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Aqueous Synthesis of $\text{Cu}_2\text{ZnSnSe}_4$ Nanocrystals

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ABSTRACT: Copper zinc tin selenide (CZTSe) nanocrystal inks are a promising candidate for the development of cheap, efficient, scalable and non-toxic photovoltaic (PV) devices. They also present an important opportunity to controllably mix copper zinc tin sulfide (CZTS) with CZTSe to produce directly spectrally tunable $\text{Cu}_2\text{ZnSn}(\text{S}/\text{Se})_4$ (CZTSSe) solid-solutions using low temperature processes. Herein we describe a one-pot, low temperature, aqueous-based synthesis that employs simultaneous redox and crystal formation reactions to yield CZTSe nanocrystal inks stabilized by $\text{Sn}_2\text{Se}_7^{6-}$ and thiourea. This versatile CZTSe synthesis is understood through the use of inductively coupled plasma mass spectrometry (ICP-MS), Raman spectroscopy, Fourier transform infrared spectroscopy and powder x-ray diffraction (PXRD). It is further shown that stoichiometrically mixed CZTSe and CZTS nanocrystal powders yield a single CZTSSe phase at annealing temperatures between 200–250 °C. This facile and low-temperature process offers a low-energy alternative for the deposition of pure CZTSe/SSe thin-films and enables the band gap to be readily tuned from 1.5 down to 1.0 eV by simple solution chemistry.

1.0. INTRODUCTION

Chalcogenide photovoltaic (PV) materials have garnered growing interest over the years as robust and inexpensive inorganic alternatives to Si-based PV.¹ These materials have gradually evolved from binary II-VI CdTe, through to ternary I-III-VI₂ CuInS_2 (CIS), quaternary I₂-III-III-VI₄ $\text{Cu}_2\text{InGaSe}_4$ (CIGSe), and even quinary I₂-II-IV-VI_x-VI_(4-x) $\text{Cu}_2\text{ZnSn}(\text{S}/\text{Se})_4$ (CZTSSe) compositions. The increasing complexity through the cross-substitution of elements allows for both the tailoring of their optoelectronic properties and the selection of less toxic and more abundant elements.² $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe), $\text{Cu}_2\text{ZnSnS}_4$ (CZTS), and CZTSSe kesterites are promising absorber materials due to their elemental abundance, environmental benignity, high absorption coefficients exceeding 10^4 cm^{-1} , p-type conductivity, and ideal direct band gaps of 1.0 eV, 1.5 eV and 1.0–1.5 eV, respectively.¹ Of these, CZTSe and CZTSSe PV devices show the most promising photo-conversion efficiencies (PCE) of 11.6%³ and 12.6%,⁴ respectively, while CZTS devices lag behind with a PCE of 8.4%.

Various methods for the fabrication of CZTSSe thin films have been developed, including quinary sputtering⁵ and CZTSSe nanoparticle deposition;^{6, 7} however, the bulk of the literature has focused on a two-step process of depositing pure CZTS or CZTSe films followed by selenization and/or sulfurization at high temperature under toxic atmospheres to form the mixed CZTSSe phase.^{4, 8–11} The deposition of CZTS and CZTSe films can be achieved by the decomposition of molten salts,^{12–14} reactive sputtering,^{15–20} electroplating,^{21–23} vapour deposition,^{24–28} precursor solution deposition,^{29–34} and nanoparticle ink sintering.^{35–57} Of these, nanoparticle routes are among the most promising due to their potential to be inexpensive and scalable, while maintaining superior phase and composi-

tional control when compared to non-solution based approaches. Although CZTS nanoparticle routes, including green and scalable syntheses, have been widely reported,^{35, 50–56} reports related to CZTSe nanoparticles are much more scarce.^{36–49, 57}

CZTSe nanoparticle syntheses typically involve the use of toxic solvents such as hydrazine,^{37, 38} or hot injection reactions in non-polar solvents that require extensive post processing.^{34, 39–45, 57, 58} This is mainly due to the difficulty in forming soluble Se anions or precursors in solution. While “greener” CZTSe nanoparticle syntheses do exist,^{46–48} these typically do not have precise elemental ratio control and use bulky aliphatic ligands to stabilize nanoparticles via steric repulsion, which leaves organic impurities in the resultant film, even after thermal annealing, hindering device performance.^{1, 59, 60}

The fundamental drawback of the superior tunability of CZTSSe is the complexity of the elemental distribution within the lattice structure. This leads to a greater number of potential anti-sites, interstitial sites, and vacancy defects in the crystal structure, and the number of these sites are further increased by heat treatment above 250 °C.^{2, 61} Selenization processes to date use temperatures of ~500 °C, which also cause a multitude of problems: (i) decomposition of CZTSSe into secondary phases and the potential loss of SnSe/SnS species if careful control of the atmosphere is not maintained;^{9, 62} (ii) inefficient use of a large excess of Se, the rarest element in the composition, of which there is only 0.05 ppm in the earth’s crust;¹¹ (iii) difficulty in controlling the exact S:Se ratio in the film and S:Se gradient with depth;^{2, 63–65} (iv) formation of a thick MoSe_2 layer of several hundred nanometers at the electrode interface that increases resistance and recombination;^{2, 4, 11, 66} (v) increased cationic disorder, due to similar atomic radii, resulting in increased band tailing and trap states;^{2, 20, 67, 68} and (vi) formation of toxic gases which makes scalability dif-

ficult and costly. A number of hypotheses have been proposed to explain the device performance gap between CZTSSe and CIGSe devices.^{2, 65-71} The most widely accepted are that the presence of a thicker MoSe₂ layer leads to resistive and recombination losses,^{2, 4, 11, 66} and cationic disorder leading to band tailing and a large V_{oc} deficit^{2, 67-69} are the primary performance loss factors. Both of these are due in part to the selenization process, and as such the potential to increase the efficiency of CZTSSe to be at parity with CIGSe (PCE 22.6%)⁷² by replacing this selenization process with a lower temperature and scalable alternative is of great interest.

At present there is no CZTSe nanoparticle synthesis that simultaneously provides stoichiometric compositional control and phase purity using a low toxicity solvent, while also yielding negligible residual carbon impurities following thermal annealing. Additionally, a low temperature and scalable alternative to current selenization processes that offer homogeneous and stoichiometric control of the S:Se ratio in the film has yet to be reported. Herein, by using a highly charged, molecular, tin selenide ligand, we demonstrate a versatile, stoichiometric, one-pot synthetic method that produces aqueous CZTSe nanoparticles on a multigram scale without the use of long-chained organic ligands. We also establish a simple process to produce single phase CZTSSe kesterite materials by mixing stoichiometric amounts of CZTS³⁵ and CZTSe nanoparticle inks followed by mild heat treatment. This process is facilitated by the short inorganic ligands present on the nanoparticle surfaces, and the small CZTSe particle sizes, which enables short diffusion distances and low sintering temperatures to produce a homogeneous distribution of S and Se in the film. The work presented here on both pure and mixed nanoparticle annealing properties, phase purity and grain growth characteristics under an inert atmosphere, lays the groundwork for the fabrication of future high efficiency PV devices.

2.0. EXPERIMENTAL SECTION

2.1. Materials

Tin powder (<45 μ m particle size, 99.8%), selenium powder (100 mesh, 99.5% or 99.99%), zinc nitrate hexahydrate (>99%), copper nitrate hemi-pentahydrate ($\geq$ 98%), ammonia (25% in water), thiourea ($\geq$ 99%), selenourea (98%), sodium borohydride (98%), sodium hydroxide ($\geq$ 97%), and methanol (99.8%) were purchased from Sigma-Aldrich. Tin diselenide (99.999%) was purchased from Chengdu Alfa Metal Material Co. All of the above reagents were used as received; however, any solvents used under inert gas were first degassed on a Schlenk line under vacuum (1 mPa) using an ultrasonic bath on a degas cycle with a power of 120 W. A cold trap was also employed to prevent any vaporized solvent reaching the vacuum pump. The tin powder and selenium powder were stored in a glove box under a nitrogen atmosphere with >1 ppm H₂O to prevent oxidation. Deionized water was obtained from a Milli-Q system (18.2 M Ω .cm resistivity). Reaction containers were polypropylene specimen containers with polypropylene screw caps purchased from Techno Plas. Note that CZTSe nanoparticles were found to adsorb strongly onto glass vessels.

2.2. Preparation of Tin Selenide Chalcogenide

Two possible routes to form aqueous tin selenide chalcogenide (SnSe-MCC) solutions were trialed for this work: (i) a hydrothermal route, modified from Loose & Sheldrick⁷³ and

(ii) a redox route, modified from Krebs & Uhlen.⁷⁴ These are shown schematically in Figure 1 a) & b).

While both experimental methods are described here, only results using the hydrothermal route are presented here. We found that the redox route required a large excess of Na₂Se, resulting in binary phase formation when synthesizing CZTSe. Some results using the redox route are included in the Supporting Information for completeness.

Hydrothermal route: Tin powder (50 mmol, 5.936 g) and selenium powder (175 mmol, 13.825 g) were added to a high pressure Teflon lined autoclave and sealed under a nitrogen atmosphere to prevent their premature oxidation. Sodium hydroxide (200 mmol, 7.999 g), Milli-Q water (30 mL), and methanol (60 mL) were quickly added to the high pressure Teflon lined autoclave in air before filling with argon and resealing. The original turbid mixture was allowed to react for 3 days with the temperature maintained at 140 °C using a chamber furnace. This yielded a transparent 0.2778 M Sn₂Se₇⁶⁻ solution (25 mmol in 2:1 methanol-water, 90 mL) with a deep-red color. This solution was then stored at 4 °C for 3 days to form crystals, which were then filtered and washed with cold methanol in a N₂ environment to give red Na₆Sn₂Se₇·16H₂O needles (23.6 mmol, 31.115 g, 94% yield). The identification of these products is provided in the SI. It is noted that at the high temperatures and pressures experienced in hydrothermal reactions there is slow methanol oxidation⁷⁵ $CH_3OH + 2H_2O \rightarrow CH_2O + 2H_3O^+ + 2e^-$ which accounts for the otherwise missing electrons in the balanced equations seen in Figure 1 a).

A colorless ammonium selenide solution was then produced by reacting selenium (2.5 mmol, 0.198 g), and sodium borohydride (5 mmol, 0.189 g) in ammonia (6.94 mL, 12.8 % in Milli-Q water) under a N₂ atmosphere with stirring until bubbling stopped. Na₆Sn₂Se₇·16H₂O (2.5 mmol, 3.296 g) was then dissolved in this ammonium-selenide solution to give the final 0.36 M SnSe-MCC precursor solution (2.5 mmol in 6.94 mL of 12.8% aqueous ammonium selenide).

Redox route: Sodium hydroxide (15 mmol, 0.600 g) was dissolved in degassed Milli-Q water (150 mL) and placed under N₂ at 1 °C. Sodium borohydride (30 mmol, 1.135 g) and selenium powder (15 mmol, 1.184 g) were added with stirring and allowed to react (~3 hours) to give a clear 0.1 M Na₂Se solution. To this solution SnSe₂ (5 mmol, 1.383 g) was added and left to react with stirring (~12 hours) to give 16.7 mM Sn₂Se₆⁴⁻ and 66.7 mM Na₂Se, which was a transparent green solution under N₂ and a transparent red solution under vacuum or air. The solution was then vacuum dried to give an orange-red mix of Na₄Sn₂Se₆·13H₂O (2.5 mmol, 2.593 g) and Na₂Se (10 mmol, 1.249 g) crystals with a final combined yield of 3.546 g (92.3%). Characterization is provided in the SI. These crystals were difficult to separate so they were all dissolved in ammonia (6.94 mL, 12.8% in Milli-Q water) under N₂ atmosphere to give the final 0.36 M SnSe-MCC precursor solution (2.5 mmol in 6.94 mL of 12.8% ammonium-selenide water). Note this green-red color change is reversible and could be cycled >20 times.

A 3-fold excess of selenium powder relative to tin diselenide is used to ensure complete reaction to form Sn₂Se₆⁴⁻; if stoichiometric quantities are used large amounts of unreacted SnSe₂ powder remains and needs to be filtered out, leaving an equivalent quantity of Na₂Se in the resultant Na₄Sn₂Se₆·13H₂O crystals. Waiting additional time made no discernible difference.

Stability: Neither aqueous SnSe-MCC solution can be stored for long periods due to a slow degradation reaction that causes an orange precipitate to form. However, the $\text{Na}_6\text{Sn}_2\text{Se}_7 \cdot 16\text{H}_2\text{O}$ and $\text{Na}_4\text{Sn}_2\text{Se}_6 \cdot 13\text{H}_2\text{O}$ crystals can be stored in a sealed container under N_2 for long periods (>30 days) and dissolved when needed.

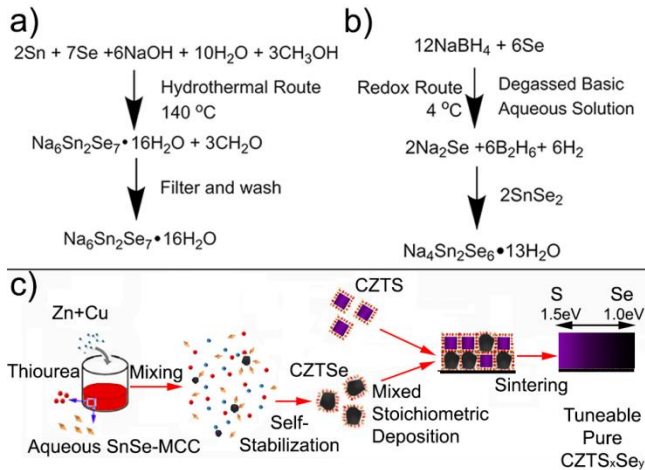


Figure 1. a) Hydrothermal reaction of metallic tin and selenium to form $\text{Na}_6\text{Sn}_2\text{Se}_7 \cdot 16\text{H}_2\text{O}$.^{73, 75} b) Redox reaction of metallic selenium to form Na_2Se and then the subsequent reaction with SnSe_2 to form $\text{Na}_4\text{Sn}_2\text{Se}_6 \cdot 13\text{H}_2\text{O}$.⁷⁴ c) A simplified process diagram for aqueous CZTSe ink preparation.

2.3. Synthesis of CZTSe Nanoparticles

A typical synthesis of CZTSe nanoparticles with an elemental ratio of 2:1:1 Cu:Zn:Sn and total metal concentration of 40 g/L is as follows: a 1 M thiourea solution (15 mmol in 15 mL of Milli-Q water) and a 0.36 M SnSe-MCC solution (2.5 mmol in 6.94 mL of 12.8% aqueous ammonium selenide) were added to Milli-Q water (42 mL, to adjust the final ink concentration to 40 g/L) at 40 °C with stirring. A 0.76 M $\text{Zn}(\text{NO}_3)_2$ solution (5 mmol in 6.54 mL of 18% ammonia solution) was then added, causing the formation of a pale orange precipitate, which redissolved within 3 minutes to return the solution to its original transparent red appearance. Once the solution was completely transparent, a 1.25 M $\text{Cu}(\text{NO}_3)_2$ solution (10 mmol in 8 mL of Milli-Q water) was added quickly with stirring, causing the immediate formation of a black CZTSe nanoparticle ink. The yield by mass was $\geq 98\%$ (3.1 g of dried CZTSe nanoparticles). This synthetic method was successfully scaled-up to produce 10 g of dried CZTSe nanoparticle powder. It should be noted that this reaction was performed inside a N_2 glove box with degassed solvents to eliminate oxygen and carbon dioxide.

CZTSe nanoparticles of different elemental ratios and concentrations can be synthesized stoichiometrically by the addition of different amounts of copper, zinc, and tin precursor solutions, while keeping a pH >11 and ~1.5-fold excess of thiourea to copper ions in solution to ensure reduction of Cu(II) to Cu(I) by thiourea. This synthesis can be varied to make any of the nanoparticle inks discussed later in this work at concentrations of up to ~90 g/L.

These CZTSe nanoparticles, once synthesized, are colloidal-stable in aqueous-based solvents with a pH ≥ 7 at low ionic strengths (<10 mM), however at higher pH of ~10 larger ionic strengths of ~0.45 M are possible.

It should be noted that selenourea is able to substitute for thiourea in the above synthesis; however, no difference in the resultant CZTSe nanoparticles was identified aside from the presence of the relevant urea derivative on the nanoparticle surface. Specifically, no sulfur was detected in the CZTSe crystals when using thiourea even with annealing. As such, based on cost and toxicity considerations, thiourea was chosen over selenourea.

2.4. Characterization

As-synthesized CZTSe powders were obtained by drying at 40 °C under N_2 . Purified CZTSe nanoparticles were obtained by adding ethanol or isopropanol as an antisolvent, centrifuging at > 4000 rcf (~5 mins), disposing of the supernatant and redispersing the precipitant in Milli-Q water. Powder samples were prepared at a concentration of 40 g/L, dried at 40 °C under N_2 for 3 days, then under vacuum (1 mPa for 1 hour) to yield a dry nanoparticle powder. Such powders were made into compacted discs with a diameter of 1.3 cm using a KBr disc manual hydraulic press with 9 tons applied for 2 minutes.

Transmission electron microscopy (TEM) images were recorded on a FEI TF 20 TEM operated with an acceleration voltage of 200 kV. 2:1:1 CZTSe nanoparticles were prepared as described above and diluted (0.5 g/L) for TEM analysis. The dilute nanoparticle dispersions (10 μL) were drop cast onto parafilm. A carbon-coated copper grid (400 mesh) pretreated with a dilute poly(dimethyldiallyl ammonium chloride) (PDMAC) solution to create a monolayer of cationic polymer was placed on top for two minutes then removed and allowed to dry.

STEM selected area electron diffraction (SAED) and energy dispersive X-ray spectroscopy (EDS) were also performed on a FEI TF 20 TEM using a HAADF detector. The sample was prepared from a compressed disc sintered at 250 °C with a S:Se ratio of 1:1 using a FEI Nova Dual Beam FIB SEM as described in the supporting information. Simulated SAED patterns were obtained using EMAPS⁷⁶.

Raman spectra were collected with a Renishaw InVia-Raman spectrometer using a $\lambda = 514$ nm laser source and Renishaw RM 1000 Raman spectrometer using a $\lambda = 325$ nm laser source over the range from 100 to 720 cm^{-1} and the peaks were fitted using Origin software.

Fourier transform infrared spectra were collected with a Perkin Elmer Spectrum One FTIR spectrometer over the range from 650 to 3600 cm^{-1} .

Zeta Potential measurements were performed using a NanoBrook ZetaPALS zeta potential analyzer. CZTSe nanoparticles were diluted to 0.5 g/L with ammonia-water to maintain a pH ~10 and 0.5 mM of NaCl added as an electrolyte. 10 measurements were performed and the average taken as the zeta potential value.

Tandem thermogravimetric analysis combined with Fourier transform infrared spectroscopy (TGA-FTIR) was conducted on a Netzsch TG 209 F1 Libra instrument in tandem with a STA 449 F1 Jupiter-FT-IR Coupling system. The CZTSe ink powders used for this analysis were synthesized at a concentration of 40 g/L with a Cu:Zn:Sn ratio of 2:1:1. The heating rate was 2.5 °C/minute with mass measured every 0.6 seconds and FTIR spectra acquired every 22 seconds. The original CZTSe mass was 42.8 mg. Two vacuum-fill cycles were performed before measurements began, and a nitrogen flow rate of 20 mL/min was applied throughout measurements. FTIR

peaks were analyzed based on reference spectra from the National Institute of Standards and Technology (NIST) database where no publications are cited.

Powder x-ray diffraction (PXRD) analysis was carried out on a Bruker D8 Advance Diffractometer between 5° and 90° using Ni-filtered Cu α radiation ($\lambda = 1.5406 \text{ \AA}$) and a step size of 0.02°. Each data set was analyzed using Rietveld refinement-based quantitative phase analysis^{77, 78} and crystal phase wt% values were calculated via the Hill and Howard algorithm.⁷⁹ An anisotropic crystallite size broadening function, adapted by Coelho⁸⁰ from March-Dollase,⁸¹ was used to improve the quality of the fit by taking into account the crystallite size and micro-strain.

Inductively coupled plasma elemental mass spectrometry (ICP-MS) was performed using a GBC Optima 9500 ICP-TOF-MS. For ICP-MS a portion of CZTSe nanoparticle powder was digested in HCl and diluted with 2% HCl in Milli-Q water to achieve ~250 ppb levels for analysis. A single calibration standard solution was purchased from Choice Analytical of 100 ppm of Au, Cu, Zn, Sn, S, and Se was diluted to multiple concentrations between 10 and 200 ppb in order to produce a calibration curve for each of the elements.

In-situ, time-resolved UV-Vis-NIR measurements were carried out using an Ocean Optics system with a DH-2000-BAL light source (balanced deuterium & halogen lamps, range: 190–2500 nm), HR2000 detector (range: 190–1100 nm), Flame NIR detector (range: 950–1650 nm) using QP600-2-SR optic fibers (600 μm , range: 300–2100 nm) with 71 ms resolution. Two detectors were used in order to capture both the UV-Vis region and NIR region, and the spectra were merged at 950 nm. The typical 50:25:25 (Cu:Zn:Sn %) composition was studied at a nanoparticle ink concentration of 0.5 g/L, selected to prevent saturation of the UV-Vis detector. The synthesis was carried out in a 1 cm pathlength quartz cuvette with a magnetic stirrer to ensure proper mixing.

Reflectance UV-Vis-NIR measurements were carried out on compacted CZTSe discs using a Perkin Elmer Lambda 1050 UV/Vis/NIR with an integrating sphere. A Kubelka-Munk transformation was used to convert reflectance spectra into equivalent absorption spectra using the reflectance of a compacted BaSO₄ disc as a reference. Note these discs were too thick to exhibit any transmission.

Photoelectron Spectroscopy in Air (PESA) measurements were carried out using a Riken Keiki AC-2 spectrometer. For all samples a power intensity of 50 nW was used. The error in the ionization energies determined from the PESA measurements on a given sample was 0.05 eV.

Scanning electron microscopy (SEM) images were recorded on a FEI Nova Dual Beam FIB SEM operated with an acceleration voltage of 20 kV, current of 2.4 nA, and magnification of 35000 $\times$.

3.0. RESULTS AND DISCUSSION

3.1. Synthesis, Morphology and Surface Chemistry of CZTSe Nanoparticles

To synthesize CZTSe nanoparticles we have built on our previous work,³⁵ while keeping to four design principles: (1) the materials and processes must be economical; (2) green and non-toxic materials and techniques must be used; (3) all techniques must be scalable; and (4) impurities, such as carbon, nitrogen and oxygen, must be minimized. Briefly, an aqueous

ammonia solvent, metal nitrates, urea derivatives, and a tin metal chalcogenide were processed at low temperature using simple and scalable methods. Most notably the need for post-processing to remove impurities and organic ligands is eliminated and only a mild heat treatment of <200 °C is required, which makes this synthesis amenable to deposition and annealing on flexible substrates, as well as commercialization.

The synthesis and use of SnSe-MCC in aqueous solution as an organic-free stabilizer utilizing electrostatic repulsion is not trivial. The synthesis of SnSe-MCC via green and non-toxic means has only been attempted a limited number of times,^{73, 74, 82} and to our knowledge has not been used as a stabilizer in aqueous solutions to date. We trialed two routes for the synthesis of SnSe-MCC crystals. Firstly, a hydrothermal route, based on that developed by Loose and Sheldrick⁷³ was modified to use stoichiometric quantities of precursors to ensure complete reaction and give a near 100% yield of Sn₂Se₇⁶⁻ in the form of Na₆Sn₂Se₇·16H₂O. Secondly, a redox route, based on that developed by Krebs & Uhlen⁷⁴ was modified to reduce the toxicity and associated risks by substituting the reported hydrogen selenide gas bubbling through solution for selenium powder and sodium borohydride. This latter method yielded the analogous SnSe-MCC Sn₂Se₆⁴⁻ in the form of Na₄Sn₂Se₆·13H₂O; however, to achieve a complete reaction of SnSe₂, a 3-fold excess of selenium was required. This resulted in a large proportion of Na₂Se crystal impurities mixed with the SnSe-MCC crystals. As such the hydrothermal route is the preferred synthetic route for SnSe-MCC. It should be noted that we also trialed selenourea as a replacement for thiourea; however we observed no difference in the resultant CZTSe particles, apart from the expected change in the surface chemistry. This suggests the urea derivatives are only a mild reducing agent to convert Cu(II) to Cu(I), and do not contribute sulfur or selenium to the resultant nanoparticles.

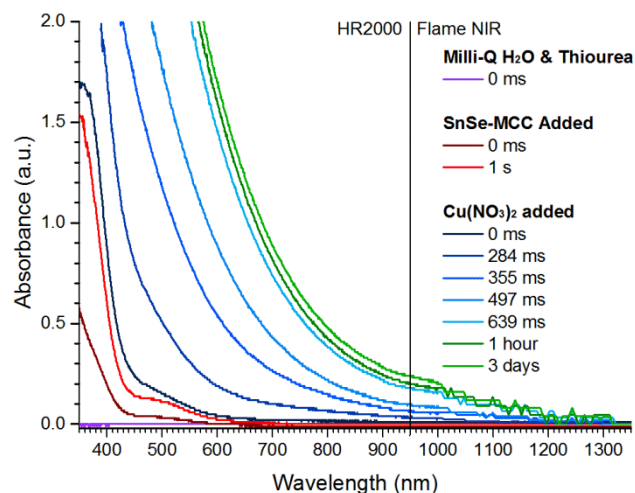


Figure 2. In-situ time resolved merged UV-Vis-NIR spectra of a 50:25:25 (Cu:Zn:Sn %) CZTSe nanoparticle ink with a concentration of 0.5 g/L. The HR2000 detector signal and Flame NIR detector signals are merged at 950 nm, highlighted by the black vertical line. The purple curve shows the baseline of Milli-Q water and thiourea solution. The red curves highlight the addition of the SnSe-MCC precursor solution. Adding the zinc precursor solution exhibited no absorbance change from the equilibrated red curve at 1s and as such spectra following the addition of Zn(NO₃)₂ were omitted. The synthesis and growth of the CZTSe nanoparticles are shown by the blue curves over the first 639 ms after the addition of the 1.25 M Cu(NO₃)₂ solution with 71 ms resolution. The green curves highlight the stability of the resultant

nanoparticle dispersion over the next 3 days on a variety of time-scales.

In order to observe the nucleation and growth of the CZTSe nanoparticles, and their subsequent colloidal stability, in-situ temporal resolved UV-Vis-NIR measurements were carried out. The purple baseline curve in Figure 2 was Milli-Q water and thiourea solution, while the red curves were collected after the addition and mixing of the SnSe-MCC solution. Adding the zinc precursor solution exhibited no absorbance change from the equilibrated red curve at 1 s and as such the series of curves were omitted. As the thiourea, SnSe-MCC and Zn^{2+} ions are stable in solution, no precipitation, nucleation, or growth occurs, and at this point we have obtained a Zn, Sn & Se containing solution of dissolved salts. In the blue curves at 0 ms the $\text{Cu}(\text{NO}_3)_2$ solution was quickly added resulting in an increasing red shift in the absorption up until ~639 ms indicating rapid CZTSe nanoparticle formation. It should be noted that Cu_2Se has the lowest solubility product ($K_{\text{sp}} = 1.58 \times 10^{-61}$) of all the species involved by over 10 orders of magnitudes,⁸³ and readily reacts to form $\text{CZTSe}_{(\text{s})}$ if zinc, tin and selenium are present. Upon addition of Cu^{2+} into solution, the Cu ions are reduced by thiourea to Cu^+ and then react with Zn, Sn and Se ions to yield CZTSe nanoparticles via $\text{Cu}_2\text{Se}_{(\text{s})} + 2\text{Cu}_{(\text{aq})}^+ + 2\text{Zn}_{(\text{aq})}^{2+} + \text{Sn}_2\text{Se}_{7(\text{aq})}^{6-} \rightarrow 2\text{Cu}_2\text{ZnSnSe}_{4(\text{s})}$. After ~639 ms the spectra remains stable with only a slight shift in absorbance over the next 3 days, which are attributed to either slight growth of particles, or fluctuation in light source intensity over time. The absorbance continuing to ~1225-1325 nm (~1.01-0.94 eV) is equivalent to or lower in energy compared to bulk CZTSe (1.0 eV), which suggests that no quantum confinement effects are present and that sub-gap or indirect absorption may be contributing to the spectrum.

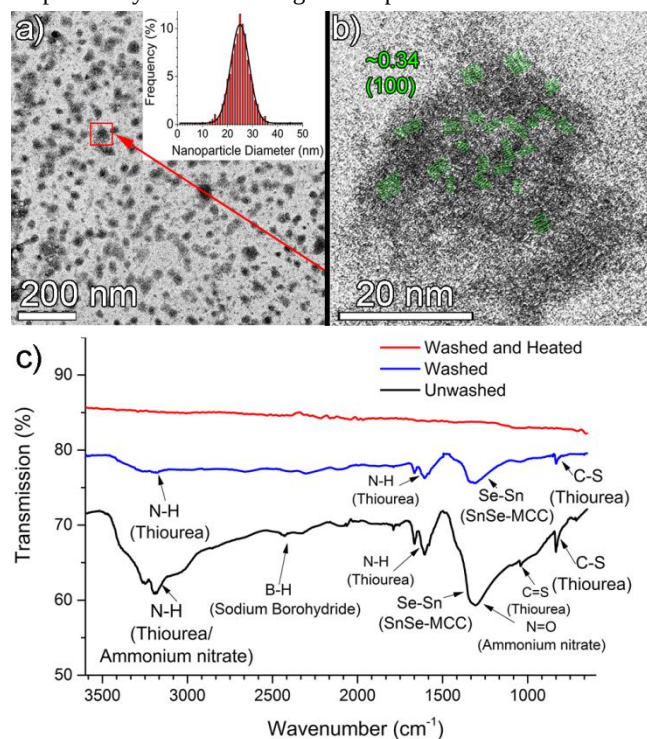


Figure 3. a) TEM image of CZTSe nanoparticles with an elemental ratio of 2:1:1 Cu:Zn:Sn produced at an original concentration of 10 g/L. Left Inset: histogram indicating a mean size of ~25 nm b) High resolution TEM image showing the presence of nano-crystalline domains within the nanoparticle with lattice spacings

of 0.34 nm (green). c) FTIR spectra showing the functional groups present in the dried CZTSe nanoparticle ink (black), twice washed and dried CZTSe nanoparticles (blue), and twice washed and annealed at 250 °C CZTSe nanoparticles (red).

We employed TEM to identify the size distribution and morphology of the CZTSe nanoparticles produced. Figure 3 a) shows globular spherical nanoparticles with a mean diameter of ~25 nm with a standard deviation of 3.6 nm. The high resolution TEM (HR-TEM) in Figure 3 b) reveals the presence of nano-crystalline regions in the CZTSe nanoparticle with lattice spacing of ~0.347 nm, consistent with the inter-planar d_{100} spacing of CZTSe;⁴⁰ however, a large fraction of the nanoparticles appear amorphous.

The nature of the surface bound molecules was investigated by FTIR. In the unwashed ink, all of the expected functional groups stemming from the original reaction chemistry are present as seen in Figure 3 c). After purification, the surface chemistry is revealed to be composed of just $\text{Sn}_2\text{Se}_7^{6-}$ anions and thiourea molecules. The former confers some negative charge on the nanoparticles, confirmed by a zeta-potential of -29 mV, while the thiourea probably provides colloidal stability via hydrogen bonding to the solvent. Upon heating at 250 °C all surface bound molecules are removed.

3.2. Thermal Decomposition Characteristics of CZTSe Nanoparticles

Nanoparticles that require minimal post-synthesis processing, such as centrifugation, filtering or precipitation steps, and have no impurities upon mild annealing, are ideal for thin film applications. In order to identify at what temperatures the different components of the unwashed CZTSe nanoparticle ink vapourise, TGA-FTIR was employed, the results are shown in Figure 4.

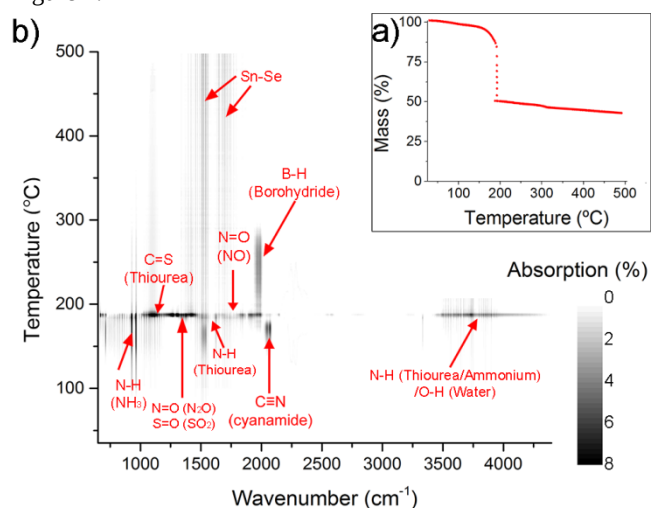
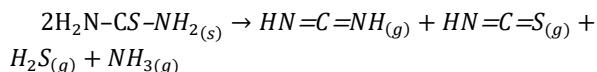


Figure 4. a) TGA of a CZTSe nanoparticle powder with an elemental ratio of Cu:Zn:Sn 2:1:1, indicating most mass loss occurs at ~187 °C. b) The corresponding FTIR spectra vs. temperature with color indicating the absorption (%) collected in tandem with the TGA in order to analyze the source of mass loss. Each set of peaks has been labelled with the corresponding functional groups and its source in the nanoparticle ink.

The initial slow mass loss evident in the TGA curve below 150 °C is due to evaporation of residual ammonia (~4.5%), followed by some loss of thiourea as cyanamide^{84, 85} and isothiocyanic acid,^{86, 87} which starts at ~150 °C via the following reaction:



In the presence of water released from other decomposition reactions at $\sim 180^\circ\text{C}$, isothiocyanic acid further decomposes via $\text{HN}=\text{C}=\text{S}_{(g)} + \text{H}_2\text{O}_{(g)} \rightarrow \text{O}=\text{C}=\text{S}_{(g)} + \text{NH}_{3(g)}$ ⁸⁸ to carbonyl sulfide. It should be noted that the amount of H_2S released is too small for the corresponding peaks to be observed in Figure 4 b); however, they are present with a maximum intensity of $\sim 0.3\%$. The sharp mass decrease between $170\text{--}187^\circ\text{C}$ ($\sim 43.6\%$) largely corresponds to the continued loss of thiourea (21.5%), then the subsequent loss of nitrate (22.1%). Between $190\text{--}280^\circ\text{C}$ the loss of borohydride (0.4%) is observed. Above 220°C loss of SnSe is observed when the vapor pressure of SnSe around CZTSe is low, as is the case here where there is a constant nitrogen flow past the detector of 20 mL/min. This is the result of slow thermal decomposition: $\text{Cu}_2\text{ZnSnSe}_4 \rightarrow \text{Cu}_2\text{S} + \text{ZnS} + \text{SnSe} + \frac{1}{2}\text{Se}_2$ ⁶². It should be noted that unlike the case with CZTS nanoparticles,³⁵ there is no loss of carbonates. This is because the reaction was carried out inside a N_2 filled glovebox using degassed solvents, resulting in the elimination of naturally dissolved carbonate in solvents from atmospheric CO_2 . This highlights the importance of air in the synthesis of carbon-free films using solvents where carbonates form.

Based on the IR results, we find that the lowest practical temperature to remove all the undesirable components in the nanocrystal ink through either decomposition and/or vaporization is $\sim 200^\circ\text{C}$. This confirms, that with mild heat treatment, the CZTSe nanoparticle ink affords a nitrogen-, oxygen-, and carbon-free CZTSe bulk material.

3.3. Phase Map of Annealed Compositionally-Variant CZTSe Nanoparticles

In order to create a compositionally dependent crystal phase map and confirm the robustness of the synthesis in terms of elemental ratios, 13 different compositions of CZTSe nanoparticles were analyzed. Samples were prepared with theoretical elemental ratios as shown in Figure 5 a) at a concentration of 40 g/L. ICP-MS was performed on small portions of washed and dried powders to compare the theoretical and experi-

mental elemental ratios. As seen in Figure 5 a), the values were found to be within measurement and pipetting errors ($<0.5\%$), thus confirming that the synthetic method yields stoichiometric precipitation of the metallic ions into nanoparticles.

Each of the 13 sample powders were prepared for PXRD and Raman by annealing at 500°C for 10 minutes under N_2 in a tube furnace. The PXRD patterns shown in Figure 5 b) indicate that the majority phase present in all 13 different compositions is stannite CZTSe (ICDD 52-0868), however a small proportion of kesterite CZTSe (ICDD 70-8930) may also be present. Stannite CZTSe is differentiated from kesterite CZTSe by the presence of two additional peaks at $\sim 31^\circ$ and 35° corresponding to the d_{200} and d_{211} planes respectively. Copper selenide peaks convoluted with the main CZTSe peaks are observed in two samples with high Cu % and low Sn % as denoted by the * in Figure 5 b). These compositions were also seen to contain copper-based secondary phases in our previous CZTS work.³⁵ Small tin selenide peaks were also expected due to the elevated annealing temperatures employed; however, these were either not present or not large enough to be observable. It is well known that PXRD alone cannot differentiate between ZnSe, Cu_2SnSe_3 and $\text{Cu}_2\text{ZnSnSe}_4$ phases due to the similarity in their diffraction patterns.^{1, 40} In order to confirm that CZTSe is indeed the majority phase, Raman analysis was performed.

The Raman spectra of the 13 samples in Figure 5 c) clearly show the characteristic CZTSe peak centered at 191 cm^{-1} with a shoulder peak at 173 cm^{-1} and broad peak at 235 cm^{-1} . On the other hand, no compositions exhibited a Cu_2SnSe_3 or ZnSe peak, even when using a 325 nm laser to excite. This suggests the majority phase present in each of the crystals is pure-phase CZTSe without any ZnSe contributions. The crystal phases observed by Raman spectroscopy are consistent with the phases observed by PXRD, including the presence of copper selenide secondary phase peaks in the same two samples (denoted by *). Additional tin selenide peaks are observed in 3 of the samples with high Sn% (denoted by Θ). This further confirms that the synthesis is stoichiometric and allows for CZTSe nanoparticles to be synthesized with tuneable composition.

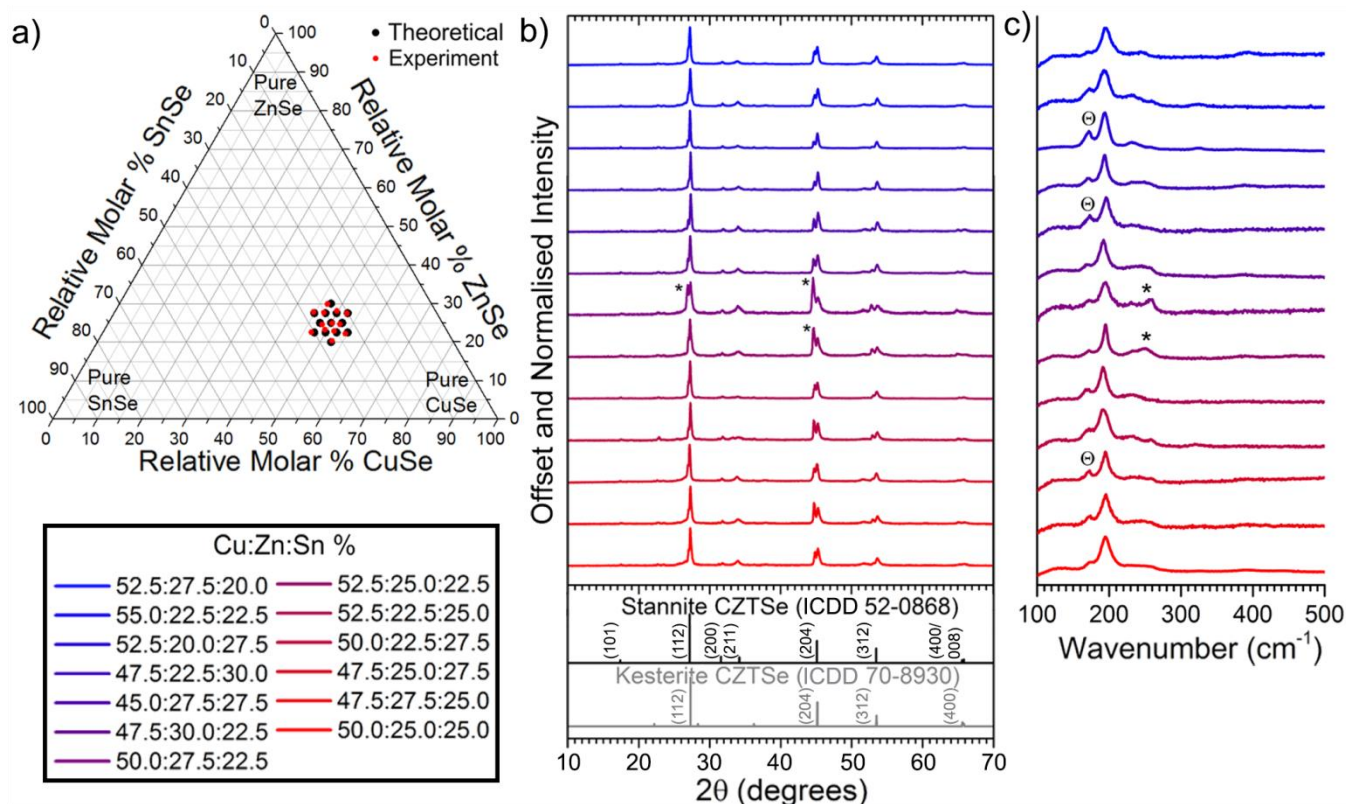


Figure 5. a) Experimental elemental ratios obtained by ICP–MS analysis (red dots) for CZTSe samples prepared for PXRD and Raman spectroscopy measurements were overlaid onto the corresponding theoretical elemental ratios (black dots). Variations between theory and experiment are within pipette and measurement error. b) PXRD patterns for the 13 different elemental ratios shown in a) after annealing at 500 °C. The majority phase in each diffraction pattern can be seen to be CZTSe. For reference, the simulated diffraction pattern of stannite CZTSe is shown below. The presence of additional copper selenide peaks are denoted by *. c) Raman spectra for the 13 different elemental ratios shown in a) after annealing at 500 °C. The majority phase in each spectra is the characteristic CZTSe peak centered at 195 cm⁻¹ with a shoulder peak at 172 cm⁻¹ and broad peak at 238 cm⁻¹, however the presence of copper selenide and tin selenide are highlighted by * and ⊖ respectively in some samples.

Crystal phase vs. temperature in unwashed CZTSe nanoparticle inks was also investigated for 50:25:25 (Cu:Zn:Sn %) CZTSe. These CZTSe powders were annealed at varied temperatures between 50 and 600 °C for 10 minutes under N₂ in a tube furnace and the resulting crystal phases were then probed by PXRD and Raman spectroscopy. Below 200 °C, PXRD measurements revealed that many different phases coexisted (Figure 6 a). This includes broad peaks at 27° and 45° 2θ originating from a stannite CZTSe phase with a <100 nm mean crystallite size as determined by an anisotropic crystallite size broadening function, adapted by Coelho⁸⁰ from March-Dollase⁸¹. The pattern at 200 °C shows a clear sharpening of the CZTSe peaks and a reduction in the additional impurity contributions. Between 200 °C and 250 °C all additional ink components are removed and the CZTSe nanoparticles sinter to yield crystallites with a mean size of ≥240 nm at 250 °C, determined via the anisotropic crystallite size broadening function (Figure 6 b). At 250 °C a range of grain sizes are observed via SEM (Figure 6 c) consisting of small grains of ~90 nm adhered to surfaces of large >1 μm grains interspersed with intermediate ~300 nm grains. A mean size of ≥240 nm seems reasonable based on our observations and thus is supported by SEM. Between 350 °C and 400 °C two additional peaks around the <112> stannite CZTSe peak at 27.2° are observed, which correspond to the characteristic triple peak structure of wurtzite-stannite CZTSe⁴⁰. These peaks account for ~2 and 5 wt% of the crystal phase at 350 and 400 °C, re-

spectively, and are not present in significant amounts (<0.5 wt%) outside this range. The CZTSe grains further grow to mean sizes ≥500 nm by 500 °C as reported in Figure 6 b). We confirmed this mean crystallite size calculated from the PXRD via SEM in Figure 6 d) where large grains between ~400 nm and ~2.5 μm are observed.

Figure 6 e) contains the corresponding Raman spectra of samples heated to ≥200 °C. We note that the spectra below this temperature were too noisy to yield identifiable peaks. A clear sharpening of the characteristic A₁, A₂ and B₂ (TO) CZTSe Raman mode peaks at 195, 172, and 238 cm⁻¹, respectively, was observed with increasing temperature.⁸⁹ We note that ZnSe was not present in the Raman at any temperature. This supports the PXRD assignments of the CZTSe phase and the gradual grain growth. By 250–300 °C in both PXRD patterns and Raman spectra, distinct and sharp CZTSe peaks with crystallite sizes ranging from ~240 to ~290 nm are observed with the lack of any secondary phase peaks. From PXRD measurements a linear trend in crystallite growth with temperature is observed between 200–400 °C, while a reduction in the rate of growth with temperature is seen between 400–600 °C as it approaches a steady state. This saturation in growth however may just be due to the inaccuracy of using the anisotropic crystallite size broadening function for larger grain sizes, or it may be associated with a progressive increase in tin selenide loss from the particles.

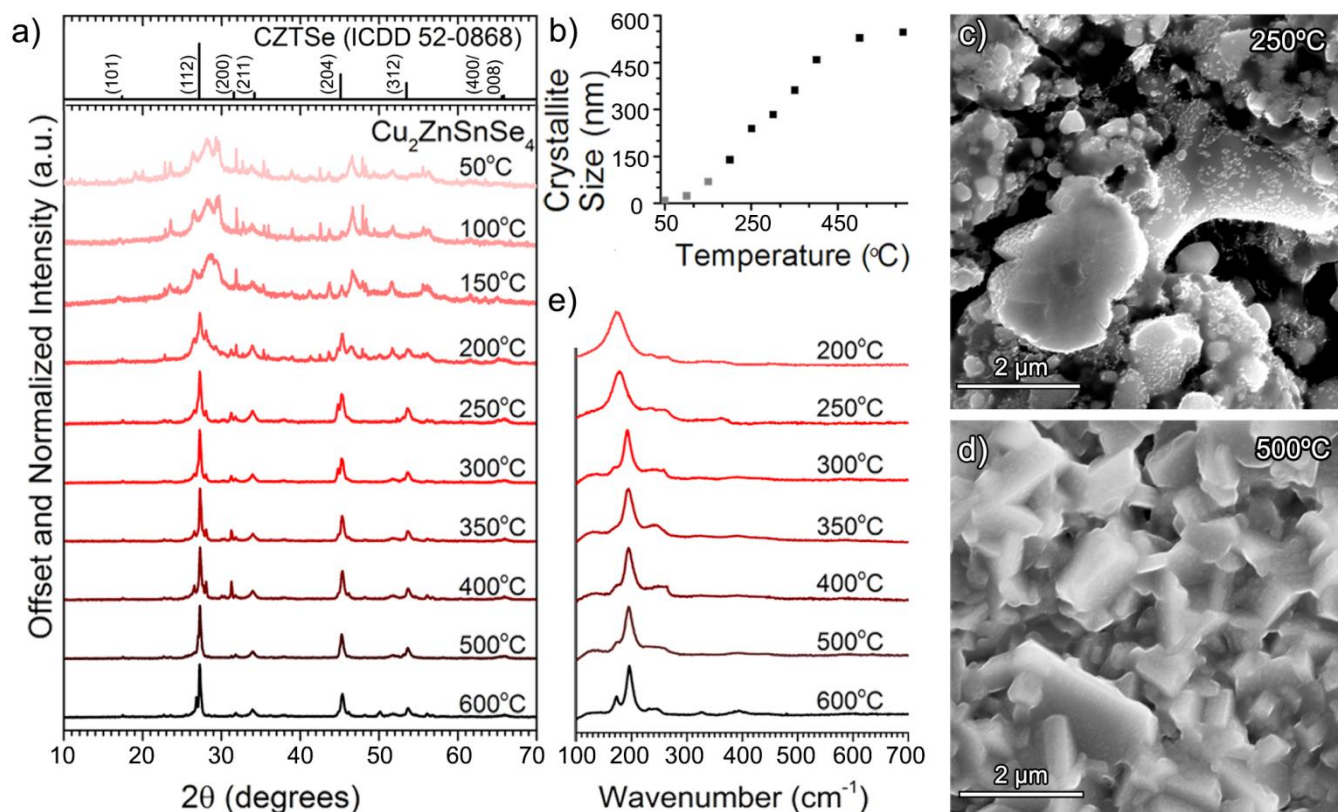


Figure 6. a) PXRD patterns of 2:1:1 CZTSe nanoparticles annealed under N₂ at 50, 100, 150, 200, 250, 300, 350, 400, 500, and 600 °C in order to capture the phase and size behavior of the crystals present with temperature. For reference, the simulated diffraction pattern of stannite CZTSe is shown below. b) Calculated mean Cu₂ZnSnSe₄ crystallite size from fits to broadened PXRD peaks. SEM images at 35,000x of CZTSe nanoparticles annealed under N₂ at c) 250 °C and d) 500 °C. e) Raman spectra of the same CZTSe nanoparticles annealed under N₂ varying temperatures in order to confirm the phase behavior identified by PXRD.

3.4. Annealing of CZTS & CZTSe Nanoparticles – Temperature and S:Se Ratio Dependence

In order to map out the processes occurring during annealing of mixtures of CZTS and CZTSe nanoparticles, a series of temperature and composition ratio dependent PXRD and Raman spectroscopy studies were conducted. It is important to determine whether a solid-solution CZTSSe phase can be achieved by simply mixing and sintering the two nanoparticle types, or whether S and/or Se vapors are required, as per more conventional processes currently used. For this set of experiments, CZTSe nanoparticles were synthesized as in the experimental section, while CZTS nanoparticles were synthesized following our previous work³⁵ in the same N₂ glovebox. These nanoparticle inks were then mixed in controlled ratios, dried under N₂ and vacuum, and finally heated to the designated temperature for 10 mins under N₂ in a tube furnace.

In Figure 7 a) the PXRD patterns collected from three mixed S:Se ratios and pure kesterite CZTS (ICDD 26-0575) and stannite CZTSe (ICDD 52-0868) are presented. A linear shift in the scattering peaks with composition is observed between the pure CZTS and CZTSe phases (Figure 7 c), and there is only a single phase present. This observation is consistent with Vegard's law, which has previously been found to hold for

CZTS and CZTSe.⁶ A comparison of the Raman spectra across the alloyed samples reveals a progressive change in the ratios and positions of the strong A kesterite CZTS (332 cm⁻¹) and A₁ stannite CZTSe (195 cm⁻¹) Raman mode peaks as a function of composition. These correspond to symmetric vibrations of the anion lattice of S and Se, respectively (Figure 7 b, d).⁸⁹ The relative intensities of the CZTS peaks are lower than that for CZTSe, which creates a noted disparity when comparing samples with different compositions. Moreover, shifts in the main Raman peaks are also noted for the mixed compositions, with the CZTSe and CZTS peaks shifting toward higher and lower wavenumbers, respectively. This is consistent with the formation of an alloyed CZTSSe phase due to the strong A kesterite CZTS and A₁ stannite CZTSe Raman modes being stretched or contracted by changes in the anionic lattice spacing.⁹⁰ It should be noted that for both CZTSe or CZTS, the stannite and kesterite phases cannot be distinguished based on Raman vibrational modes because the crystal lattices are too similar. The assignment of kesterite CZTS and stannite CZTSe used when referring to the Raman modes is to give precise vibrational mode assignment, due to the difference in symmetries, and are based on their PXRD patterns alone.

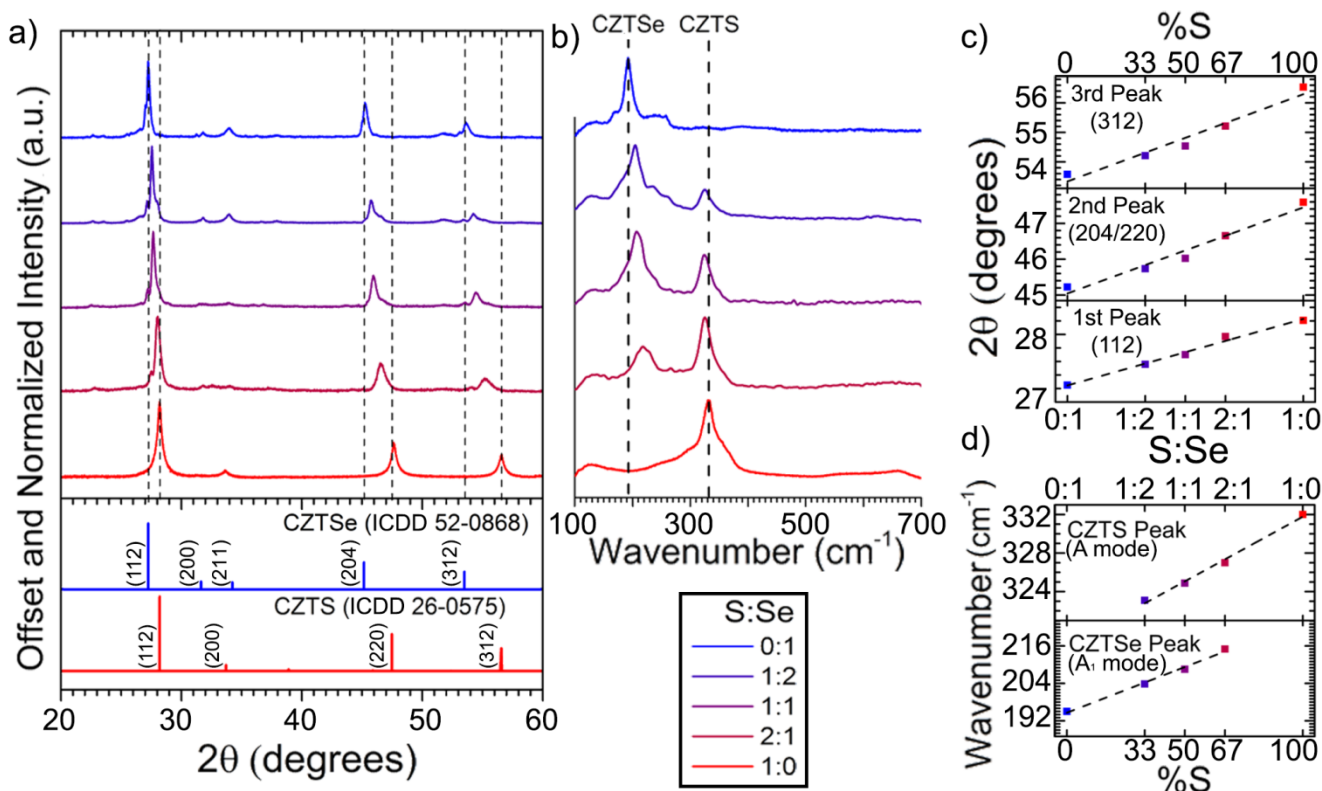


Figure 7. a) PXRD patterns of different ratios of mixed CZTS and CZTSe nanoparticles (varied bulk S:Se ratios) annealed under N₂ at 500 °C. For reference, the simulated diffraction patterns of stannite CZTSe and kesterite CZTS are shown below. Black dashed lines are used as guides to better illustrate the shift of peaks due to S:Se ratio. b) Raman spectra of the corresponding mixed nanoparticle powders. Black dashed lines are used as guides for the position of the center of the corresponding CZTS and CZTSe Raman peaks to better illustrate the shift due to S:Se ratio. c) Plots of the three major PXRD peak shifts with varied S:Se ratio. d) Plots of the CZTS and CZTSe peak shifts with varied S:Se ratio.

Compacted discs of the heat treated powders were used to investigate the optoelectronic properties of three mixed alloyed CZTSSe with different S:Se ratios and pure CZTS and CZTSe. Reflectance UV-Vis-NIR spectra were converted to equivalent absorption using the Kubelka-Munk function with BaSO₄ as a reference. Clear red-shifts in equivalent absorbance UV-Vis-NIR spectra are observed for higher Se (see Figure 8 a). These spectra were then converted into the corresponding Tauc plots in Figure 8 b) and the band gaps for each S:Se ratio calculated. Mixing stoichiometric amounts of CZTS and CZTSe and sintering at 250 °C results in linear shifts in the band gaps of CZTSSe between 1.51 eV and 1.05 eV for pure CZTS and pure CZTSe, respectively, as seen in Figure 8 d). This is consistent with previous reports of CZTSSe with different S:Se ratios.^{1, 91}

By utilizing PESA the valence band edge of semiconductors can be obtained (Figure S1), which when coupled with the bandgap of the material, can be used to determine the conduction band edge.⁹² The valence band edge energies for the pure CZTS and CZTSe are within the expected error for PESA of 0.05 eV to their theoretical and experimental values of ~5.1 eV and ~4.95 eV respectively^{45, 93-96}. Based on these valence band energies, and the corresponding band gaps, band diagrams have been constructed for different S:Se ratios and are presented in Figure 8 c). These show the relative positions of the valence band edge and conduction band edge and exhibit the expected broadening profile with decreasing valence band edge and increasing conduction band edge with increased sulfur doping.

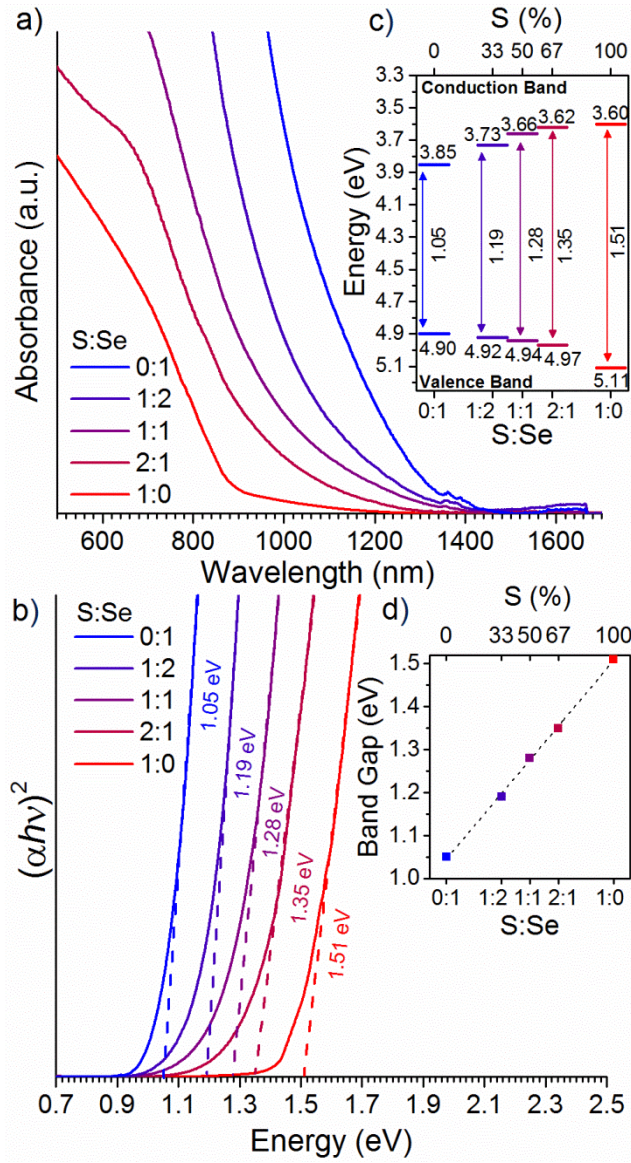


Figure 8. a) UV-Vis-NIR reflectance spectra converted into equivalent absorbance spectra using the Kubelka-Munk function with BaSO₄ as reference, and b) corresponding Tauc plots of compacted discs containing different ratios of mixed CZTS and CZTSe nanoparticles (varied bulk S:Se ratios) annealed under N₂ at 250 °C. c) Band diagram of the different S:Se ratio CZTSSe materials calculated from the valence band from PESA and

band gap from Tauc plots. d) Calculated band gap as a function of the S:Se ratio, showing the expected linear dependence with S:Se ratio.

To further probe the alloying process, in Figure 9 a) we show the PXRD following annealing at different temperatures of 1:1 S:Se ratio ($\text{Cu}_2\text{ZnSnS}_2\text{Se}_2$) powder samples. This sample is taken as a representative across the composition range, as all mixed CZTS/CZTSe powders show the same phase and crystallite size dependence with temperature. Below 200 °C, the PXRD patterns (Figure 9 a) show overlapping broad peaks originating from CZTSe and CZTS, along with the many impurity peaks remnant of the original synthesis. The presence of the $\text{Cu}_2\text{ZnSnS}_2\text{Se}_2$ phase starts to become evident at 200 °C, with the emergence of distinct CZTSSe scattering contributions appearing between the CZTS and CZTSe peaks. This corresponds to the temperature where all additional ink components are removed allowing particles to more easily contact each other. By 250 °C, the kesterite/stannite $\text{Cu}_2\text{ZnSnS}_2\text{Se}_2$ phase with a mean crystallite size of ≥ 90 nm is observed, determined via the anisotropic crystallite size broadening function (Figure 9 b). It should be noted it is not currently possible to determine whether the CZTSSe phase is pure kesterite, stannite or a mix by either Raman spectroscopy or XRD as their spectra are so similar. The relative peak positions used to distinguish these phases are so fine they are difficult to resolve for pure CZTS and CZTSe. This is further exacerbated by the relatively large shifts due to the effect of the S:Se ratio found in CZTSSe, especially when peak broadening is considered. At 250 °C a range of grain sizes are observed via SEM (Figure 9 c) from small grains of ~ 30 nm to larger agglomerates of ~ 300 nm grains spanning >1 μm . A mean size of ≥ 90 nm seems reasonable based on our observations and thus is supported by SEM. At progressively higher temperatures, the PXRD patterns exhibit a continued sharpening of the CZTSSe peaks, with the crystallites reaching a size of ≥ 400 nm by 500 °C determined via PXRD (Figure 9 b). We confirmed this calculated mean grain size via SEM in Figure 9 d) where large grains between ~ 250 nm and ~ 2 μm are observed. It is interesting to note that the extent of growth in these alloys is reduced compared to pure CZTSe. As shown in Figure 9 e), Raman measurements of the CZTSSe powders corroborate the PXRD. Notably, reliable analysis were only possible at temperatures of 200 °C and above, consistent with the increasing crystallite sizes and reduction of impurities in the powders.

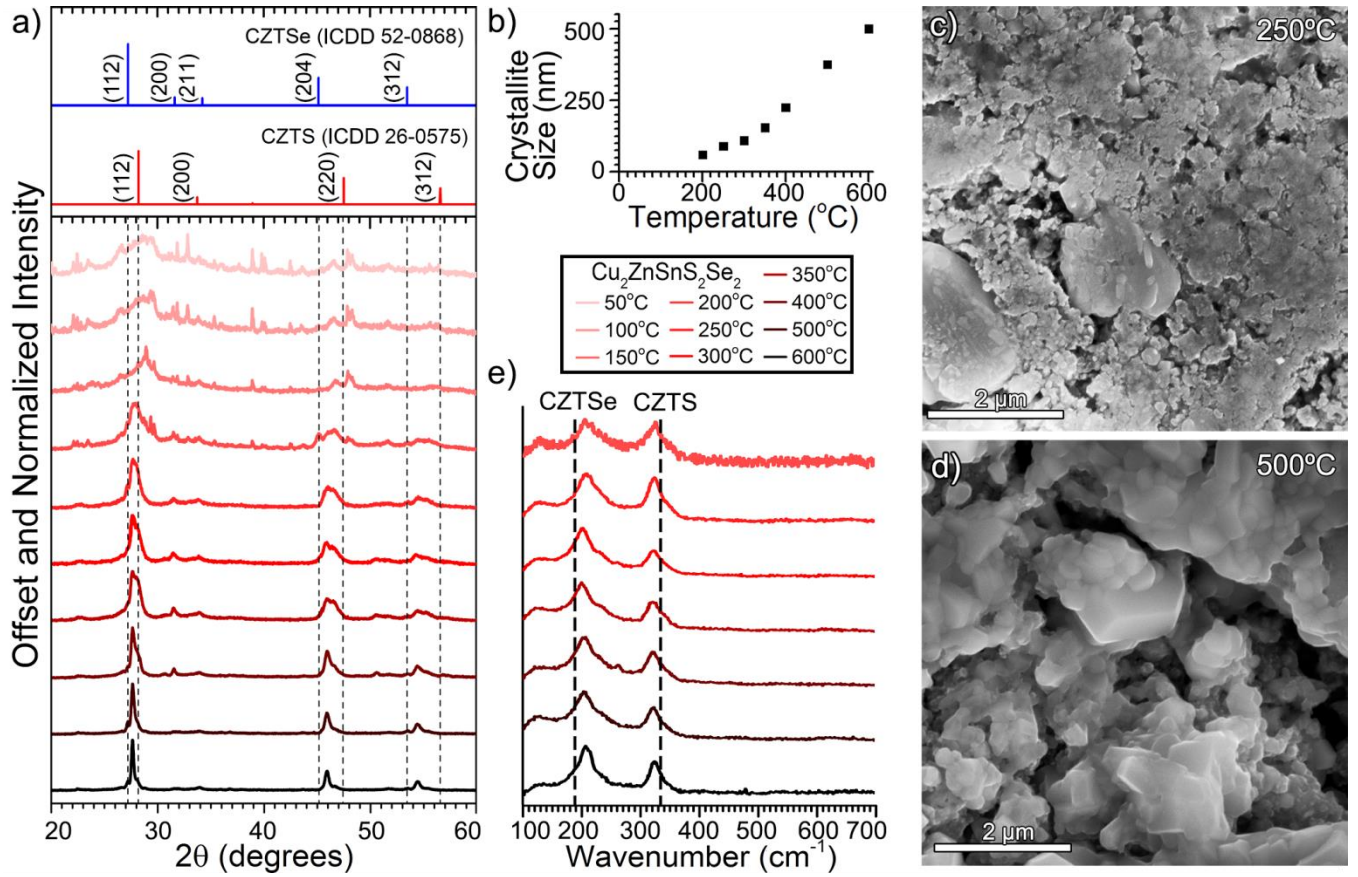


Figure 9. a) PXRD patterns of mixed CZTS and CZTSe nanoparticles with a ratio of S:Se of 1:1. All samples were annealed under N_2 at their corresponding temperatures. The presence of $Cu_2ZnSnS_2Se_2$ phase due to sintering of CZTS and CZTSe nanoparticles becomes evident above 200 °C, with the peaks sharpening as the crystals grow with temperature. For reference, the simulated diffraction patterns of stannite CZTSe and kesterite CZTS are shown below. Black dashed lines are used as guides to better illustrate the shift of peaks due to S:Se ratio. b) Calculated mean $Cu_2ZnSnS_2Se_2$ crystallite size from fits to broadened PXRD peaks. SEM images at 35,000x of mixed CZTS and CZTSe nanoparticles with a ratio of S:Se of 1:1 annealed under N_2 at c) 250 °C and d) 500 °C. e) The corresponding Raman spectra confirming the growth of $Cu_2ZnSnS_2Se_2$ phase as seen in a) with black dashed lines as guides for the position of the center of the corresponding CZTS and CZTSe Raman peaks to better illustrate the shift due to S:Se ratio. Note the spectra were too noisy to identify peaks at temperatures < 200 °C and as such were omitted.

To confirm homogeneous distribution of sulfur and selenium in the crystals after mild sintering, dark field STEM energy dispersive X-ray spectroscopy (EDS) mapping was utilized on the 1:1 S:Se ratio ($Cu_2ZnSnS_2Se_2$) compressed disc sample sintered at 250 °C. The results are presented in Figure 10 a-c. The sample corresponds to the image in Figure 9d. Sample preparation procedures for the compressed disc are presented in the supporting information. The area mapped is taken as representative of the entire sample, and clearly shows that S and Se are homogeneously distributed across the sample. The Cu, Zn and Sn EDS maps (not shown) likewise show identical distributions of S and Se. The dark patches in Figure 10 b) & c) with low X-ray counts correspond to thinner areas or voids in the sample and match the darker patches evident in the dark field STEM image (Figure 10 a). The EDS plot of the same area in Figure 10 d) indicates that the expected elemental ratio of ~2:1:1:2:2 Cu:Zn:Sn:S:Se for $Cu_2ZnSnS_2Se_2$ is present in the sample indicating that no loss of metals occurs below 250 °C.

Selected area electron diffraction (SAED) was subsequently performed on the largest crystal in the bottom middle of Figure 10 a) in order to get the highest resolution pattern possible, and compared to simulated SAED patterns^{76, 97} (Figure 10 e-g). [010] Simulated kesterite $Cu_2ZnSnS_2Se_2$ (Figure 10 e) is most consistent with the positions and intensities of the experimental SAED pattern in Figure 10 f) and suggests single phase. The experimental SAED pattern also exhibits the characteristic kesterite/stannite [010] angle of 63.4°. It should be noted that [010] stannite $Cu_2ZnSnS_2Se_2$ (Figure 10 g) can be differentiated from [010] kesterite $Cu_2ZnSnS_2Se_2$ (Figure 10 e) by its missing 4 superlattice reflections at 303, 30-3, -303, and -30-3, and the relative intensities of 200, -200, 101, 10-1, -101, 004, and 00-4. This analysis confirms that the crystals obtained are of single phase, and suggests that they are kesterite $Cu_2ZnSnS_2Se_2$.

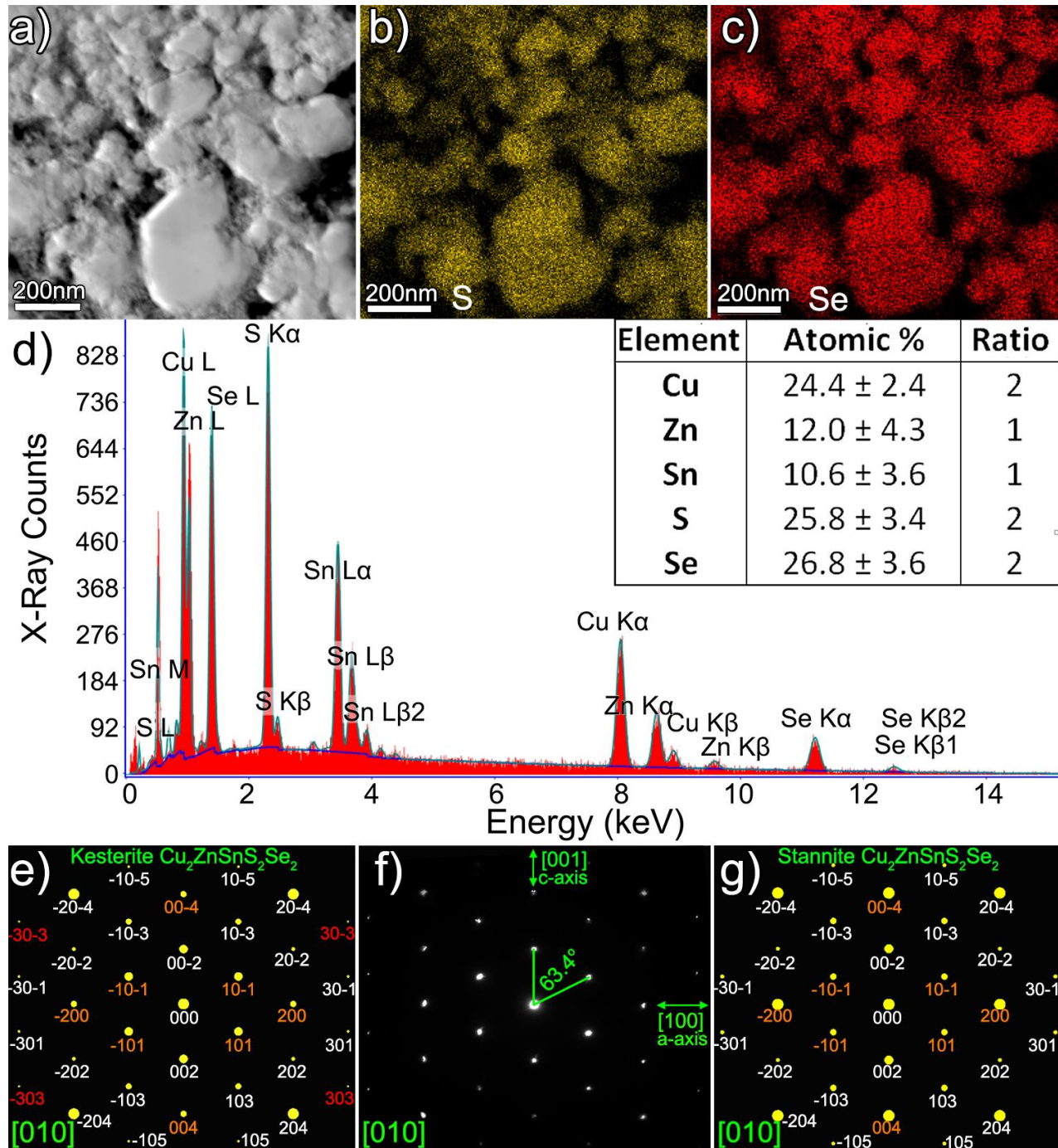


Figure 10. Mixed CZTS and CZTSe nanoparticles with a ratio of S:Se of 1:1 sintered at 250 °C under N₂ atmosphere were analyzed using dark field STEM. a) Original STEM image with b) sulfur and c) selenium EDS map showing homogeneous distribution throughout the crystals. d) The EDS quantitative plot of the same area indicating the expected Cu₂ZnSnS₂Se₂ elemental ratio. SAED was performed on the largest crystal in the STEM image (a) and compared with simulated diffraction patterns. e) Simulated [010] kesterite Cu₂ZnSnS₂Se₂ SAED pattern, f) experimental SAED pattern, and g) simulated [010] stannite Cu₂ZnSnS₂Se₂ SAED pattern. Labels in orange represent differences in diffraction intensities, while labels in red represent additional reflections present between kesterite and stannite simulated patterns.

These PXRD, Raman spectroscopy, and STEM EDS & SAED results illustrate that by mixing stoichiometric quantities of CZTS and CZTSe nanoparticles, then heating to only 250 °C, an alloyed CZTS₂Se₂ phase with controlled S:Se ratio can be achieved. This provides an important, low temperature alternative to the more traditionally employed selenization or sulfurization processes used to synthesize comparable alloys. These processes are typically carried out at >450 °C under flowing hydrogen sulfide/selenide or vapourised elemental

sulfur/selenium, with great practical challenges in controlling the exact proportion of S:Se in the resulting material. In contrast, the process developed here is chemically benign, provides precise stoichiometric tunability, and is amenable to low-temperature processing (<300 °C). Importantly, below 300 °C the cationic ordering in the lattice can be reversibly altered by careful control of ramping rates.^{2, 67, 68} This suggests that our process has the potential to also decrease the cationic disordering in the lattice structure, which has to date been the

primary cause in limiting the success of these materials for use in photovoltaics².

4.0. CONCLUSION

Aqueous SnSe-MCC solutions were produced using green and non-toxic synthetic methods. These were used as precursors for CZTSe nanoparticle synthesis and as organic-free colloidal stabilizers for their dispersion in water. The stannite CZTSe nanoparticles were obtained using simultaneous reduction and crystal formation reactions. Thiourea or selenourea was used to reduce Cu(II) to Cu(I), and Zn^{2+} , $\text{Sn}_2\text{Se}_7^{6-}$, and Se^{2-} are present as the sources of zinc, tin and selenium, respectively. The as-synthesized nanoparticles were found to be polycrystalline and have a mean diameter of ~ 25 nm. ICP-MS measurements were conducted on 13 samples of different elemental compositions, and the CZTSe nanoparticle synthesis was determined to retain its solution-phase elemental stoichiometry. PXRD and Raman spectroscopy were utilized to build crystal phase maps of nanoparticles with different Cu:Zn:Sn ratios. Consistent across the different stoichiometries, thermal treatment of the nanoparticle ink caused evaporation/decomposition of ammonia, thiourea and associated nitrate ligands at ~ 200 °C, to yield largely impurity free CZTSe products by ~ 250 °C. The alloying of CZTS and CZTSe nanoparticles to give CZTSSe was also confirmed through a combination of PXRD, Raman, UV-Vis-NIR and PESA with respect to temperature and S:Se ratio. The fully alloyed CZTSSe phase was found to be achieved at temperatures between 200–250 °C across all S:Se ratios studied here. Achieving such alloyed phases at these low temperatures presents a viable alternative to the more traditionally adopted selenization or sulfurization processes used to make comparable materials. The CZTSe nanocrystals produced in this work are considered to be ideal for producing impurity-free CZTSe/SSe films with precise bandgap control using a scalable, non-toxic, and low cost synthesis that is amenable to printing processes. Future work will focus on the formulation of tailored inks suitable for printing and the assessment of the resulting materials for use within functional solar cells devices.

SUPPORTING INFORMATION

PESA plots showing valence band edge fits, characterization of $\text{Na}_6\text{Sn}_2\text{Se}_7 \cdot 16\text{H}_2\text{O}$ and $\text{Na}_4\text{Sn}_2\text{Se}_6 \cdot 13\text{H}_2\text{O}$, redox route CZTSe nanoparticle characterization, and TEM sample preparation for SAED and EDS. (PDF)

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