S₃ (211) peak as a function of precursor layer annealing temperature (red = 120 °C, black = 160 °C, blue = 200 °C, pink = 250 °C, green = 300 °C). Using the Scherrer formula, average crystallite size can be estimated to be ~ 82 nm, 91 nm, 106 nm, 117 nm and 137 nm for the films annealed at 120 °C, 160 °C, 200 °C, 250 °C and 300 °C respectively. We note that the associated error in these values will increase as the FWHM of the peaks approaches that of a large single crystal, although the trend remains striking.

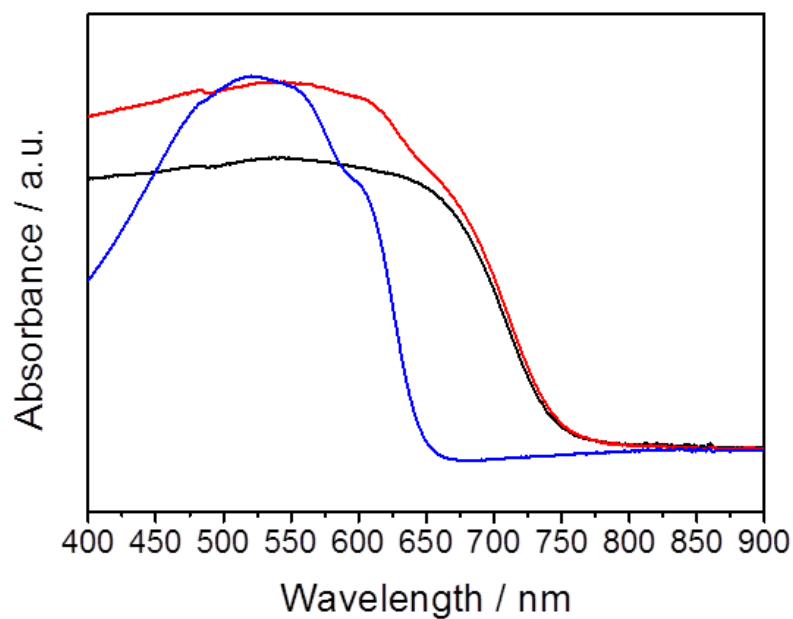


Figure 4 – Absorption spectra of Sb₂S₃ film (black curve), pristine P3HT film (blue curve) and Sb₂S₃/P3HT composite film (red curve).

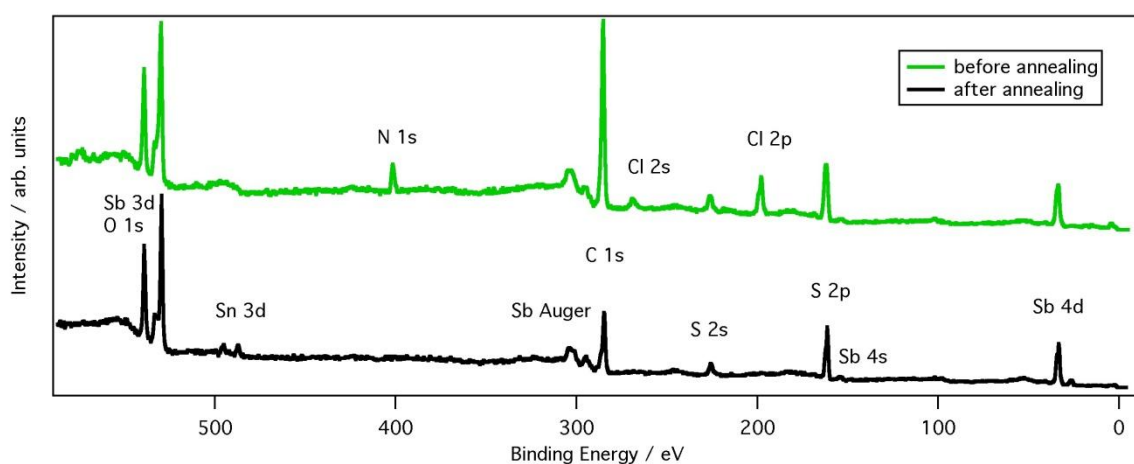


Figure 5 – XPS overview measurements before and after thermal annealing at 160°C showing all the elemental core-levels in the samples. Also visible is the Sn 3d level from the conducting glass substrate. Nitrogen and chlorine disappear upon annealing together with most of the carbon. Some carbon and oxygen are still present after annealing, which is expected on the surface of samples prepared outside of ultrahigh vacuum.

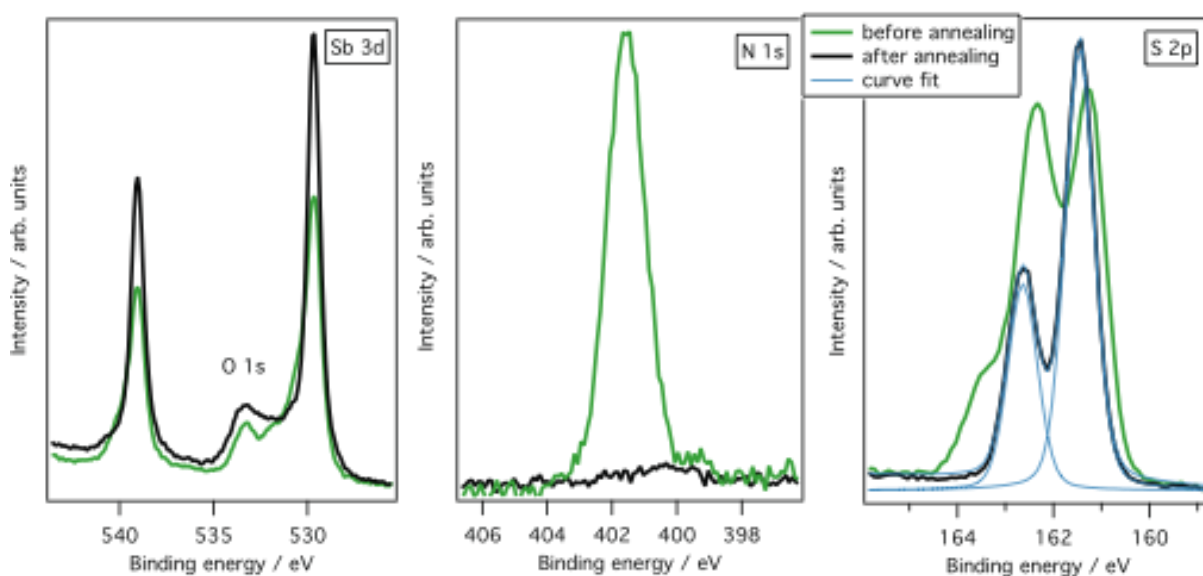


Figure 6 - XPS measurements of the Sb 3d, N 1s and S 2p core levels before and after annealing at 160°C. The nitrogen signal disappears during annealing. The antimony Sb 3d and sulphur S 2p core level peaks become narrower with annealing, indicating a more ordered structure. Furthermore, after annealing, the S 2p core level can be fitted with one peak doublet (S 2p_{1/2} and S 2p_{3/2}) with narrow peaks (FWHM 0.72eV) showing that all sulphur atoms are chemically equivalent.

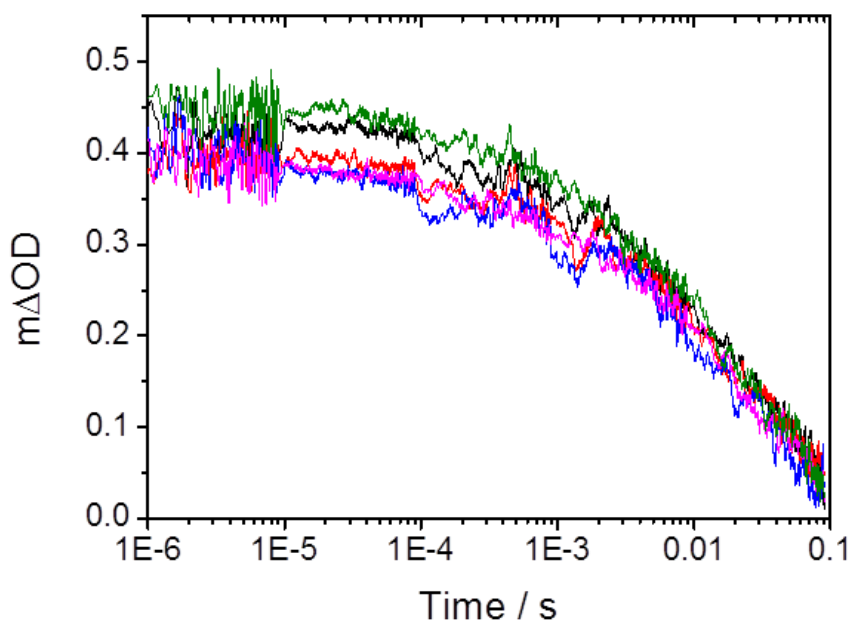


Figure 7 – Decay in transient absorption of P3HT hole polaron at 980 nm for $\text{Sb}_2\text{S}_3/\text{P3HT}$ films as a function of laser excitation wavelength (black trace – 450 nm, red – 510 nm, blue – 567 nm, pink – 620 nm and green – 650 nm). $\text{Sb}(\text{EX})_3$ precursor layer was annealed at 160 °C. Signals are scaled to account for small differences in the number of photons incident upon the sample at the excitation wavelength. Laser power = $10.2 \mu\text{J cm}^{-2}$ (450 nm), $9.4 \mu\text{J cm}^{-2}$ (510 nm), $8.4 \mu\text{J cm}^{-2}$ (567 nm), $8.4 \mu\text{J cm}^{-2}$ (620 nm), $8.7 \mu\text{J cm}^{-2}$ (650 nm).

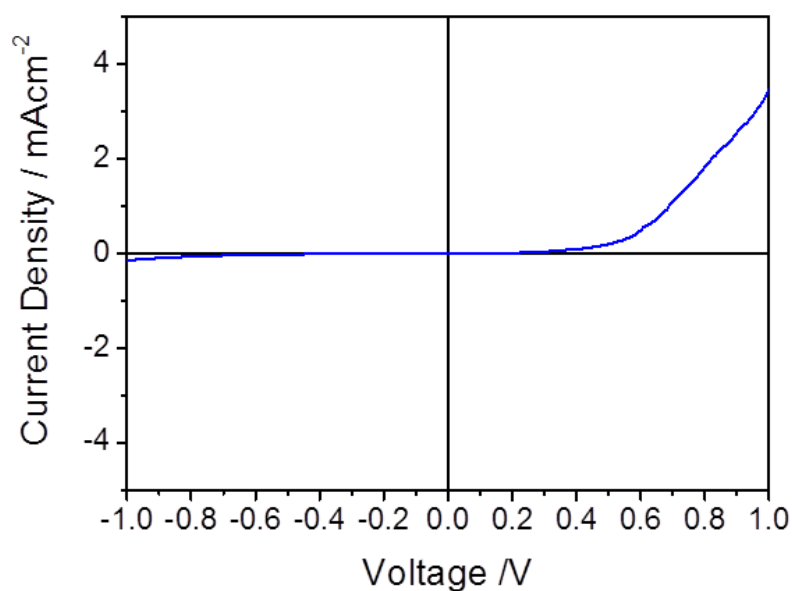


Figure 8 – Current-voltage response of an $\text{ITO}/\text{TiO}_2/\text{CdS}/\text{Sb}_2\text{S}_3/\text{P3HT}/\text{PEDOT:PSS}/\text{Ag}$ photovoltaic device in the dark.

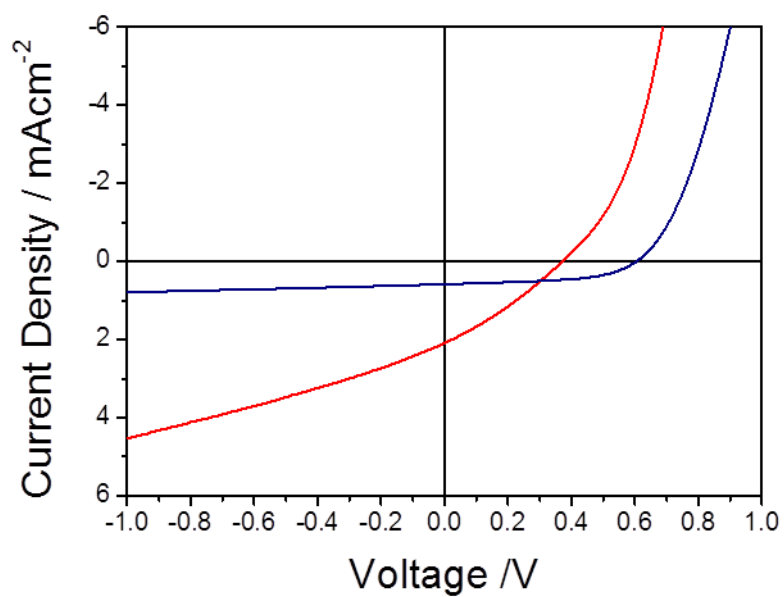


Figure 9 – Current voltage response of an ITO/TiO₂/CdS/P3HT/PEDOT:PSS/Ag (blue trace - $J_{SC} = 0.58$ mA cm⁻², $V_{OC} = 0.60$ V, FF = 0.52, PCE = 0.19 %) and an ITO/TiO₂/Sb₂S₃/P3HT/PEDOT:PSS/Ag (ref trace - $J_{SC} = 2.09$ mA cm⁻², $V_{OC} = 0.37$ V, FF = 0.30, PCE = 0.23 %) device under 1 Sun illumination.

References

- [1] N. Bansal, F. T. F. O'Mahony, T. Lutz, S. A. Haque, *Adv. Energy Mater.* **2013**, Available Online, DOI:10.1002/aenm.201300017.
- [2] a) S. Messina, M. Nair, P. Nair, *Thin Solid Films* **2007**, *515*, 5777-5782; b) S. Dowland, T. Lutz, A. Ward, S. P. King, A. Sudlow, M. S. Hill, K. C. Molloy, S. A. Haque, *Adv. Mater.* **2011**, *23*, 2739-2744.
- [3] M. Bäessler, J. O. Forsell, O. Björneholm, R. Feifel, M. Jurvansuu, S. Aksela, S. Sundin, S. L. Sorensen, R. Nyholm, A. Ausmees, S. Svensson, *J. Electron. Spectrosc. Relat. Phenom.* **1999**, *101-103*, 953-957.