SI: Contamination-Free Selenium Solutions in Amines for Nanoparticle Synthesis

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EXPERIMENTAL PROCEDURES:

Chemicals

Selenium powder (100 mesh 99.99% Aldrich), selenium pellets (<5mm 99.999% Aldrich), sulfur powder (99.98% Aldrich), oleylamine (80-90% Acros-Organics), ethanethiol (97% Aldrich), butylamine (99.5% Sigma-Aldrich), 1-dodecanethiol (98% Aldrich), 1-propanethiol (99% Aldrich), oleic acid (99% Sigma-Aldrich), octadecene, lead oxide (99.99% Aldrich), copper (II) acetylacetonate (99.99% Aldrich), indium (III) acetylacetonate (99.99% Aldrich), zinc acetylacetonate hydrate powder (99.995% Aldrich), tin (IV) bis(acetylacetonate) dibromide (98% Aldrich). All chemicals were used as received unless otherwise noted.

Selenium dissolution

At room temperature elemental selenium was combined with desired amine and thiol. The reaction proceeded readily with adequate stirring resulting in selenium dissolution completion after a short period of time (between 1 second and 1 hour depending on choice of amine and thiol as well as selenium concentration and surface area).

Sulfur-free 1 molar Selenium Solution in Oleylamine

One molar selenium in oleylamine (OLA) solution was formed by addition of 10 ml of OLA, 10 mmol of selenium powder (789.6 mg), and 5ml of ethanethiol to a 100 ml round bottom three neck flask fitted with a condenser, thermocouple, and septa on the three ports. The solution was heated to 40°C and gentle vacuum was pulled on the flask for five minutes with subsequent one minute of argon back fill through the condenser. The vacuum and back fill procedure was repeated three times to quickly remove oxygen from the system. After the third argon back fill the vacuum was returned to remove the unreacted ethanethiol from solution. Once the system was no longer actively boiling at 40°C, the temperature was increased while the solution was still under vacuum to 120°C. When the solution successfully reaches 120°C while under vacuum the diethyldisulfide has been removed (see Fig S1) and the solution contains only OLA and dissolved selenium. At this point the solution was cooled under a blanket of argon to room temperature and stored under argon for use in subsequent reactions.

GC-MS measurements

The capillary gas chromatography/mass spectrometry analyses were carried out using an Agilent 5975C (Agilent Labs, Santa Clara, CA) mass spectrometer system. Typical electron energy was 70eV with the ion source temperature maintained at 250°C. The individual components were separated using a 30 meter DB-5 capillary column (250μm i.d. X 0.25μm film thickness). The initial column temperature was set at 40°C (for 3 minutes) and programmed to 320°C at 10.0°C per minute. The flow rate is typically set at 1ml/min. The injector temperature was set at 250°C. Solutions were diluted in dichloromethane.

Selenium nanoparticle formation

Utilizing the sulfur-free selenium solution described above, 5ml of the sulfur-free selenium solution was injected into 20ml of hexane that had been stored with normal atmospheric air and believed to contain equilibrium oxygen concentrations. The sudden oxygen exposure of the solution breaks the reduced selenium stability and results in the rapid formation of selenium nanoparticles. The nanoparticles were cleaned from extra oleylamine through washing with isopropanol and hexane and extracted from solution through centrifugation using a Beckman Allegra X-22 centrifuge.

Sulfur free cuprous selenide nanoparticle formation

1 mmol copper (II) acetylacetonate [$Cu(acac)_2$] was added with 10 ml OLA into a 100 ml round bottom three neck flask fitted with a condenser, thermocouple, and septa on the three ports. After purging the system of oxygen through the use of three sets of five minute vacuum followed by one minute argon pressure at both room temperature and again at 120°C the temperature was raised to 225°C and the appropriate 0.5ml of sulfur-free selenium solution was injected. The reaction was allowed to continue for 1 minute followed by removal of heat and natural cooling to room temperature. After opening the flask unreacted selenium precipitated and was dissolved back into solution through the addition of 5ml of ethanethiol. The nanoparticles were cleaned from extra solvent through washing with isopropanol and hexane and extracted from solution through centrifugation using a Beckman Allegra X-22 centrifuge.

Sulfur contaminated cuprous selenide nanoparticle formation

One molar selenium in OLA and dodecanethiol (DDT) solution was formed by addition of 5 ml of OLA, 10 mmol of selenium powder (789.6 mg), and 5ml of DDT into a 100 ml round bottom three neck flask fitted with a condenser, thermocouple, and septa on the three ports. After purging the system of oxygen through the use of three sets of five minute vacuum followed by one minute argon pressure at both room temperature and again at 120°C the system was cooled to room temperature.

1 mmol copper (II) acetylacetonate [$Cu(acac)_2$] was added with 10 ml OLA into a 100 ml round bottom three neck flask fitted with a condenser, thermocouple, and septa on the three ports. After purging the system of oxygen through the use of three sets of five minute vacuum followed by one minute argon pressure at both room temperature and again at 120°C the temperature was raised to 225°C and 0.5ml of selenium in OLA-DDT solution was injected. The reaction was allowed to continue for 1 minute followed by removal of heat and natural cooling to room temperature. After opening the flask unreacted selenium precipitated and was dissolved back into solution through the addition of 5ml of ethanethiol. The nanoparticles were cleaned from extra solvent through washing with isopropanol and hexane and extracted from solution through centrifugation using a Beckman Allegra X-22 centrifuge.

Cuprous sulfo-selenide nanoparticle formation

One molar total chalcogen in OLA solution was formed by addition of 10 ml of OLA, 5 mmol of selenium powder (394.8 mg), 5 mmol of sulfur powder (160.3 mg), and 5ml of ethanethiol to a 100 ml round bottom three neck flask fitted with a condenser, thermocouple, and septa on the three ports. The solution was heated to 40°C and gentle vacuum was pulled on the flask for five minutes with subsequent one minute of argon back fill through the condenser. The vacuum and back fill procedure was repeated three times to quickly remove oxygen from the system. After the third argon back fill the vacuum was returned to remove the unreacted ethanethiol from solution. Once the system was no longer actively boiling at 40°C, the temperature was increased while the solution was still under vacuum to 120°C. When the solution successfully reaches 120°C while under vacuum the diethyldisulfide has been removed and the solution contains only OLA dissolved selenium and dissolved sulfur. At this point the solution was cooled under a blanket of argon to room temperature and stored under argon for use below.

1 mmol copper (II) acetylacetonate [Cu(acac)$_2$] was added with 10 ml OLA into a 100 ml round bottom three neck flask fitted with a condenser, thermocouple, and septa on the three ports. After purging the system of oxygen through the use of three sets of five minute vacuum followed by one minute argon pressure at both room temperature and again at 120°C the temperature was raised to 225°C and 0.5ml of the selenium and sulfur in OLA solution was injected. The reaction was allowed to continue for 1 minute followed by removal of heat and natural cooling to room temperature. After opening the flask unreacted selenium precipitated and was dissolved back into solution through the addition of 5ml of ethanethiol. The nanoparticles were cleaned from extra solvent through washing with isopropanol and hexane and extracted from solution through centrifugation using a Beckman Allegra X-22 centrifuge.

Lead selenide nanoparticle formation

1mmol of lead oxide, 10 ml octadecene, and 150 µl of oleic acid were added into a 100 ml round bottom three neck flask fitted with a condenser, thermocouple, and septa on the three ports. After purging the system of gaseous oxygen through the use of three sets of five minute vacuum followed by one minute argon pressure at both room temperature and again at 120°C the temperature was raised to 140°C for 30 minutes to allow the formation of lead oleate. Three milliliters of one third molar sulfur-free selenium solution prepared as above but with less selenium was injected and the reaction was allowed to continue for 1 minute followed by removal of heat and natural cooling to room temperature. After opening the flask unreacted selenium precipitated and was dissolved back into solution through the addition of 5ml of ethanethiol. The nanoparticles were cleaned from extra solvent through washing with isopropanol and hexane and extracted from solution through centrifugation using a Beckman Allegra X-22 centrifuge.

Copper Indium Selenide (CISe) nanoparticle formation

1 mmol copper acetylacetonate (Cu-Acac), 1mmol indium acetylacetonate (In-Acac), and 10 ml OLA were added into a 100 ml round bottom three neck flask fitted with a condenser, thermocouple, and septa on the three ports. After purging the system of oxygen through the use of three sets of five minute vacuum followed by one minute argon pressure at both room temperature and again at 120°Cthe temperature was raised to 225°C and three milliliters of one molar sulfur-free selenium solution was injected and the reaction was allowed to continue for 30 minutes followed by removal of heat and natural cooling to room temperature. After opening the flask unreacted selenium precipitated and was dissolved back into solution through the addition of 5ml of ethanethiol. The nanoparticles were cleaned from extra solvent through washing with isopropanol and hexane and extracted from solution through centrifugation using a Beckman Allegra X-22 centrifuge.

Copper Zinc Tin Selenide (CZTSe) nanoparticle formation

2 mmol copper acetylacetonate (Cu-Acac), 1mmol zinc acetylacetonate (Zn-Acac), 1mmol tin acetylacetonate, and 6 ml OLA were added into a 100 ml round bottom three neck flask fitted with a condenser, thermocouple, and septa on the three ports. After purging the system of oxygen through the use of three sets of five minute vacuum followed by one minute argon pressure at both room temperature and again at 120°C, the Cu-Zn-Sn solution was cooled to room temperature. Meanwhile in a separate flask, 10 ml of OLA was purged of oxygen through the use of three sets of five minute vacuum followed by one minute argon pressure at both room temperature and again at 120°C and subsequently heated to 250°C. At 250°C six milliliters of one molar sulfur-free selenium solution and 6ml of the Cu-Zn-Sn solution were injected, and the reaction was allowed to continue for 30 minutes followed by removal of heat and natural cooling to room temperature. After opening the flask unreacted selenium precipitated and was dissolved back into solution through the addition of 5ml of ethanethiol. The nanoparticles were cleaned from extra solvent through washing with isopropanol and hexane and extracted from solution through centrifugation using a Beckman Allegra X-22 centrifuge.

pXRD Measurements

PXRD was performed with Scintag X2 diffractometer employing Cu Kα radiation at standard room temperature and pressure conditions. Nanocrystals were coated over a fused quartz substrate except for the copper-chalcogenides which were coated on molybdenum coated glass. Copper-chalcogenide pXRD were aligned such that the molybdenum (110) peak location was exactly 40.50 and noise was reduced for display through three point adjacent averaging.

FE-SEM EDS Measurements

EDS measurements of nanoparticles on a silicon wafer substrate were performed in a FEI Quanta 3D FEG Dual-beam scanning electron microscope equipped with a Oxford INCA Xstream-2 silicon drift detector with Xmax80 window and an accelerating voltage of 20kV.

ADDITIONAL DATA:

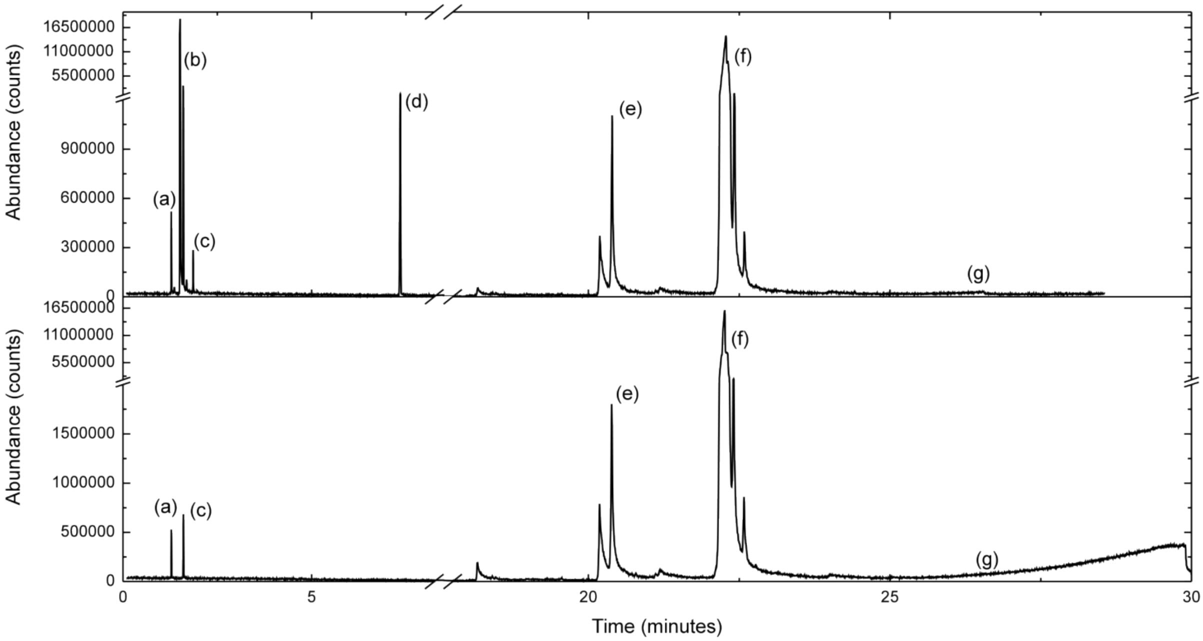

Fig. S1 GCMS data of selenium dissolved in oleylamine before (top) and after (bottom) ethanethiol and diethyldisulfide removal. Components observed are (a) Se_1, (b) ethanethiol, (c) dichloromethane used as dilutant, (d) diethyldisulfide, (e) hexadecylamine contaminant in oleylamine (see Fig S2), (f) oleylamine, and (g) Se_8. Other minor peaks are contaminants of OLA (see Fig S2). Of note is the complete removal of sulfur containing components (b and d) enabling pure selenide reactions.

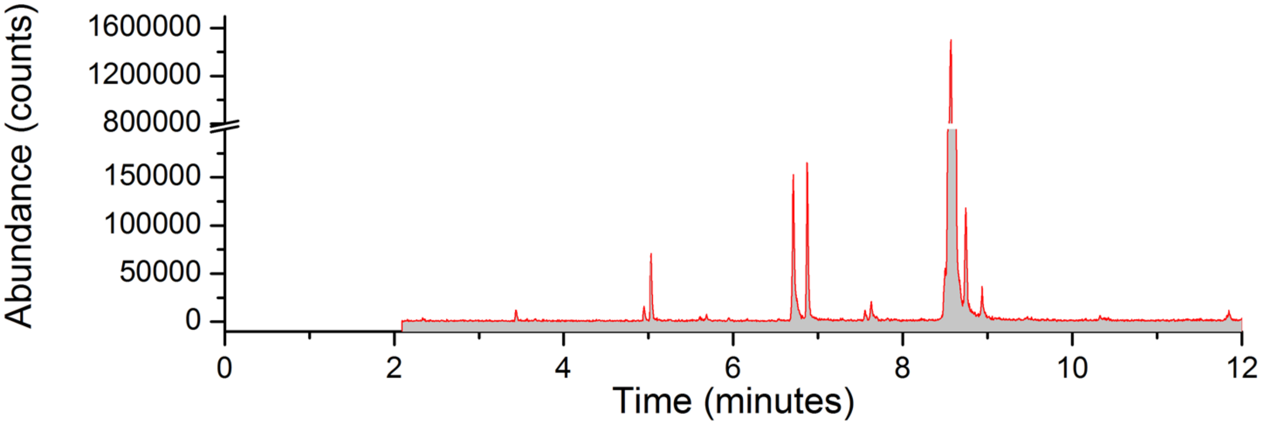

Fig. S2 GCMS spectra of oleylamine only showing the additional peaks identified in the manuscript as belonging to the impure oleylamine. Note that this run was done under different ramp rate than others shown.

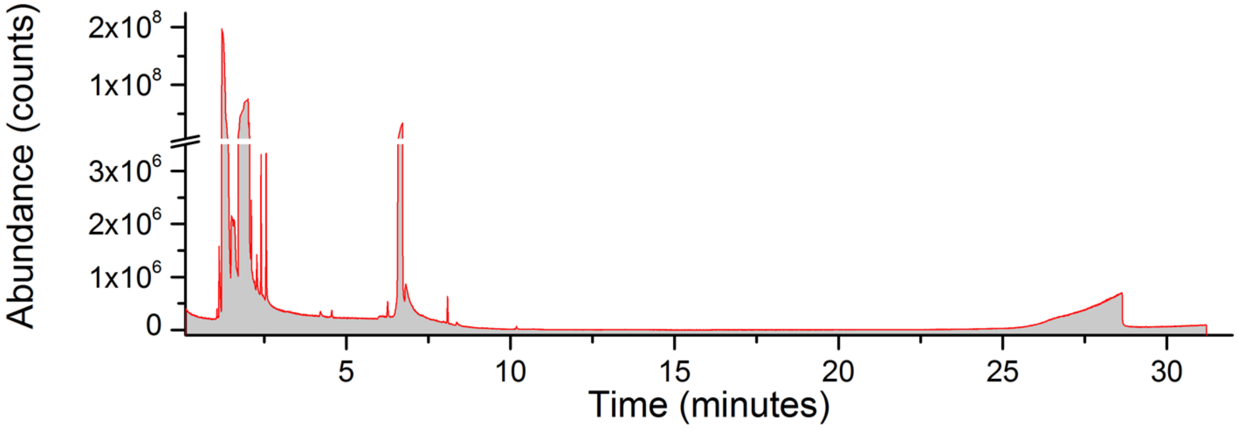

Fig. S3 GCMS spectra of selenium dissolved in butylamine and ethanethiol showing no additional components than what was observed with heavier amines. The dominant peaks are, in order of occurrence, ethanethiol, butylamine, diethyldisulfide, and finally Se8.

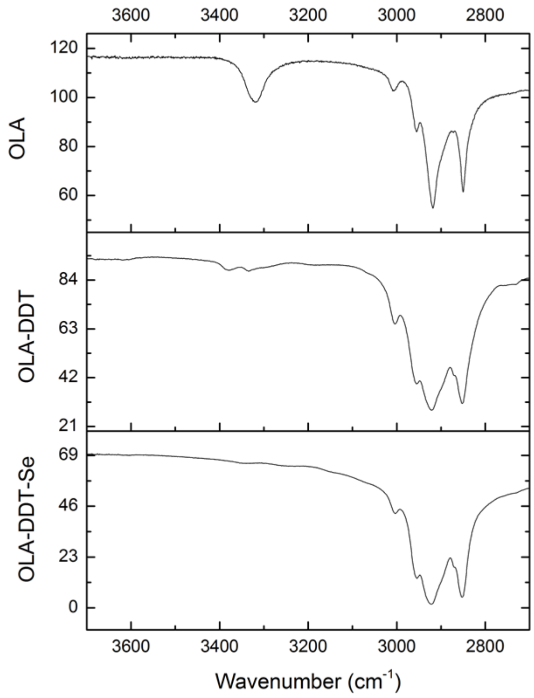

Fig. S4 FTIR data of, from top, only oleylamine, oleylamine and dodecanethiol mixed in a 1:1 volumetric ratio, 1:1 oleylamine and dodecanethiol saturated with selenium. Of note is the complete disappearance of the 3300 cm-1 N-H stretch peak as the amine switches to become aminium with a corresponding broad N+-H stretch near 3000 cm-1. For FTIR measurements samples were compressed between two potassium bromide disks. The Thermo-Nicolet Nexus 670 FTIR instrument was used to analyze the specimens after allowing the system to purge for ten minutes with nitrogen. Measurements were made in transmission mode by collecting 64 scans with a resolution of 2 cm-1 wavelength.

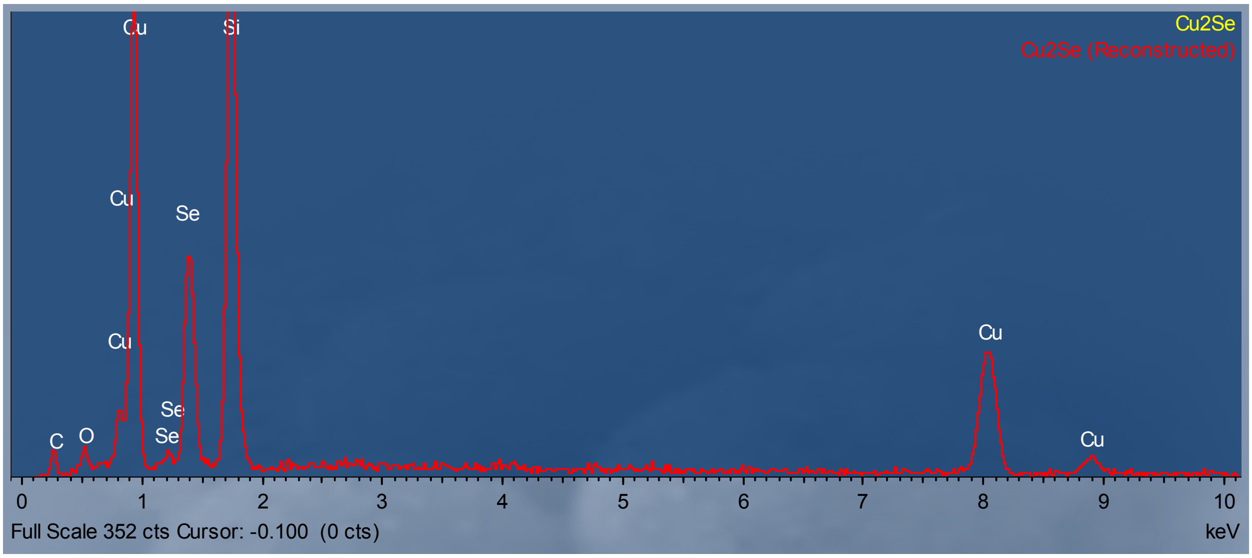

Fig. S5 Field emission scanning electron microscope (FE-SEM) based energy dispersive x-ray spectroscopy (EDS) spectra and subsequent reconstruction of copper selenide shown in manuscript Figure 3 item (a). Calculated atomic concentrations are: Copper (30.44%), and Selenium (15.56%). Resulting in a final Cu:Se stoichiometry of 2.00: 1.02. Absent is the primary sulfur Kα x-ray at 2.308 keV showing pure selenide formation. Silicon signal came from the substrate, and was removed in the calculation of composition. Other elements detected include carbon (42.98%), and oxygen (11.02%).

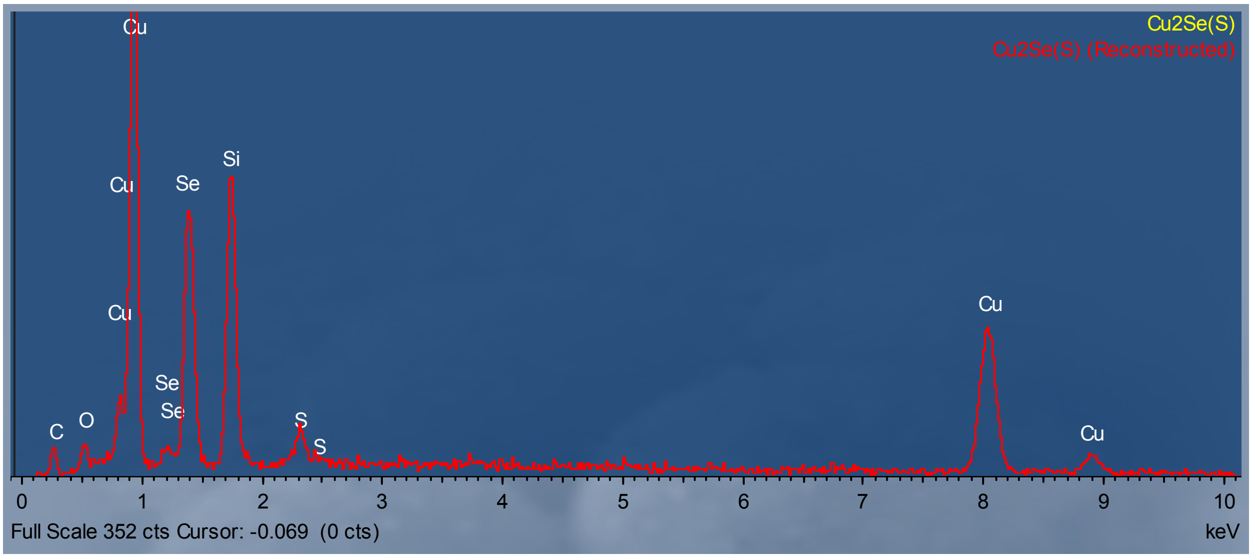

Fig. S6 FE-SEM based EDS spectra and subsequent reconstruction of copper selenide-sulfide shown in manuscript Figure 3 item (b). Calculated atomic concentrations are: Copper (27.46%), Sulfur (2.38%), and Selenium (14.68%). Resulting in a final Cu:S:Se stoichiometry of 2.00: 0.17: 1.07. Silicon signal came from the substrate, and was removed in the calculation of composition. Other elements detected include carbon (45.41%), and oxygen (10.07%).

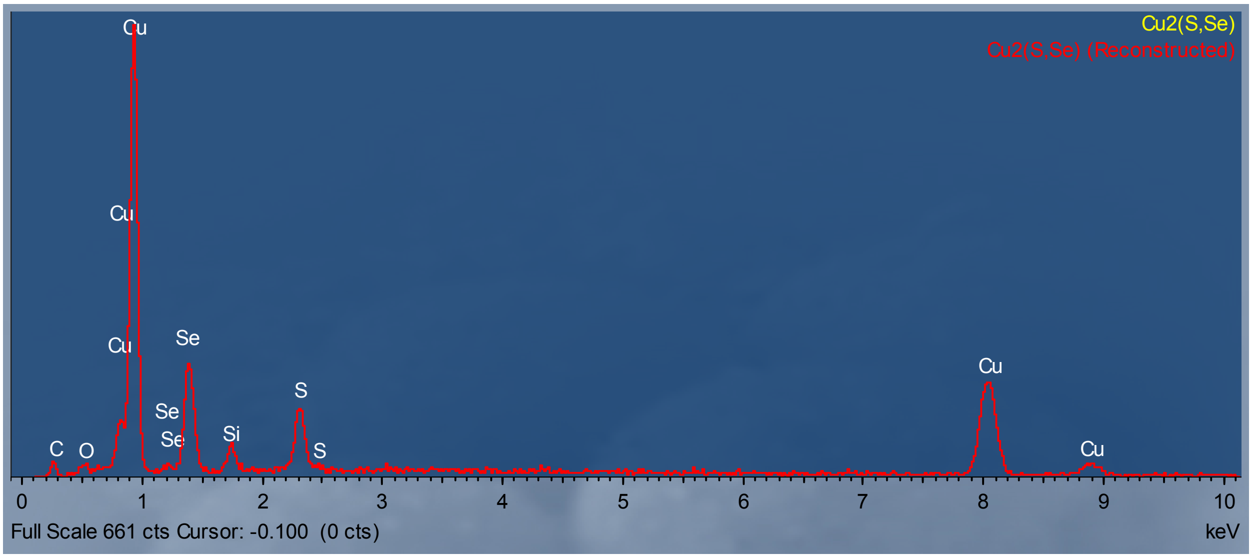

Fig. S7 FE-SEM based EDS spectra and subsequent reconstruction of copper selenide-sulfide shown in manuscript Figure 3 item (c). Calculated atomic concentrations are: Copper (33.53%), Sulfur (8.03%), and Selenium (11.87%). Resulting in a final Cu:S:Se stoichiometry of 2.00: 0.48: 0.71. Silicon signal came from the substrate, and was removed in the calculation of composition. Other elements detected include carbon (42.61%), and oxygen (3.96%).

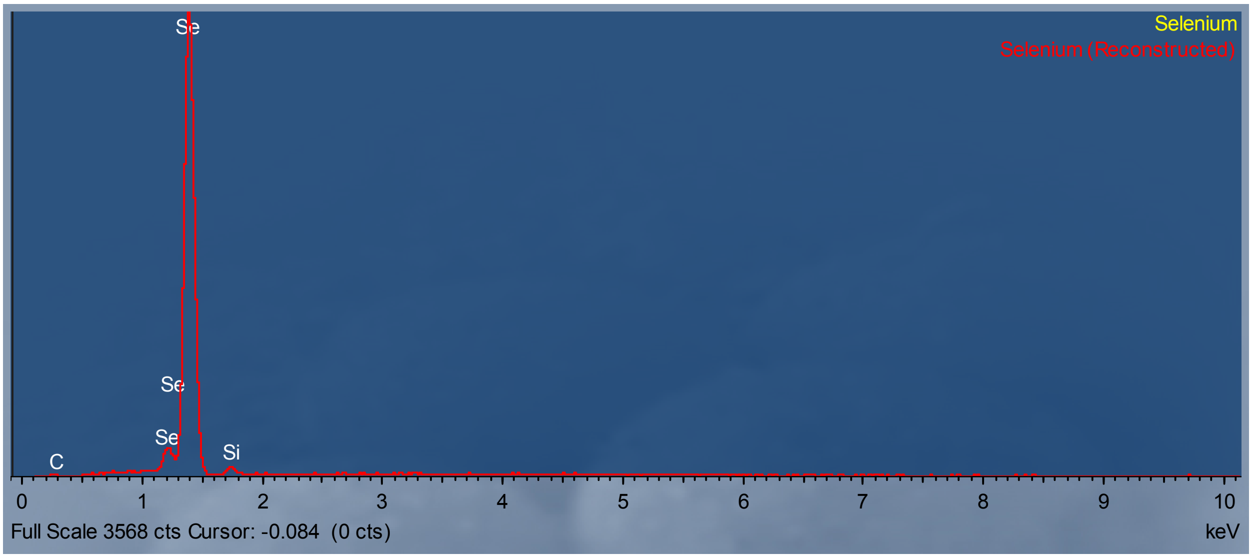

Fig. S8 FE-SEM based EDS spectra and subsequent reconstruction of selenium shown in manuscript Figure 4 item (a). Calculated atomic concentrations show Selenium (62.80%). Absent is the primary sulfur Kα x-ray at 2.308 keV. Silicon signal came from the substrate, and was removed in the calculation of composition. The other element detected is carbon (37.20%).

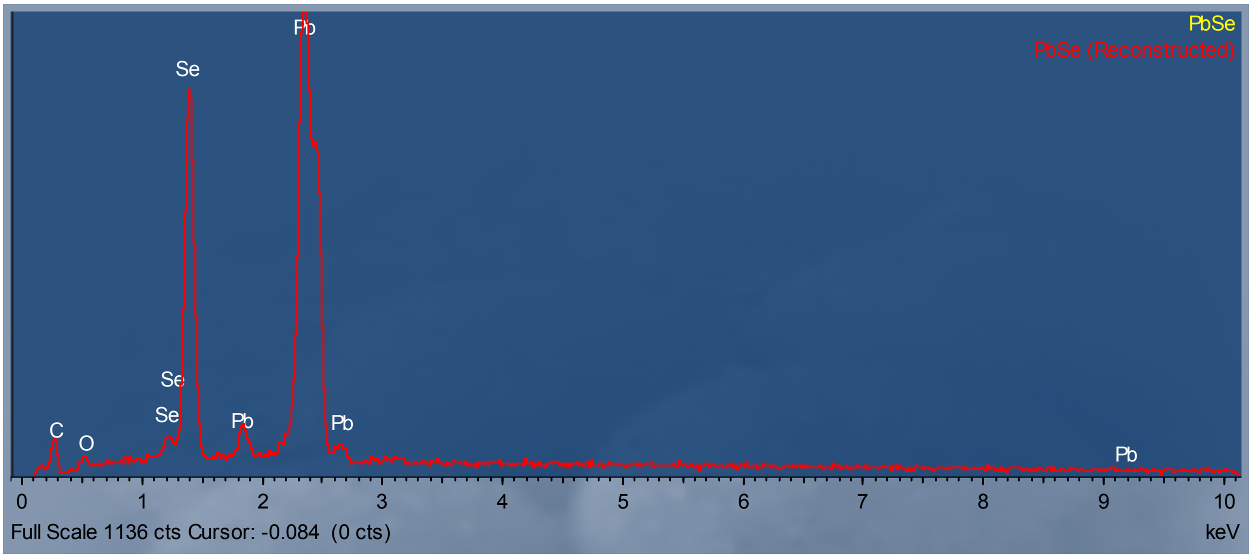

Fig. S9 FE-SEM based EDS spectra and subsequent reconstruction of lead-selenide shown in manuscript Figure 4 item (b). Calculated atomic concentrations are: Lead (18.16%) and Selenium (20.36%). Resulting in a final Pb:Se stoichiometry of 1.00:1.12. Due to close proximity of both the sulfur Kα and lead Mα x-rays at 2.308 and 2.345 keV it is difficult to ensure that no sulfur is present, although trends from other materials, GCMS data, as well as the software calculations show it is not present. Other elements detected include carbon (52.39%), and oxygen (9.09%).

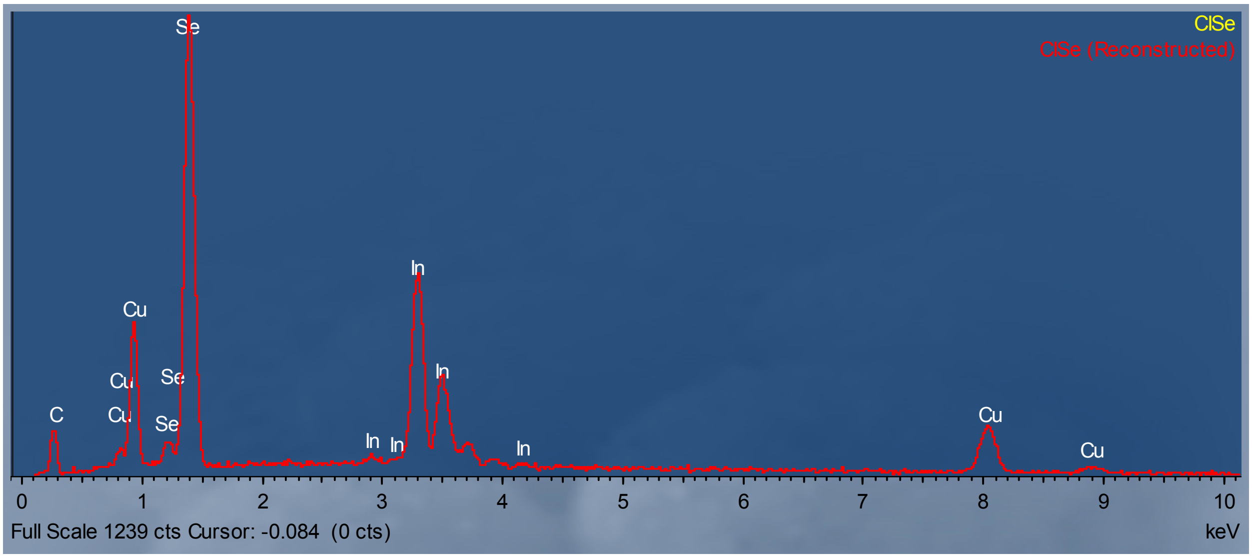

Fig. S10 FE-SEM based EDS spectra and subsequent reconstruction of copper indium selenide shown in manuscript Figure 4 item (c). Calculated atomic concentrations are: Copper (9.14%), Indium (10.56%), and Selenium (20.56%). Resulting in a final Cu:In:Se stoichiometry of 0.87: 1.00: 1.95. Absent is the primary sulfur Kα x-ray at 2.308 keV showing pure selenide formation. Silicon signal came from the substrate, and was removed in the calculation of composition. Carbon is also detected (59.73%) in the spectra.

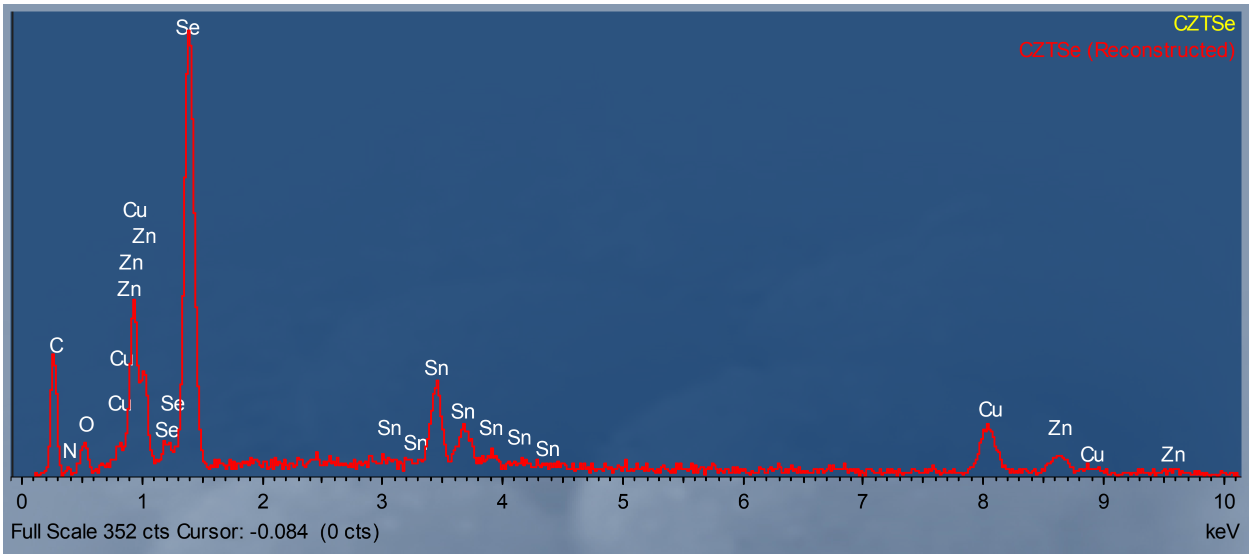

Fig. S11 FE-SEM based EDS spectra and subsequent reconstruction of copper zinc tin selenide shown in manuscript Figure 4 item (d). Calculated atomic concentrations are: Copper (4.26%), Zinc (2.44%), Tin (2.23%), and Selenium (8.92%) resulting in final Cu:Zn:Sn:Se ratio of 1.91:1.09:1.00:4.00 which is close to planned copper poor and zinc rich composition desired for this material. Absent is the signal for sulfur at 2.3 keV showing pure selenide formation. Other elements observed include carbon (64.91%), nitrogen (8.56%), and oxygen (8.68%).