

Electronic Supplementary Information

Facile dissolution of selenium and tellurium in a thiol-amine solvent mixture under ambient conditions

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Experimental

Reagents. Selenium (–200 mesh, 99.999% metals basis, Alfa Aesar), finely powdered tellurium (–200 mesh, 99.8% metals basis, Aldrich), high-purity tellurium (–60 mesh, 99.999% metals basis, Alfa Aesar), ethanethiol (97%, Alfa Aesar), antimony (powder, 99.5%, Strem), and tin (granules, 30 mesh, 99.5+%, Aldrich) were used as received. Ethylenediamine ($\geq 99\%$, Aldrich), 2-mercaptoethanol (99+%, Aldrich), and 1,2-ethanedithiol (98+%, Alfa Aesar) were purified before use, as described below.

Drying and purification of solvents. Ethylenediamine (1 L) was stirred with excess CaH_2 under a nitrogen atmosphere for 3 d, and then allowed to settle. The liquid was cannula transferred to a large flask containing *ca.* 1 g Na and boiling chips. The flask was part of a setup incorporating two condensers, to allow for either reflux or distillation. The solvent was refluxed for ~7 h, by which time the liquid had turned intensely dark blue, indicating the absence of H_2O or O_2 . The liquid was then slowly distilled, discarding the first fraction (*ca.* 50 mL) and leaving a large undistilled fraction.

2-mercaptoethanol and 1,2-ethanedithiol were purified by adding a very large excess (*ca.* 50% vol.) of 3A molecular sieves (previously dried at 350 °C, 2 d, flowing nitrogen), sparging with nitrogen, then standing ≥ 3 days with occasional shaking. The liquid was removed by cannula so then it could be slowly distilled under nitrogen. The first fraction (*ca.* 10-20% vol) was discarded, and a large undistilled fraction (*ca.* 30%) was left.

Preparation of saturated chalcogen solutions. A large excess of selenium (typically 3.2 g) or tellurium (typically 1.3 g; 200 mesh powder for more rapid approach to saturation) was purged with nitrogen and then ethylenediamine (3 mL) and thiol (0.75 mL) were injected. The initial stage of selenium dissolution was accompanied by substantial heat output, and brief cooling in water was required for the Se/EtSH/en mixture to prevent volatilization of EtSH. The EtSH/en mixtures were stirred for 4.5 h whereas the more viscous mercaptoethanol/en mixtures were stirred for 18 h (selenium) or 48 h (tellurium) to ensure saturation. The en/1,2-ethanedithiol mixtures suffered from crystallization of solid $(\text{enH}^+)_2(\text{edt}^{2-})(\text{en})$ adduct, as we reported previously (*J. Am. Chem. Soc.* **2013**, *135*, 15722.) and had to be frequently warmed to re-liquefy and permit stirring. In the final step, the solutions were filtered under nitrogen (450 nm PTFE membrane) to remove undissolved chalcogen. In the case of selenium in EtSH/en, a small amount of a colorless liquid separated;

this was discarded and only the main Se-rich phase was filtered.

Preparation of Sb–Se precursor solution. Ethylenediamine (4 mL) and EtSH (1.25 mL) were added to a mixture of selenium (12 mmol, 950 mg) and antimony (8.05 mmol, 980 mg; only a small excess is required) under nitrogen. (Note: 1.25 mL EtSH was used rather than 1 mL to offset possible evaporative losses) The mixture was warmed and stirred (60 °C, 2 h), then cooled to room temperature and filtered (450 nm PTFE membrane), resulting in a clear orange Sb–Se precursor solution. The solution was stored under nitrogen and appeared stable at room temperature and insensitive to light.

Preparation of Sn–Te precursor solution. The procedure followed that for Sb–Se, but using tellurium (3.0 mmol, 380 mg, 60 mesh, 99.999% grade) and tin (6.0 mmol, 710 mg; 30 mesh granules) and stirring for 3 h. The result was a clear red solution. Storage stability appeared similar to the Sb–Te precursor solution and was surprisingly good for a tellurium compound; nevertheless, it was kept in the dark as a precaution.

Crystallization of Se, Te, Sb_2Se_3 , and SnTe from solution. Solution (0.5–1 mL) was drop cast onto a silicon wafer on an aluminium heating block. A cover was immediately applied and the air expelled by a vigorous nitrogen purge. Slow heating to *ca.* 100 °C removed the bulk of the volatiles, after which the nitrogen flow was slowed and the temperature more quickly ramped to the set point. A heating cycle typically took 20-30 min to reach set point temperature, followed by 30 min cooling back to room temperature. The product was scraped from the silicon using a razor blade and finely ground before further analysis. The following set point temperatures were used:

- 150 °C tellurium from mercaptoethanol/en
- 250 °C selenium from EtSH/en and mercaptoethanol/en; Sn–Te and Sb–Se precursor inks
- 300 °C selenium from 1,2-ethanedithiol/en
- 350 °C tellurium from 1,2-ethanedithiol/en

For tellurium dissolved in EtSH/en, a different technique was employed to recover the solute. A slow nitrogen flow was passed over a filtered saturated solution at room temperature. Lustrous metallic grey tellurium crystals grew over a period of a few days, apparently driven by loss of EtSH, since a large volume of liquid was still present. When the liquid turned colorless, it was removed and the crystals washed several times with isopropanol.

Spin coating. Solutions were diluted for spin coating in the following proportions: 1 vol precursor solution plus 3

vol en (for Sn–Te) or 10 vol en (for Sb–Se). The diluted solutions were spin coated on UV-ozone cleaned borosilicate glass microscope slides using the following conditions: flowing nitrogen, acceleration = 770 rpm s⁻¹, 1250 rpm, 4 min. The films were then heated to 250 °C under nitrogen.

Thermogravimetric analysis (TGA), including concentration determination. Chalcogen or metal chalcogenide precursor solution (3–5 drops from a 25G needle = 25–40 mg) was placed in a tared alumina pan mounted in a TA Instruments Q50 TGA. The furnace was pre-positioned in a semi-raised state so it could be closed quickly to minimize evaporation. The following program was employed: initial nitrogen flow = 60 mL min⁻¹, increase flow to 200 mL min⁻¹, isothermal (25 °C) 20 min (*purge step*), ramp 5 °C min⁻¹ to 125 °C, isothermal 20 min (*drying step*), cool to 30 °C, nitrogen flow 60 mL min⁻¹, equilibrate at 30 °C, ramp 10 °C min⁻¹ to final temp (*analysis step*); final temp = 360 °C (selenium), 410 °C (tellurium), or 460 °C (Sb–Se or Sn–Te). Since the selenium and tellurium solutions were saturated, the solubility expressed as mass% solute was directly read from the data at an appropriate temperature (250 °C for selenium from all solvent mixtures, 150 °C for tellurium from EtSH/en and mercaptoethanol/en, and 350 °C for tellurium from 1,2-ethanedithiol/en). For studying the loss of organics from the dried material, the data was re-plotted to show only the analysis step.

Other instrumentation and analysis. Powder XRD data were obtained using a Rigaku Ultima IV diffractometer (zero-diffraction Si substrate, Cu K_α radiation, continuous scan, 0.05° step size, 1° min⁻¹ scan rate). EDX data were obtained using an AMETEK EDAX model APOLLO X detector (50 live s count time, 12.80 μs amp) mounted on a JEOL JSM-7001F SEM (15 kV accelerating voltage, beam current adjusted to give ~30–35 % dead time); data were gathered for several large areas and the mean taken. FT-IR spectroscopy was done on a Bruker Vertex 80v using powdered samples dispersed in KBr pellets. The change in electrical conductivity on adding EtSH to en was qualitatively assessed by measuring the resistance between two Pt wires dipped in a nitrogen-purged cuvette of liquid using a G W Instec LCR-816 meter (1.275 V 2 kHz AC output). Raman spectra of the solutions were recorded under ambient conditions using a Horiba Jobin Yvon, equipped with a liquid sample holder. An excitation source of 785 nm from a diode laser was employed at a power level of 50 mW. Solution NMR spectra were recorded at 400 MHz for ¹H and 76 MHz for ⁷⁷Se using a Varian Mercury 400MR spectrometer. Chemical shifts for ¹H NMR were referenced internally to the residual proton signal for benzene-*d*₆ at 7.16 ppm. Chemical shifts for ⁷⁷Se NMR were referenced externally to diphenyl diselenide in benzene-*d*₆ at 460 ppm. Benzene-*d*₆ was purchased from Cambridge Isotopes Labs and used as received.

Table S1. Solubilities of grey selenium and tellurium in 1:4 vol/vol thiol/ethylenediamine solvent mixtures, expressed as wt% solute in the saturated solution.

Solvent mixture	Se solubility (wt%)	Te solubility (wt%)
en/EtSH	38 ^a	9.3 ^b
en/2-mercaptoethanol	40	2.2
en/1,2-Ethanedithiol	44 ^c	4.6 ^c

^a Se-rich phase; $\rho = 1.42$ g/mL (Se-rich phase only), concentration = 540 mg/mL. ^b $\rho = 0.99$ g/mL, concentration = 92 mg/mL.

^c The solutions had to be warmed to allow stirring and filtration because of solvent crystallization; therefore, the true room temperature solubilities are probably slightly lower than the figures given.

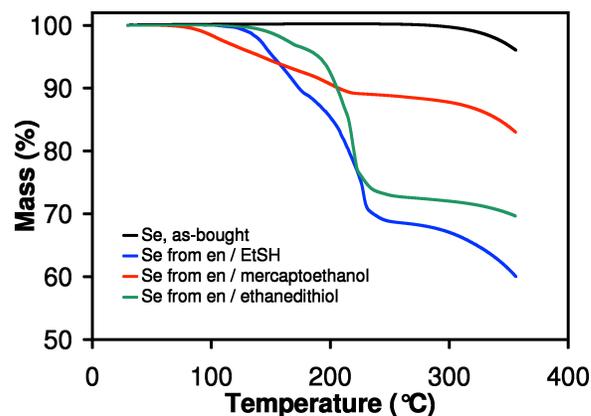


Fig. S1 TGA data for as-bought selenium and selenium solutions. All data were acquired under the same conditions, *i.e.* after a 125 °C *in-situ* drying step.

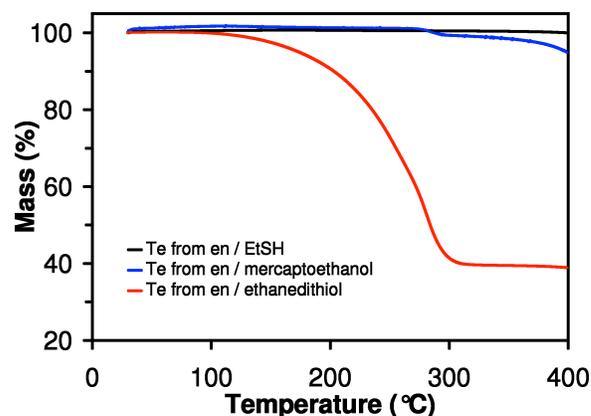


Fig. S2 TGA data for tellurium solutions after a 125 °C *in-situ* drying step.

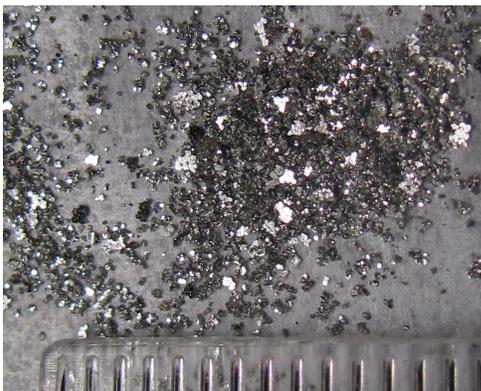


Fig. S3 Photograph of macroscopic silver-grey tellurium crystals grown from a tellurium solution in EtSH/en by partial evaporation under flowing nitrogen at room temperature. Each division on the scale represents 1 mm.

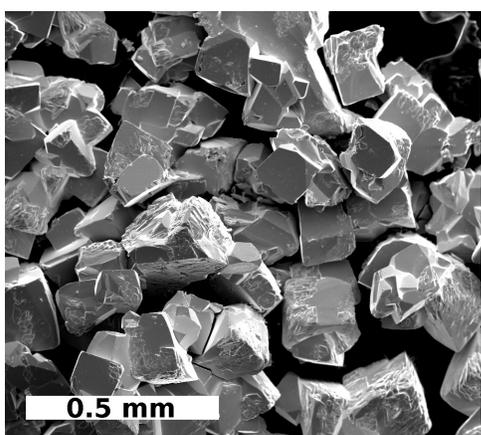


Fig. S4 Low magnification SEM image of tellurium crystals grown from tellurium dissolved in EtSH/en by partial evaporation under flowing nitrogen at room temperature.

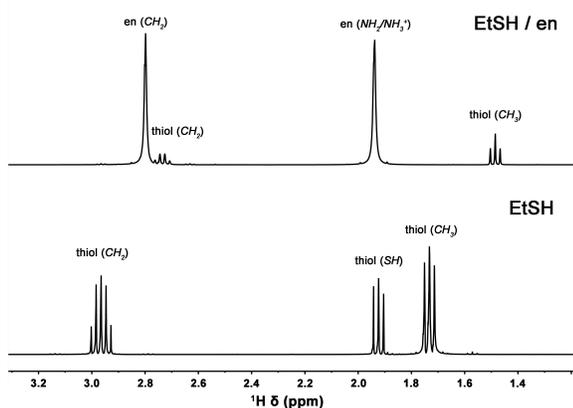


Fig. S5 ^1H NMR spectra comparing neat EtSH to the EtSH/en solvent mixture. The thiol splitting pattern and the absence of the S-H resonance in EtSH/en suggests that the thiol is partially deprotonated, as corroborated by electrolytic conductivity data.

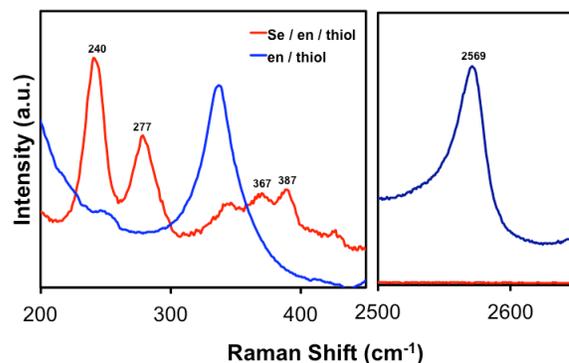


Fig. S6 Raman spectra taken before and after dissolution of selenium in EtSH/en at 36 wt%.

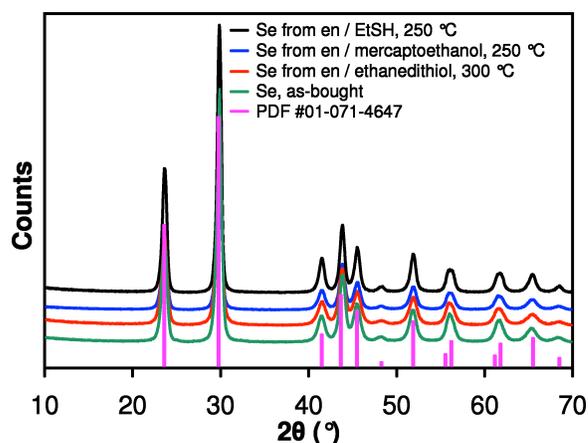


Fig. S7 XRD patterns of reference (as-bought) selenium, and selenium recovered from solution by evaporation and heat-treatment at the temperatures given. All diffraction patterns correspond to the hexagonal grey allotrope of selenium.

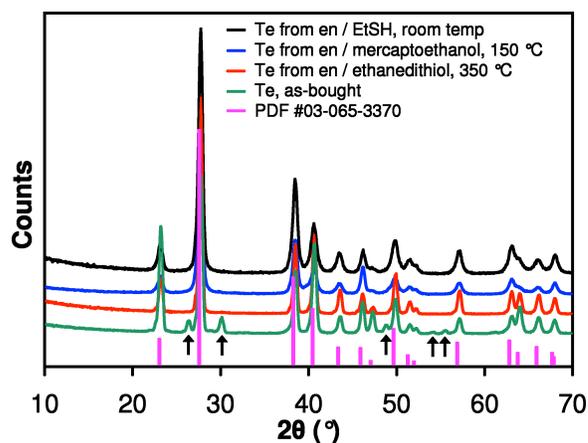


Fig. S8 XRD patterns of reference (as-bought) tellurium, and tellurium recovered from solution by evaporation and heat-treatment at the temperatures given. All diffraction patterns correspond to the usual hexagonal tellurium crystal structure. The black arrows indicate peaks assigned to a TeO_2 impurity (PDF #01-071-4822, tetragonal) in the as-bought Te. Solution-recovered material was TeO_2 free.

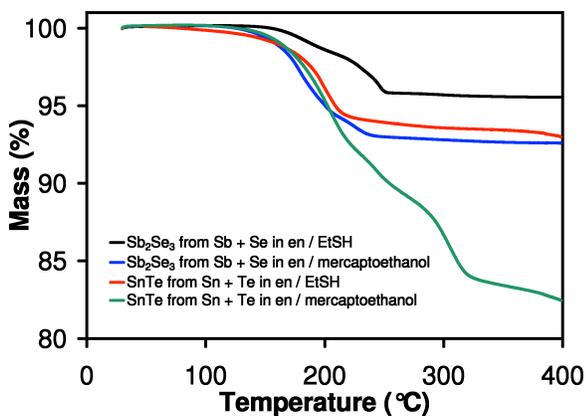


Fig. S9 TGA data for Sb–Se and Sn–Te precursor solutions after a 125 °C *in-situ* drying step.

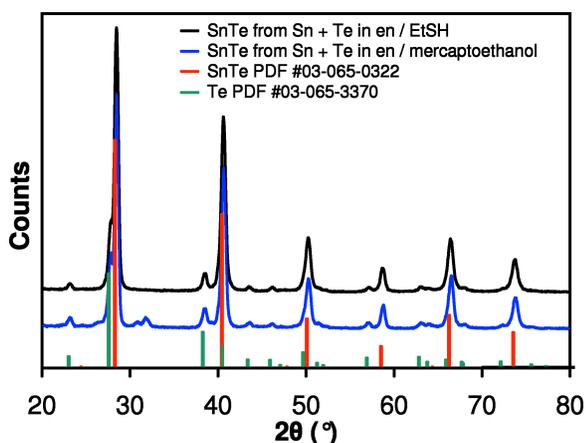


Fig. S10 XRD patterns for SnTe prepared by thermolysis of Sn–Te precursor solutions at 250 °C (from EtSH/en) or 350 °C (from mercaptoethanol/en). Both appear to be cubic rock salt SnTe with tellurium as a secondary phase. The small peaks at 31–32° in the lower diffraction pattern are of unknown origin.



Fig. S11 Photograph of spin coated SnTe film on borosilicate glass.

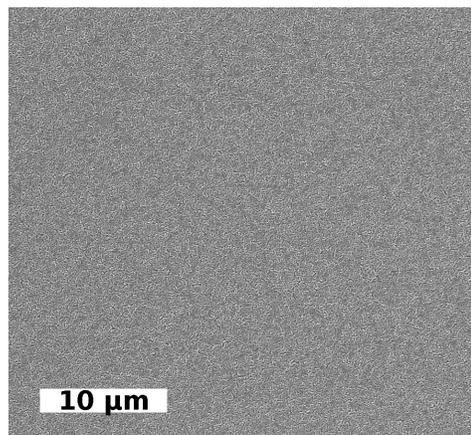


Fig. S12 SEM image showing a large area (1262 μm²) of a spin coated SnTe film on borosilicate glass. The film is smooth and free of macroscopic imperfections at this and larger scales.

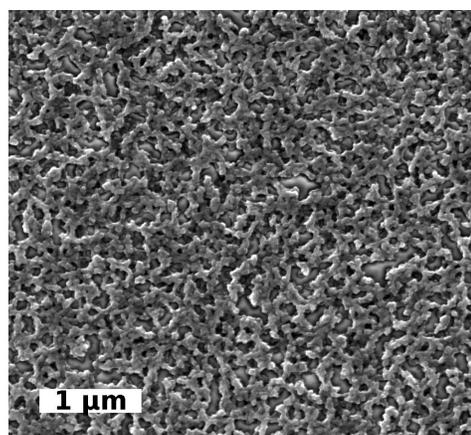


Fig. S13 High-magnification SEM image showing the fully interconnected nanostructure of an SnTe film spin coated on borosilicate glass.

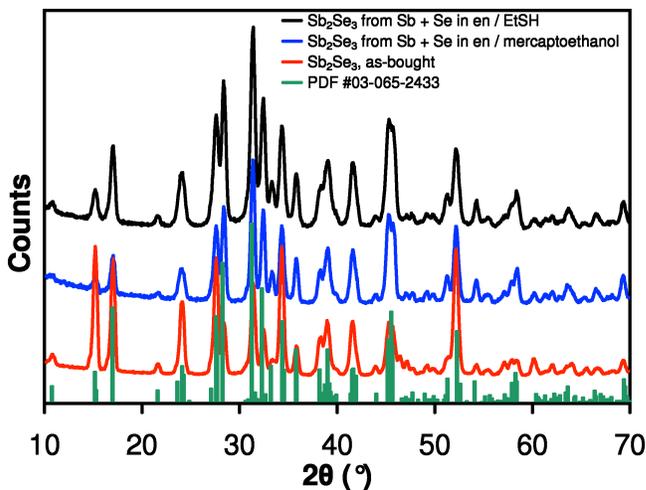


Fig. S14 XRD patterns for Sb₂Se₃ prepared by thermolysis of Sb–Se precursor solutions at 250 °C, with a reference sample of Sb₂Se₃ shown for comparison. All diffraction patterns appear to be in the orthorhombic stibnite phase of Sb₂Se₃ with no discernable secondary phases.