Supporting Information

Solution Deposition of a Bournonite $CuPbSbS_3$ Semiconductor Thin Film from the Dissolution of Bulk Materials with a Thiol-Amine Solvent Mixture

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Characterization. *Thermal gravimetric analysis* (TGA) was performed on a TA Instruments TGA Q50 instrument and samples were run in an alumina crucible under a flowing nitrogen atmosphere with a heating rate of 5 ˚C min^{-1}. The TGA samples were prepared by drying the ink in an alumina crucible to 140 ˚C under a flowing nitrogen atmosphere in an aluminum annealing chamber prior to TGA analysis to avoid excess corrosion of the thermocouple in the TGA. *Fourier transform infrared* (FT-IR) spectra were measured on a Bruker Vertex 80 spectrometer. The samples were prepared by drop casting the $CuPbSbS_3$ ink onto a ZnSe window and drying to 100 ˚C before annealing to 450 ˚C under a flowing stream of nitrogen. FT-IR spectra were background corrected with ~20 iterations. *Scanning electron microscopy* (SEM) was performed on a JEOL JSM-7001F scanning electron microscope with an operating voltage of 10 kV. The films were scored with a diamond scribe and broke in half before they were sputtered with argon before SEM imaging. *Inductively-coupled plasma optical emission spectroscopy* (ICP-OES) was performed on an iCap 7400 ICP. All powder samples were digested with 2 mL of concentrated nitric acid and subsequently diluted to 25 mL with Millipore water in a volumetric flask. Copper, lead, and antimony ICP standards were prepared at different concentrations (0.1 ppm, 0.8 ppm, 2 ppm, 5 ppm, 10 ppm) to construct a five-point calibration curve from which the sample concentrations of Cu, Pb, and Sb could be determined. *Raman* spectra were conducted on 570 nm bournonite thin films on glass substrates annealed to 450 °C for 20 min using a Horiba XploRA confocal Raman microscope with 785 nm excitation. The Raman microscope was covered with a black tarp to reduce ambient light exposure. *X-ray photoelectron spectroscopy* (*XPS*) was performed using a Kratos Axis Ultra X-ray photoelectron spectrometer with a monochromatic aluminum anode. An operating current of 5 mA and voltage of 12 kV with a step size of 0.1 eV, a pass energy of 20 eV, and a pressure range of $9 \times 10^{-8} - 1 \times 10^{-9}$ Torr was used to acquire 20 high resolution scans for each element. XPS was done on thin films deposited on Si/SiO_2 substrates using the solution deposition method described in the main text. In situ Ar^+ ion beam milling was done for 5 min. *Photoconductivity measurements* were performed on a basic device architecture whereby the absorber layer was deposited on a glass substrate patterned with parallel FTO electrodes with a spacing of ~20 μm that was pre-cleaned as described in the main text. The cleaned FTO substrates were masked with Kapton tape to leave bare FTO for the electrode connections and the $CuPbSbS_3$ absorber layer was deposited as described in the main text. The Kapton mask was peeled off and the final anneal to 450 °C for 20 min was done without Kapton tape. Photoconductivity measurements were performed in air at 25 °C using a Keithley 2420 Sourcemeter (sensitivity = 100 pA) in the dark and under white light illumination from an AM1.5G filtered 300 W Xe arc lamp (Asahi Spectra HAL-320W).

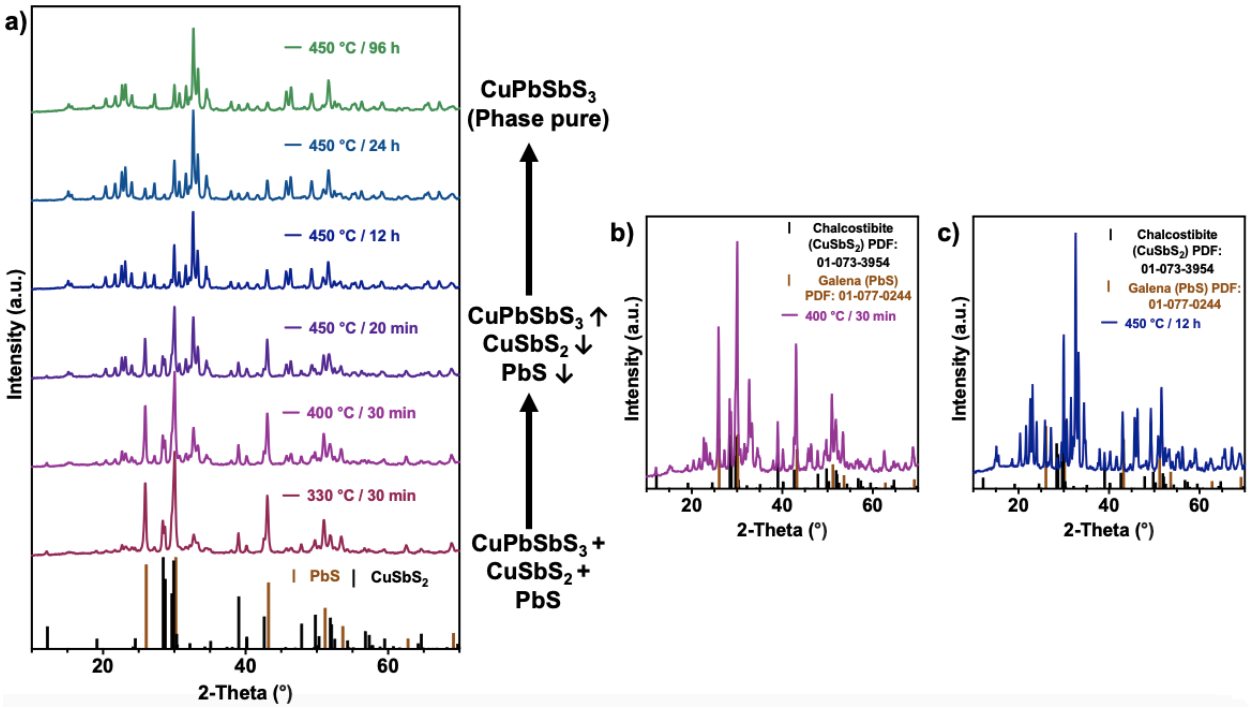

Figure S1. (a) Ex situ powder XRD patterns of a dropcast ink annealed to various temperatures and times showing the phase evolution of $CuPbSbS_3$ indexed with $CuSbS_2$ and PbS. (b) Powder XRD pattern of dropcast ink annealed to 400 ˚C for 30 min showing substantial PbS and $CuSbS_2$ impurities. (c) Powder XRD pattern of dropcast ink annealed to 450 ˚C for 12 h showing reduced PbS and $CuSbS_2$ impurities.

Table S1. Structural parameters of phase-pure bournonite $CuPbSbS_3$ extracted from Rietveld analysis.

Space Group	*Pmn2₁*
a (Å)	7.8158(58)
b (Å)	8.1515(17)
c (Å)	8.6729(54)
V (Å^3)	552.5634(34)
$\alpha = \beta = \gamma$	90˚
R_{wp}	4.96%
χ^2	2.48

Atom	Multiplicity	Occupancy	*x*	*y*	*z*	U_{iso} (Å^2)
Cu_1	4	1.0	0.25038(9)	0.26601(5)	0.40833(1)	0.0167(7)
Pb_1	2	1.0	0.0	0.07523(4)	0.994008	0.0102(9)
Pb_2	2	1.0	0.0	0.44129(3)	0.67268(6)	0.00100
Sb_1	2	1.0	0.0	0.92307(8)	0.54000(1)	0.00100
Sb_2	2	1.0	0.0	0.50855(9)	0.15134(9)	0.00100
S_1	2	1.0	0.0	0.22264(8)	0.28514(1)	0.00100
S_2	2	1.0	0.0	0.75425(5)	0.75841(6)	0.00100
S_3	4	1.0	0.24232(8)	0.10121(2)	0.64531(3)	0.00100
S_4	4	1.0	0.26614(8)	0.58338(3)	0.45166(7)	0.00100

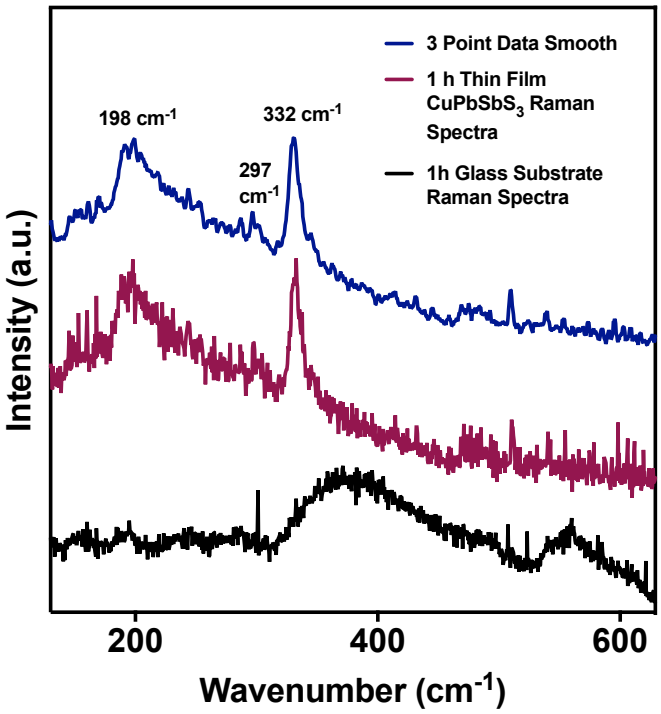

Figure S2. Raman spectra of a 570 nm $CuPbSbS_3$ thin film on glass annealed to 450 °C for 20 min, along with a blank borosilicate substrate.

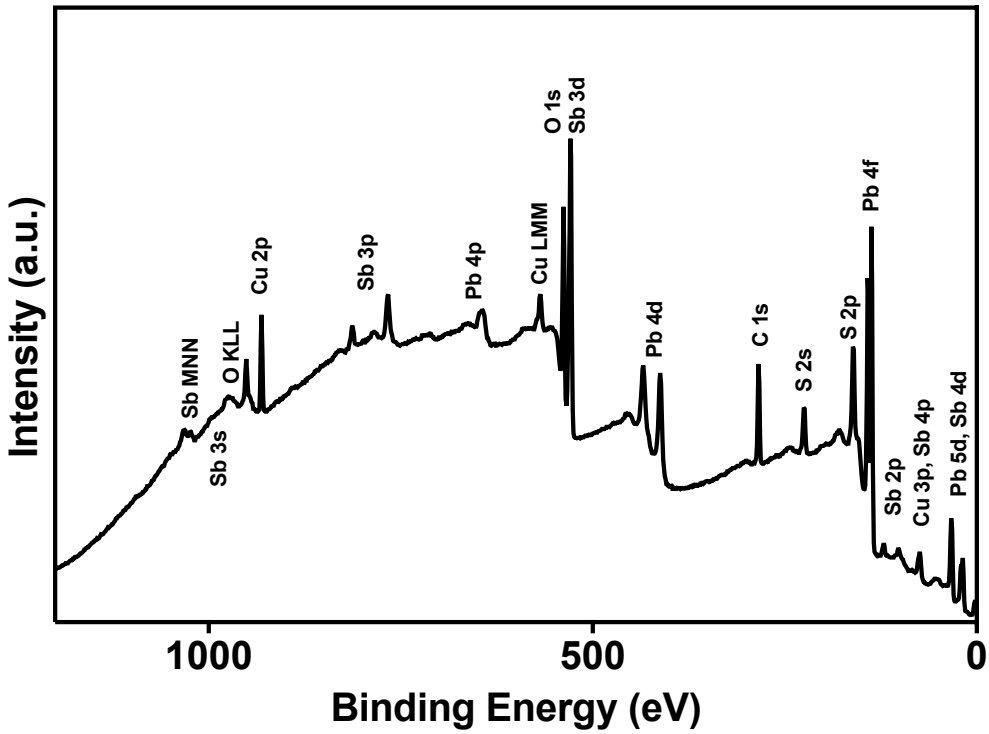

Figure S3. XPS survey scan of thin film $CuPbSbS_3$ on Si/SiO_2 before in situ Ar^+ ion beam milling.

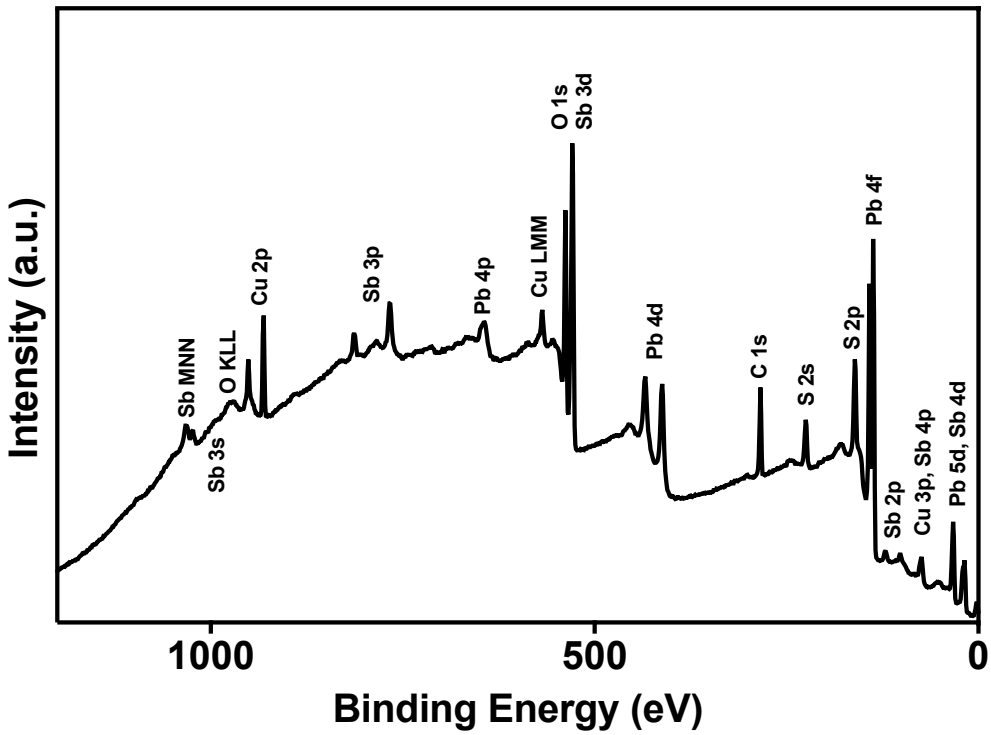

Figure S4. XPS survey scan of thin film $CuPbSbS_3$ on Si/SiO_2 after in situ Ar^+ ion beam milling.

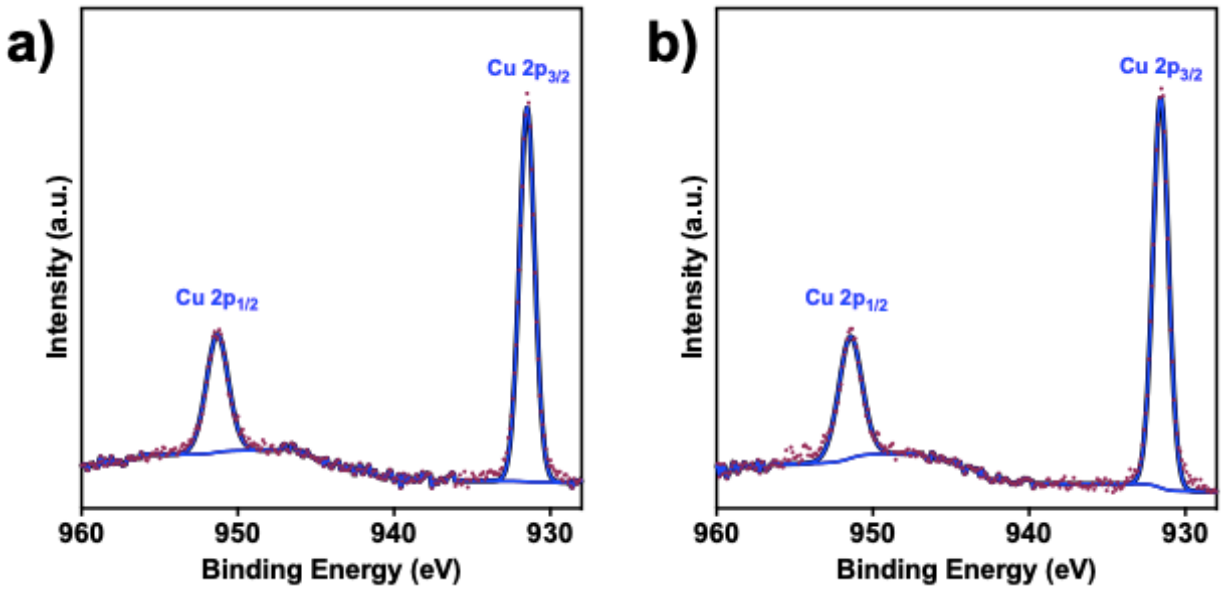

Figure S5. High-resolution XPS spectra for (a) Cu 2*p* before in situ Ar^+ ion beam milling, and (b) Cu 2*p* after milling.

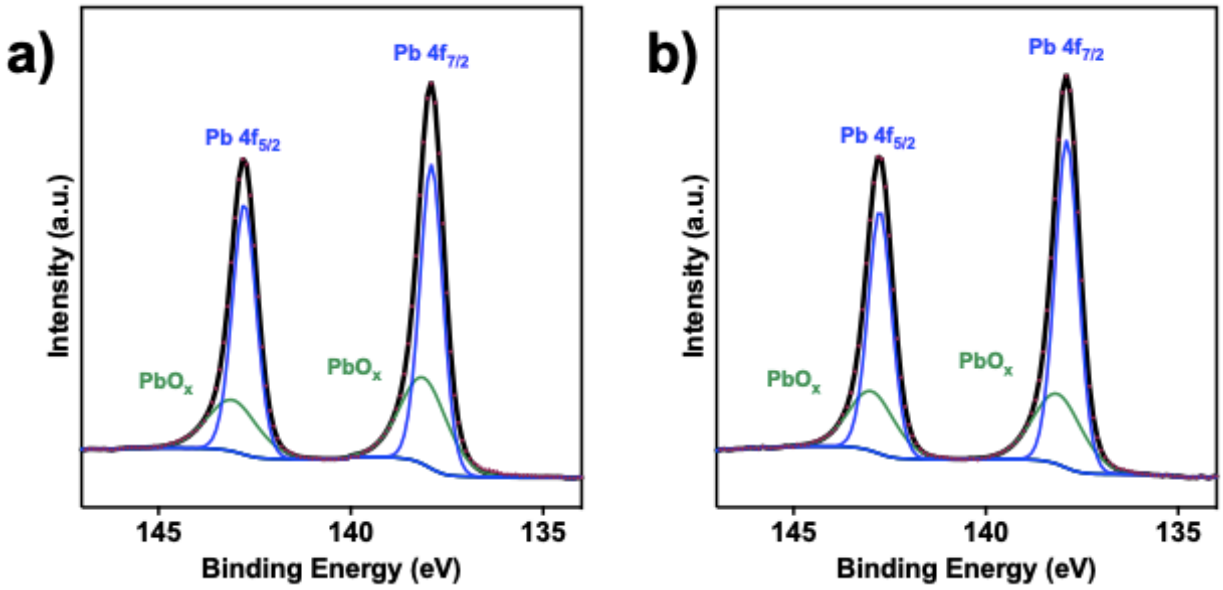

Figure S6. High-resolution XPS spectra for (a) Pb 4*f* before in situ Ar^+ ion beam milling, and (b) Pb 4*f* after milling.

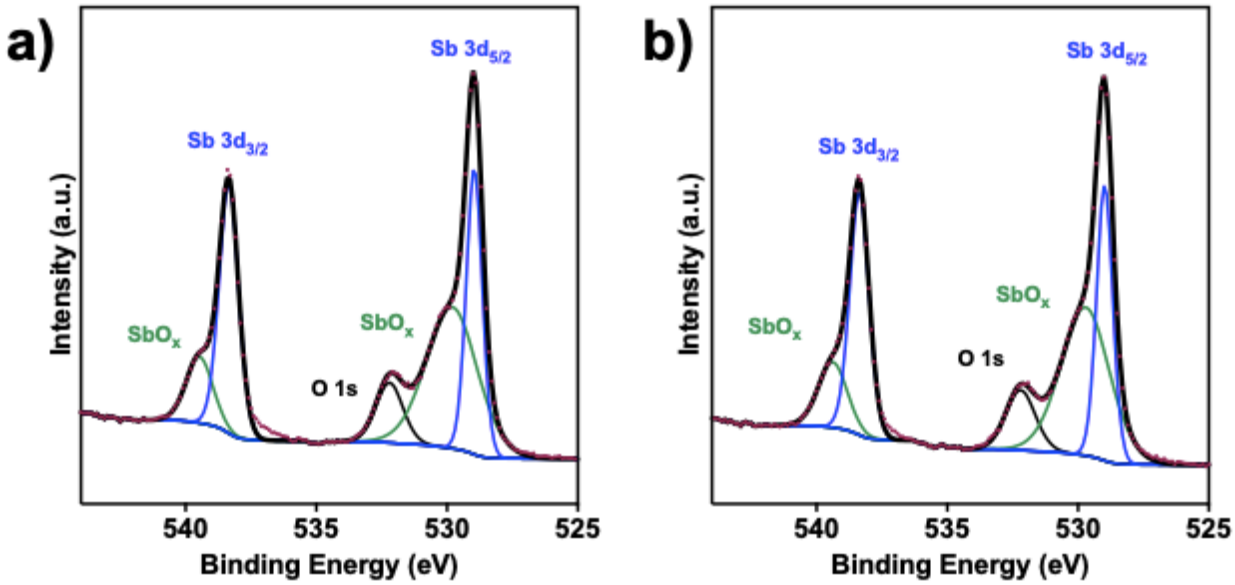

Figure S7. High-resolution XPS spectra for (a) Sb 3*d* before in situ Ar^+ ion beam milling, and (b) Sb 3*d* after milling.

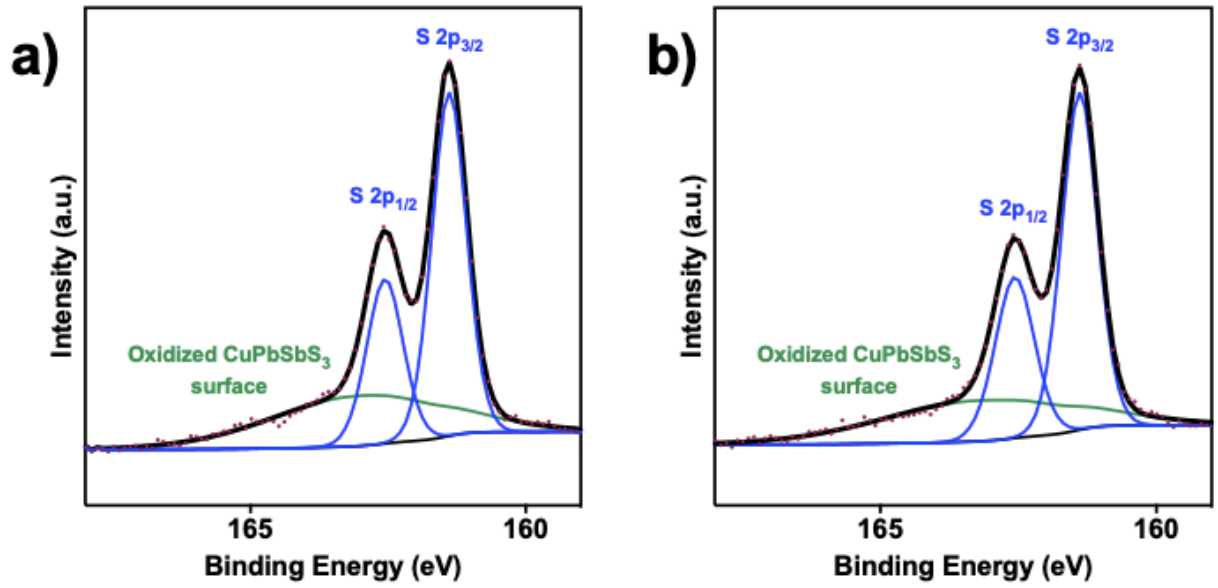

Figure S8. High-resolution XPS spectra for (a) S 2*p* before in situ Ar^+ ion beam milling, and (b) S 2*p* after milling.

Table S2. Peak positions and peak splitting from the high-resolution XPS spectra of $CuPbSbS_3$ thin films on Si/SiO_2 before in situ Ar^+ ion beam milling.

Element	Peak Splitting (eV)	Peak ID	Binding Energy (eV)
Cu	19.8	$2p_{1/2}$	951.3
		$2p_{3/2}$	931.5
Pb	4.8	$4f_{5/2}$	142.7
		$4f_{7/2}$	137.9
Pb (surface PbO_x)	4.9	$4f_{5/2}$	143.0
		$4f_{7/2}$	138.1
Sb	9.3	$3d_{3/2}$	538.3
		$3d_{5/2}$	529.0
Sb (surface Sb_xO_y)	9.6	$3d_{3/2}$	539.5
		$3d_{5/2}$	529.9
S	1.1	$2p_{1/2}$	162.5
		$2p_{3/2}$	161.4
S (surface SO_x)		$2p$	163.1

Table S3. Peak positions and peak splitting from the high-resolution XPS spectra of $CuPbSbS_3$ thin films on Si/SiO_2 after in situ Ar^+ ion beam milling.

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		$4f_{7/2}$	138.1
Sb	9.3	$3d_{3/2}$	538.3
		$3d_{5/2}$	529.0
Sb (surface Sb_xO_y)	9.5	$3d_{3/2}$	539.4
		$3d_{5/2}$	529.9
S	1.1	$2p_{1/2}$	162.5
		$2p_{3/2}$	161.4
S (surface SO_x)		$2p$	163.1

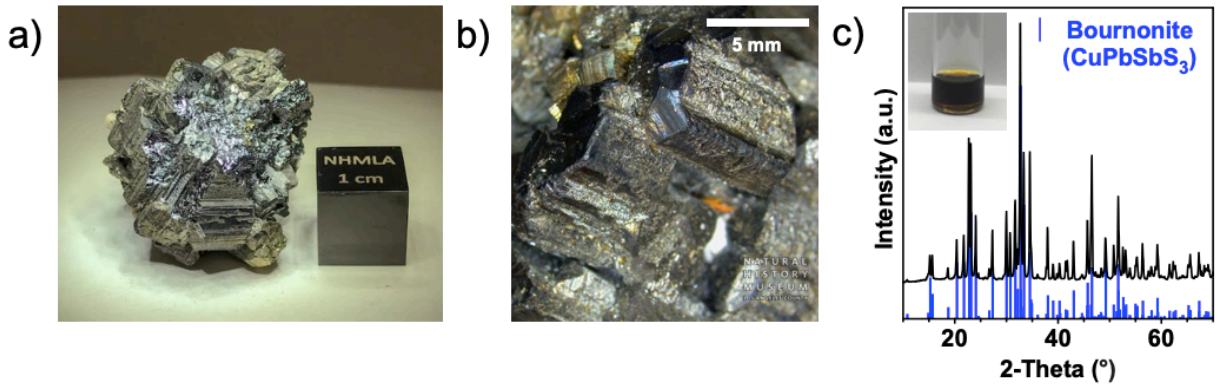

Figure S9. (a,b) Natural bournonite sample obtained from the Los Angeles County Natural History Museum (catalog number: NHMLA 67450, mined from Chihuahua, Mexico), and (c) powder XRD pattern of natural sample indexed to $CuPbSbS_3$ (PDF: 01-073-5993). Inset shows fully dissolved ink.

Figure S10. Photograph of $CuPbSbS_3$ inks prepared from the dissolution of CuO, PbO, and Sb_2S_3 in a 1:4 (v/v) mixture of EDT and en (left), and an ink of a natural bournonite sample (right) dissolved in the same solvent mixture with the same concentration (~60 mg mL^{-1}). Solid components of inks are shown in front of vials.

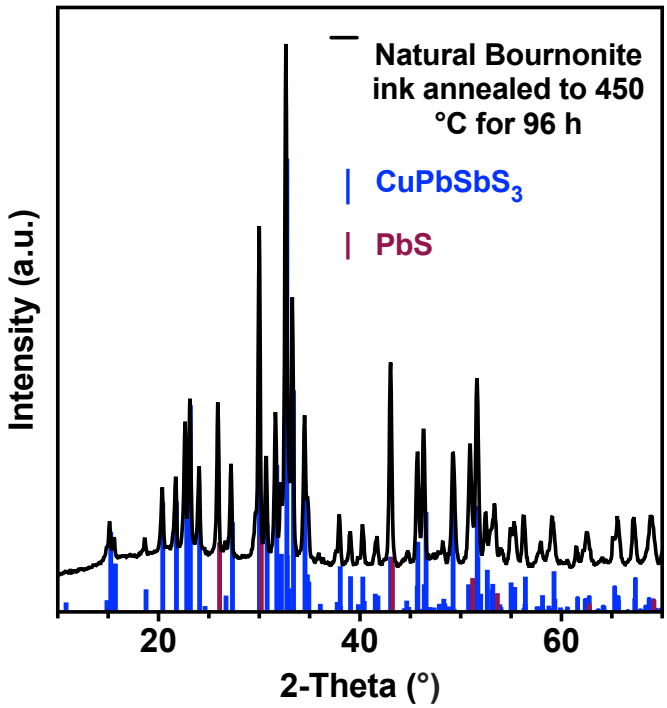

Figure S11. Powder XRD pattern of ink of natural bournonite sample annealed to 450 ˚C for 96 h and indexed to $CuPbSbS_3$ (PDF: 01-073-5993) and PbS (PDF: 01-077-0244).

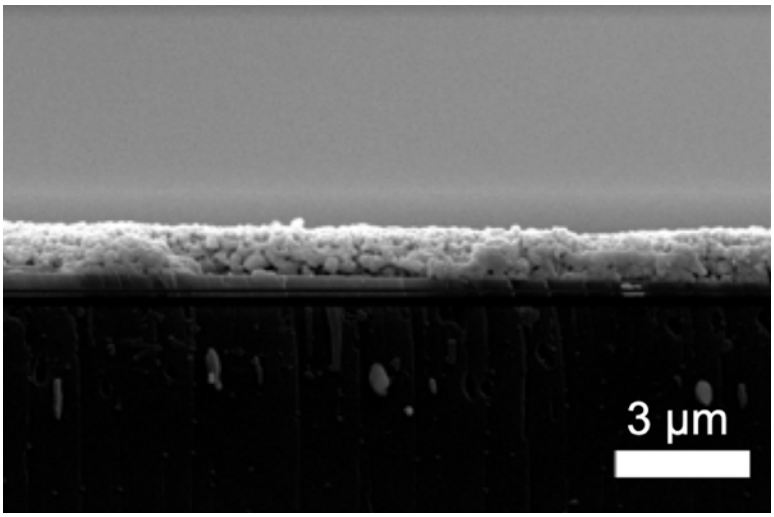

Figure S12. Cross-sectional SEM image of a ~1 µm $CuPbSbS_3$ thin film derived from 3 coats spun at 2000 rpm and annealed to 390 ˚C for 10 min between each coat.

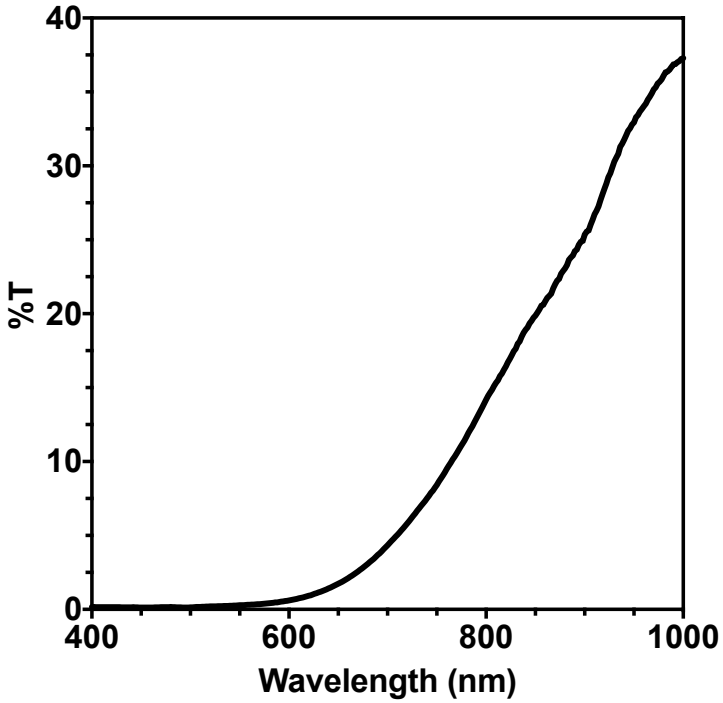

Figure S13. Transmittance spectrum in an integrating sphere using a 570 nm thin film of $CuPbSbS_3$.

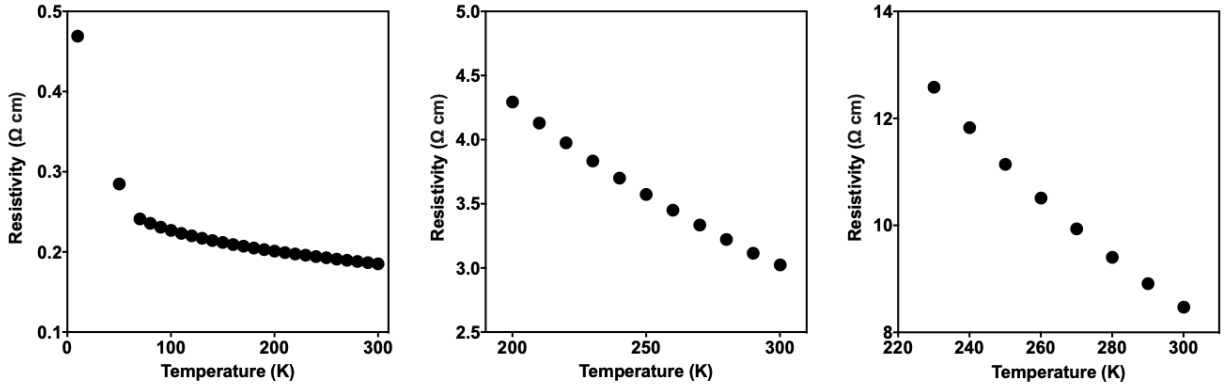

Figure S14. Representative resistivity measurements on different solution processed bournonite thin film samples. Plots are representative of semiconducting nature of $CuPbSbS_3$. Resistances were collected until ohmic contact was lost (data omitted).

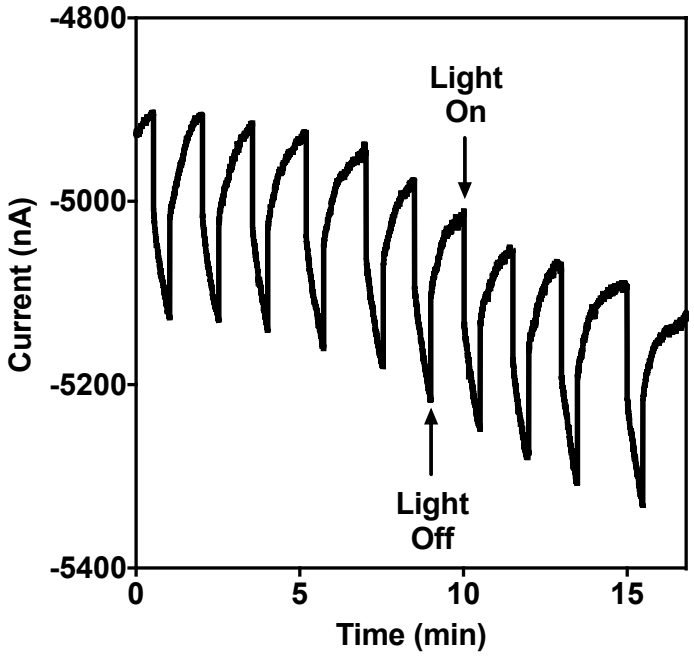

Figure S15. Transient photoresponse at 25 ˚C under ambient conditions of a $CuPbSbS_3$ thin film deposited on patterned FTO. The device was tested under chopped white light at -500 mV. A 300 W Xe arc lamp calibrated to AM1.5G was employed for this measurement. Arrows indicate when light was turned on or off.

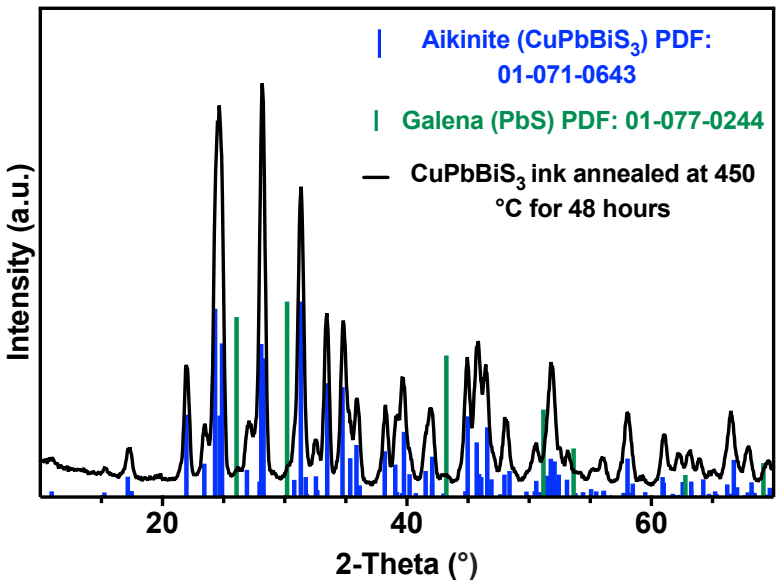

Figure S16. Powder XRD pattern of aikinite $CuPbBiS_3$ ink annealed to 450 °C for 48 h and indexed to $CuPbBiS_3$ (PDF: 01-071-0643) and PbS (PDF: 01-077-0244).