

## Supporting Information

### Room temperature aqueous $\text{Sb}_2\text{S}_3$ synthesis for inorganic-organic sensitized solar cells with efficiencies of up to 5.1 %

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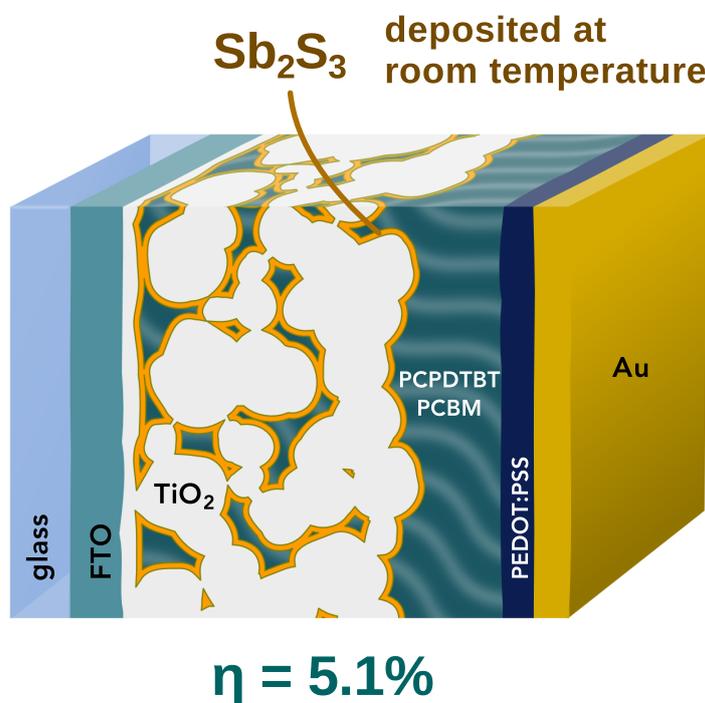


Figure S1: Graphical TOC.

## Experimental Methods

### Solar cell preparation

Glass substrates with a conductive fluorine doped tin-oxide layer (FTO,  $8\ \Omega/\square$ , Sigma-Aldrich) were coated with a hole-blocking compact  $\text{TiO}_2$  layer by a sol-gel spin-coating process. Mesoporous titania anodes with a thickness of  $1\ \mu\text{m}$  were fabricated by screen-printing a paste consisting of  $\text{TiO}_2$  with 50 nm average particle size followed by sintering at  $550\ ^\circ\text{C}$  for 2 h. To reduce surface traps, the anode was immersed in a 40 mM aqueous  $\text{TiCl}_4$  solution at  $65\ ^\circ\text{C}$  for 1 h and resintered at  $500\ ^\circ\text{C}$  for 1 h.

For the reference low-T samples, we used the standard aqueous deposition route of  $\text{Sb}_2\text{S}_3$  in a chemical bath of  $\text{SbCl}_3$  (Sigma-Aldrich,  $\geq 99.0\%$ ) and  $\text{Na}_2\text{S}_2\text{O}_3$  ( $\geq 98.0\%$ , Sigma-Aldrich) with a deposition temperature below  $10\ ^\circ\text{C}$ , as described previously [?]. For the RT deposition, 800 mg  $\text{SbCl}_3$  were dissolved in 2.5 ml acetone followed by the addition of 72.5 ml deionized water. Antimony chloride hydrolysed which lead to a cloudy solution with white precipitate. 3.95 g  $\text{Na}_2\text{S}_2\text{O}_3$  in 25 ml  $\text{H}_2\text{O}$  was added while stirring. The substrates were immediately vertically immersed immediately into the solution. The deposition of  $\text{Sb}_2\text{S}_3$  was indicated by an orange colour change of the bath. The substrates were left in

the chemical bath for 1 h. After deposition the orange substrates were rinsed in deionized water and dried with nitrogen. To form brown crystalline  $\text{Sb}_2\text{S}_3$ , the samples were annealed in an argon atmosphere at  $300^\circ\text{C}$  for 5 min. As a hole conducting material, PCPDTBT (poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta [2,1-b;3,4-b]dithiophene)-alt-4,7(2,1,3-benzothiadiazole)]) was dissolved in 1,2-dichlorobenzene (15 mg/ml) and 5 mg/ml PC<sub>70</sub>BM ([6,6]-Phenyl C71 butyric acid methyl ester) were added and spin-coated at 2000 RPM for 60 s onto the substrates. Gold electrodes (100 nm) were evaporated using a thermal evaporator. The active area ( $9.6\text{ mm}^2$ ) of the solar cells was defined using a metal mask.

## Material characterization

X-ray diffraction was carried out using a Bruker D8  $\theta/\theta$  (fixed sample) set-up with a LynxEye position sensitive detector and a standard SC detector with auto-absorber and graphite 2<sup>nd</sup> beam monochromator. The set-up uses a Bragg Brentano para-focusing geometry and operates in reflection mode. X-ray photoelectron spectra (XPS) were measured in an ultra-high vacuum chamber of an ESCALAB 250Xi. The measurements were carried out using a XR6 monochromated Al $\alpha$  source (1486.6 eV) and a pass energy of 20 eV. Photothermal deflection spectra (PDS) were measured with a Light Support MKII 100 W Xenon arc source coupled with a CVI DK240 monochromator. A Qioptiq 670 nm fiber-coupled diode laser was used for the probe beam.

## Optoelectronic measurements

An ABET Technologies (Model 11016 Sun 2000) solar simulator with a xenon arc lamp was used and the solar cell response was recorded using a Keithley 2635 sourcemeter. The intensity of the solar simulator was calibrated to  $100\frac{\text{mW}}{\text{cm}^2}$  using a silicon reference cell from Czibula & Grundmann (FHG-ISE, RS-OD4).

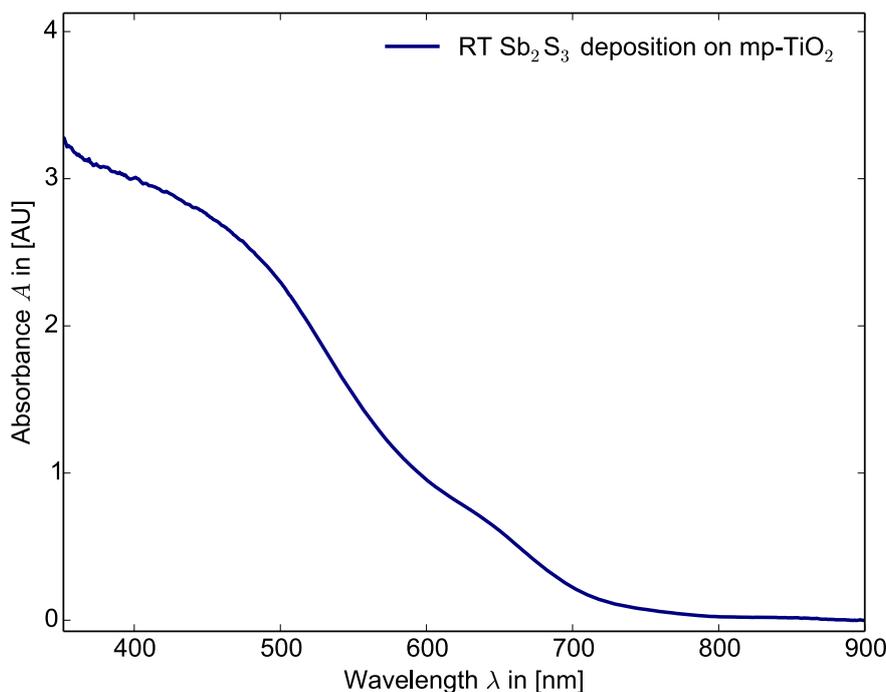


Figure S2: UV-vis spectrum of crystalline  $\text{Sb}_2\text{S}_3$  deposited by the RT method on a  $1\ \mu\text{m}$  thick mesoporous  $\text{TiO}_2$  layer.

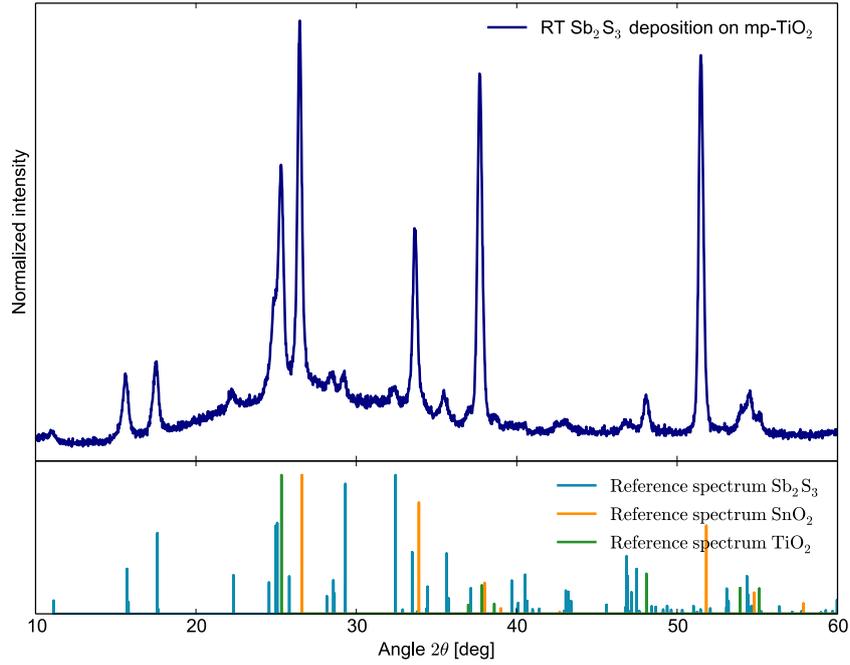


Figure S3: XRD spectrum of crystalline Sb<sub>2</sub>S<sub>3</sub> deposited by the RT method on a mesoporous TiO<sub>2</sub> layer. The substrate is glass with fluorine doped tin oxide (FTO) film. Reference spectra for Sb<sub>2</sub>S<sub>3</sub>, TiO<sub>2</sub> (anatase) and SnO<sub>2</sub> are shown below the measurement.

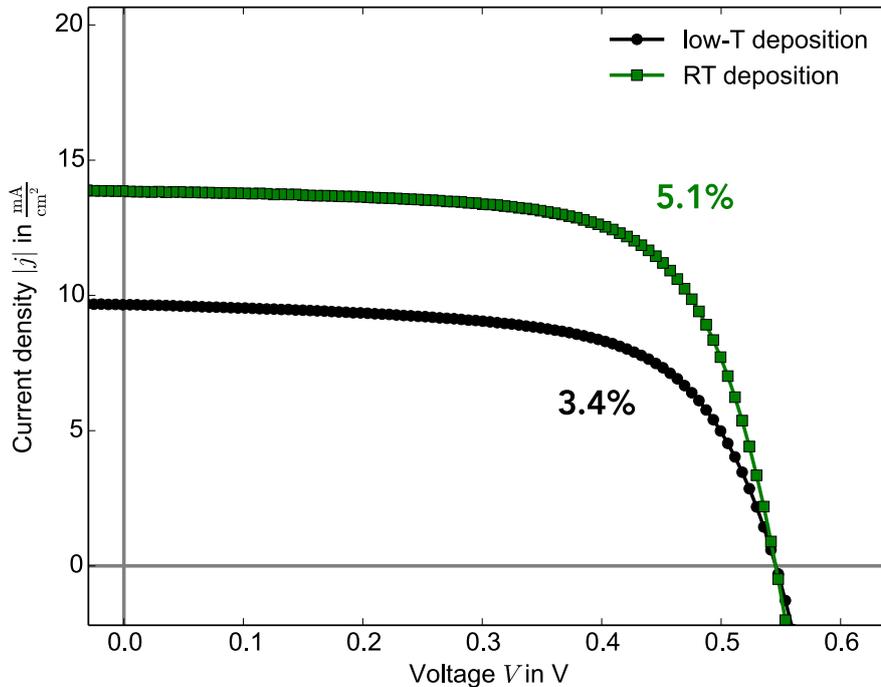


Figure S4: Current-voltage characteristic of the best performing low-T deposited Sb<sub>2</sub>S<sub>3</sub> solar cell compared to the best performing RT deposited device. We note that we did not optimize the low-T solar cells to the same extent as the RT devices.

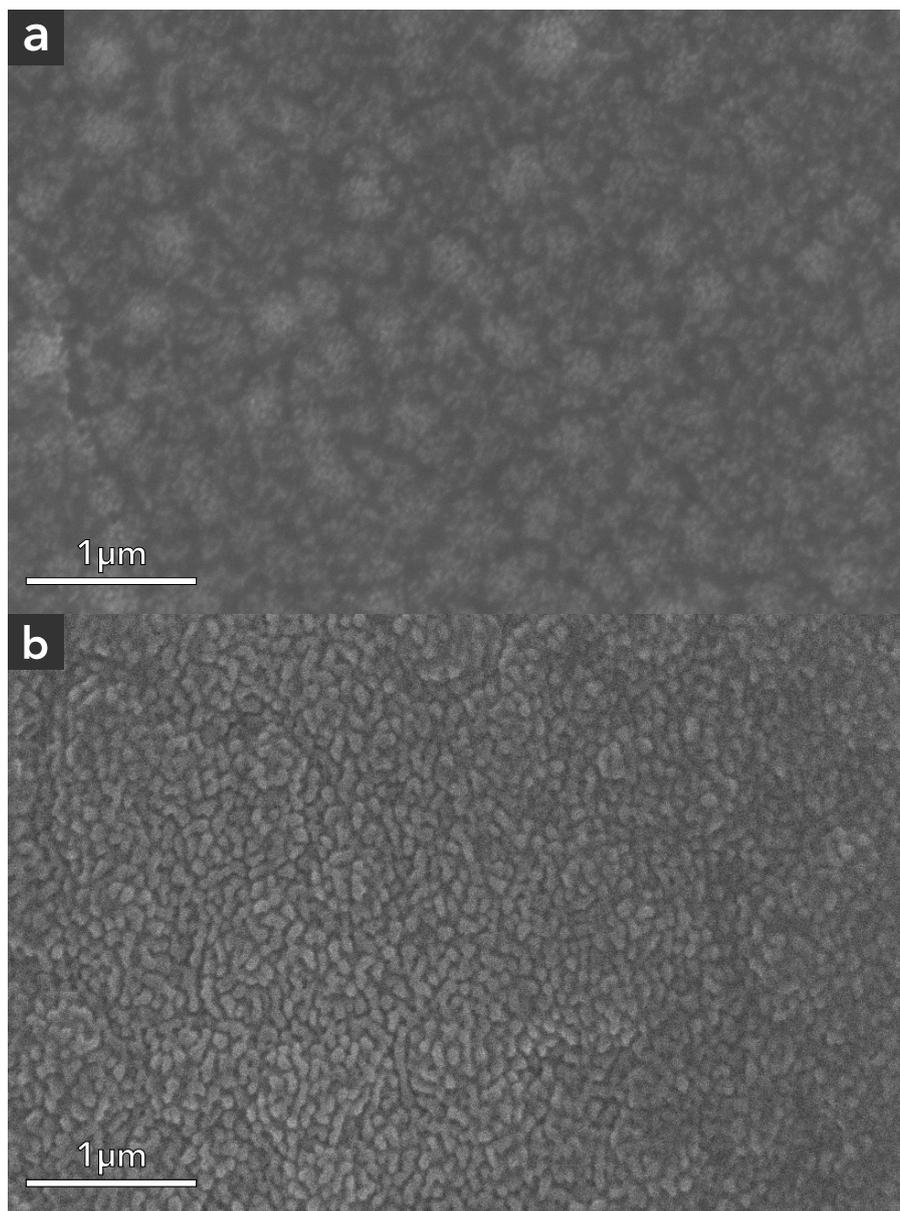


Figure S5: Top view scanning electron microscopy images of films made by (a) the low-T deposition method of  $\text{Sb}_2\text{S}_3$  and (b) the RT technique. Both films are deposited directly onto FTO-glass substrates.

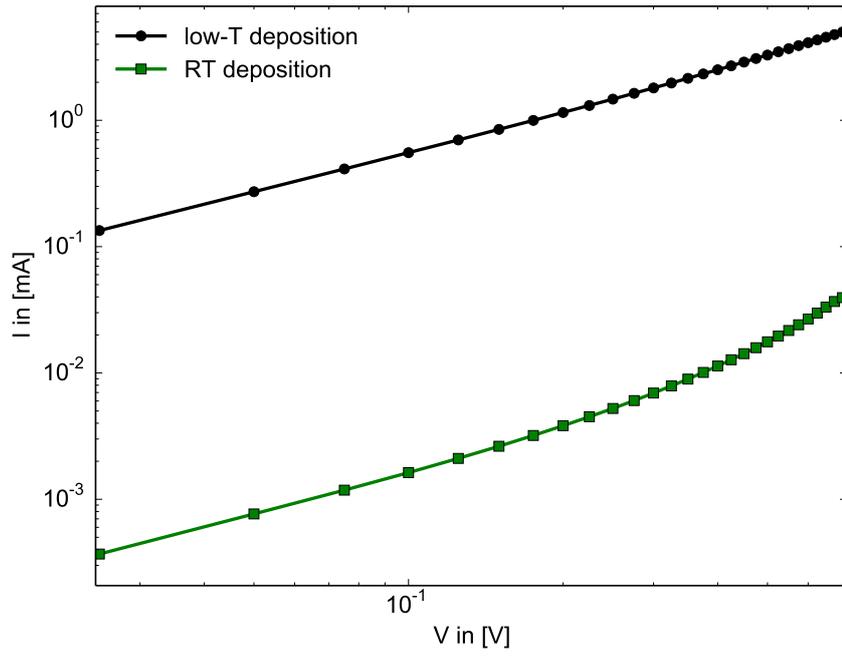


Figure S6: Averaged (12 samples each) current-voltage measurements of crystalline  $\text{Sb}_2\text{S}_3$  films with comparable thickness on a compact  $\text{TiO}_2$  layer in the dark. The RT deposition method shows a much lower conductivity.

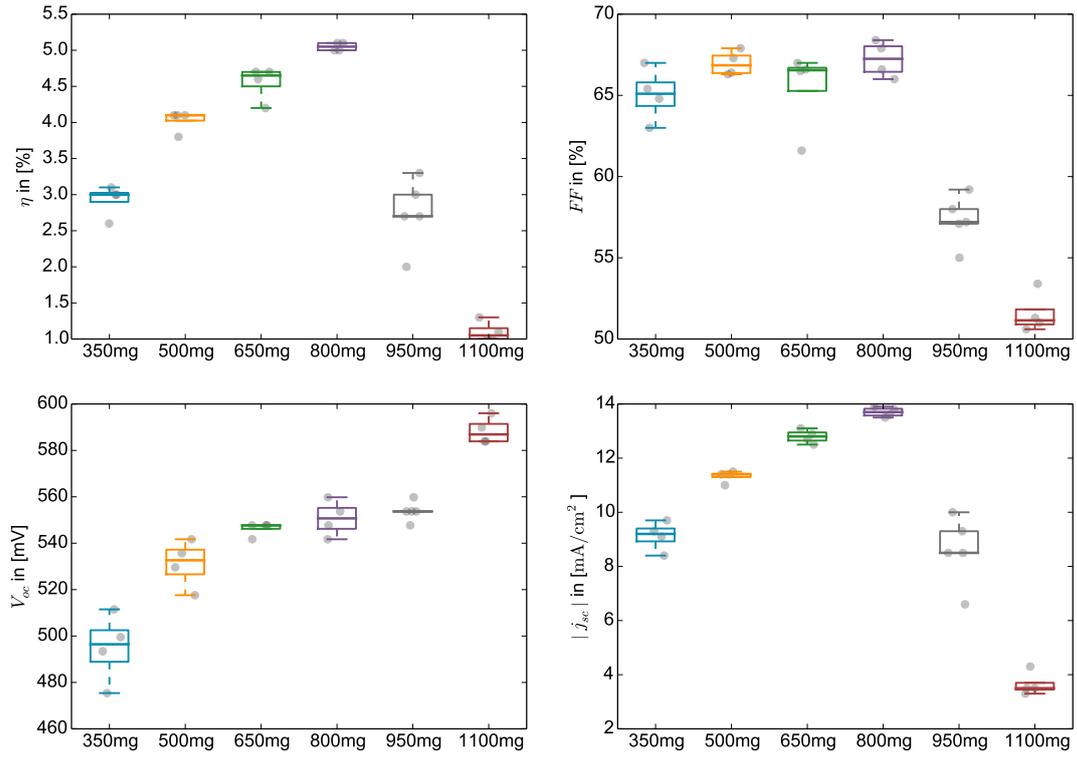


Figure S7: Photovoltaic parameters of  $\text{Sb}_2\text{S}_3$  sensitized solar cells in dependence of the initial  $\text{SbCl}_3$  concentration. The labels of the x-axis refer to the mass of  $\text{SbCl}_3$  per 100 ml total solution of the chemical bath. The deposition time was kept constant at 1 h.

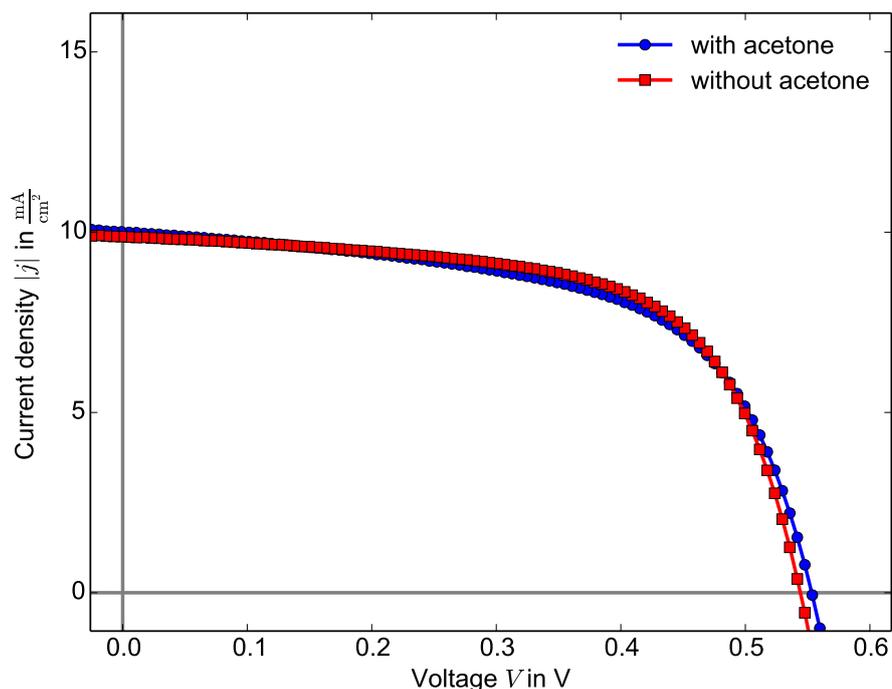


Figure S8: Influence of the dissolution of  $\text{SbCl}_3$  in acetone on the photovoltaic performance. For the blue curve ('with acetone'),  $\text{SbCl}_3$  was dissolved in Acetone before the addition of water, which induces the hydrolysis. For the red curve ('without acetone'),  $\text{SbCl}_3$  was directly hydrolysed in its granular form.

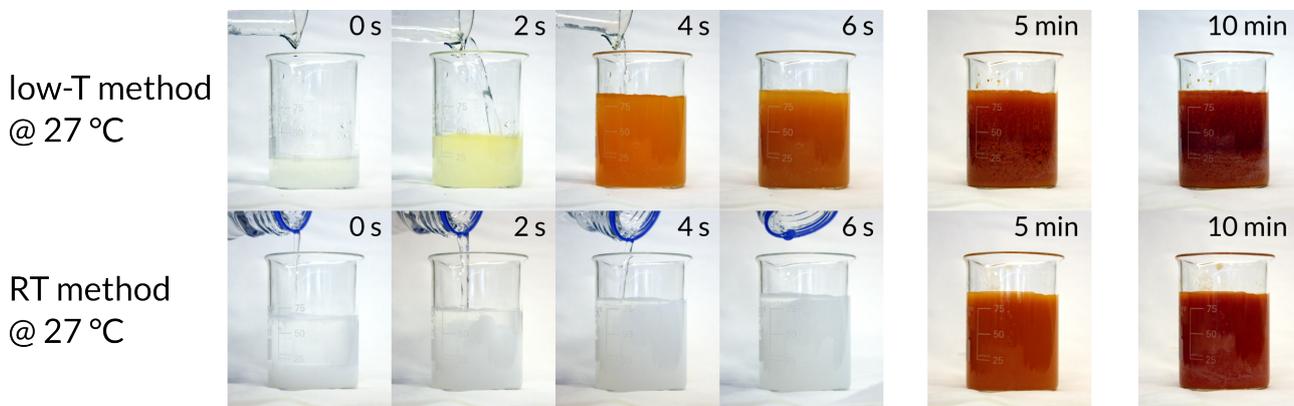


Figure S9: Photographic time series of the low temperature (low-T) method carried out at room temperature ( $27^\circ\text{C}$ ) in comparison with our RT method at  $27^\circ\text{C}$ . If the RT method is carried out at lower temperatures, the reaction rate is even slower.

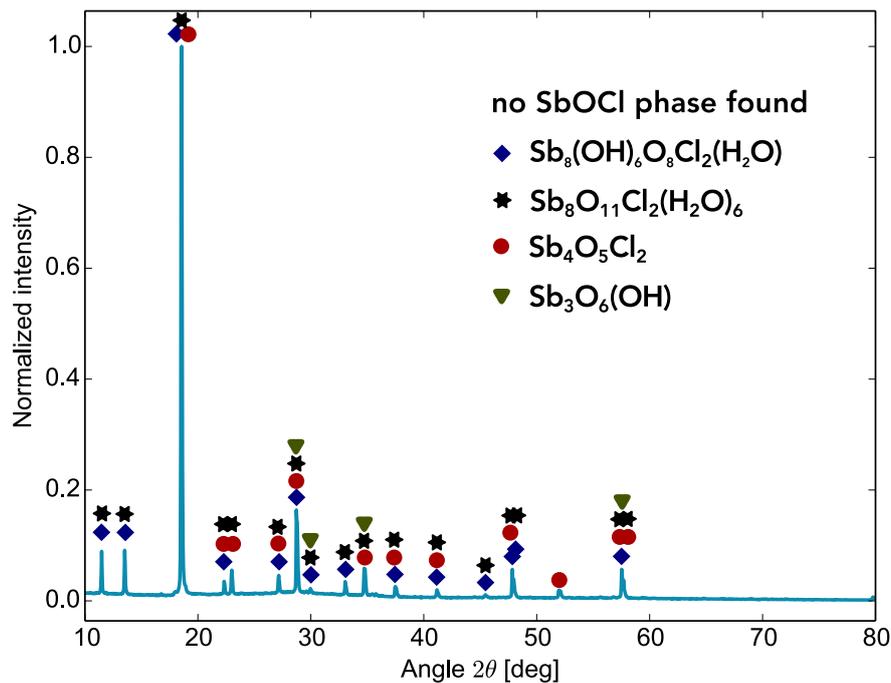


Figure S10: XRD spectrum of the intermediate precipitate which is the product of the hydrolysis of  $\text{SbCl}_3$ . Possible peaks of compounds containing antimony, oxygen and chlorine were detected by the software HighScore (PANalytical). The  $\text{SbOCl}$  reference did not match any of the peaks in the measured spectrum.

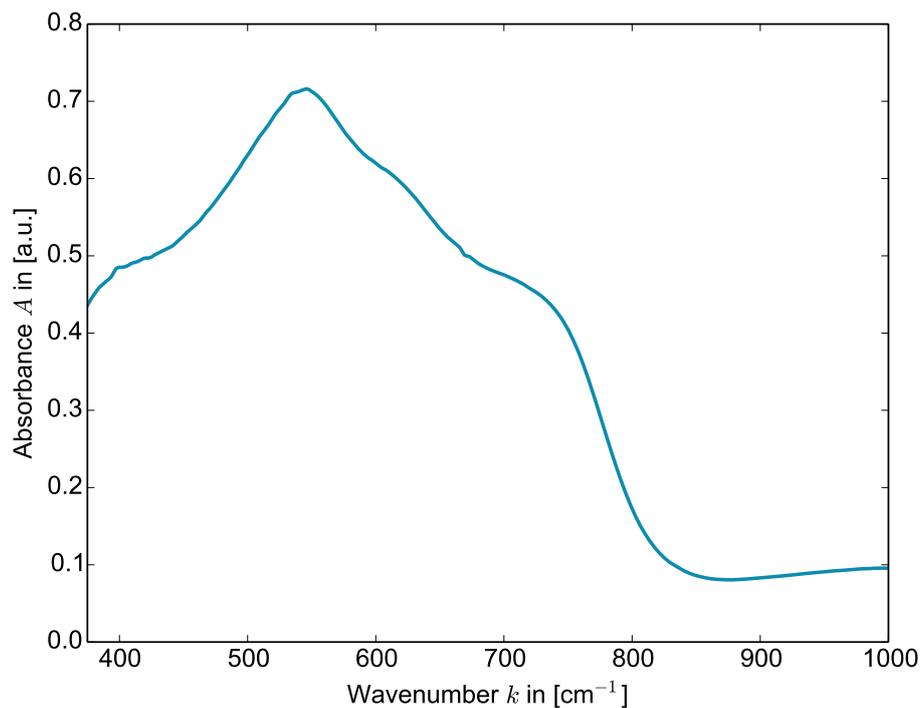


Figure S11: FTIR spectrum of the intermediate precipitate (hydrolysed  $\text{SbCl}_3$ ).

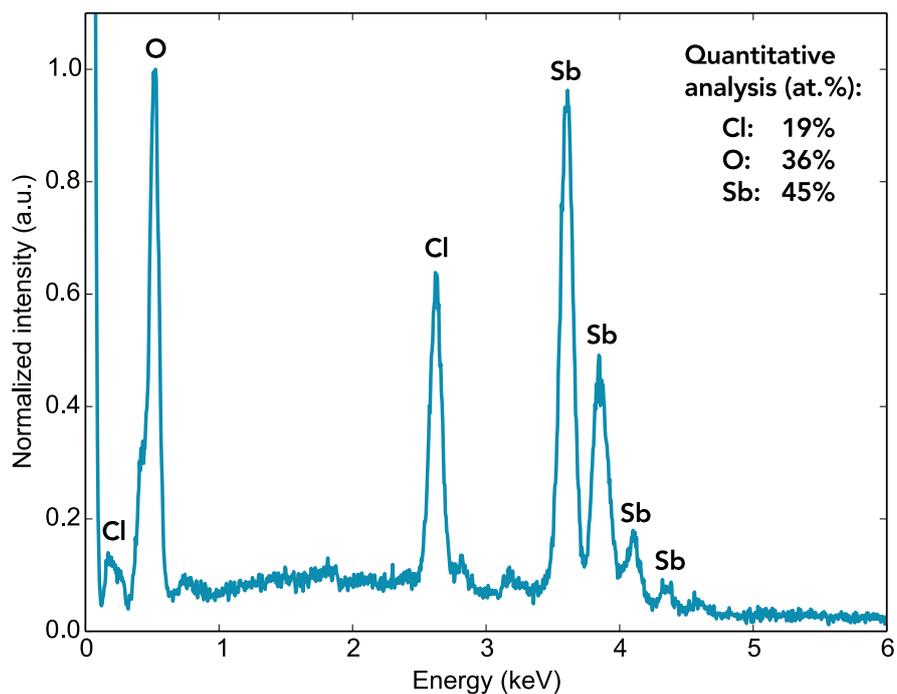


Figure S12: EDX spectrum of the intermediate precipitate (hydrolysed  $\text{SbCl}_3$ ). The result of the quantitative analysis (in atomic percent) is shown as inset.

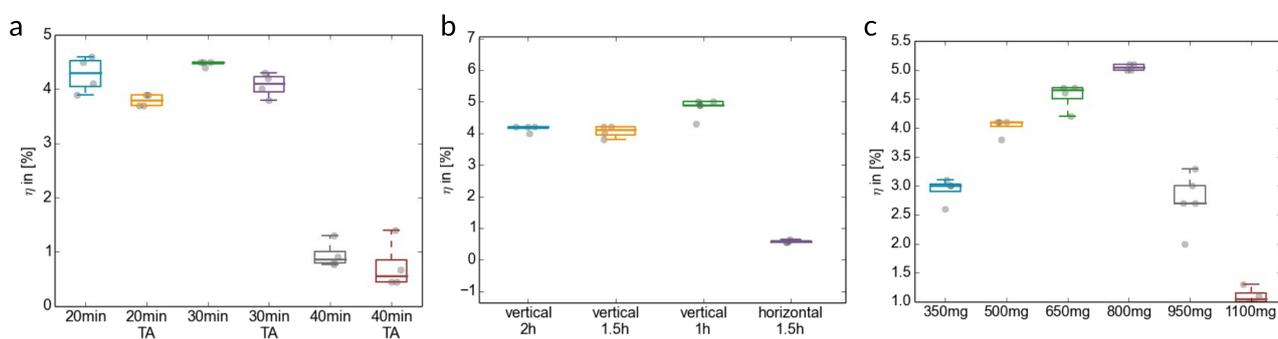


Figure S13: Power conversion efficiencies for three different batches, showing the reproducibility, as deviations from batch to batch and from device to device are small. a) Different deposition times and thioacetamide post-treatment for horizontally placed samples in the chemical bath. b) Different deposition times and sample orientations in the chemical bath. c) Different  $\text{SbCl}_3$  concentrations for a 1h deposition time and vertically oriented samples.