Temporal growth studies of $\text{Cu}_2(\text{M})\text{SnS}_4$ (M=Zn, Mn, Fe, Co) nanoparticles formation

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NANYANG
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**TEMPORAL GROWTH STUDIES OF
 $\text{Cu}_2(\text{M})\text{SnS}_4$ (M= Zn, Mn, Fe, Co)
NANOPARTICLES FORMATION**

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ENERGY RESEARCH INSTITUTE @ NTU (ERI@N)**

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Abstract

In the last few decades, there has been much emphasis placed on the development of solar harvesting materials. Multi-component (Cu-(M)-Sn-S) materials which is made up of naturally abundant components are highly promising as solar harvesting materials. However to realize an efficient solar harvesting device from these materials, several challenges such as: producing single phase material, controlling appropriate carrier concentration with good carrier transport properties, suitable bandgap, matching band energy level, doping control and minimal intrinsic defect states need to be overcome. These fundamental properties of the materials can be controlled if there is understanding of the material formation mechanism, kinetics and thermodynamics. The objective of this thesis is to investigate the synthesis of pure CMTS; $\text{Cu}_2\text{-M-Sn-S}_4$ (M=Zn, Fe, Mn, Co), based semiconductors as potential solar harvesting materials for both solar cell and solar fuel applications. From these studies, crucial growth steps have been pinpointed and conflicting growth kinetics have been solved via a proposed reaction pathway.

In the initial stage of the study, the synthesis of $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) nanoparticles was used as a model system to establish general reaction conditions for the synthesis of CMTS nanoparticles. Three key research foundations were laid. Firstly, Surface-enhanced Raman scattering (SERS) spectroscopy is demonstrated for the first time to be a sensitive characterization tool for unambiguous characterization of phases present in as-synthesized nanoparticles. This resolves the inability to differentiate mixed compositional phase (e.g., CZTS, CTS and ZnS) by powder X-ray diffraction (XRD) and conventional Raman spectroscopy. Secondly, the growth of CZTS is established to proceed strictly via formation of Cu_{2-x}S nuclei, followed by diffusion of Sn^{4+} to form Cu_3SnS_4 and lastly diffusion of Zn^{2+} to form $\text{Cu}_2\text{ZnSnS}_4$ phase. Lastly, the reaction kinetics of Sn^{4+} ion were identified to be the limiting factor for CZTS nanoparticles' purity. It is demonstrated that by carefully controlling the reactivity of organometallic ligand complex, it is possible to achieve balance in the reaction kinetics allowing one to synthesize CZTS phase without any observable binary/ternary phase from XRD and SERS.

Following on, using the knowledge gained from the first study, a model study is presented to highlight the complexity of phase transition via cation exchange to form multi-component sulfide nanomaterials ($\text{Cu}_{29}\text{S}_{16}$ to Cu_4SnS_4 to $\text{Cu}_2\text{ZnSnS}_4$). Using transmission electron microscopy (TEM) and XRD, direct evidence indicates that the phase transformation of binary $\text{Cu}_{29}\text{S}_{16}$ to ternary Cu_4SnS_4 proceeds via sequential three steps reaction processes involving two intermediate phases ($\text{P12}_{1n1} \text{ Cu}_{31}\text{S}_{16}$ and $\text{P12}_{1c1} \text{ Cu}_{32}\text{S}_{16}$) while preserving the anionic framework of $\text{Cu}_{29}\text{S}_{16}$. In addition, the ex-situ growth study of CZTS from CTS reveals a negative domino cationic exchange growth effect resulting in precipitation of parasitic phases. Furthermore, the use of HR-HAADF imaging with Z-contrast capability enables the visualization of Sn fixed occupancy sites in our as-synthesized quaternary CZTS nanoparticles. This confirms that the crystal does not follow the commonly accepted $\text{P6}_3\text{mc}$.

Lastly, using the knowledge gained from the first two studies, $\text{Cu}_2\text{-M-Sn-S}_4$ (M= Fe, Mn, Co) nanoparticles synthesis were carried out based on reaction conditions obtained from the initial study to identify conflicting growth mechanism. It is revealed that $\text{Cu}_2(\text{M})\text{SnS}_4$ nanoparticles proceed via two different reaction pathways. Growth of $\text{Cu}_2(\text{Mn})\text{SnS}_4$ nanoparticles is similar to $\text{Cu}_2(\text{Zn})\text{SnS}_4$ nanoparticles where ternary Cu-Sn-S phase is the intermediate phase. On the other hand, the growth of $\text{Cu}_2(\text{Co})\text{SnS}_4$ and $\text{Cu}_2(\text{Fe})\text{SnS}_4$ proceeds via an intermediate ternary Cu-(M)-S phase. XRD characterization of as-synthesized $\text{Cu}_2(\text{M})\text{SnS}_4$ nanoparticles revealed CZTS and CMTS to crystallize in hexagonal crystal structure while CFTS and CCTS crystallize in zinc blende crystal structure. In addition, as a proof of concept, the as-synthesized chemically treated CZTS and CMTS nanoparticles are drip-casted to form thin film solar cells. We demonstrated an encouraging power conversion efficiency of 1.16% (CZTS) and 0.078% (CMTS).

In the three hypothesis proposed for this thesis, the first hypothesis on SERS having the capability to characterize nanomaterials unambiguously is proven to be true. For the second hypothesis that the growth of CZTS nanoparticle proceeds via nucleation of Cu-S phase, followed by formation of ternary Cu-Sn-S phase is

proven to be accurate. Lastly, for the third hypothesis that the growth of $\text{Cu}_2(\text{M})\text{SnS}_4$ (M= Mn, Co and Fe) nanoparticles follows the growth of CZTS nanoparticles, $\text{Cu}_2\text{MnSnS}_4$ is proven to follow the growth of CZTS nanoparticles while $\text{Cu}_2(\text{M})\text{SnS}_4$ (M= Co and Fe) show interesting growth phenomena which prompt the need for further investigations.

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“Logic will get you from A to B. Imagination will take you everywhere”-Albert Einstein

In the beginning of my PhD program, I see myself as Sun Wukong in the Chinese novel “Journey to the West”: Going on an adventurous journey, meeting monstrosity demons and heavenly fairies; Crossing vast greenies on a magical cloud, discovering divine oasis and crossing paths with mystical beasts. Well, this tiny little fantasy of mine did last me for only one month and I am back to reality.

–Joel Tan

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“I want to be the bridge to the next generation” – Michael Jordan

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180 °C showing crystal phase Pc $Cu_{29}S_{16}$ + $P2_1/n$ $Cu_{31}S_{16}$ + $Pnma$ Cu_4SnS_4 , (iv) 200 °C showing crystal phase of $P2_1/n$ $Cu_{31}S_{16}$ + $Pmna$ Cu_4SnS_4 , (v) 230 °C showing crystal phase $P2_1/c$ $Cu_{32}S_{16}$ + $Pmna$ Cu_4SnS_4 . Standard XRD of (vi) $Pnma$ Cu_4SnS_4 , (vii) Pc $Cu_{29}S_{16}$, (viii) $P2_1/n$ $Cu_{31}S_{16}$ and (ix) $P2_1/c$ $Cu_{32}S_{16}$.

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Figure 5.16 Elemental mapping of nanoparticles obtained during ex-situ study during the growth of $\text{Cu}_2\text{ZnSnS}_4$ from Cu_4SnS_4 at 10, 20, 40, 60 and 90 mins.

Figure 5.17 XRD spectrum of as-synthesized CZTS nanoparticles after addition of Zn^{2+} into Cu_4SnS_4 nanoparticles solution, heated and immediately quenched upon reaching targeted temperature. **(i)** as-synthesized Cu_4SnS_4 nanoparticles showing crystal phase of *Pnma* Cu_4SnS_4 . Solution quenched at **(ii)** 140 °C showing crystal phase of *P2₁/c* $\text{Cu}_{32}\text{S}_{16}$ + *Pnma* Cu_4SnS_4 , **(iii)** 160 °C showing crystal phase of *P2₁/c* $\text{Cu}_{32}\text{S}_{16}$ + *Pnma* Cu_4SnS_4 + wurtzite $\text{Cu}_2\text{ZnSnS}_4$, **(iv)** 180 °C showing crystal phase of *P2₁/c* $\text{Cu}_{32}\text{S}_{16}$ + *Pnma* Cu_4SnS_4 + wurtzite $\text{Cu}_2\text{ZnSnS}_4$, **(v)** 200 °C showing crystal phase of *P2₁/c* $\text{Cu}_{32}\text{S}_{16}$ + wurtzite $\text{Cu}_2\text{ZnSnS}_4$. Standard XRD of **(vi)** *Pnma* Cu_4SnS_4 , **(vii)** *P2₁/c* $\text{Cu}_{32}\text{S}_{16}$.

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Figure 5.20 (i) Elemental mapping of as-synthesized Cu-Zn-Sn-S nanoparticles on various TEM carbon grid spots. **(ii)** HR-BF imaging, **(iii)** HR-HAADF imaging, **(iv)** CRISP-treated HR-HAADF image, **(v)** JEMS simulated HR-HAADF image along $\langle 001 \rangle$ zone axis, **(vi)** JEMS simulated crystal potential along $\langle 001 \rangle$ zone axis, **(vii)** FFT image of **(viii)**, and **(ix)** JEMS simulated TEM diffraction pattern along $\langle 100 \rangle$ zone axis. **(j)** Rietveld refinement of XRD pattern, **(x)** peak fitting of SERS spectrum and **(xi)** XPS characterization of Cu-Sn-S nanoparticles.

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Figure 5.23 Rietveld refinement of (ii) CZTS quarter.

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Figure 6.1 Raman spectra of phases formed during growth of $\text{Cu}_2\text{MnSnS}_4$ nanoparticles.

Figure 6.2 Raman spectra of phases formed during growth of $\text{Cu}_2\text{FeSnS}_4$ nanoparticles.

Figure 6.3 Raman spectra of phases formed during growth of $\text{Cu}_2\text{CoSnS}_4$ nanoparticles.

Figure 6.4 Raman spectra of phases formed during growth of $\text{Cu}_2\text{ZnSnS}_4$ nanoparticles.

Figure 6.5 X-ray diffraction (XRD) patterns were obtained using a Bruker D8 Advance with Cu K α radiation(1.5406 Å) at 0.02°/s scan rate, 1 s accumulation time, and in 2 θ ranging from 20° to 70°.

Figure 6.6 TEM images (top row) and SERS spectra (bottom row) of CMTS nanoparticles synthesized using different reaction setup at 1 mL dodecanethiol amount: a and b) Cu₂FeSnS₄, c and d) Cu₂CoSnS₄, e and f) Cu₂MnSnS₄, g and h) Cu₂ZnSnS₄.

Figure 6.7 TEM images (top row) and SERS spectra (bottom row) of CMTS nanoparticles synthesized using different reaction setup at 5 mL dodecanethiol amount: a and b) Cu₂FeSnS₄, c and d) Cu₂CoSnS₄, e and f) Cu₂MnSnS₄, g and h) Cu₂ZnSnS₄.

Figure 6.8 PV performance of thin film solar cell fabricated using CZTS and CMTS nanoink. Red line shows the best PV performance out of 6 PV cells while the black line shows the worse PV performance out of 6 PV cells.

Figure 6.9 Light microscopic image of thin film absorber layer.

Figure 7.1 Schematic illustration of reaction setup showing two possible reaction pathway. Fe²⁺ as used as an example.

Figure 7.2 XRD and SERS characterization of as-synthesized Cu₂(M)SnS₄ nanoparticles using CE approach.

Figure 7.3 Schematic of coffee stain formation for an evaporating drop with pinned contact lines (a) and with mobile contact lines (b) leading to solute concentration in a single spot. Contact line mobilization is achieved by applying an AC voltage between the interdigitated electrodes (short red and blue lines) in (b).

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Figure 7.4 Zoom out and zoom in bright field light microscopic image of thin film formed from varying in the concentration (v/v %) of hexanol and IPA in CZTS nanoink.

Abbreviations

Acac	Acetylacetonate ion
ADF	Annular dark field
BF	Bright field
BSE	Backscattering electron
CCTS	$\text{Cu}_2\text{CoSnS}_4$
CE	Cation exchange
CFTS	$\text{Cu}_2\text{FeSnS}_4$
CIGS	$\text{Cu}(\text{In},\text{Ga})\text{S}_2$
CMTS	$\text{Cu}_2\text{MnSnS}_4$
CTS	Copper tin sulfide
CZTS	$\text{Cu}_2\text{ZnSnS}_4$
DDT	Dodecanethiol
DF	Dark field
EDX	Energy dispersive X-ray spectroscopy
EF	Enhanced factor
EM	Electron microscopy
EM	Electromagnetic mechanism
FFT	Fast fourier transform
GGA	Generalized gradient approximation
HAADF	High angular annular dark field
HR	High-resolution
HSAB	Pearson's hard and soft acids and bases
J_{sc}	Short-circuit current density
LSPR	Localized surface plasmon resonance
Oac	Acetate ions
Oam	Oleylamine
ODE	Octadecene
PBE	Perdew–Burke–Ernzerhof

PV	Photovoltaic
SEI	Secondary electron image
SEM	Scanning Electron Microscopy
SERS	Surface Enhanced Raman Scattering
STEM	Scanning Transmission Electron Microscopy
TEAM	Transmission Electron Aberration-Corrected Microscope
TEM	Transmission Electron Microscopy
TOP	Tri-octylphosphine
TOPO	Tri-octylphosphine oxide
UN	United Nations
VASP	Vienna Ab-initio Simulation Package
V_{oc}	Open-circuit voltage
WZ-KS	Wurtzite-Kesterite
WZ-S	Wurtzite-Stannite
XRD	X-ray diffraction
ZSW	Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden- Württemberg

Chapter 1

Introduction

In this chapter, the hypotheses, objective, overview and outcomes of this dissertation are presented. In the hypotheses/problem statement section, the key areas motivating this research and the hypotheses to be tested are highlighted. Next, in the objective section, the goal of this dissertation, which is to understand $\text{Cu}_2(\text{M})\text{SnS}_4$ ($\text{M}=\text{Zn}$, Co , Mn and Fe) nanoparticles are presented. Following on, an outline of the individual chapters covered in this dissertation will be highlighted in the overview section. Lastly, the novel outcomes arising from this thesis are summarized in the findings and outcome/originality section.

1.1 Hypotheses/Problem statements

The quaternary material $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) has gained much attention in recent years as a solar harvesting material. Various methods have been deployed to fabricate CZTS and CZTSe thin films suitable for solar cell applications. However, these methods usually involve high-vacuum deposition techniques in thermal evaporation systems, complex equipment requirements in co-evaporation techniques or highly flammable chemicals.¹⁻⁵ To avoid high vacuum processing, fabrication of CZTS thin films from solution-based approaches (e.g, spray-pyrolysis, spin coating, nanoink printing) is especially noteworthy.⁶⁻¹¹ Among the solution-based approaches, fabrication of thin film solar via nanoparticles solution (nanoink) shows the greatest potential. For the other solution-based approaches, the formation of thin film involves multiple solid state reactions during post-deposition annealing process.¹² Due to the difficulty of diffusion of ions in the solid state, the composition of the CZTS film has a tendency to be nonhomogeneous, hence leading to precipitation of secondary phases in the crystal matrix. On the other hand, the nanoink fabrication approach allows the pre-formation of ideal nanoparticles properties (phase purity and stoichiometry), and hence allows the formation of thin film with greater homogeneity and phase purity during post-deposition annealing process.¹²

The importance of phase purity in CZTS thin film is due to the detrimental effect on the electrical performance of the device arising from the secondary phases. As a multi-component semiconductor, the possibility of multiple phases (crystal and compositional) formation poses a great challenge to all researchers. For example, copper sulfide (Cu-S) phase, which is highly conducting, results in short-circuiting of CZTS device.^{13,14} Tin sulfide (Sn-S, a n-type semiconductor of ~2.2 eV bandgap) phase, when present in significant amounts may result in a second diode formation with opposite polarity to CZTS.¹⁵ This acts as a barrier for charge transport and reduces the PV cell fill factor. In addition, the presence of zinc sulfide (Zn-S) phase acts as an insulator in CZTS matrix, reducing electron-hole pair generation and conductivity of the absorber layer due to its large bandgap ~3.5 - 3.7 eV.^{16,17} Lastly, the formation of ternary phases such as copper-tin-sulfide (Cu-

Sn-S), results in metallic characteristic in CZTS.¹⁸ This ultimately enhances electron-hole pair recombination and lowers the open-circuit voltage (V_{OC}).

To date, most efforts have only been focusing on the identification of detrimental secondary phases and their effects on the electrical characteristics through device fabrication. However, little is known on how to control the reaction kinetics to avoid secondary phases formation during the synthesis stage. To obtain phase pure inorganic nanoparticles, the reactivity of the cations and anions should be well balanced.¹⁹ As the reactivity of the cations is inversely proportional to the stability of the metallo-organic precursors, Pearson's hard and soft acids and bases (HSAB) principle is generally used to predict the stability of metal-ligand complex (metallo-organic precursors).²⁰ However, due to the involvement of multiple cations precursors in CZTS reaction system, it has been proposed to be impossible to predict the reactivity and the reaction sequences of the cations using HSAB.¹⁹ In addition, there is currently no generally agreed growth mechanism of CZTS nanoparticles, therefore it is impossible to identify the crucial growth kinetics of intermediate phase, which may otherwise affect the phase purity of the final CZTS nanoparticles product.^{21,22} Since the reactivity of the cations affects the reaction kinetics, the usage of wrong precursor choices may result in premature formation of parasitic phases, which may disrupt the growth of CZTS phase and leads to multiple phases formation. In addition, there has only been theoretical calculation on the enthalpies of formation of the various possible phases and theoretical simulated phase diagrams describing the range of elemental composition favoring pure phase CZTS formation.^{23,24} However, there is no direct experimental proof reported on phase purity control.

Unavoidably, the key to explaining growth phenomena, understanding reaction pathway and optimizing reaction procedures is based on the knowledge of the microscopic mechanism of structural transformation. Therefore, two crucial areas have been identified to have inadequate emphasis in literature, namely: *i*) the accuracy in characterization of $Cu_2(M)SnS_4$ nanomaterials and *ii*) the structural growth mechanism of $Cu_2(M)SnS_4$ phase.

1.1.1 Hypothesis #1: It is plausible to increase Raman signal and resolution of nanoparticles with Surface Enhanced Raman Scattering spectroscopy (SERS)

As CZTS is a quaternary sulfide compound, there is a possibility of parasitic formation of ternary and binary sulfide phases. Based on the elemental make up of CZTS, the possible combination of secondary phases can consist of Cu_{2-x}S , ZnS , Sn_xS_y and Cu_xSnS_y phases. However, it is challenging to distinguish Cu_xSnS_y , ZnS phases from CZTS phase due to similar crystal structures with similar lattice spacings.² The difference in the diffraction angles (2Θ) is beyond the resolution limitation of powder X-ray diffraction (XRD), hence they show overlapping diffraction patterns causing them to be indistinguishable from one another.

On the other hand, Raman spectroscopy has been demonstrated to possess the capability of distinguishing CZTS phase and other secondary phases that may form during CZTS formation.^{2,25,26} In conventional Raman spectroscopy, when a monochromatic light is shone on a material, the incident electromagnetic field induces a dipole moment, which in turn radiates light as its characteristic oscillation frequencies.^{27,28} However, due to the small Raman cross section of nanoparticles, reported Raman signals have always been very broad and ambiguous. In the first hypothesis, SERS is proposed to increase the accuracy of CZTS nanoparticle characterization. The usage of SERS will increase the Raman cross section and give better signal resolution and counts. In SERS spectroscopy, due to the usage of noble metal substrate (e.g Au, Ag), there will be a redistribution of electromagnetic field around the metal surface when an electromagnetic wave (light) interacts with it. This results in localized regions of stronger electromagnetic field, and hence allows coupling of intense electromagnetic fields with the particle of interest. Theoretically, due to these electromagnetic fields, the enhancement factor of SERS spectroscopy is E^4 (E is the intensity of the electric field).²⁷ By testing this hypothesis, we will pioneer the use of SERS for inorganic nanostructure characterization. In return, we will be able to unambiguously identify the phases present in CZTS nanoparticles. This will allow us to study the growth of CZTS

nanoparticles accurately and identify parasitic growth phenomena with respect to changing reaction parameters.

1.1.2 Hypothesis #2: The reaction pathway to form CZTS should start with binary Cu-S, followed by diffusion of Sn^{4+} into Cu-S to form ternary Cu-Sn-S, and finally diffusion of Zn^{2+} into ternary Cu-Sn-S to form quaternary Cu-Zn-Sn-S

There have been few reports describing the growth mechanism of CZTS nanoparticles. Commonly, the growth mechanism is reported to proceed via the nucleation of binary Cu_{2-x}S phase followed by the formation of a ternary intermediate phase and finally the formation of quaternary $\text{Cu}_2\text{ZnSnS}_4$ phase. However, there is no commonly agreed intermediate phase, as both ternary Cu-Sn-S and Cu-Zn-S phases have been reported previously.²¹

In the second hypothesis, the growth of $\text{Cu}_2\text{ZnSnS}_4$ nanoparticle is proposed to follow a fixed pathway with Cu-Sn-S being the intermediate phase. The reaction should proceed via formation of a Cu-S binary nanoparticle, which acts as the seed for the incorporation of Sn^{4+} ions to form ternary Cu-Sn-S. This in turn acts as the intermediate phase for the incorporation of Zn^{2+} to obtain quaternary Cu-Zn-Sn-S nanoparticle. The proposal of this sequential growth is based on the reported observation of rapid formation of Cu-S binary phase due to its high reactivity with sulphur and reported inability to form Cu-Zn-S ternary phase but Cu-S/Zn-S hetero-phase instead.^{29,30} By testing this hypothesis, we are able to identify and prove that the formation of CZTS phase is governed by a set of parameters. In return, this set of parameters will allow us to gain control of forming pure-phase CZTS nanoparticles.

1.1.3 Hypothesis #3: It is still plausible to obtain pure-phase wurtzite nanoparticles by substitution of Zn^{2+} with Co^{2+} , Mn^{2+} and Fe^{2+}

In the third hypothesis, it is proposed that Zn^{2+} in CZTS can be replaced by Mn^{2+} , Co^{2+} , and Fe^{2+} . Being isovalent to Zn^{2+} and having similar atomic radii, the formation of $\text{Cu}_2(\text{M})\text{SnS}_4$ ($\text{M}=\text{Mn}^{2+}$, Co^{2+} and Fe^{2+}) nanoparticles should follow

the same mechanism as that of CZTS nanoparticle.^{31,32} The proposed feasibility of this reaction is based on widely established cationic exchange chemistry, where cation in a crystal lattice can be displaced by ions of similar charge. In our approach, instead of replacing Zn^{2+} from its crystal lattice after formation of the nanoparticles, we replaced Zn^{2+} in the reaction solution to form $\text{Cu}_2(\text{M})\text{SnS}_4$ nanoparticles with their respectively substituted cations.

By testing this hypothesis, we are able to provide a general synthetic route to obtain wider range of quaternary compounds with various functionalities. In CZTS, due to small chemical and size disparities, there is high tendency for the formation of Zn_{Cu} and Cu_{Zn} defects resulting in shorter electron-hole pair lifetime. On the other hand, when $\text{M} = (\text{Mn}^{2+}, \text{Co}^{2+} \text{ and } \text{Fe}^{2+})$, there is a lower tendency to form substitution defects in the crystal lattices due to preferential ionic occupancy in the crystal lattice as a result of larger chemical and size disparities to Cu^+ atoms. Besides minimizing substitutional defect within the crystal structure, $\text{Cu}_2(\text{M})\text{SnS}_4$ is characterized to have suitable bandgaps of 1.0-1.5 eV for solar harvesting.³³ In addition, they exhibit magnetic and catalytic properties making them multifunctional materials.³⁴⁻³⁷

1.2 Objective and Scope

The objective of this thesis is to understand the reaction pathway and conditions to form pure phase $\text{Cu}_2(\text{M})\text{SnS}_4$ ($\text{M} = \text{Zn}^{2+}, \text{Mn}^{2+}, \text{Co}^{2+} \text{ and } \text{Fe}^{2+}$) nanoparticles by heating up method.

To fulfil the above-mentioned objective, the scope of this thesis is divided into:

1. Establishing fundamental growth parameters of wurtzite CZTS nanoparticles using Surface Enhanced Raman Scattering (SERS) spectroscopy.
2. Establishing sequential phase (compositional and crystal) changes during alloyed-cation exchange growth approach to synthesize CZTS from binary Cu-S nanoparticles.
3. Identification of the preferential growth pathway of $\text{Cu}_2(\text{M})\text{SnS}_4$ ($\text{M} = \text{Mn}^{2+}, \text{Co}^{2+} \text{ and } \text{Fe}^{2+}$) nanoparticles.

4. Revealing general synthetic route to synthesize pure-phase $\text{Cu}_2(\text{M})\text{SnS}_4$ ($\text{M}=\text{Zn}^{2+}$, Mn^{2+} , Co^{2+} and Fe^{2+}) nanoparticles.

1.3 Dissertation Overview

This thesis addresses the need for unambiguous characterization, understanding of formation kinetics, pathway and mechanism of CMTS phase to achieve single-phase CMTS nanoparticle ink. A total of 7 chapters are presented and organised as follows:

Chapter 1 provides the rationale for this research and outlines the objective and scope for this study.

Chapter 2 reviews the literature concerning the current progress in CZTS nanoparticle synthesis and characterization.

Chapter 3 discusses the principles underlying the synthesis / characterization / modeling techniques employed and the methods of data analysis, including errors.

Chapter 4 elaborates on the usage of SERS spectroscopy to investigate the synthetic pathway of single phase quaternary wurtzite CZTS nanoparticles.

Chapter 5 explains the temporal changes during CE growth of Cu_{2-x}S nanoparticles to quaternary CZTS nanoparticles.

Chapter 6 elaborates on the investigation of $\text{Cu}_2(\text{M})\text{SnS}_4$ nanoparticles formation while identifying peculiar reaction pathway from CZTS.

Chapter 7 demonstrates how the thesis hypotheses have been proven, and how the design target has been met and addressed. It includes the opportunities and strategies for future work.

1.4 Findings and Outcomes/Originality

This research led to several novel outcomes by:

1. Demonstrating for the first time, SERS spectroscopy is an excellent characterization tool for CZTS nanoparticles.
2. Establishing the synthetic route of CZTS nanoparticles formation and determining the conditions to achieve pure phase CZTS nanoparticles.
3. Revealing the preferential formation of crystal structures (wurtzite and stannite) and the pure-phase formation in CMTS (M=Mn, Fe, Co and Zn) nanoparticles.
4. Discovering direct evidence that CZTS nanoparticles follow either $Pmn2_1$ or Pc crystal structure instead of the generally accepted $P6_3mc$.
5. Highlighting the complex nature of cationic exchange reaction to form quaternary Cu_2ZnSnS_4 .
6. Demonstrating for the first time, carbon-free printable nano-ink made from pure single-phase CMTS nanoparticles.

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Chapter 2

Literature Review

In this chapter, an overview on the need for solar energy to solve the energy crisis is presented. The summary on the development of thin film solar cell material is presented in a few sections. These sections include i) the types of materials being studied for solar harvesting, ii) the synthetic methods commonly adopted in the synthesis of nanomaterials, iii) the progress in $\text{Cu}_2(\text{M})\text{SnS}_4$ ($\text{M}=\text{Zn}$, Mn , Fe and Co) nanomaterial synthesis and iv) the various methods used to characterize the as-synthesized materials. Lastly, questions arising from the literature review and the context of the PhD are presented.

2.1 Overview

In recent years, there have been an increasing emphasis on sustainable development of energy resources due to the increased awareness of the potential threats posed by global warming.¹ The United Nations (UN) Framework Conventions on Climate Change's warning of the finiteness of fossil resources has led to an unavoidable need to shift from non-renewable resources to renewable and sustainable energies. Consequently, the need for high energy production and low greenhouse gas emission are essential for achieving sustainability. Currently, nuclear power plant is the widest used CO₂ free power generator in many countries such as Japan and China, but it is not a long term solution to solve the energy crisis. Not only do nuclear power plants require uranium as fuel, uranium is rare and there are still unsolved problem arising from the radioactive waste discharges from the power plants.² The occurrence of a nuclear disaster as evidenced in the Tohoku earthquake in Japan in 2011 is a somber reminder of the severity of the downside of nuclear energy sources.

Needless to say, to achieve sustainability, technologies must be based on energies that are inexhaustible. These energies can be classified into solar power, hydropower, wind power, tidal/wave power, and biofuel, with solar power being the most promising renewable energy source. The sun provides approximately 10^{16} Watt to the Earth per day, which is about 10 000 times the amount needed to meet the Earth's energy consumption in a year.³ Photovoltaic (PV) cells, utilizing solar energy to produce electricity, are leading front contenders for the future clean energy source. Materials such as binary and quaternary alloy/compound films with suitable band gaps and high optical absorption coefficients have been reported to date.^{4,5} On the down side, binary systems are generally far too expensive and toxic for large-scale commercial applications. These systems includes GaAs, CdTe, InP etc.⁶ In recent years, research focuses are shifting towards quaternary compound materials such as copper-indium-gallium-sulphide (CIGS) and copper-zinc-tin-sulfide (Cu-Zn-Sn-S). PV cell using CIGS as absorber layer has achieved ~21.7% efficiency at the Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg (ZSW).⁷ However, due to its requirements for gallium and indium,

which are rare metals, $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) is deemed to be a better candidate. $\text{Cu}_2\text{ZnSnS}_4$ (CZTS), a quaternary chalcogenide p-type semiconductor, is actively studied as a new photovoltaic material due to its high absorption coefficient ($\sim 10^4 \text{ cm}^{-1}$), optimal direct band energy ($\sim 1.0 - 1.5 \text{ eV}$), as well as naturally abundant and nontoxic elemental components. Its bandgap tunability can be achieved by substituting S with selenium (Se) at various concentrations. Its potential as a new solar harvesting material is proven by achieving a nearly 2-fold increase in solar efficiency within a period of 4 years. The current record solar cell efficiency of 12.6% was from a device fabricated via non-vacuum processes, making CZTS an ideal material with lower production costs.⁸

Various methods have been deployed to fabricate CZTS and CZTSe thin films for solar cell applications. However, these methods usually involve high-vacuum environment, complex equipment or highly flammable chemicals. In addition, high temperature fabrication of CZTS film has a tendency to form unwanted CTS phases.⁹ To avoid high vacuum processing, fabrication of CZTS films from quaternary CZTS nanoparticles ink (nanoink) is especially noteworthy, as it simplifies processing steps. In 2013, a report by Yang Yang *et al* pointed out the advantage of CZTS nanoink approach. In his report, nanoink approach is described to bypass random phase formation during thin film fabrication as CZTS phase are “preformed” during nanoparticles synthesis.¹⁰ As a result, it is desirable to develop a robust solution-based process for CZTS nanoparticles for the fabrication of CZTS based devices.

2.1.1 Progress in the field of CZTS nanoparticle synthesis

In the past two decades, the progress in semiconductors nanocrystals synthesis has expanded rapidly. Various types of semiconductors nanocrystals can now be obtained. They include, **II-VI** ($\text{Cd}(\text{S},\text{O})$, HgTe , $\text{Zn}(\text{S},\text{O})$), **IV-VI** ($\text{Pb}(\text{S},\text{Se},\text{Te})$), **III-V** (InP , InAs), **IV** (Si , Ge), **I-V-VI** ($\text{Cu}(\text{In},\text{Ga})(\text{S},\text{Se})_2$) and **I-II-IV-VI** ($\text{Cu}_2\text{ZnSnS}_4$) to name a few.¹¹⁻²⁴ **I-II-IV-VI** nanoparticles, $\text{Cu}_2\text{ZnSnS}_4$ to be specific, were only reported in 2009 by Guo *et al.*²⁰ In less than one decade, progress in CZTS synthesis protocols has led to the development of various recipes to obtain

CZTS nanoparticles. These recipes highlighted changeable organometallic precursors, varying reaction temperatures, better class of sulfur source, scalable reaction procedures and even doping.^{18,25-33}

The driving factor behind nanoparticle approach over other solution-based approach lies on the potential of pre-formation of ideal nanoparticles properties (phase purity and stoichiometry). The underlying key to this success is the formation of nanocrystals in a carefully controlled environment, allowing the precursors to interact more homogeneously with greater diffusivity to reach thermodynamically stable phase.¹⁰ In CZTS nanoparticle-based solar cell approach, it starts with the synthesis of CZTS nano-ink, followed by deposition of nano-ink on substrate and finally post-deposition treatment to form CZTS thin film. Utilization of carefully synthesized nanocrystals bypasses the process of random phase formation during post-deposition treatment, therefore ensuring greater control over phase purity and stoichiometry compositions. In general, synthesis of nanomaterials can be classified into either *direct approach* or *post synthetic approach*. In *direct approach*, strategies to synthesize nanomaterials include sol-gel processes, hot-injection, heating-up, hydrothermal and co-precipitation to name a few.³⁴⁻⁴³ While *post synthetic approach* can be generalized as involving a cationic or anionic exchange processes.⁴⁴⁻⁴⁹

In this dissertation, both direct and post synthetic approach will be studied. We will be focusing on hot-injection and heating-up in direct approach and cationic exchange in post synthetic approach.

2.1.1.1 Direct approach- Hot Injection and heating-up method

Wet-chemical colloidal syntheses are unparalleled in their ability to grow a wide range of particle types, while offering control over particle size and shape, and minimizing particle polydispersity. The foundation of the wet-chemical synthesis of colloids dates back over 150 years to the pioneering work of Faraday, in which he added a strong reducing agent (phosphorus) to an aqueous solution of gold chloride to yield nanosized gold colloid.⁵⁰ Spawned from the pioneering work of Henglein *et al* and Bruson *et al* on CdS colloids, Murray *et al* popularized the hot-

injection synthetic method to produce semiconductors nanocrystals.⁵¹⁻⁵⁹ This approach can be generalized as injection of organometallic reagents solution into hot coordinating solvents, or vice versa, for pyrolysis of precursor to occur instantaneously at elevated temperature. Another synthetic approach is known as the “non-injection approach” (also known as heating-up approach).⁶⁰ This approach can be generalized as mixing all the chemical reagents into a reaction vessel and heating them up to induce nucleation and growth of nanocrystals. Based on these two synthesis approaches, various reaction conditions to synthesize CZTS have been reported, of which a few are summarized in **Table 2.1**

Table 2.1 Chemical synthesis methods for quaternary metal chalcogenide nanocrystals.^a

Authors	Chemical Reagents	Method	Size (nm) and morphology	Ref
Guo et al	Cu(acac) ₂ , Zn(acac) ₂ , Sn(bis-acac dibromide) ₄ , S, OLA	HI	15-25	20
Riha et al	Cu(acac) ₂ , Zn(ac) ₂ , Sn(Oac) ₄ , S, OLA, TOPO	HI	13, irregular faceted shape	27
Lu et al	CuCl ₂ , ZnCl ₂ , SnCl ₄ , DDT, OLA or OA	HI	With OLA: 20 x 28, prisms With OA: 14 nm thick plates	26
Singh et al	Cu(acac) ₂ , Zn(Oac) ₂ , Sn(Oac) ₄ , tert-DDT, DDT, TOPO, ODE	HI	35 x 11, nanorods	33
Rath et al	CuI, ZnCl ₂ , SnI ₄ , S, OLA	HI	7-10	61
Saha et al	CuCl ₂ , ZnCl ₂ , SnCl ₄ , S, OLA	HI	7-9	62
Cao et al	CuCl ₂ , Zn(Oac) ₂ , SnCl ₄ , S, EDA	HU/A	5-32, aggregated	63
Yang et al	Cu(acac) ₂ , Zn(Oac) ₂ , SnCl ₂ , S, OLA	HU	11, irregular	64
Hara et al	Cu(NO ₃) ₂ , Zn(NO ₃) ₂ , SnCl ₄ , S, OLA	HU	10-15, aggregated	65
Khare et al	Cu(S ₂ CNEt ₂) ₂ , Zn(S ₂ CNEt ₂) ₂ , Sn(S ₂ CNEt ₂) ₄ , OLA	HU	2-7, faceted	66
Shi et al	CuCl, ZnCl ₂ , SnCl ₂ , S, EDA	HU	μm, nanowires	67
Zhou et al	CuCl ₂ , ZnCl ₂ , SnCl ₄ , thiourea, PVP, EG	HU/A	500, flower-like	68
Shavel et al	CuCl ₂ , ZnO, SnCl ₄ , S, OLA, ODE	HU	15, irregular faceted shape	69
Regulacio et al	Cu(S ₂ CNEt ₂) ₂ , Zn(S ₂ CNEt ₂) ₂ , Sn(S ₂ CNEt ₂) ₄ , hexadecanethiol, trioctylamine	HU	15 x 8, elongated	32

^a ODE: octadecene, DDT: dodecanethiol, OA: oleic acid, OLA: oleylamine, EDA: ethylenediamine, TOPO: trioctylphosphine oxide, PVP: polyvinylpyrrolidone, EG: ethylene glycol, TEG: triethylene glycol, acac: acetylacetonate, Oac: acetate, HI: hot-injection, HU: heating-up, and A: autoclave.

In 2009, Guo *et al* first demonstrated the synthesis of CZTS nanoparticles via the hot injection method.²⁰ By optimizing the stoichiometry composition, the group managed to improve the efficiency of their PV device by 10-fold. Since then, numerous groups began reporting various wet-chemistry reaction methods to prepare CZTS nanoparticles. In their report, nanoparticle synthesis was carried out using copper (II) acetylacetonate, zinc (II) acetylacetonate and tin (IV) bisacetylacetonate dibromide as the cation sources and elemental sulfur as the sulfur source. Metal precursors were dissolved in oleylamine and heated to 225 °C, at which point elemental sulfur was rapidly injected to the reaction mixture.

Figure 2.1 XRD patterns (a) of as-synthesized kesterite CZTS nanoparticles coated on Mo coated soda lime glass (black line) and after annealing under a selenium (Se) atmosphere at 500 °C for 20 mins (red line). Diffraction peaks of the selenized films shift systematically to the left due to the increase in lattice parameter with Se replacing sulfur (S) in the CZTS matrix. (b) TEM image of the CZTS nanoparticles. Reproduced with permission from Reference 20. Copyright 2009, American Chemical Society.

The obtained nanoparticles were polydisperse in the size range of 15 – 25 nm (**Figure 2.1**), with the elemental composition of synthesized CZTS nanoparticles measured by EDX analysis showing them to be zinc poor and copper rich $\text{Cu}_{2.12}\text{Zn}_{0.84}\text{Sn}_{1.06}\text{S}_4$. These nanoparticles gave a poor power conversion efficiency of only 0.74% and 0.80% when they were selenized at 450 °C and 500 °C respectively. In an attempt to increase the efficiency of their device, Guo *et al* increased the precursor concentration of Zn cations to give zinc rich and copper poor CZTS nanoparticles. The overall composition was designed to keep copper

poor to avoid formation of binary and/or ternary phases of copper chalcogenide in the final film. The revised

Figure 2.2 SEM (a) image of CZTSSe device showing CZTSSe on Mo-substrate with CdS as the buffer layer and ZnO and ITO as electrode. (b) I-V characteristics of the best performing CZTSSe solar cell measured in the dark, as fabricated, and after light soaking for 15 mins under AM 1.5 illumination. The reported device parameters are calculated based on total device area (0.472 cm²). Reproduced with permission from Reference 25. Copyright 2010, American Chemical Society.

Figure 2.3 (a) TEM, (b) HRTEM and (c) SEM images of CZTS nanoparticles. In (b), nanoparticle is imaged down the [110] crystallographic zone axis. (d) XRD pattern of CZTS nanoparticles. The red reference pattern is simulated with CaRine Crystallography 3.1 software using space group I4 and lattice parameters a=b=5.427 Å and c=10.848 Å for kesterite CZTS (JCPDS no. 26-0575). e) I-V characteristic of a CZTS nanoparticle PV device. Reproduced with permission from Reference 70. Copyright 2009, American Chemical Society.

CZTS nanoparticle composition of $\text{Cu}_{1.31 \pm 0.02}\text{Zn}_{0.91 \pm 0.03}\text{Sn}_{0.95 \pm 0.02}\text{S}_4$ gave a power conversion efficiency of 7.2 % (**Figure 2.2**).²⁵ Not only did Guo *et al* demonstrate the importance of CZTS atomic composition, they devised a robust, solution based method for the fabrication of efficient CZTS thin film solar cells. However, the power conversion efficiency is still not ideal which could be due to the presence of secondary phases.

Steinhagen *et al* reported a new reaction procedure for the synthesis of CZTS nanoparticles.⁷⁰ By utilizing tri-octylphosphine oxide (TOPO) and oleylamine as coordinating solvent and copper (II) acetylacetonate, zinc (II) acetate and tin (IV) acetate and elemental sulfur as precursors, CZTS nanoparticles of 10.9 ± 2.9 nm in average size and a composition of $\text{Cu}_{2.308}\text{Zn}_{1.01}\text{Sn}_{1.20}\text{S}_{3.70}$ are obtained. A photovoltaic device fabricated using these nanoparticles showed power conversion efficiency of 0.23 % with an open circuit of 321 mV, current density 1.95 mA cm^{-2} and fill factor of 0.37 as shown in **Figure 2.3**.

Figure 2.4 (a) TEM images and (b, c) HRTEM images of nanoprisms prepared in dodecanethiol and oleylamine. (d) TEM images and (e, f) HRTEM images of nanoplates prepared in DDT and oleic acid (OA). (g) XRD patterns of CZTS nanoparticles. For reference the stimulated XRD pattern of wurtzite CZTS and the XRD pattern of kesterite CZTS (JCPDS 26.0575) are shown below. The scheme of the proposed crystal structure of wurtzite is given in the top right corner. Reproduced with permission from Reference 26. Copyright 2011, Wiley.

Lu *et al* reported another interesting approach for synthesis of CZTS nanoparticles in which copper (II) chloride, zinc (II) chloride and tin (IV) chloride were used as metal sources while dodecanethiol was used as sulfur source.²⁶ The metal cations reacted with dodecanethiol at 120 °C to form metal-thiolate complexes and were hot-injected into oleylamine or oleic acid at 240 °C. The reaction was kept at this temperature for 1 hr to complete the growth of the nanoparticles. The nanoparticles obtained are wurtzite hexagonal crystallites with elemental composition of $\text{Cu}_2\text{ZnSnS}_4$. By using oleylamine, CZTS nanoprisms with a width of 20 nm and a height of 28 nm were obtained (**Figure 2.4**). Lattice fringes with an interplanar spacing of 0.33 nm are assigned to the [100] planes of wurtzite CZTS, and 0.32 nm to the [002] plane. Oleic acid gave nanoplates with lattice fringes of 0.33 nm assigned to [100] planes. It was reported that the metal-thiolate complexes influenced the cation's reactivity, hence adjusting the chemical environment favored the formation of wurtzite crystal structure.

Figure 2.5 (a) DF-STEM image showing a 3D superstructure of CZTS nanorods. (b) Top-down HRTEM image showing the closed-packed monolayer of CZTS nanorods. The inset shows an HRTEM image of a single nanorod. (c, d) Scanning electron microscopy (SEM) and HRTEM images showing top-down and side views of a multilayer assembly of CZTS nanorods. Reproduced with permission from Reference 33. Copyright 2012, American Chemical Society.

In another study, Singh *et al* reported the first morphology control of CZTS nanoparticles.³³ By using a mixture of two thiol ligands (dodecanethiol and tert-dodecyl mercaptan), preferential growth along the [002] direction was controlled, allowing them to obtain rod-like CZTS nanoparticles. In a typical synthesis, copper (II) acetylacetonate, zinc (II) acetate, tin (IV) acetate, and TOPO are mixed with 10 mL of 1-octadecene in a three neck round-bottom-flask and the solution was evacuated at room temperature to remove oxygen. The solution was then heated to 240–260 °C under an argon atmosphere. At 150–160 °C, a mixture of dodecanethiol and tert-dodecyl mercaptan were quickly injected into the flask, resulting in an immediate color change from dark-green to wine-red and then finally to brown. After injection, the reaction was allowed to proceed for 15–30 mins with continuous stirring to obtain their wurtzite CZTS nanorods.

2.1.1.2 Post synthetic approach - Cation exchange method

Ionic exchange method has been around for more than two decades. The general concept of this method is the substitution of ions in an extended solid (starting material) by ions dissolved in a solution. However, most of the work on cationic exchange (CE) has been carried out on binary compounds while little study has been carried out on multinary compounds. In 2014, Wu *et al* reported a synthetic protocol for the formation of quaternary CZTS 2D nanoparticles via CE, with CuS nanoparticles as the starting material (**Figure 2.6**).⁷¹ In this report, CuS nanoparticles were synthesized via reaction of CuI with elemental sulphur in oleylamine at 120 °C for 6 hrs. A CE reaction to form CZTS was then carried out by adding zinc 2,4-pentanedionate monohydrate (0.2 mmol) and tin(IV) chloride bis(2,4-pentanedionate) (0.2 mmol) into CuS nanoparticles solution. The reaction was kept at 260 °C for 2 hrs to allow complete reaction to take place.

Figure 2.6 TEM (a,b) and HRTEM (c,d) images of synthesized CZTS nanoplates. e) STEMEDS mapping of a single CZTS nanoplate shown in Figure 1b. f) XRD pattern of CZTS nanoplates. Reproduced with permission from Reference 71. Copyright 2014, Wiley.

Figure 2.7 Conventional TEM images of pristine (a), and exchanged Cu-rich (b), and Zn-rich (c) nanoparticles. Inset in (a) shows corresponding nanoparticles arranged vertically. (d-f) High-angle annular dark field (HAADF) scanning TEM (STEM) observations of the nanoparticles shown in (a-c); insets below display their corresponding STEM-EDS spectra where the main peaks of S, Sn, Cu, Zn, and Se are shown consistent with chemical compositions of $\text{Cu}_{1.82}\text{Se}_{0.74}\text{S}_{0.26}$, $\text{Cu}_{0.54}\text{Zn}_{0.31}\text{Sn}_{0.23}\text{Se}_{0.79}\text{S}_{0.21}$, and $\text{Cu}_{0.15}\text{Zn}_{0.88}\text{Sn}_{0.04}\text{Se}_{0.75}\text{S}_{0.25}$ for the pristine, Cu-rich, and Zn-rich samples, respectively. Reproduced with permission from Reference 72. Copyright 2014, American Chemical Society.

In the same year, Lesnyak *et al* reported the formation of CZTS_{Se} nanoparticles from $\text{Cu}_{2-x}\text{Se}_y\text{S}_{1-y}$ nanoparticles via a CE reaction.⁷² In a typical reaction, $\text{Cu}_{2-x}\text{Se}_y\text{S}_{1-y}$ nanoparticles were synthesized via reacting $\text{Cu}(\text{acac})_2$ (262

mg) with elemental Se and dodecanethiol at 220 °C for 4 mins. The CE reaction to form CZTSSe nanoparticles was carried out via addition of trioctylphosphine (TOP), ZnCl₂ and Sn(acac)₂Cl₂ into Cu_{2-x}Se_yS_{1-y} nanoparticles solution and allowed to react for 20 mins at 100 °C. In the report, diffusion of Zn²⁺ into Cu_{2-x}Se_yS_{1-y} nanoparticles was reported to be faster than Sn⁴⁺. The authors attributed this phenomena to the larger charge density of Sn⁴⁺ ions hampering their diffusion within the crystal matrix.

2.1.2 Progress in the field of CZTS phase characterization

As a quaternary sulfide compound, there is a high possibility of parasitic formation of secondary phases. These secondary phases includes binary (i.e. copper sulfide, zinc sulfide, tin sulfide) and ternary (copper-tin-sulfide) compounds. These binary phases have been reported to degrade the performance of PV cell. Copper sulfide (Cu-S) phase, which is highly conducting, results in short-circuiting of CZTS device.^{73,74} Tin sulfide (Sn-S, a n-type semiconductor of ~2.2 eV bandgap) phase, when present in significant amounts may result in a second diode formation with opposite polarity to CZTS.⁷⁵ This acts as a barrier for charge transport and reduces the PV cell fill factor. In addition, the presence of zinc sulfide (Zn-S) phase acts as an insulator in CZTS matrix, reducing electron-hole pair generation and conductivity of the absorber layer due to its large bandgap ~3.5 - 3.7 eV.^{76,77} Lastly, the formation of ternary phases such as copper-tin-sulfide (Cu-Sn-S), results in metallic characteristic in CZTS.⁷⁸ This ultimately enhances electron-hole pair recombination and lowers the open-circuit voltage (V_{OC}). X-ray diffraction (XRD) has been widely used as the main characterization tool to analyse material crystal structure and phase purity. There are currently two known crystal phases for CZTS; wurtzite and kesterite. The wurtzite crystal structure is generally accepted to follow *P6₃mc* wurtzite ZnS crystal structure, with the cation (Cu⁺, Sn⁴⁺ and Zn²⁺) randomly occupying Zn²⁺ site, and a unit cell parameter of $a=b=3.838$ Å and $c=6.338$ Å.²⁶ On the other hand, kesterite CZTS crystallizes with a *I-4* space group, and a unit cell parameter of $a=b=5.435$ Å and $c=10.843$ Å.²⁰

Figure 2.8 Diffractograms of $\text{Cu}_2\text{ZnSnS}_4$ films before and after annealing. (a) Diffractogram of a $\text{Cu}_2\text{ZnSnS}_4$ nanorod film, showing wurtzite $\text{Cu}_2\text{ZnSnS}_4$ reflexes. (b) Diffractogram of a $\text{Cu}_2\text{ZnSnS}_4$ nanorod film after annealing to 400 °C, showing kesterite $\text{Cu}_2\text{ZnSnS}_4$ reflexes. Reproduced with permission from Reference 79. Copyright 2014, Nature.

Mainz *et al*, presented a report on the XRD study of CZTS crystal transformation.⁷⁹ The as-synthesized metastable (wurtzite) CZTS nanocrystals shows a characteristic diffraction pattern of a hexagonal crystal structure with three main diffraction peaks at $\sim 27^\circ$, 28° and 30° of [100], [002] and [101] crystal planes respectively. Upon heating to 400 °C, wurtzite CZTS nanocrystals undergo a crystal phase change to kesterite crystal structure. The XRD pattern of kesterite CZTS shows a characteristic diffraction pattern of a zinc blende crystal structure. The diffractograms shows a main diffraction peak at $\sim 28^\circ$, a small peak at 33° , two secondary diffraction peaks at $\sim 47^\circ$ and $\sim 56^\circ$ from [112], [200], [220] and [312] lattice planes.

Table 2.2: Main XRD peaks and orientation planes for tetragonal and wurtzite CZTS, tetragonal and orthorhombic CTS and cubic-ZnS.

Wurtzite ²⁶ Cu ₂ ZnSnS ₄		Tetragonal ⁸⁰ Cu ₂ ZnSnS ₄		Orthorhombic ⁸¹ Cu ₃ SnS ₄		Tetragonal ⁸² Cu ₂ SnS ₃		Cubic-ZnS ⁸³	
2 Θ	hkl	2 Θ	h k l	2 Θ	hkl	2 Θ	hkl	2 Θ	hkl
26.70	1 0 0			27.04	2 1 0				
				27.68	0 2 0				
28.10	0 0 2	28.44	1 1 2	28.49	0 0 2	28.54	1 1 1	28.50	1 1 1
30.26	1 0 1			30.64	2 1 1				
				31.21	0 2 1				
		32.93	2 0 0						
		33.02	4 0 0	33.89	1 1 2	33.07	2 0 0	33.03	2 0 0
39.19	1 0 2			39.24	2 2 1				
47.32	1 1 0	47.33	2 0 4	47.39	4 0 0	47.47	2 2 0	47.40	2 2 0
51.23	1 0 3			51.82	2 1 3				
		56.09	3 1 2			56.32	3 1 1	56.24	3 1 1
		56.20	1 1 6						
		76.41	3 3 2			76.68	3 3 1	76.56	3 3 1

As CZTS is a quaternary sulfide compound, there is a possibility of the parasitic formation of ternary and binary sulfide phases. Based on the elemental make up of CZTS, the possible combination of secondary phases can consist of Cu_{2-x}S, ZnS, Sn_xS_y and Cu_xSnS_y phases. The formation of Cu_{2-x}S and Sn_xS_y phases can be easily differentiated from CZTS phase as they have different crystal structures and lattice spacings from all other possible phases. However the challenge lies on differentiating Cu_xSnS_y, ZnS phases from CZTS phase. As these phases possesses lattice planes of similar lattice spacings, they exhibit overlapping diffraction patterns with one another and with CZTS phase. As the difference in diffraction angle (2 Θ) is beyond the resolution limitation of XRD, these phases become indistinguishable from one another. As shown in **Table 2.2**, a comparison chart of the diffraction peaks of wurtzite CZTS, kesterite CZTS, orthorhombic Cu₃SnS₄, tetragonal Cu₂SnS₃ and cubic ZnS highlights the similarity in diffraction peaks of these five phases.

From **Table 2.2**, it can be seen that the phase identification of samples constituted by a phase mixture can be a difficult task if only the XRD technique is used. The use of High Resolution XRD technique combined with numerical methods, such as Rietveld refinement, can help, but it will always depend on the quality of the sample, namely the crystallinity, compactness and particle size. Therefore, XRD alone is not sufficient to resolve the different phases that may be present in the sample.

2.1.2.2 Raman characterization of CZTS

Figure 2.9 Raman spectra of a zinc/copper/tin thin film stack sulfurized at (A) $T_s = 500\text{ }^{\circ}\text{C}$ and (B,C) at $T_s = 400\text{ }^{\circ}\text{C}$. (B) and (C) show the Raman spectra of the film sulfurized at $T_s = 400\text{ }^{\circ}\text{C}$ at 2 different locations on the film. Raman spectra of copper/tin thin film stack sulfurized at (D, E) $T_s = 500\text{ }^{\circ}\text{C}$ and (F) $T_s = 400\text{ }^{\circ}\text{C}$. (D, E) show the Raman spectra of the film sulfurized at $T_s = 500\text{ }^{\circ}\text{C}$ at 2 different locations on the film. Reproduced with permission from Reference 9. Copyright 2011, AIP.

As discussed, during the formation of CZTS nanoparticles, there is a tendency for secondary phases to form. Some of the possible secondary phases, such as ZnS and CTS, have crystal structures similar to that of CZTS with nearly indistinguishable X-ray diffraction (XRD) patterns. This has made identification of the phases present in CZTS films difficult. Raman spectroscopy has been

demonstrated to possess the capability of distinguishing CZTS phase and other secondary phases that may form during CZTS formation.

Table 2.3. Summary of the Raman peaks location of the CZTS, ternary and binary phases.

Phase	Raman scattering peak (cm ⁻¹)	Ref
CZTS	289, 339, 350, 37	84-86
CTS (tetragonal)	297, 337, 352	9,82
CTS (cubic)	267, 303, 356	9,82
CTS (orthorhombic)	318	81
ZnS	275, 352	87
SnS	160, 190, 219	88,89
SnS ₂	314	89,90
Sn ₂ S ₃	32, 60, 307	89
CuS	475	91

Cheng *et al* demonstrated the capability of using Raman spectroscopy to distinguish between CZTS and other secondary phases that may form during CZTS formation.⁹ Figures 2.7a, b and c show the Raman spectra of CZTS film synthesized through sulfurization of layered stack of zinc/copper/tin. Raman spectra of CZTS film obtained at 500 °C (**Figure 2.9a**) shows the strongest peak at 338 cm⁻¹ and is accompanied by a wide shoulder that can be assigned to two weaker peaks at 358 and 372 cm⁻¹ as well as a weak peak observed at 288 cm⁻¹. Raman spectra from film sulfurized at 400 °C (**Figures 2.9b, c**) shows peaks corresponding to CZTS (288, 338 and 372 cm⁻¹) and secondary phase corresponding to CTS (298 and 322 cm⁻¹). **Figures 2.9d, e and f** show the Raman spectra of CTS synthesized through sulfurization of layered Cu/Sn stack. Raman spectra of CTS shows intense peaks at 298 and 356 cm⁻¹ which are expected from cubic Cu₂SnS₃ and peaks at 268, 318 and 375 cm⁻¹ are assigned to Cu₂Sn₃S₇. In addition, collective reports from the Raman spectroscopy study on binary and ternary chalcogenide materials have provided the database for the identification of secondary phases that are most likely to form during CZTS phase formation. They are summarized in **Table 2.3**. All materials have their own unique characteristic phonon modes. This uniqueness allows them to differentiate themselves from one another even if they have similar

crystal structures. Hence, Raman spectroscopy has been shown to be a useful complementary technique to identify the phases present.

2.1.3 Progress in the field of $\text{Cu}_2(\text{M})\text{SnS}_4$ (M=Fe, Co and Mn) research

Within the **I-II-IV-VI** class of quaternary compound, earth abundant $\text{Cu}_2(\text{M})\text{SnS}_4$ (M=Fe, Co and Mn) quaternary semiconductor compounds have received great attention as potential solar harvesting materials in recent years. This is due to their crystal structures' similarity to that of CZTS, suitable band gaps and high absorption coefficients.

Table 2.4 Chemical synthesis methods for quaternary metal chalcogenide nanocrystals.^a

Author	Compound	Chemical reagent	Method	Sample	Ref
Himmrich <i>et al</i>	$\text{Cu}_2\text{MnSnS}_4$ $\text{Cu}_2\text{FeSnS}_4$ $\text{Cu}_2\text{CoSnS}_4$ $\text{Cu}_2\text{ZnSnS}_4$	Elemental Cu, Mn, Fe, Co, Zn, Sn and S	Melt 700-900 °C	Large particles	84
Khadka <i>et al</i>	$\text{Cu}_2\text{Zn}_x\text{Fe}_{1-x}\text{SnS}_4$ ($0 \leq x \leq 1$)	CuCl_2 , FeCl_3 , ZnCl_2 , SnCl_4 , thiourea, elemental S	Spray pyrolysis 500 °C 25 mins	Thin film	92
Chen <i>et al</i>	$\text{Cu}_2\text{Zn}_x\text{Mn}_{1-x}\text{SnS}_4$ ($0 \leq x \leq 1$)	CuCl_2 , $\text{Mn}(\text{Oac})_2$, $\text{Zn}(\text{Oac})_2$, SnCl_2 , thiourea, 2-methoxy ethanol and acetyl acetone	Sol gel 580 °C 10 mins	Thin film	93
Prabhakar <i>et al</i>	$\text{Cu}_2\text{FeSnS}_4$	CuCl_2 , FeCl_3 , SnCl_2 , thiourea, deionized water	Spray pyrolysis 400-600 °C 30 mins	Thin film	94
Cui <i>et al</i>	$\text{Cu}_2\text{MnSnS}_4$ $\text{Cu}_2\text{FeSnS}_4$ $\text{Cu}_2\text{CoSnS}_4$ $\text{Cu}_2\text{NiSnS}_4$	CuCl , SnCl_2 , $\text{Co}(\text{NO})_3$, FeCl_2 , $\text{Ni}(\text{NO}_3)_2$, MnCl_2 , CS_2 , hexylamine and 3-mercaptopropionic acid	Solvothermal 180 °C 2 hrs	Nanoparticles	95
Zhang <i>et al</i>	$\text{Cu}_2\text{FeSnS}_4$	$\text{Cu}(\text{acac})_2$, $\text{Fe}(\text{acac})_3$, SnCl_2 , oleylamine and elemental S	Hot-injection 280 °C 1.5 hrs	Nanoparticles	96
Yan <i>et al</i>	$\text{Cu}_2\text{FeSnS}_4$	$\text{Cu}(\text{acac})_2$, $\text{Fe}(\text{acac})_3$, SnCl_4 , oleylamine, dodecanethiol and tert-dodecanethiol	Heating up method 210 °C 30 mins	Nanoparticles	97
Gillorin <i>et al</i>	$\text{Cu}_2\text{CoSnS}_4$	CuCl_2 , CoCl_2 , SnCl_4 , $\text{CS}(\text{NH}_2)_2$, ethanol, 25% tetramethylammonium hydroxide in methanol and ascorbic acid	Solvothermal 200 °C 16 hrs	Quantum dots	98
Liang <i>et al</i>	$\text{Cu}_2\text{MnSnS}_4$	$\text{Cu}(\text{Oac})_2$, SnCl_4 , $\text{Mn}(\text{Oac})_2$, oleylamine and elemental S	Hot-injection 270 °C 30 mins	Na nanoparticles	99

^a Oac: acetate ion, acac: acetylacetonate ion

2.1.3.1 Synthesis of $\text{Cu}_2(\text{M})\text{SnS}_4$ (M=Fe, Co and Mn) materials

Fig. 2.10 Low resolution and high resolution TEM and SAED images of zincblende and wurtzite Cu_2MSnS_4 (M = Co, Fe, Ni, Mn) nanocrystals. (a–c) $\text{Cu}_2\text{CoSnS}_4$; (d–f) $\text{Cu}_2\text{FeSnS}_4$; (g–i) $\text{Cu}_2\text{NiSnS}_4$; (j–l) $\text{Cu}_2\text{MnSnS}_4$ rods (aspect ratio 4.4); (m and n) $\text{Cu}_2\text{MnSnS}_4$ rods (aspect ratio 9.4). Reproduced with permission from Reference 95. Copyright 2012, Wiley.

Various fabrication methods used to synthesize CMTS materials are summarized in **Table 2.4**. In 1992, Himmrich *et al* reported synthesizing $\text{Cu}_2(\text{M})\text{SnS}_4$ (M=Mn, Zn, Fe and Co) using the melt approach.⁸⁴ In the report, stoichiometric mixtures of the elements were grounded carefully in a vibrational mill, pressed to pellets under a pressure of 10^8 Pa, sealed in evacuated silica glass ampoules, and tempered in tube furnaces at 700–900 °C. Recently, Lopez *et al* reported using similar method to synthesize $\text{Cu}_2\text{Mn}_x\text{Co}_{1-x}\text{SnS}_4$.¹⁰⁰ In the report, stoichiometric mixtures of the elements were mixed and sealed under Ar atmosphere in evacuated quartz ampoules and heated at 850 °C for 72 hrs. Chen *et al*, reported thin film fabrication of $\text{Cu}_2\text{Mn}_x\text{Zn}_{1-x}\text{SnS}_4$ solid solution via sol-gel

technique.⁹³ Stoichiometric amounts of CuCl_2 , $\text{Mn}(\text{CH}_3\text{COO})_2$, $\text{Zn}(\text{CH}_3\text{COO})_2$, SnCl_2 , thiourea, 2-methoxy ethanol and acetyl acetone were mixed homogenously to form the precursor solutions. The precursor solutions were spin-coated onto sodium lime glass for a few times to achieve desired thickness followed by annealing at 580°C for 10 mins under a N_2 atmosphere.

To date, there are only a few papers discussing the synthesis of $\text{Cu}_2(\text{M})\text{SnS}_4$ ($\text{M}=\text{Mn}, \text{Zn}, \text{Fe}$ and Co) nanoparticles. In 2012, Cui *et al* reported a general strategy for the synthesis of quaternary semiconductor $\text{Cu}_2(\text{M})\text{SnS}_4$ ($\text{M}=\text{Mn}, \text{Ni}, \text{Fe}$ and Co) using solvothermal method.⁹⁵ A typical reaction proceeded via dissolving stoichiometric amounts of CuCl , SnCl_2 , $\text{Co}(\text{NO}_3)_3$, FeCl_2 , $\text{Ni}(\text{NO}_3)_2$, MnCl_2 , CS_2 in hexylamine and 3-mercaptopropionic acid. The solution mixture was transferred to a Teflon-lined stainless steel autoclave and heated at 180°C for 2 hrs.

2.1.3.2 Crystal structure studies of $\text{Cu}_2(\text{M})\text{SnS}_4$ ($\text{M}=\text{Fe}, \text{Co}$ and Mn) materials

Figure 2.11 Crystal structure of (a) stannite $\text{Cu}_2\text{FeSnS}_4$ and (b) Kesterite $\text{Cu}_2\text{ZnSnS}_4$. Reproduced with permission from Reference 92. Copyright 2014, American Chemical Society.

$\text{Cu}_2\text{FeSnS}_4$ (CFTS) quaternary compound is a naturally occurring mineral. It crystallizes in a stannite crystal structure with a space group of $I2m$. The difference between kesterite CZTS and stannite CFTS lies in the ordering of cations in the tetragonal sublattices. In the stannite structure, Fe atom occupies the origin

2a (0,0,0) and Cu occupies the 4d (0,1/2,1/4) site. However, in the kesterite structure, Cu atoms are located at both 2a (0,0,0) and 2c (0,1/2,1/4) sites and Zn occupies the 2d (0,1/2,3/4) site. Sn resides at 2b (0,0,1/2) in both structures while the anion S lies on the (110) mirror plane at 8i (x,y,z) for stannite and 8g (x,y,z) for kesterite as illustrated in **Figure 2.11**.⁹²

Figure 2.12 XRD patterns (a,b) and Raman spectra (c,d) of as-sprayed and postsulfurized $\text{Cu}_2\text{Fe}_x\text{Zn}_{1-x}\text{SnS}_4$ ($0 \leq x \leq 1$) films. Reproduced with permission from Reference 92. Copyright 2014, American Chemical Society.

In 2014, the effect of replacing Zn with Fe on optical properties and band gap tuning was reported by Khadka *et al.*⁹² In their report, it was observed that for all values of x ($0 \leq x \leq 1$) in $\text{Cu}_2\text{Fe}_x\text{Zn}_{1-x}\text{SnS}_4$, the absorption coefficients were measured to be above $1 \times 10^4 \text{ cm}^{-1}$ in the visible range, while the bandgap changed from $\sim 1.46 \text{ eV}$ ($x = 0$) to $\sim 1.36 \text{ eV}$ ($x = 1$). In addition, XRD and Raman characterizations are summarized in **Figure 2.12**. It was reported that there was a crystal phase change from kesterite to stannite when $x \geq 0.4$. Raman study showed that CFTS phase has a main peak at 318 cm^{-1} which redshifted with increasing

amount of Zn^{2+} composition to 338 cm^{-1} . In the same year, Prabhakar *et al* reported using CFTS as the photocathode in a dye-sensitized solar cell achieving an encouraging efficiency of 8.03%.⁹⁴ All these reports highlight the potential of $\text{Cu}_2\text{Fe}_x\text{Zn}_{1-x}\text{SnS}_4$ as a good solar harvesting material.

In 2012, Lopez *et al* presented a report on the crystal structure studies of $\text{Cu}_2\text{Mn}_{1-x}\text{Co}_x\text{SnS}_4$ ($0 \leq x \leq 1$) solid solutions.¹⁰⁰ Both $x=0$ $\text{Cu}_2\text{MnSnS}_4$ (CMTS) and $x=1$ $\text{Cu}_2\text{CoSnS}_4$ (CCTS) are found to crystallize in the space group $I2m$ (stannite). On the other hand, for materials ($0.25 \leq x \leq 0.75$), the $\text{Cu}_2\text{Mn}_{1-x}\text{Co}_x\text{SnS}_4$ solid solutions crystallize in the space group I (kesterite). The XRD and Raman characterizations are summarized in **Figure 2.13**. The Raman spectroscopy characterization of CCTS shows a main peak at 324 cm^{-1} and it red shifted with increasing Mn^{2+} composition to give 329 cm^{-1} (CMTS).

Figure 2.13 XRD diffraction pattern for $\text{Cu}_2\text{Mn}_x\text{Zn}_{1-x}\text{SnS}_4$ ($0 \leq x \leq 1$) compounds. Reproduced with permission from Reference 100. Copyright 2013, American Chemical Society.

2.2 Questions arising from the growth mechanism of $\text{Cu}_2(\text{M})\text{SnS}_4$ ($\text{M} = \text{Zn}, \text{Mn}, \text{Co}, \text{Fe}$) nanoparticles

Firstly, there have been few reports describing the growth mechanism of CZTS nanoparticles. Commonly, the growth mechanism is reported to proceed via the nucleation of a binary Cu_{2-x}S phase followed by the formation of a ternary intermediate phase and finally the formation of quaternary $\text{Cu}_2\text{ZnSnS}_4$ phase. However, the ternary intermediate phase has been reported by some groups to be a ternary Cu-Sn-S phase while some other groups reported it to be a ternary Cu-Zn-

S phase instead. This discrepancy shows the need to resolve the growth mechanism of CZTS, so as to improve the synthesis approach and control the purity of CZTS nanomaterials.

Secondly, there have been a strong interest in $\text{Cu}_2(\text{M})\text{SnS}_4$ materials due to their magnetic properties, potential solar harvesting capability and catalytic properties. However, there have been few reports on the formation mechanism of $\text{Cu}_2(\text{M})\text{SnS}_4$ (M= Mn, Co, Fe) nanoparticles. The formation of CMTS, CCTS and CFTS are thought to be more challenging than CZTS due to the possibility of forming ternary thiospinel (e.g CuFeS_2 , CuCoS_2 , CuMnS_2) secondary phases. Therefore, there is a need to identify the preferential growth pathway and growth kinetics of these materials so as to increase the purity of as-synthesized materials.

2.3 Question arising from the characterization accuracy of $\text{Cu}_2(\text{M})\text{SnS}_4$ (M= Zn, Mn, Co, Fe) nanoparticles

The ability to differentiate secondary phases from the main phase is crucial as it increases the accuracy of material purity characterization. Secondary phases may contribute to unwanted characteristics such as decrease in charge carrier lifetime, increase in resistivity or even cause short circuitry in fabricated devices. However, conventional Raman spectroscopy is unsuitable for nanoparticles characterization and XRD is unable to differentiate materials with the same crystal structure and similar lattice parameters. Hence, a new characterization technique with high sensitivity and capability of differentiating the various phases from one another is required.

2.4 PhD in context of literature

Synthesis and characterization of quaternary semiconductor $\text{Cu}_2(\text{M})\text{SnS}_4$ (M=Zn, Fe, Mn, Co) nanoparticles are considered in this thesis. Designated objectives to fulfil the first phase of the study involves introduction of SERS spectroscopy, enthroned with higher detection limit over regular Raman spectroscopy for unambiguous compositional phase characterization technique of nanoparticles. This is followed by ex-situ study on temporal changes during CZTS

nanoparticles phase formation to pinpoint purity-limiting reaction steps and establishment of guidelines for the formation of pure single-phase CZTS nanoparticles. Next, the compatibility evaluation of established guidelines from CZTS nanoparticles formation on synthesis of $\text{Cu}_2(\text{M})\text{SnS}_4$ (M=Fe, Mn, Ni, Co) nanoparticles is verified to identify peculiar reaction mechanism in formation of $\text{Cu}_2(\text{M})\text{SnS}_4$ derivatives. Lastly, we aim to establish a general synthetic protocol that allows i) the formation of phase pure $\text{Cu}_2(\text{M})\text{SnS}_4$ nanomaterials and ii) ex-situ monitoring of reaction progress while allowing adjustment (e.g addition of chemicals) to the reaction mixture to avoid secondary phases formation.

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Chapter 3

Experimental Methodology

In this chapter, the rationale, the synthesis methods and the characterization and analysis techniques are presented. In the rationale section, the key reasons behind the selection of chemical precursors, synthetic protocols, characterization techniques used and data analysis methods are elaborated. Next, in the synthesis section, the formation mechanism of nanoparticles via heating-up method are presented. Following this, in the characterization section, the working principles of instrument used and the analysis techniques are elaborated. Finally, the principles behind the simulation (VASP) are discussed.

3.1 Rationale for selection of materials and methods

3.1.1 Materials

3.1.1.1 Solvents

Based on recent reports on the formation of CZTS nanoparticles, the temperature required to carry out the reaction is in the range of 230-250 °C.^{1,2} Therefore when choosing chemical precursors, there are a few points to take note of which listed as follows: (i) *Solvent*: The boiling point of the solvent used must be higher than 250 °C so as to be able to attain the required temperature for reaction. Therefore octadecene, a long chain hydrocarbon alkene, with a boiling point of 315 °C was used as the solvent. (ii) *Capping agent*: Reaction at 250 °C provides a lot of thermal energy, therefore the selected capping agent used to stabilize the nanoparticles during growth must be thermally stable at 250 °C. Based on the requirements of high boiling point and good thermal stability at 250 °C, oleylamine and dodecanethiol were chosen as the capping agents. Oleylamine is an unsaturated fatty amine with a high boiling point of 364 °C, while dodecanethiol is a saturated fatty thiol with a boiling point of 266 °C.

3.1.1.2 Cation precursors

Metallo-organics precursors such as zinc acetate, copper acetate and tin acetate are used as cation sources to synthesize CZTS nanoparticles. There are a few advantages of using metallo-organic precursors over inorganic salts (e.g Zn(X) (X=Cl⁻, Br⁻, NO₃⁻, SO₄²⁻) and a few are listed as follows. (i) *Absence of halide ions* (e.g Cl⁻, Br⁻): This is to avoid possible incorporation of unwanted elements into CZTS nanoparticles.³ (ii) *Side reaction*: Recently, copper nitrate salts has been reported to form copper nitride (Cu₃N) nanoparticles, while metal sulfates (M(SO₄)) have been reported to form metal sulfide, oxide compounds M(S,O).⁴ On the other hand, there are no known side reactions arising from metallo-organic precursors. (iii) *Reactivity of cations*: A metallo-organic precursor is a metal-ligand complex, consisting of a metal ion center bonded to anionic organic ligands. The anionic organic ligands counter balance the charge of the metal ions and at the same time affect the reactivity of the metal ions.^{5,6} The reactivity of the metal ion is affected

by the stability of the metal-ligand complex, which is determined by the type of ligand binding to it, and an example of metal-ligand complex that is more stable than copper acetate is copper acetylacetonate.⁷ By controlling the reactivity of the metal ion, one can influence the reaction kinetics, therefore allowing one to carry out kinetics study on the formation of CZTS nanoparticles.

3.1.2 Methods

3.1.2.1 Synthetic approaches

The heating-up approach is used as the main synthesis method in this dissertation. Inherent within this method are a number of advantages and they are listed as follows.⁸ (i) *Homogenous mixing*: Chemical reagents (metal precursors and capping agents) are mixed together in the solvent while heated to an elevated temperature allowing homogenous mixing of precursors. This homogenous mixing at elevated temperature allows elimination of volatile compounds (e.g water) under vacuum, which may otherwise disrupt the growth of the nanoparticles. In addition, this allows the precursors to be heated evenly, achieving a more homogenous reaction later on. (ii) *Reproducibility*: After the precursors are pre-mixed with mild heating, the temperature is increased to provide the reaction with sufficient energy for the reaction to start. These specific sequences minimize random errors as a result of human involvements. An example of a human involvement that contributes to high error margin is the need to add a fixed amount of chemicals at a fixed temperature, which is a step required in the hot-injection method. (iii) *Scalability*: The scale of the reaction is limited by the effective heat transfer in the reaction mixture to ensure homogenous reaction. Therefore, the scale of nanoparticles reaction can be much larger as compared to other synthetic methods.

3.1.2.2 Electron microscopy (EM)

The synthesized nanomaterials are less than 100 nm in size, therefore EM is required to visualize the morphologies and crystal lattices of the nanomaterials.⁹ Due to the usage of electron beams as the characterization probe, the resolution limit of EM can be as small as 0.5 Å.¹⁰ There are two commonly used EM

techniques, namely transmission electron microscopy (TEM) and scanning electron microscopy (SEM).

TEM is capable of imaging nanoparticles based on phase contrast and Z-contrast. Phase contrast TEM imaging visualizes materials based on the *i*) density of the unit cell of the phases present and *ii*) thickness of the nanoparticles.¹¹ Phase contrast TEM images can provide structural information of the nanoparticles morphologies (e.g circular, cubic) and coating of materials (e.g Au/SiO₂ core/shell structure). Next, Z-contrast TEM imaging visualizes materials based on atomic number (Z number). Two different materials with different average Z number will appear differently in the same focus plane.¹² The materials with a higher Z number will appear brighter as compare to the materials with lower Z number (e.g Au atoms will be brighter than Zn atoms).¹³ Lastly, EM is capable of providing high resolution (HR) imaging. Due to constructive interference of the electron beam with the crystal zone axis, an ordered pattern (lattice image) can be generated on the detector which corresponds to the crystal symmetry of the zone axis in the focus plane. Using this information and simulated HRTEM image, one can identify the zone axis of the nanoparticle.

Next, scanning electron microscopy (SEM) is commonly used to provide information on the surface of thin film samples.¹⁴ Due to the detection of secondary electrons to produce an image, a secondary electron image (SEI) provides three dimensional information on a two dimensional image. The corners and edges of the sample will appear brighter than the flat surface therefore providing an “outline” contrast, hence the 3D effect. SEI images can tell one the sample thickness, crystal size, visual compactness of crystals and even spatial location of materials on substrates.

3.1.2.3 Energy dispersive X-ray (EDX) spectroscopy

EDX spectroscopy identifies elements present and their atomic weight percentage in the sample.¹⁵ When an incident electron beam ejects an electron from the inner shell of an element, the filling up of the electron vacancy in the inner shell by an electron from an outer shell releases energy in the form of an X-ray. As each

element has a unique set of electrons in their atomic orbitals, these causes each element to have their own unique X-ray emission spectrum. The intensity of the X-ray measured can be quantified, therefore information on elemental distribution across the sample to check for homogeneity and the stoichiometry ratio of elements in the synthesized material can be provided.

3.1.2.4 Powder X-ray diffraction (XRD)

When a sample is irradiated with X-rays, the X-rays are scattered by the periodic long-range array of atoms.¹⁶ The scattering of X-rays produced a diffraction patterns that contains information about the atomic arrangement (crystal structure) and the lattice parameters of the material. Analysis of XRD spectrum (diffractogram) provides information on the crystalline content, identification of crystal structure and the composition percentage of each material phase.

3.1.2.5 Surface enhanced Raman scattering (SERS) spectroscopy

In SERS spectroscopy, Raman scattering is enhanced due to the redistribution of electromagnetic field around the SERS substrate (noble metal such as Ag and Au).¹⁷ This results in localized regions of strong electromagnetic field, allowing coupling of intense electromagnetic fields with the molecule/particle of interest. The electromagnetic field increases the intensity of incident light, providing more photons for excitation of Raman modes, therefore increasing the intensity of Raman scattering. The Raman signal is further magnified when dipole moment of the molecule/particle vibration mode couples with the oscillating electromagnetic field, leading to a greater increase in the intensity of Raman scattering. These enhancements allow low detection limit of molecular concentration and reduces ambiguity in identification of molecules.

3.2 Principle behind synthesis approach

3.2.1 Heating-up method

The fundamental concept of forming nanoparticles via heating-up methods can be summarized as follows:⁸ Firstly, the chemical precursors are mixed

homogeneously and heated up to ensure complete dissolution of precursors in the reaction apparatus. Next, when the reaction is heated up further, the increase in thermal energy converts the precursors to reactive species. As the temperature increases further, the increasing thermal energy will eventually triggers the nucleation of nascent crystallites. Lastly, when the temperature is kept at the designated reaction temperature, the nuclei will grow into mature nanocrystals. To explain the principles behind these reaction mechanism, an overview of the time dependent profiles of the key reaction parameters for a simulated heat-up synthesis is shown in (**Figure 3.1**)

Figure 3.1 Simulated evolution of the prominent reaction parameters during the heating of a precursor solution during a typical heat-up synthesis. The temperature is ramped at 23 K min⁻¹ up to 523 K for the first half of the simulation and then maintained at this temperature for the duration of the simulation. Reproduced with permission from Reference 8. Copyright 2015, American Chemical Society.

Stage 1: Formation of reactive species. This stage refers to the reaction of chemical precursor to form reactive species as the temperature increases. The chemical precursors is define at (P), whose reactivity is dependent on the stability of the metal-ligand complex. The rate of formation of reactive species (M) from the precursors is denoted as k_f and the reactive species formation reaction can be expressed as equation (3.1)¹⁸

$$\text{Rate equation: } \frac{d[M]}{dt} = -\frac{d[P]}{dt} = A \cdot [P] \cdot e^{\left\{\frac{-E_a}{RT_v}\right\}} \quad (3.2)$$

Equation (3.2) relates the rate of reaction to the Arrhenius equation. A is the prefactor, E_a is the activation energy for the precursors decomposition or disassociation, and T_v is the temperature of the solution within the reaction vessel.

Stage 2: Nucleation. LaMer was the first to propose a classic precipitation reaction in a closed system.¹⁹ The reaction starts with the formation of free reactive species [M] from the chemical precursors used. As the temperature increases, the thermal energy increases the conversion of precursors to reactive species, nucleation than occurs when the [M] is raised above the critical (nucleation) concentration $[M_c]$ known as supersaturation point. The rate of nucleation $\left(\frac{dN}{dt}\right)$, climbs from an infinitesimal rate to a maximum. In addition, there will be a drastic increase in nuclei concentration ($[NCs]$) and a moderate growth of the nuclei (mean radii) above the size of the reactive species, with the standard deviation (SD) of the particle size distribution (PSD) reaching its maximum. The rapid broadening of the PSD is caused by the disparity between the size of the growing nuclei and the formation of new (smaller) nuclei. As the reactive species are used up during the formation of nuclei, the concentration of reactive species [M] eventually drops below $[M_c]$ and nucleation ceases.

Stage 3: Growth. The stage is defined by a decrease in the rate of nucleation $\left(\frac{dN}{dt}\right)$ as the supersaturation has reached its maximum and begins to decline due to the rapid growth of the existing nuclei. For the newly formed nuclei having a radius (a), [M] is still well above its equilibrium reactive species concentration, $[M_a]$ (concentration of reactive species required to prevent the dissolution of particles with $r \geq a$), upon the cessation of nucleation.²⁰ As such, all particles with $r > a$ will grow through the accretion of reactive species. Although [M] is still well above

$[M_{\infty}]$ (the concentration of reactive species in equilibrium with a flat surface), as reactive species is consumed throughout the reaction, $[M]$ eventually drops below $[M_a]$ and coarsening (Ostwald ripening) follows.²¹ In this case all particles with $r < a$ dissolve in order to support the growth of larger particles. As a consequence favorable growth dynamics, the particle size distribution then narrows as the average nanocrystals size reaches its maximum.

Stage 4: Equilibrium. This stage is defined by the depletion of the remaining precursor and while the average size and particle size distribution and the concentration of the nanocrystals remain constant. At this point the reaction would typically be cooled and the NCs isolated and purified.

3.2.2 Cationic exchange

The fundamental concept of cationic exchange (CE) involves the substitution of cations in an extended solid with those in the solution. Necessary factors for a successful CE reaction are that the thermo-stability of the products are higher than those of the reactants, and that the kinetics of ionic exchange are energetically favourable on the solid surface and in the extended solid.²²

The synthetic feasibility of a cation exchange reaction is determined by its net thermodynamic driving force and intervening activation barriers. An example to illustrate the thermodynamics involved is illustrate as the following:

Overall reaction:

A and B are representative of divalent cations while S is the counter divalent anion. By rewriting this overall reaction equation into two electrochemical half reaction equations (3.4, 3.5)

Half reaction equation:

Standard free energy of formation (ΔG_f^0) compound:

Standard reduction potential (E^0) of the element:

Each of these equations (3.4, 3.5) can be further decomposed into the corresponding standard free energy of formation (ΔG_f^0) of each phase (3.6, 3.7) and the standard reduction potential (E^0) of the metal ion in the electrochemical half reactions (3.8, 3.9). Thus, the overall free energy of the reaction can be written as (3.10):

Overall free energy of the reaction:

$$\Delta G_{reaction} = (\Delta G_f^0)_{BS} - (\Delta G_f^0)_{AS} - 2F[(E^0)_{B^{2+}} - (E^0)_{A^{2+}}] \quad (3.10)$$

where F is Faraday's constant. A quantitative measure of the favorability of a given reaction is the difference in Gibbs free energy (ΔG). In a reaction with sufficient activation energy, when the calculated energetics of the process indicate that ΔG is negative, it means that the reaction will be spontaneous.^{23,24} By contrast, if conditions indicated a positive ΔG , then energy, usually in the form of heat or electricity, would have to be added to the reacting system for the reaction to occur.

3.3 Principle behind characterization tools and techniques

3.3.1 Powder X-ray diffraction (XRD)

Powder XRD is commonly used to study the degree of crystallinity, identify the crystalline phases, the lattice spacing of the unit cell and the amount of the phases that are present in a material. There are four major components of a XRD machine, (i) X-ray source, (ii) sample holder, (iii) goniometer and (iv) detector. Measurement is carried out by irradiating the sample (crystal) with X-ray.^{16,25} When the X-rays hit the sample (crystal), the X-rays are deflected at specific angles characteristic to the crystal structure of its unit cell. The detector then moves along the goniometer measuring the intensity of the deflected X-rays across a range of degree (°). The intensity measured is plot against the angle of the detector giving rise to a diffraction pattern plot (diffractogram). The diffractogram allows one to interpret the crystal structure of the material via Bragg's Law²⁶

$$2d\sin\Theta = n\lambda \quad (3.11)$$

where d is the lattice spacing of the crystal plane present in the crystal unit cell, Θ is the angle measured by the detector, n is an integer and λ is the wavelength of the X-ray.

Figure 3.2 Pictorial illustration of path taken by deflected X-ray.

As shown in **Figure 3.2** the incoming beam (coming from X-ray source) hits the sample and gets deflected by the atoms (black dots) in the crystal lattice. The angle (Θ) of deflection follows the incident angle (angle between the X-ray source and the lattice plane of the atoms deflecting the X-ray beam).²⁷ For a

crystalline sample, the X-ray waves that are deflected by the lattice planes are separated by a lattice spacing (d). When the deflected waves exiting the crystal interfere constructively, they remain in phase, therefore the difference in the path length of each wave through each lattice planes is a multiple integer of the wavelength ($n\lambda$). The difference in the distance between waves that gets deflected along AC' and the wave that gets transmitted (AB) through the lattice plane and deflected along BC is as follows:

$$f(x) = (AB + BC) - (AC') \quad (3.12)$$

When the waves undergoes constructive interference and the path difference is any integer multiplication of the wavelength than the equation follows:

$$(AB + BC) - (AC') = n\lambda \quad (3.13)$$

Since,

$$AB = BC = \frac{d}{\sin\theta} \text{ and } AC = \frac{2d}{\tan\theta} \quad (3.14)$$

Therefore,

$$AC' = AC \cdot \cos\theta = \frac{2d}{\tan\theta} \cos\theta = \frac{2d}{\sin\theta} \cos^2\theta \quad (3.15)$$

Substituting (3.14 and 3.15) back into (3.13),

$$\left(\frac{d}{\sin\theta} + \frac{d}{\sin\theta} \right) - \left(\frac{2d}{\sin\theta} \cos^2\theta \right) = n\lambda$$

$$\left(\frac{2d}{\sin\theta} \right) - \left(\frac{2d}{\sin\theta} \cos^2\theta \right) = n\lambda$$

$$\left(\frac{2d}{\sin\theta} \right) (1 - \cos^2\theta) = n\lambda$$

$$\left(\frac{2d}{\sin\theta} \right) (\sin^2\theta) = n\lambda$$

$$2d\sin\theta = n\lambda$$

Figure 3.4 Illustration of X-ray diffraction occurring in the crystal lattice of 2 crystal samples of different lattice spacing.

As the angles between the X-ray beam and different lattice planes in the crystal structure are different, and different crystal structure have their unique set of lattice planes, this gives every crystal structure their characteristic set of diffraction patterns.²⁸ In addition, the lattice spacing is affected by the size the element present (e.g a gold atom is bigger than a copper atom), a larger lattice spacing will have a slightly smaller diffraction angle since $\sin\Theta = \frac{\lambda}{2d}$ (**Figure 3.4**).

3.3.2 Electron Microscopy (EM)

The maximum theoretical resolution of any microscopy is half of the wavelength $\left(\frac{\lambda}{2}\right)$ of the probe (e.g visible light, X-ray, electron beam).²⁹ As shown in Figure 3.5, the highest resolution (differentiation 2 points apart) for a human eye is $\sim 100 \mu\text{m}$, while for a light microscope it is $\sim 100 \text{ nm}$ and an electron microscope it is $\sim 1 \text{ \AA}$.³⁰ Therefore, to visualize materials at the nanometer (nm) length scale, an electron microscope is required (**Figure 3.5**).

Figure 3.5. A resolution comparison between human eye, light microscope and electron microscope. Copyright. 2012. University of Waikato. All Rights Reserved.

A general layout of an electron microscope consists of,^{31,32} (i) *electron gun*. An electron gun is a device capable of producing electrons beam to be used for the probing of materials. Electron guns used in electron microscope include tungsten hairpin, LaB₆, field emission and Schottky guns.^{33,34} (ii) *Thick metallic casing*. As electrons are used as the probe for imaging, an electron microscope has to operate under vacuum due to the short penetration depth of electrons. A thick metallic casing to house the electron microscope is to provide structural integrity as the pressure in the internal chamber is very low. (iii) *Electromagnet*. The glass lenses used in light microscopes to focus light beams on sample are not compatible with electron beams.¹⁰ Due to the shallow penetrating depth of electrons, a glass lens will block all electrons from coming into contact with the samples. To focus an electron beam, electromagnets are required to act as lenses to converge the electron beams. By using electromagnets, magnetic fields are generated, which interact with the electron beams, and by regulating the electric current in the electromagnet, the strength of the magnetic field can be tuned to align the electron beam to bring the sample to focus. (iv) *Detectors*. There are several types of detectors in an electron microscope which give different information of the samples. Examples of detectors used in electron microscope include a Everhart-Thornley detector to detect secondary electrons, which is also known as a secondary electron imaging detector (SEI detector), backscattered electron (BSE) detectors to detect electrons emitted at high angle, and for energy-dispersive X-ray (EDX) spectroscopy for elemental

analysis (**Figure 3.6**).³⁵ (v) *Sample holder*. A conductive sample holder is required to prevent electrons from accumulating on the samples during electron beam irradiation. In addition, there is a difference in the holder used in transmission electron microscope (TEM) and scanning electron microscope (SEM). The holder of a TEM has a window in the center to allow electrons to transmit while the holder of a SEM has a continuous surface.

Figure 3.6 Electron beam interactions with electrons in the elements. The inner electron shells of atoms are labelled according to standard notation (the innermost states are K, L etc). a) Low-angle scattering - electrons scattered in this way pass to the next layer of atoms with very little loss of energy, b) back (or high-angle) scattering, c) emission of a secondary electron and characteristic x-rays and d) emission of an Auger electron.

3.3.2.1 Scanning Electron Microscopy (SEM)

Scanning electron microscope (SEM) probes the surface of the sample using an electron beam.³⁶ It is usually used to characterize the surface of materials, and information obtainable includes:³⁷

(i) *Surface Topography*. When an electron from the electron beam interacts with the electron cloud surrounding the atom in the sample, there is a possibility of ejecting an electron from the K-shell of the atom (**Figure 3.6**). The ejected electron

(secondary electron) possesses low-energy and the image arising from this is called the secondary electrons image (SEI). The secondary electrons are collected by the SEI detector and the information is processed to give a two-dimensional image. The brightness contrast (intensity of a pixel) of the image depends on the amount of secondary electrons ejected from the region and reaching the detectors. The intensity of secondary electrons ejected depends largely on, (i) *the probe's incident angle on the sample surface*. The higher the angle, the higher the intensity. (ii) *The direction of the surface*. Surfaces facing the detector will have a higher counts of secondary electrons. Therefore, by scanning the sample with the electron beam, a two dimensional intensity contrast map is generated by measuring the secondary electron intensity across the area. Due to the different in the intensity on the edges, sides and corners, the two dimensional map have a three-dimensional appearance hence providing the topography information of a sample surface.

(ii) *Compositional difference*. When an electron from the electron beam approaches the nucleus of an atom, there is a possibility of the electron being scattered at a large angle and re-emerging from the sample surface. The high angle scattered electrons (backscattered electrons) possess higher energy than secondary electrons and the image arising from this is called the backscattered electrons image (BSE). When the e-beam penetrates a sample, the energy spreads in a cone-shaped pattern. As the BSE signal originates from deeper in the sample, the area contributing to the signal is larger than the electron beam size, hence resulting in a lower resolution than SEI. In addition, the possibility of backscattering electrons increases with the atomic number. Therefore, heavier elements will have a higher backscattered electrons count, hence appearing stronger in intensity. This provides compositional information to differentiate multiple compositional phases in a sample. An example is differentiating Cu_{2-x}S from Cu_2SnS_3 , where Cu_2SnS_3 has a higher average Z number, therefore regions in the sample at which are Cu_2SnS_3 rich will appear brighter under BSE imaging.

3.3.2.2 Transmission Electron Microscopy (TEM) / Scanning Transmission Electron Microscope (STEM)

TEM and STEM generally operates at a high acceleration voltage of 80-300 keV.³⁵ Due to the high acceleration voltage, TEM and STEM are capable of atomic resolution imaging. This is due to the fact that an electron wavelength is defined by the de Broglie wavelength equation^{38,39}

$$\lambda = \frac{h}{mv} \quad (3.15)$$

where λ is the wavelength, h is the planck constant, m is the mass of the particle and v is the velocity of the particle. Hence, the wavelength of electron decreases with increasing acceleration voltage as velocity of electron increases. The different between TEM and STEM is that conventional TEM uses a wide-spread parallel electron beam as the probe while STEM uses a highly converged electron beam as the probe.

The classical phase contrast model is used to explain the principle behind the imaging using TEM and STEM.^{30,40,41} When the electron beam is shone on the sample, electrons penetrate the sample and interact with the nuclei of the atoms. An electron is attracted by a nucleus via Coulombic interaction, and the path of the electron is deflected towards the core. The force of the deflection is defined by the Coulombic force and defined as⁴²

$$F_1 = \frac{q_1 q_2}{4\pi\epsilon_0} \cdot \frac{(r_1 - r_2)}{|r_1 - r_2|^3} \quad (3.16)$$

where $(r_1 - r_2)$ is the distance between the nucleus and the electron, $|r_1 - r_2|^3$ is the unit vector, ϵ_0 is the dielectric constant and q_1 is the charge at position r_1 and q_2 is the charge at position r_2 . The closer the distance between the electron and nucleus (smaller Δr), the larger the Coulombic force (F) and the greater the scattering angle will be. Various imaging modes in conventional TEM and STEM can be summarized as:

Figure 3.7 Pictorial illustration of how objective aperture is used to obtain a) bright field, b) dark field and c) high resolution images. Copyright *ETH* Zürich (Source: <http://www.microscopy.ethz.ch/elmi-home.htm>).

(i) *Conventional TEM.* Conventional TEM is commonly used to obtain bright field (BF), dark field (DF) and high resolution (HR) images and a pictorial illustration of how such images are obtained is shown in **Figure 3.7**.

Firstly, in BF imaging mode, the magnetic lenses focuses the back focal plane such that it falls on the objective aperture.^{43,44} The objective aperture is a piece of metal foil containing numerous windows opening with various sizes. It is used to control the amount of electrons and selectively permit a specific area of electrons to be transmitted from the sample to the detectors. In BF imaging, the direct electron beam (electron beam along optic axis) is allowed to pass through. BF images have a bright background (high electron counts from direct electron beam) and the sample appears darker (low electron count) due to the scattering of electrons when they interact with the sample. Therefore, in BF imaging, mass-thickness and atomic number contribute to the image formation. Regions in the samples with heavy atoms or which are thicker have higher populations of electrons getting scattered therefore the rate of electrons (electron counts per second) reaching the detector is lesser hence giving a darker contrast. Hence giving BF

images the characteristic contrast of having a bright background with sample appearing dark.

Next, in DF imaging mode, the opening in the objective aperture is shifted away from the direct electron beam.⁴¹ The objective aperture only allows diffracted beams to pass through. As the detector is not receiving any direct electron beam counts, the background of DF images are black and since the diffracted electrons originates from the sample, the sample signal from the samples will have a higher electron counts per second therefore appearing brighter. Hence giving DF image the characteristic contrast of having a black background with sample appearing brighter.

Lastly, to obtain a lattice image (high resolution) of the crystalline sample, a large objective aperture (large window opening) has to be used to allow multiple beam, including direct electron beam, to pass through. The image is formed by the interference of the diffracted beams with the direct beam. During measurement, electron beam must be aligned parallel to the zone axis of the crystalline sample. This is because HRTEM mode measures the intensity of a complex exit wave (wave function of the electron exiting the sample) generated by a sample at a given focal plane, which arises from the interference of the wave function in the focal plane. An electron exit wave from the focal plane can be expressed as^{45,46}

$$\psi_0(\vec{r}) = a(\vec{r}) \cdot e^{[i \cdot \phi(\vec{r})]} \quad (3.17)$$

where $a(\vec{r})$ and $\phi(\vec{r})$ are the wave amplitude and phase respectively and $(\vec{r})$ represents the spatial coordinate. The propagation of $\psi_0(\vec{r})$ to an observation plane in the small angle scattering limit can be calculated in real space using a convolution operation with a Fresnel diffraction operator. The exit wave then passes through the imaging system where it propagates to the image wave. The relationship between exit wave and image wave can be described by the contrast transfer function

$$\text{CTF}(u) = A(u) \cdot E(u) \cdot \sin[\chi(u)] \quad (3.18)$$

where $A(u)$ is the *aperture function*, $E(u)$ describes the attenuation of the wave for higher spatial frequency u , is called the *envelope function*. $\chi(u)$ is a function of the aberrations of the electron optical system. The sinusoidal term of the CTF determines the sign with which components of frequency u will contribute to the contrast in the final image. If one takes into account only spherical aberration to third order and defocus, χ is rotationally symmetric about the optical axis of the microscope and thus only depends on the modulus $u = |u|$, given by

$$\chi(u) = \left(\frac{\pi}{2} \cdot C_s \cdot \lambda^3 \cdot u^4\right) - (\pi \cdot \Delta f \cdot \lambda \cdot u^2) \quad (3.19)$$

where C_s is the spherical aberration coefficient, λ is the electron wavelength, and Δf is the defocus value. In TEM, defocus can easily be controlled and measured to high precision. Thus one can easily alter the shape of the CTF by defocusing the sample. Contrary to optical applications, defocusing can actually increase the precision and interpretability of the micrographs. Hence, the recorded image is NOT a direct representation of the sample's crystallographic structure, therefore requiring HRTEM simulation to support the claim.⁴⁶

Figure 3.8 Pictorial illustration of the detectors present in the TEM as seen along a) cross-section and b) 3-dimension.

(ii) *STEM*. There are commonly three detectors used during STEM imaging. Bright field (BF) detector used for BF-STEM imaging is placed at the same site as

the aperture in BF-TEM, while annular dark field (ADF) detector for ADF-STEM imaging is a disk with a hole in its center where the BF detector is installed (**Figure 3.8**). Lastly, high angular annular dark field (HAADF) detector for HAADF-STEM imaging is also a disk with a hole, but the disk diameter and the hole are much larger than in the ADF detector is situated in between ADF and the sample.

Firstly, the principle behind BF-STEM imaging is the same as BF-TEM imaging where the detector detects the electron count from the direct beam. The difference between BF-STEM and BF-TEM lies on the scanning motion of the electron probe. As the electron beam scans the sample, the detector measures the rate of electron counts at each localized area. Due to the scattering of electrons in the sample, the electrons counts will be lesser when the electron is passing through the sample as compared to the carbon grid, therefore the differences in electron counts contributes to the contrast in BF-STEM imaging.

Next, the principle behind the contrast in ADF-STEM imaging is the same as DF-TEM and difference lies in the scattered electrons signal coming from localized area during the probe scans.⁴⁷ Finally, the HAADF-STEM imaging detects electrons that are scattered to higher angle and almost all electrons are contributed by incoherent Rutherford scattering therefore achieving Z-contrast imaging. The heavier the atoms, the greater in the intensity of the scatter electrons, hence heavier atoms will appear brighter.

Lastly, to obtain high-resolution (HR) STEM imaging, besides aligning the beam to the zone axis of the crystalline sample, the instrument itself has to be fitted with the necessary hardware.⁴⁸ The resolution of electron microscopes is limited not by the electron wavelength, but by intrinsic imperfections of electron lenses. These are referred to as spherical and chromatic aberrations because of their similarity to aberrations in optical lenses (**Figure 3.9**).⁴⁹ Chromatic aberrations in TEM refers to the failure of the electromagnetic lens failing to focus electrons of various wavelength to common focus point. While spherical aberrations in TEM refers to the failure to converge electrons from various spatial position along the plane of the focusing element (electromagnetic field generated by the electromagnets). Those aberrations are reduced by installing in a microscope a set

of specially designed auxiliary "lenses" which are called aberration correctors. These optical corrections allows the convergent of electron beam to a smaller area, therefore increasing resolution of the probe scan. An example of an aberration corrected TEM is the Transmission Electron Aberration-Corrected Microscope (TEAM).⁵⁰ The electron source is a Schottky type field emission gun with a relatively low energy spread of 0.8 eV at 300 keV. With a chromatic aberrations (Wien-filter type monochromator), this spread is further lowered to 0.13 eV at 300 keV and 0.08 eV at 80 kV. In addition, the condenser lens, and the objective lens are equipped with fifth-order spherical aberration correctors. These corrections allow a HRSTEM imaging to achieve a spatial resolution below 0.5 Å.

Figure 3.9 Pictorial illustration of chromatic and spherical aberrations.

3.3.3 Energy Dispersive X-ray Spectroscopy (EDX)

When an electron beam interacts with the sample, X-ray photons are generated. Each X-ray photons possesses characteristic energy that are specific to the elements present in the sample, and these specifically provide electron microscopes capabilities for analytical characterization.^{37,41,51} Typically, the energy of X-rays analyzed usually ranges from 0.1 to 20 keV. In addition, X-ray photons whose energy levels have no relationship to any elements contribute to the continuum background noise of the spectrum.^{52,53} These background photons originate from the loss of electron energy when it undergoes deceleration in the Coulombic field of the sample atoms. This radiation is referred to as bremsstrahlung, or “braking radiation”. The energy loss, $\Delta E = h \cdot \nu$, where h is Planck’s constant

and ν is the frequency of the electromagnetic radiation.⁵⁴ The intensity of these background signal increases with beam current, atomic number, sample thickness and beam energy.

When an electron from the electron beam interacts with the tightly bound electrons in the inner shell of an atom in the sample, the incident electron may provide energy to the electron in the shell. When there is sufficient energy ($E > E_b$), where E is the energy absorbed by the electron in the shell, and E_b is the binding energy of electron to the shell, the electron will be ejected. The ejected electron leaves behind an ion (now positively charged) in an excited state as shown in **Figure 3.6**. This excited state lasts for 1 ps, after which the ion relaxes to its ground state (lowest energy state) by filling up the inner-shell electron vacancy with the other shell electrons. The transition of electrons from the higher energy outer shell to the lower energy inner shell involves releasing energy. From the Planck equation, the wavelength of this energy falls in the X-ray region, and the detection and analysis of this X-ray is called energy dispersive X-ray spectroscopy.

K-series X-ray involves filling the vacant state in the innermost electron shell (K shell) with an electron transition from the next shell out (L shell). Therefore, the energy difference between K shell and L shell equals to the energy of the K_α X-ray produced. When the transition to fill the vacant K shell is from the outer most M shell, the X-rays resulting from the electronic relaxation are called K_β X-rays. The energy difference between K and M shell is greater than K and L shell, therefore K_β X-rays are of higher energy than K_α X-rays. As each element has its own specific energies of the electrons in the shells (atomic energy levels), the energy levels between the electron shells will be unique to each element, therefore from the X-rays generated, identification of the elements present in the sample can be achieved.

3.3.4 Surface Enhanced Raman Scattering (SERS)

Firstly, the working principle behind conventional Raman spectroscopy will be explained. In 1928, Chandrasekhara Venkata Raman observed inelastic

scattering of light, later known as the Raman effect.⁵⁵ When a monochromatic light is shone on a material, the incident electromagnetic field induces a dipole moment, which in turn radiates light at its oscillation frequencies.¹⁷ The dipole moment may radiate at several frequencies as shown in **Figure 3.10**:

1. Stokes scattering: the wavelength of the emitted photon is red shifted with respect to excitation source.
2. Rayleigh scattering: the wavelength of the absorbed and emitted photons is the same as the excitation source.
3. Anti-Stokes scattering: the wavelength of emitted photon is blue shifted with respect to excitation source.

In Raman spectroscopy, the Raman signal comes from the inelastic scattering of light due to interaction with the vibrational modes of a molecule. The inelastic scattering process involves the instantaneous absorption and emission of photons by the molecule. The inelastic scattering due to the energy transfer between photons and molecular vibration during their interaction is an example of Raman scattering and allows identification of molecules based on their unique set of fingerprint scattering peaks.⁵⁶

Figure 3.10 Simplified Jablonski diagram of Raman process. Note that the virtual state is not a real physical state.

Using electromagnetic mechanism (EM) enhancement model, the working principle of surface enhanced Raman scattering (SERS) spectroscopy will be explained. SERS spectroscopy was first observed in the 1970s, where adsorption of pyridine on silver nanoparticles surface exhibited enhancement in Raman intensities.^{57,58} SERS spectroscopy involves the use of a metal surface (e.g metal nanoparticles, rough metal surface). When an electromagnetic wave (light) interacts with a metal surface (Ag, Au), the fields at the surface are different than those observed in the far field. If this field enhances the intensity of the incident and scattered fields, then there is the possibility of a large enhancement of the intensity of the Raman scattering.⁵⁹ This change in field surrounding the metal surface is due to the localized surface plasmon resonance (LSPR). The LSPR occurs when the collective oscillation of valence electrons of the atoms in the metal nanoparticles is in resonance with the frequency of the incident light (**Figure 3.**) The magnitude of the electromagnetic field outside a spherical nanoparticle (E_{out}) can be expressed as⁶⁰⁻⁶²

$$E_{out}(x, y, z) = E_0(\hat{\mathbf{z}}) - \left\{ \alpha \cdot E_0 \left\{ \frac{x}{r^3} - \left[\left(\frac{3z}{r^5} \right) \cdot (x\hat{\mathbf{x}} + y\hat{\mathbf{y}} + z\hat{\mathbf{z}}) \right] \right\} \right\} \quad (3.20)$$

where x , y and z are the Cartesian coordinates; r is the radial distance; $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$ and $\hat{\mathbf{z}}$ are the Cartesian unit vectors; α is the metal polarizability expressed as

$$\alpha = g \cdot a^3 \quad (3.21)$$

where a is the radius of the sphere and g is defined as

$$g = \frac{\varepsilon_{in} - \varepsilon_{out}}{\varepsilon_{in} + 2\varepsilon_{out}} \quad (3.22)$$

where ε_{in} is the dielectric constant of the metal nanoparticle, and ε_{out} is the dielectric constant of the external environment. Based on equation (3.22), the value

of g is the biggest when the value of $(\varepsilon_{in} + 2\varepsilon_{out})$ approaches zero. Therefore the strength of the electromagnetic field is the strongest when $\varepsilon_{in} \approx -2\varepsilon_{out}$.

The intensity of scattered Raman is linear with the incident field intensity (E_0^2).⁶³ As the intensity of the electromagnetic field at the nanoparticle surface increases, the increase in scattered Raman intensity is the absolute square of E_{out} . When g is large, the maximum enhancement approaches

$$|E_{out}|^2 = 4E_0^2|g|^2. \quad (3.23)$$

In addition, when a monochromatic light is shone on a material, the incident electromagnetic field induces a dipole moment, which in turn radiates light at its oscillation frequency as discussed in the conventional Raman effect. This change in dipole moment radiates light, and there is a probability that the radiated light is Stokes shifted by the vibrational frequency of the molecule. This emitted photon from the induced dipole is also capable of enhancement. To a first-order approximation, the enhance emission can be modeled using equation (3.23), therefore the overall enhancement factor (EF) contributed by the enhancement in scattered Raman ($|E_{out}|^2$) and emitted photons ($|E'_{out}|^2$) can be described as⁶⁴

$$EF = \frac{|E_{out}|^2 \cdot |E'_{out}|^2}{|E_0^2|^2} = 4 \cdot |g|^2 \cdot |g'|^2 \quad (3.23)$$

where the primed symbols refer to the field evaluated at the scattered frequency of the photons from induced dipole oscillation. This expression describes the theoretical EF resulting from the EM mechanism of SERS. If the Stokes shift in the radiated light is small, the values of g and g' can be evaluated at the same frequency/wavelength such that the $EF \approx g^4$ which is commonly referred to as E^4 enhancement in SERS spectroscopy.

3.4 References

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Chapter 4

Understanding the Synthetic Pathway of a Single Phase Quaternary Semiconductor Using Surface Enhanced Raman Scattering: A Case of Wurtzite $\text{Cu}_2\text{ZnSnS}_4$ Nanoparticles

Pure-phase $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) is an essential prerequisite for achieving high-efficiency CZTS thin-film solar cell device. In this report is presented a study on achieving selective phase formation in CZTS nanoparticles by ligand control. Surface-enhanced Raman scattering (SERS) spectroscopy is utilized for the first time as a sensitive characterization tool for nanoparticles so as to differentiate the mixed compositional phase (e.g., CZTS, CTS and ZnS), which are not differentiable by X-ray diffraction. Due to the superior sensitivity and selectivity of SERS, the growth pathway of CZTS nanoparticles via hot-injection is revealed to involve 3 growth steps. It is identified that single-phase CZTS nanoparticles can be synthesized via careful balancing the formation rate of CTS phase with the rate of Zn^{2+} diffusion into CTS phase. It is demonstrated that this critical balance can be achieved by using 1 mL of thiol with copper (II) acetate, tin (IV) acetate and zinc (II) acetylacetonate metal salts to synthesize the CZTS phase without any binary/ternary phase observable by XRD and SERS.

4.1 Introduction

$\text{Cu}_2\text{ZnSnS}_4$ (CZTS), a quaternary p-type semiconductor, has been actively studied as a photovoltaic material due to its optimal band energy $\sim 1.0\text{--}1.5$ eV, high absorption coefficient ($\sim 10^4$ cm^{-1}), as well as being composed of nontoxic and naturally abundant elements.¹⁻³ Currently, the best reported device made from CZTS shows only 12.6% efficiency, which is less than 50% of the theoretical maximum power conversion efficiency of 29.4%.^{4,5} This huge gap between the experimental and theoretical power conversion efficiencies can be attributed to a few factors, such as the complicated nature of the surface and bulk defects, lack of stoichiometric control, as well as the difficulty of ensuring pure-phase CZTS during fabrication.⁶

Recently, the wet-chemistry approach to the synthesis of CZTS nanoparticles has attracted much attention. This is due to the versatility of CZTS nanoparticles to be used as inks in a wide range of printing techniques, such as screen printing, roll-to-roll, and spray pyrolysis.⁷⁻¹³ One of the challenges faced in the synthesis of CZTS nanoparticles is the formation of binary (i.e., copper sulfide, tin sulfide and zinc sulfide) and ternary sulfides (Cu-Sn-S derivatives).^{14,15} Among these secondary phases, conducting phases (CTS and Cu_{2-x}S) are most detrimental to the electrical performance of CZTS devices as they lead to quenching of electron-hole pairs and short-circuiting.^{16,17} Consequently, the ability to prepare pure phase CZTS nanoparticles has become the top priority in improving the efficiency of CZTS nanoparticle-based solar cells. Fusion of CZTS nanoparticles to form bulk thin film avoids random nucleation faced by other solution process method.¹⁸ It is therefore important to understand the synthetic chemistry and growth mechanism of CZTS nanoparticles so as to achieve reproducible synthetic route for the formation of single-phase CZTS nanoparticles. Reports on the synthesis of CZTS nanoparticles can be collectively classified as studying of the effect of various thiol source, capping agents, and metal salt precursors on the resulting CZTS crystal structures (e.g., kesterite (k), wurtzite (w)), morphology, and elemental composition of CZTS nanoparticles.^{7,13,19-25} While the influence of the metal salts used on the formation of chalcopyrite phases (e.g. CuS, $\text{Cu}_{31}\text{S}_{19}$) has been

investigated before, there is currently no study on the influence of the metal salt precursors on formation of CZTS compositional phases (e.g., CZTS, CTS).²⁶

There are currently two primary characterization techniques (X-ray diffraction and Raman spectroscopy) used to characterize the crystal structure and compositional purity of as-synthesized nanoparticles. However, there are inherent complications related to the use of these techniques during characterization of compositional purity of CZTS nanoparticles.²⁴ XRD is unable to differentiate the presence of CTS (stannite/orthorhombic) and CZTS (wurtzite/kesterite) phases accurately due to the overlapping of diffraction peaks.¹² On the other hand, Raman spectroscopy has the ability to resolve various compositional phases from one another due to their characteristic vibrational modes; bulk CZTS (338 cm^{-1}), Cu_3SnS_4 (318 cm^{-1}), Cu_2SnS_3 (298 cm^{-1}) and Cu_{2-x}S ($269, 301$ and 470 cm^{-1}).^{12,27,28} However, the sensitivity of regular Raman spectroscopy is poor as a result of the small Raman scattering cross sections of the nanoparticles.²⁹ This small Raman scattering cross section however can be increased by using surface-enhanced Raman scattering (SERS) spectroscopy.³⁰

Herein, is demonstrated the use of SERS spectroscopy as a sensitive characterization technique to accurately differentiate Raman peaks of various compositional phases present in the as-synthesized CZTS nanoparticles. With this capability, it is intended to investigate the formation pathway of CZTS nanoparticles by altering the coordinating strength of the chelating ligands (acetate (OAc) and acetylacetonate (acac)), that is of different binding strengths. The influence of having a metal salt (Cu^{2+} , Zn^{2+} and Sn^{4+}) with more strongly bound ligand on the formation of CZTS is examined, and the crucial reaction steps to achieve pure CZTS-phase is revealed. On the basis of our findings, an optimal set of conditions is established to synthesize CZTS nanoparticles with low polydispersity. The synthetic mechanism revealed in this work may be used to help produce other $\text{Cu}_2(\text{M})\text{SnS}_4$ (where $\text{M}=\text{Ni}, \text{Co}, \text{Fe}, \text{Mn}$) quaternary materials that have been recently been studied with possible applications in magnetic, optoelectronics and electronic devices.³¹

4.2 Experimental Methods

4.2.1 Chemicals and materials

All chemicals purchased were used without further purification. Copper(II) acetate monohydrate ($\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$, Aldrich, >98%), copper(II) acetylacetonate ($\text{Cu}(\text{acac})_2$, Aldrich, 97%), zinc acetate dihydrate ($\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, Aldrich, >98%), zinc acetylacetonate ($\text{Zn}(\text{acac})_2$, Aldrich, 97%), tin(IV) bis(acetylacetonate) dichloride ($\text{Sn}(\text{acac})_2\text{Cl}_2$, Aldrich, 98%), tin(IV) acetate ($\text{Sn}(\text{OAc})_4$, Aldrich), trioctylphosphine oxide (TOPO, Aldrich, 90%), 1-octadecene (ODE, Aldrich, 90%), 1-dodecanethiol (DDT, Aldrich, 98%), and oleylamine (OAm, Acros, 97%).

4.2.2 Synthesis

Figure 4.1 Synthetic approach for CZTS nanoparticles. Degas and dehydration: Reaction mixture was subjected to vacuum for 30 mins at room temperature to remove oxygen and water from the system. This is to prevent oxidation of metal cations during reaction. Stage 2. Incubation: reaction was then rapidly heated while under vacuum to remove all traces of water, to dissolve metal cations and preheat the mixture for DDT and OAm injection. Stage 3. Hot-injection: sulfur source (DDT) and capping ligand (OAm) were hot-injected into the reaction mixture to introduce sulfur anions. Stage 4. Rapid heating: it is essential to heat the reaction mixture rapidly to ensure homogenous reaction at designated temperature.

In a typical reaction, stoichiometric amount (Cu : Zn : Sn; 2 : 1.1 : 1) of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ / $\text{Cu}(\text{acac})_2$ (0.442 mmol), $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ / $\text{Zn}(\text{acac})_2$ (0.234 mmol) and $\text{Sn}(\text{OAc})_4$ / $\text{Sn}(\text{acac})_2\text{Cl}_2$ (0.221 mmol) were added into a 50 mL three-neck round bottom flask contained TOPO (1.37 mmol) and 10 mL of ODE. Reaction mixture was allowed to heat to 150 °C at 10 °C/min under vacuum. A 1-5 mL volume of DDT and 1-5 mL of Oam (Oam/DDT, 1:1) were injected at 150 °C and allowed to hold under vacuum for 10 mins and after which allowed to heat to 240 °C under N_2 gas. During the heating process, reaction mixtures were allowed to react

for 90 mins once the temperature exceeded 200 °C. After 90 mins of reaction, the reaction mixture is stopped by removal of heating mantle and allowed to cool naturally to room temperature. Quenching of the reaction was carried out by adding 2 mL volume of toluene to the reaction mixture at 80 °C as discussed by Singh et al. As-synthesized nanoparticles were then washed with 1% v/v dodecanethiol/hexane and ethanol in a ratio of 1:5 and centrifuged twice at 7500 rpm for 3 mins to remove excess ligands from the nanoparticles. The nanoparticles were collected and stored in vial and allowed to dry in a self-built N₂ box for storage. Dried nanoparticles can be dispersed in either hexane, chloroform or toluene solvent.

4.2.3 Scanning electron microscope (SEM)

Sample preparation for SEM-energy dispersive X-ray (EDS) measurement was carried out by dripping a concentrated CZTS nanoparticles solution (40 mg/mL, hexane) onto a Si wafer substrate (10 mm x 10 mm) and allowing it to dry to form a flat film in an enclosed Petri dish. The film was ensured to be thick enough by having no Si signal from the Si wafer during measurement. The film was analysed within the day of sample preparation using a JEOL-JSM-7600F scanning electron microscope operating at an acceleration of 30 kV and a current of 8 mA with acquisition time at 10 min/map at 5K magnification. The final elemental composition was calculated by averaging 9 EDS mappings measurement of (50 µm x 50 µm/map). When the error margin was above 20%, the samples were prepared again and reanalysed. Samples thickness check for SERS spectroscopy was carried out by scratching the layer of CZTS film off and imaging the nanoparticles using JEOL-JSM-7600F scanning electron microscope operating at an acceleration of 5 kV without conductive coating.

4.2.4 Bright-field transmission electron microscope (BFTEM)

Samples preparation for BFTEM were carried out by dripping 1 drop (~10 µL) of diluted CZTS nanoparticles solution (4 mg/mL, hexane) on a TEM full carbon copper grid (Ted Pella) and allowing it to dry. BFTEM images were

obtained using a JEOL-JEM-1400 electron microscope at an accelerating voltage of 100 kV while high resolution BFTEM (HR-BFTEM) images were obtained using a JEOL-JEM-2010 electron microscope at an accelerating of 200 kV.

4.2.5 X-ray diffraction (XRD)

Sample preparation for XRD characterization was carried out by dripping a concentrated CZTS nanoparticles solution (40 mg/mL, hexane) onto a Si wafer substrate (15 mm x 15 mm) and allowing it to dry to form a film. XRD patterns were obtained using a Bruker D8 Advance with Cu K α radiation (1.5406 Å) at 0.02 °/s scan rate, 2 secs accumulation time, and in 2θ ranging from 20° to 70°. All powder patterns were refined using the Topas. Quantitative Rietveld refinement was carried out using the Fundamental parameters approach, using accepted structural models obtained from the ICSD database of the respective components with just instrumental parameters refined i.e. background (5-term Chebyshev polynomial, zero error and 'crystallite size' to model the microstructure-controlled line broadening.

4.2.6 Surface enhanced Raman scattering (SERS)

A 50 nm thick Au film on Si was prepared using thermal evaporation to serve as a substrate for SERS measurements. The thickness of the Au film was monitored by quartz crystal microbalance, and the deposition rate was 0.5 Å/s. A diluted CZTS nanoparticle solution in hexane was then drop-casted (20 μ L, 4 mg/mL) onto a Au-coated Si wafer (5 mm $\times$ 5 mm) to form a thin film ($\sim 10 \pm 5$ nm) for SERS measurements. Both Raman and SERS spectroscopies were performed using a Horiba JY LabRAM HR Raman system with an excitation wavelength of 632.5 nm (power = 0.95 mW) supplied by an argon laser. All mapping experiments were performed using a 100 $\times$ objective lens (NA = 0.9) with 30 s accumulation time between 200 and 1000 cm^{-1} and stage movement of 5 μ m steps.

4.3 Principal outcomes

4.3.1 SERS spectroscopy as a superior characterization tool

Figure 4.2 a) TEM images of as-synthesized CZTS nanoparticles. Powder X-ray diffraction patterns of b) as-synthesized CZTS nanoparticles, c) simulated CZTS, d) kuramite CTS, e) kesterite CZTS and f) wurtzite ZnS. g) Raman and h) surface-enhanced Raman Scattering spectra of as-synthesized CZTS nanoparticles containing multiple phases. The inset shows the nanoparticle obtained from Sn-acac 1 mL DDT used for the Raman and SERS spectroscopy.

As-synthesized nanoparticles with plates-like morphology were obtained with low polydispersity, with an average size of 10 ± 3 nm (**Figure 4.2a**). XRD characterization (**Figure 4.1b**) revealed it a wurtzite crystal structure. However, due to overlapping diffraction peaks in the standard XRD patterns of the possible phases of ZnS (w), CTS (k), CZTS (k), and CZTS (w) (**Figure 4.2c-f**), it is not possible to determine the purity and identity of the compositional phases present using XRD. Conventional Raman measurement (**Figure 4.2g**) showed an ambiguous peak at ~ 326 cm^{-1} , hinting at the possible presence of multiple phases. This is resolved by SERS spectroscopy measurement. SERS measurements (**Figure 4.2h**) are carried out on a thin film ($\sim 10 \pm 5$ nm) of the same as-synthesized CZTS nanoparticles drop-casted on a 50 nm thick gold film (**Figure 4.3**). Five distinct peaks could be observed, which can be unambiguously assigned to CZTS (293, 335 and 372 cm^{-1}), CTS (320 cm^{-1}) and ZnS phases (351 cm^{-1}) respectively.^{28,32,33} The preliminary

characterization of the as-synthesized CZTS nanoparticles highlights the need for a highly sensitive characterization tool and the superiority over conventional Raman spectroscopy and XRD in detection of secondary phases present. From here onward, SERS will be used as the main characterization tool to identify the phases present in the as-synthesized CZTS nanoparticles. XRD coupled with Rietveld refinements will be used to determine the crystal structures of the nanoparticles based on the phases identified from SERS.

Figure 4.3 a) Bright field optical image of a SERS substrate, b) bright field optical image of scratched SERS film for AFM measurement, c) SEM image of large scale nanoparticles assembling into a thin layer, and d) higher magnification of SEM image showing assembly of CZTS nanoparticles.

4.3.2 Establishing the growth mechanism of CZTS nanoparticles

To thoroughly study the growth steps involved during CZTS nanoparticles formation that could not be achieved with XRD, a study was carried out using SERS on the reaction reported by Liao et al³⁴ with modifications. An ex-situ time-growth study was performed to monitor the reaction progress during CZTS phase formation. Aliquots were withdrawn from the reaction mixture at regular time intervals, and the corresponding morphology and compositional phases present in the as-synthesized nanoparticles were examined by TEM and SERS respectively. After 2 mins of reaction, a broad peak at $\sim 290\text{ cm}^{-1}$ corresponding to Cu_{2-x}S phase (**Figure 4.4b**) was observed with the TEM showing the formation of $\sim 4\text{ nm}$ nuclei seed crystals when the reaction solution turned black.³² After 8 mins of reaction, three

Raman peaks were observed at 260 and 289 cm^{-1} corresponding to Cu_{2-x}S phase and at 320 cm^{-1} corresponding to the CTS phase (**Figure 4.4d**) respectively.^{35,36} The formation of Cu_{2-x}S /CTS nanoparticles indicate the diffusion of Sn^{4+} into Cu_{2-x}S nuclei seed crystals which also lead to the growth of nanoparticles to ~ 8 nm (**Figure 4.4c**). Upon allowing the reaction to proceed further, SERS characterization of aliquots extracted after 12 mins showed three Raman peaks (**Figure 4.4f**) at 298 cm^{-1} (CTS phase) and at 334 and 372 cm^{-1} (CZTS phase) respectively. TEM characterization (**Figure 4.4e**) revealed a mixture of 2 populations of nanoparticles with sizes of ~ 3 nm and ~ 10 nm. Finally, after 90 mins of reaction, three distinctive Raman peaks (**Figure 4.4h**) corresponding to CZTS phase at 292, 335 and 372 cm^{-1} were observed along with an increase in nanoparticles size to ~ 14 nm (**Figure 4.4g**). This finding of CZTS nanoparticles growth proceeding from Cu_{2-x}S nuclei complements recently reported experimental observation.^{23,34,37} In addition, it has been demonstrated by using SERS, that the growth of CZTS undergoes an intermediate phase (CTS) which has not been identified until now.³⁷

Figure 4.4 CZTS nanoparticles extracted at different reaction times at 240 °C. a) TEM images and b) SERS spectra at 2 mins, c) TEM images and d) SERS spectra at 8 mins, e) TEM images and f) SERS spectra at 12 mins, g) TEM images and h) SERS spectra at 90 mins. i) Pictorial representation of the three step growth process for the formation of CZTS nanoparticles.

From this growth study, a sequential three step growth mechanism has been proposed. The first step involved the nucleation of Cu_{2-x}S nanoparticles, followed by the diffusion of Sn^{4+} into Cu_{2-x}S nanoparticles to form CTS nanoparticles and lastly the diffusion of Zn^{2+} into CTS nanoparticles to form CZTS nanoparticles. The sequence of Sn^{4+} diffusion into Cu_{2-x}S nanoparticles first rather than Zn^{2+} cations is agreeable to reports on the unfavorable formation of the Cu–Zn–S ternary system but as heterogeneous Cu_{2-x}S –ZnS nanoparticles instead.^{38,39} In addition, the observation of smaller nanoparticles alongside larger nanoparticles (**Figure 4.4e**) during the growth of CZTS nanoparticles suggest that the growth proceeds via Ostwald ripening. These finding highlights the growth specificity of CZTS nanoparticle thus realizing the need to identify the purity-determining growth step. To study the importance of growth rate at each step, a stronger binding ligand was used to reduce the reactivity of the cations at each growth step (**Figure 4.3.viii**). An OAc–metal complex is less stable than an acac–metal complex because the former forms a less stable four-membered ring with the metal cation as compared to a more stable six-membered ring formed by the metal–acac complex.⁴⁰

4.3.3 Understanding the ligand effect on CZTS nanoparticle formation

A systematic study was carried out to elucidate the effect of ligand binding strength has on CZTS nanoparticles formation (**Table 4.1**). OAc reaction (all metal salts ligands are acetate ions) served as a control experiment, while Cu-acac reaction (Cu^{2+} metal salt with acetylacetonate as ligand) demonstrated the effect of reducing Cu^{2+} reactivity during Cu_{2-x}S phase growth. The Sn-acac reaction (Sn^{4+} metal salt with acetylacetonate as ligand) showed the effects of reducing Sn^{4+} reactivity during the diffusion of Sn^{4+} into Cu_{2-x}S to form the CTS phase. Lastly, the Zn-acac reaction (Zn^{2+} metal salt with acetylacetonate as ligand) highlighted the effect of reducing Zn^{2+} reactivity during Zn^{2+} diffusion into the CTS phase to form the CZTS phase. SERS was used to characterize all as-synthesized nanoparticles from the various reaction series with the amount of 1-dodecenthiol (DDT) kept constant at 1 mL to fix the amount of sulphur in the reaction.

Table 4.1 Four different reaction setups are carried out to study the effect of cations reactivity on CZTS phase formation: **I) Oac**; all cations are binded to acetate ligands, **II) Cu-acac**; acetate ligands on Cu cations are substituted with acetylacetonate ligands, **II) Sn-acac**; acetate ligands on Sn cations are substituted with acetylacetonate ligands and **IV) Zn-acac**; acetate ligands on Zn cations are substituted with acetylacetonate ligands.

Reaction Setup	Metal precursor		
	Cu salt:	Sn salt:	Zn salt:
I Oac	$\text{Cu}(\text{OAc})_2$	$\text{Sn}(\text{OAc})_4$	$\text{Zn}(\text{OAc})_2$
II Cu-acac	$\text{Cu}(\text{acac})_2$	$\text{Sn}(\text{OAc})_4$	$\text{Zn}(\text{OAc})_2$
III Sn-acac	$\text{Cu}(\text{OAc})_2$	$\text{Sn}(\text{acac})_2\text{Cl}_2$	$\text{Zn}(\text{OAc})_2$
IV Zn-acac	$\text{Cu}(\text{OAc})_2$	$\text{Sn}(\text{OAc})_4$	$\text{Zn}(\text{acac})_2$

Ligands:

acetate ions
(OAc)

acetylacetonate
ions (acac)

First, the control experiment with all metal salts having acetate ions as ligands (OAc reaction series) was carried out. The SERS spectrum (**Figure 4.5b**) of as-synthesized nanoparticles obtained from the OAc reaction shows three peaks at ~ 292 , 336 , and 372 cm^{-1} indicating compositionally pure CZTS phase. In addition, TEM imaging of CZTS nanoparticles (**Figure 4.5a**) shows bricklike morphology with a size distribution of $9 \pm 3\text{ nm}$ and XRD characterization with Rietveld refinement showed pure wurtzite (CZTS) crystal structure (**Figure 4.6**).

Figure 4.5 TEM images (left column) and SERS spectra (right column) of CZTS nanoparticles synthesized using different reaction setup at 1 mL dodecanethiol amount: a and b) Setup I – **Oac**, c and d) Setup II - **Cu-acac**, e and f) Setup III - **Sn-acac**, g and h) setup IV - **Zn-acac**.

Figure 4.6 Rietveld refinement of **OAc** reaction setup for 1 mL DDT. (Please see annex 1 for refined lattice parameters)

Next, Cu^{2+} with a stronger binding acetylacetonate ligand ($\text{Cu}(\text{acac})_2$) was used. The SERS spectrum (**Figure 4.5d**) of nanoparticles obtained from the Cu–

acac reaction shows three peaks at ~ 290 , 334 , and 371 cm^{-1} , indicating compositionally pure CZTS phase. TEM imaging of as-synthesized nanoparticles obtained from Cu–acac (**Figure 4.5c**) shows random oval-like morphology with a size distribution of $9 \pm 4\text{ nm}$ and pure wurtzite (CZTS) crystal structure (**Figure 4.7**). The lack of consistent morphology as compared to OAc (**Figure 4.5a**) suggests nonhomogeneous growth of CZTS nanoparticles. This implies that reduction of Cu^{2+} reactivity inhibits homogeneous growth of nanoparticles but does not affect the phase transformation during CZTS nanoparticle formation. There is no difference in compositional phase purity between the OAc reaction (**Figure 4.5b**) and the Cu–acac reaction (**Figure 4.5d**) because of the much higher affinity of Cu^{2+} over Sn^{4+} and Zn^{2+} to the sulfur source (DDT) despite having acac as the chelating ligand.⁴¹ This leads to the rapid formation of the Cu_{2-x}S phase, which has been shown earlier to be essential for the formation of CZTS nanoparticles. During the reaction, Cu^{2+} is readily reduced to Cu^+ by DDT due to its low reduction potential of $+0.159\text{ V}$ versus NHE. The higher affinity of Cu^+ to DDT arises from the better soft–soft compatibility between these two ionic species as compared to Sn^{4+} and Zn^{2+} with DDT.^{42,43} The ranking of the cations can be ranked as $\text{Cu}^+ > \text{Cu}^{2+}$ and $\text{Zn}^{2+} > \text{Sn}^{4+}$.^{35,36} Consequently, the influence of acac on Cu^{2+} reactivity shows little effect on the formation of CZTS nanoparticles due to the high affinity of Cu^{2+} for thiol.

Figure 4.7 Rietveld refinement of **Cu–acac** reaction setup for 1 mL DDT. (Please see annex 2 for refined lattice parameters)

Next, Sn^{4+} with stronger binding acetylacetonate ligand ($\text{Sn}(\text{acac})_2\text{Cl}_2$) was used. SERS (**Figure 4.5f**) characterization of nanoparticles obtained from the Sn–

acac reaction shows five peaks which were assigned to CZTS (290, 335, and 371 cm^{-1}), CTS (320 cm^{-1}), and ZnS (shoulder at 354 cm^{-1}) respectively. TEM imaging of as-synthesized nanoparticles obtained from the Sn–acac reaction shows uniform square-like nanoparticles (**Figure 4.5e**) with a narrower size distribution of 10 ± 3 nm and a mixture of wurtzite (CZTS) and stannite (CTS) crystal structures (**Figure 4.8**). It is proposed that the decrease in the reactivity of Sn^{4+} slows the diffusion of Sn^{4+} into Cu_{2-x}S nanoparticles thus affecting the rate of CTS nanoparticle formation. As established earlier, the growth route of the CZTS phase is highly specific. Since the formation of the CTS phase is an intermediate phase before the diffusion of Zn^{2+} occurs for formation of CZTS nanoparticles, the diffusion of Zn^{2+} ions into the CTS phase is slowed down too. A possible explanation for the presence of CZTS, CTS, and ZnS phases is the result of slowing down of Zn^{2+} ions consumption, leading to the reaction of thiol with excessive Zn^{2+} to form ZnS, possibly as a heterophase on Cu_{2-x}S /CTS nanoparticles.^{38,39} The formation of ZnS deprives the reaction system of Zn^{2+} for the phase transformation from the CTS phase to the CZTS phase, hence giving rise to CTS, CZTS, and ZnS phases.

Figure 4.8 Rietveld refinement of Sn-acac reaction setup for 1 mL DDT. (Please see annex 4 for refined lattice parameters)

Finally, Zn^{2+} with stronger binding acetylacetonate ligand ($\text{Zn}(\text{acac})_2$) was used. SERS (**Figure 4.5h**) characterization of as-synthesized nanoparticles obtained from the Zn–acac reaction shows three peaks at 292, 334, and 370 cm^{-1} indicating a compositionally pure CZTS phase. TEM imaging of CZTS nanoparticles obtained from Zn–acac (**Figure 4.5g**) shows bricklike morphology with a size distribution of 9 ± 3 nm and pure wurtzite (CZTS) crystal structure (**Figure 4.9**). The size distribution is much narrower as compared to the product of OAc reaction (**Figure 4.5a**). This suggest a more homogeneous nanoparticle growth with reduced Zn cation reactivity, while at the same time producing compositional pure CZTS phase. The observation of compositionally pure CZTS is unexpected from the Zn–acac reaction. The reduced Zn^{2+} reactivity is proposed to hinder the rate of Zn^{2+} diffusion into CTS to form the CZTS phase, and formation of CTS should be observed. The absence of the CTS phase is likely due to the affinity of Zn^{2+} for DDT and the small ionic radius of Zn^{2+} (74 pm).⁴⁴ Due to the small ionic radius, diffusion of Zn^{2+} into the growing CTS lattice is still highly favourable despite using a more stable chelating ligand, hence resulting in the formation of compositionally pure CZTS. It is shown here that the rate of formation of the CTS phase is crucial in ensuring pure CZTS phase formation and the need to balance the rate of all three growth steps to achieve pure CZTS phase is critical. These findings further prompt the need to establish the possible effect of thiol concentration on CZTS nanoparticle formation as the amount of sulfur (DDT) can influence the rate of phase formation.

Figure 4.9 Rietveld refinement of **Zn-acac** reaction setup for 1 mL DDT. (Please see annex 3 for refined lattice parameters)

4.3.4 Understanding the Influence of Thiol Concentration on CZTS Nanoparticle Formation

Based on the rate of reaction equation; $r_{ab} = k_a[a]^x \times k_b[b]^y$, the alteration of the concentration of non-pseudo zero order reactants will affect the reaction rate. Since the amount of the metal ions has to stay constant, the influence of the amount of sulphur (DDT) used during reaction on the rate of reaction was studied. The amount of DDT was increased from 1 mL (used in all previous reactions above) to 5 mL, which amount was used for all the subsequent reactions. SERS characterization (**Figure 4.10b**) of as-synthesized nanoparticles obtained from the OAc reaction series shows five peaks, which can be assigned to CZTS (290, 336, and 371 cm^{-1}), CTS (320 cm^{-1}), and ZnS (shoulder at 355 cm^{-1}) respectively. In addition, TEM imaging reveals nanorods-like morphology (**Figure 4.10a**) with a size distribution of 21 ± 5 nm and a mixture of wurtzite (CZTS) and stannite (CTS) crystal structures (**Figure 4.11**) are obtained. In comparison to 1 mL of DDT used previously (**Figure 4.5b**) that gives pure CZTS phase, using 5 mL DDT gives mixed phases. The same observation was noted for the Cu-acac and Zn-acac reactions series, where SERS spectra of the products of both the Cu-acac (**Figure 4.10d**) and Zn-acac (**Figure 4.10h**) reactions show five peaks which were assigned to CZTS ($\sim 290, 335$, and 371 cm^{-1}), CTS (~ 320 cm^{-1}), and ZnS (shoulder at ~ 355 cm^{-1}) respectively. TEM images shows all as-synthesized nanoparticles to possess nanorod-like morphology (**Figure 4.10c** and **4.10g**) with a mixture of wurtzite (CZTS) and stannite (CTS) crystal structures being obtained as well (**Figures 4.12** and **4.13**). The observation of a mixed compositional phase can be ascribed to mismatched reactivities leading to sequential phase segregation and non-uniform elemental distribution.⁴⁵

Figure 4.10 TEM images (left column) and SERS spectra (right column) of CZTS nanoparticles synthesized using different reaction setup at 5 mL dodecanethiol amount: a and b) Setup I – **Oac**, c and d) Setup II - **Cu-acac**, e and f) Setup III - **Sn-acac**, g and h) setup IV - **Zn-acac**.

Figure 4.11 Rietveld refinement of **OAc** reaction setup for 5 mL DDT. (Please see annex 1 for refined lattice parameters)

Figure 4.12 Rietveld refinement of **Cu-acac** reaction setup for 5 mL DDT. (Please see annex 2 for refined lattice parameters)

Figure 4.13 Rietveld refinement of **Sn-acac** reaction setup for 5 mL DDT. (Please see annex 4 for refined lattice parameters)

Figure 4.14 Rietveld refinement of **Zn-acac** reaction setup for 5 mL DDT. (Please see annex 3 for refined lattice parameters)

On the other hand, when 5 mL of DDT was used in the Sn-acac reaction series, SERS characterization (**Figure 4.10f**) of as-synthesized nanoparticles shows a decrease in the relative peak intensity of the CTS phase (shoulder at 320 cm^{-1}) with respect to the CZTS peak ($\sim 335\text{ cm}^{-1}$). A small shoulder at $\sim 354\text{ cm}^{-1}$ indicates the presence of a small amount of ZnS phase. These two observations imply that less CTS and ZnS phases are present in the Sn-acac reaction series as compared to OAc, Cu-acac, and Zn-acac reaction series when 5 mL of DDT is used in the reaction. TEM characterization (**Figure 4.10e**) of as-synthesized nanoparticles shows bullet-like morphology with a size distribution of $\sim 20 \pm 5\text{ nm}$ and XRD characterization reveals a mixed of wurtzite (CZTS) and stannite (CTS) crystal structures (**Figure 4.14**). This phenomenon is again in contrast to when 1 mL of DDT is used in Sn-acac reaction series, where the formation of CTS and ZnS were prominently observed. This opposing trend of phase formation with varying DDT concentrations (**Figure 4.15**) shows that the order of reaction for sulfur is non-pseudo zero order ($d \neq 0$) in the formation of CZTS nanoparticles.

Figure 4.15 SERS spectra comparison for a) OAc, b) Cu-acac, c) Zn-acac and d) Sn-acac with increasing amount of DDT (1 mL to 5 mL).

4.3.5 Relative growth rates of CZTS phase

Cross referencing of two observation as discussed above permits the derivation of two crucial growth parameters. First, the purity of CZTS nanoparticles is controlled by the relative rates of formation of the CTS phase. Secondly, the rate of formation is highly dependent on the amount of DDT used. The obtaining of CZTS nanoparticles with higher phase purity from Sn–acac reaction with 5 mL DDT as compared to 1 mL of DDT confirms that the rate of ZnS formation is not accelerated by increasing the amount of thiol source. This observation ruled out the formation of the ZnS phase observed in the OAc, Cu–acac and Zn–acac reactions with 5 mL of DDT being a result of the increase in the rate of ZnS phase formation, which in turn deprives the reaction system of free Zn^{2+} cations to convert the CTS to the CZTS phase. Next, the obtaining of CZTS nanoparticles with higher purity phase from the Sn–acac reaction compared to the nanoparticles obtained from the OAc, Cu–acac, and Zn–acac reactions using 5 mL of DDT and 5 mL of oleylamine (Oam) confirms that there is no ligand hindering effect arising from the high amount of DDT and Oam added. Therefore, it is proposed that the purity of CZTS nanoparticles is controlled by the relative rates of formation of CTS and Zn^{2+} doping into CTS. The rate of CTS formation is accelerated by the presence of a large excess of sulfur source when the DDT volume is increased from 1 to 5 mL (**Figures 4.15**). As the rate of CTS formation increases, the diffusion rate of Zn^{2+} into the CTS matrix has to be comparable with the rate of CTS phase formation to completely transform the CTS phase into the CZTS phase. The fact that both CTS and ZnS phases are observed (**Figures 4.15a-c**) suggests that the diffusion rate of Zn^{2+} is slower than the rate of CTS phase formation, leaving the unreacted Zn^{2+} to react with DDT to form the ZnS phase for the OAc, Cu–acac, and Zn–acac reactions. On the other hand, when 5 mL of DDT is used in the Sn–acac reaction, the SERS spectra (**Figures 4.15d**) shows a decrease in CTS peak intensity (shoulder at 320 cm^{-1}) with respect to the CZTS peak ($\sim 336\text{ cm}^{-1}$). A small shoulder at $\sim 354\text{ cm}^{-1}$ indicates the presence of a small amount of the ZnS phase. This phenomenon with 5 mL of DDT can be ascribed to the rate of CTS phase formation increasing to a level comparable to Zn^{2+} doping leading to the formation

of the CZTS phase. The presence of a shoulder at 320 cm^{-1} (CTS phase) indicates that even with 5 mL of DDT, the rate of CTS phase formation is still slower than the Zn^{2+} diffusion process and the formation of the ZnS phase (shoulder at 354 cm^{-1}) inhibits the complete conversion of CTS to CZTS.

a)

$$\text{Eqn (1)} \quad R_{\text{CTS}} = k_{\text{Cu}^{2+}} [\text{Cu}^{2+}]^a k_{\text{Sn}^{4+}} [\text{Sn}^{4+}]^c k_{\text{S}^{2-}} [\text{S}^{2-}]^d$$

$$\text{Eqn (2)} \quad R_{\text{CZTS}} = k_{\text{Cu}^{2+}} [\text{Cu}^{2+}]^a k_{\text{Zn}^{2+}} [\text{Zn}^{2+}]^b k_{\text{Sn}^{4+}} [\text{Sn}^{4+}]^c k_{\text{S}^{2-}} [\text{S}^{2-}]^d$$

b)

Figure 4.16 a) Proposed equations for rate of reaction of CTS and CZTS phase and b) proposed relative rates of reaction for CTS formation and Zn^{2+} doping.

To summarize the mechanism of CZTS nanoparticle formation, the proposed relative reaction rates are shown in **Figure 4.16**. For the OAc, Cu–acac, and Zn–acac reactions series with 1 mL of DDT, the formation of pure-phase CZTS is obtainable as a result of comparable relative rates of CTS phase formation and Zn^{2+} doping. However with 5 mL of DDT, the relative rate of CTS phase formation is much higher than Zn^{2+} doping resulting in incomplete CTS phase conversion and ZnS phase formation. On the other hand, due to the decrease in reactivity of Sn^{4+} in the Sn–acac reaction, with 1 mL of DDT, the relative rate of CTS phase formation is much lower than for the OAc, Cu–acac, and Zn–acac reactions. Assuming the reactivity of Zn^{2+} doping remains unchanged and there are less CTS nanoparticles to react with, the excess Zn^{2+} ions react with DDT to form the ZnS phase. By increasing the DDT volume to 5 mL, the rate of CTS phase formation increases hence providing more CTS phase for Zn^{2+} doping to take place. This phenomenon results in purer CZTS-phase nanoparticles as can be seen in **Figures 4.15** for the

Sn–acac reaction. Therefore, on the basis of the observation of the Sn–acac reaction, the preferential formation of the CZTS phase over the CTS phase is highly dependent on the rate of CTS phase formation for a comparable rate of Zn^{2+} doping into the crystal lattice.

4.3.6 Understanding the influence of TOPO ligand on elemental composition

Figure 4.17 TEM images of as-synthesized nanoparticles.

The elemental composition of CZTS nanoparticles has been shown to influence the efficiency of device performance significantly.⁸ Hence it is critical to have the capability to optimize the elemental composition of CZTS nanoparticles while ensuring the formation of single-phase CZTS nanoparticles. By using energy-dispersive X-ray (EDX) characterization, it is observed that all as-

synthesized nanoparticles (**Figure 4.17**) show a common trend of being compositionally Zn poor ($(\text{Zn}/\text{Sn}) \sim 0.5\text{--}0.7$) for low DDT amounts and having higher Zn content ($(\text{Zn}/\text{Sn}) \sim 0.8\text{--}1.0$) for higher DDT amount for all reaction setups (**Figure 4.18**). It is noted that the Zn–acac reaction setup that gives the purest CZTS phase with 1 mL of DDT (**Figure 4.18a**) is Zn poor, which is not ideal for thin-film fabrication.

Figure 4.18 EDS analysis of CZTS film of a) OAc, b) Cu-acac, c) Sn-acac and d) Zn-acac.

A further study to optimize the elemental composition was carried out by adjusting the concentration of trioctylphosphine oxide (TOPO) amount based on the molar ratio of TOPO to the cations (**Figure 4.19**). Initially, following the work of Singh et al, $1.5\times$ TOPO was used for all reaction setups.²² It was observed that, by lowering the TOPO amount, it was possible to get higher Zn content while maintaining CZTS-phase purity as shown in **Figure 4.19b**. It was found that, at $0.75\times$ TOPO, the highest consistency was obtained with the lowest error margin (less than $\pm 5\%$ from SERS and energy-dispersive spectroscopy (EDS) characterization). This can be explained as TOPO has a known synergistic effect on ensuring high reproducibility and at the same time influencing the incorporating

of Zn into the nanoparticles. The elemental composition (**Figure 4.19a**) of nanoparticles obtained from the Zn–acac reaction with 1 mL of DDT was optimized to a near stoichiometric ratio of copper ($\text{Cu}/\text{Sn}+\text{Zn} = 0.9 \pm 0.1$

Figure 4.19 a) Zn–acac with varying TOPO mole ratio at 1 mL DDT. b) SERS of CZTS nanoparticles (Zn–acac) at varying TOPO mole ratio. c) HRTEM image of a CZTS nanoparticle (Zn–acac) at 0.75× TOPO.

Figure 4.20 XPS analysis of Zn–acac 1 mL DDT CZTS nanoparticles.

to zinc ($\text{Zn/Sn} = 1.1 \pm 0.1$) that has been reported to yield high CZTS device efficiency. From the high-resolution TEM (HRTEM) image (**Figure 4.19c**) of optimized CZTS nanoparticles, a lattice constant of 6.4 Å is indexed to the (0001) plane and a lattice constant of 3.5 Å is indexed to the (1010) plane 90° to the (0001) plane. The growth along the (002) plane is in agreement with a previous report on the selective growth of wurtzite crystal along the *c* axis.^{22,46}

In addition, X-ray photoelectron spectroscopy (XPS) measurement (**Figure 4.20**) of CZTS nanoparticles shows distinctive peaks at 931.22 and 951.06 eV corresponding to Cu^+ , 1047.52 and 1043.2 eV corresponding to Zn^{2+} , 485.6 and 489.12 eV corresponding to Sn^{4+} , and 161.76 and 162.60 eV corresponding to S^{2-} . This XPS data confirms that the oxidation numbers of the elements (i.e., Cu^+ , Zn^{2+} , Sn^{4+} , S^{2-}) of the final product agrees with the expected values corresponding to the CZTS quaternary system.

4.4 Conclusion

SERS has been demonstrated for the first time to be a sensitive tool for material phase characterization, enabling monitoring the growth mechanism of CZTS nanoparticles to proceed via three growth steps. It was found that the formation of CZTS phase proceeds via nucleation of Cu_{2-x}S nanoparticles followed by diffusion of Sn^{4+} into Cu_{2-x}S nanoparticles to form kinetically driven CTS nanoparticles and lastly diffusion of Zn^{2+} into CTS nanoparticles to form CZTS nanoparticles. The most crucial growth step to ensure a pure CZTS phase has been revealed to be the growth of the intermediate CTS phase. The selective CZTS phase formation over the CTS phase has been shown by carefully maintaining the rate of CTS phase formation to be similar to the rate of Zn^{2+} ion diffusion via controlling the coordinating strengths of the chelating ligands of metal precursors. It was also found that CTS formation is very sensitive to the reactivity of Sn precursor and the amount of sulfur source. After a systematic study, the most optimized reaction conditions to form pure CZTS nanoparticles was found to be using a low DDT volume of 1 mL and using $\text{Cu}(\text{Oac})_2$, $\text{Zn}(\text{acac})_2$, and $\text{Sn}(\text{oac})_4$ as the metal precursors. Not only can this study serve as a platform to explain the formation of

other CMTS (i.e., $M = \text{Co}^{2+}, \text{Ni}^{2+}, \text{Mn}^{2+}, \text{Fe}^{2+}$) nanoparticles, this ability to produce pure-phase CZTS nanoparticles holds the potential to achieve higher solar cell efficiency and even enable large-scale production of devices.

4.5 References

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Chapter 5

Structural Investigation of Phase Transformation of Multinary-Sulfide Nanomaterial via Cation Exchange

The delivery of multi-component nanomaterials requires control of conflicting crystallization processes to avoid the parasitic precipitation of secondary phases. Unfortunately, such knowledge is not transferrable across different chemistries, and ab initio calculation remains qualitative at best. This work presents a model study to highlight the complexity of phase transition via cation exchange to form multi-component sulfide nanomaterials ($\text{Cu}_{29}\text{S}_{16}$ to Cu_4SnS_4 to $\text{Cu}_2\text{ZnSnS}_4$). This is the first time direct evidence has been shown on the phase transformation of binary $\text{Cu}_{29}\text{S}_{16}$ to ternary Cu_4SnS_4 to quaternary $\text{Cu}_2\text{ZnSnS}_4$ occurring via alloyed cationic exchange in a fixed anionic framework. Tracing the structural changes of binary $\text{Cu}_{29}\text{S}_{16}$ growth to ternary Cu_4SnS_4 revealed a sequential three steps reaction processes involving two intermediate phases ($P12_1n1$ $\text{Cu}_{31}\text{S}_{16}$ and $P12_1c1$ $\text{Cu}_{32}\text{S}_{16}$) while preserving the anionic framework of $\text{Cu}_{29}\text{S}_{16}$. In addition, the ex-situ growth study of CZTS from CTS reveals a negative domino CE growth effect resulting in precipitation of parasitic phases. Furthermore, the use of HR-HAADF imaging with Z-contrast capability enables the visualization of Sn fixed occupancy sites in the as-synthesized quaternary CZTS nanoparticles. This confirms that the crystal does not follow the commonly accepted $P6_3mc$ structure.

5.1 Introduction

Nanomaterials exhibit size- and shape- dependent functional properties, where they can find applications in optics, electronics, catalysis and photovoltaics.¹⁻⁷ The formation of nanomaterials can be controlled via direct and post-synthetic approaches. In the first, particle formation promulgates initially via conversion of precursors to reactive species, followed by nucleation and growth.⁸ The chemical specificity of the sequential growth steps is highly dependent on the reaction kinetics that ultimately control purity. In particular multi-element nanomaterials require control of conflicting crystallization processes to avoid the parasitic precipitation of secondary phases.^{9,10} When the goal is phase-pure products through direct synthesis, competing processes must be discerned and controlled. Unfortunately, such knowledge is not transferrable across different chemistries, and *ab initio* calculation remains qualitative at best. On the other hand, post-synthetic modification of particles has proven predictable and reproducible for a range of nanomaterials.^{11,12}

Advances in post-synthetic modification chemistry, specifically cation exchange (CE), provides pathways to previously unavailable nanomaterials including multi-component nanomaterials (e.g metallo-organic framework, sulfides, oxides and halides), epitaxial-core-shell and epitaxial-hetero nanostructures.^{5,13-19} Essentially, cation exchange enables tailoring of optical, electronic and magnetic properties through transportation of dissolved cations into the extended solid.⁷ Two factors are necessary for successful CE, the first is that the thermodynamic stability of the products has to exceed that of the reactants, and second is that the CE reaction on the solid surface and in the extended solid must be energetically favourable. Novel materials with enhanced and tailored functionality (e.g bandgap, photoluminescence and catalysis) are obtainable with ternary and quaternary compounds.^{15,20,21} Key challenges include non-uniform growth rates, disrupting morphology due to Kirkendall ripening or competitive growth kinetics.^{22,23} To date, most CE work has been on binary systems rather than ternary and quaternary systems.^{11,12} In particular, the kinetics of the competing parallel reaction are poorly understood and the microstructural transformations

accompanying multi-component CE growth require optimization to control such syntheses.²⁰

$\text{Cu}_2\text{ZnSnS}_4$ (CZTS) is a quaternary compound that shows potential as a thin film photovoltaic (PV) material due to its high solar absorption coefficient and composed of abundant elements.^{24,25} Here, a CE growth model that accounts for the temporal changes in crystal structures, the impact of interfacial plane alignment of the hetero-phase, and the elemental distribution of the binary host component $\text{Cu}_{26}^+\text{Cu}_3^{2+}\text{S}_{16}^{2-}$ ($\text{Cu}_{29}\text{S}_{16}$) nanoparticles that then form ternary $\text{Cu}_4^+\text{Sn}^{4+}\text{S}_4^{2-}$ (CTS) and quaternary $\text{Cu}_2^+\text{Zn}^{2+}\text{Sn}^{4+}\text{S}_4^{2-}$ (CZTS) sequentially will be presented. Ex-situ studies using Z-contrast scanning transmission microscopy (STEM), phase contrast high resolution transmission electron microscopy (HRTEM) and energy dispersive X-ray (EDX) are used to monitor the structural and compositional changes during each growth phase. In addition, temperature-dependent studies with surface enhanced Raman scattering (SERS) spectroscopy analysis and powder X-ray diffraction (XRD) examined the kinetics and energetic barriers towards structural transformations. To determine the chemical potential and thermodynamics reaction pathway, first-principles calculations using Vienna Ab initio Simulation Package (VASP) were carried out. During the growth of CTS, Sn^{4+} diffuses into $\text{Cu}_{29}\text{S}_{16}$ and induces a series of phase transformations while the transformation into CZTS is accompanied by multiple parasitic phase formation reactions.

5.2 Experimental Methods

5.2.2 Chemicals and materials

Copper(II) acetate monohydrate ($\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$, Aldrich, >98%), zinc acetylacetonate ($\text{Zn}(\text{acac})_2$, Aldrich, 97%), tin(IV) acetate ($\text{Sn}(\text{OAc})_4$, Aldrich), 1-octadecene (ODE, Aldrich, 90%), 1-dodecanethiol (DDT, Aldrich, 98%) and oleylamine (OAm, Acros, 97%) were used without further purification.

5.2.2 Synthesis of nanoparticles

5.2.2.1 Synthesis of $\text{Cu}_{29}\text{S}_{16}$ nanoparticles

In a typical synthesis, 0.455 mmol of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (Sigma-Aldrich $\geq 98\%$) is added to 1 mL of oleylamine (Oam, Acros Organics 80-90%) and 9 mL of 1-octadecene (Sigma-Aldrich 90%) in a three-necked round bottom flask (RBF) and heated to 130 °C under reduced pressure before adding 1.5 mL of dodecanethiol (DDT, Sigma-Aldrich $\geq 98\%$) followed by further heating to 150 °C for 10 mins under reduced pressure. The solution was heated rapidly (10 °C/min) to 230 °C and reacted for 60 mins under an N_2 environment. The reaction was stopped by removing the RBF from the heating mantle and allowed to naturally cool to 160 °C before placing it in a water bath for rapid cooling to 100 °C (for synthesis of Cu_4SnS_4 nanoparticles) or room temperature (for characterization). Nanoparticles for characterization were washed via the addition of 20 mL of hexane to the reaction solution and centrifuged 3 times at 10000 rpm for 3 mins and allowed to dry in a self-built N_2 box.

5.2.2.2 Synthesis of Cu_4SnS_4 nanoparticles.

A solution of Sn^{4+} salt (0.225 mmol of $\text{Sn}(\text{Oac})_4$ (Sigma-Aldrich) dissolved in 1 mL DDT and 1 mL Oam) was added to a freshly prepared solution of $\text{Cu}_{29}\text{S}_{16}$ nanoparticles when it had cooled to 80 °C. The reaction mixture was then heated rapidly (10 °C/min) to 150 °C under reduced pressure and the temperature was raised (10 °C/min) to 230 °C. The mixture was allowed to react at that temperature for 60 mins under a N_2 atmosphere. The reaction was stopped by removing the RBF from the heating mantle and allowed to cool naturally to 160 °C before placing it in a water bath for rapid cooling to 100 °C (for synthesis of $\text{Cu}_2\text{ZnSnS}_4$ nanoparticles) or room temperature (for characterization). Nanoparticles for characterization were washed via the addition of 20 mL of hexane to the reaction solution and centrifuged 3 times at 10000 rpm for 3 mins and allowed to dry in a self-built N_2 box.

5.2.2.2 Synthesis of $\text{Cu}_2\text{ZnSnS}_4$ nanoparticles

0.225 mmol of $\text{Zn}(\text{acac})_2 \cdot x\text{H}_2\text{O}$ (assuming 1 part H_2O , Sigma-Aldrich powder) was added to a freshly prepared Cu_4SnS_4 nanoparticles solution when it had cooled to 80 °C. The reaction mixture was then heated rapidly (10 °C/min) to 150 °C under reduced pressure. The temperature was raised (10 °C/min) to 240 °C and the mixture was allowed to react at this temperature for 90 mins under N_2 environment. The reaction was stopped by removing the RBF from the heating mantle and allowed to cool naturally to 160 °C before placing it in a water bath for rapid cooling to room temperature. Nanoparticles for characterization were washed via the addition of 20 mL of hexane to the reaction solution and centrifuged 3 times at 10000 rpm for 3 mins and allowed to dry in a self-built N_2 box.

5.2.3 Characterization

5.2.3.1 Powder X-ray diffraction

XRD samples were prepared by drop casting a concentrated nanoparticles solution on a Si wafer (1.5 x 1.5 cm) to form a thick and dense film. Patterns were recorded using a Bruker D8 diffractometer with a $\text{Cu-K}\alpha$ radiation source ($\lambda_1 = 1.54056 \text{ \AA}$, $\lambda_2 = 1.54439 \text{ \AA}$) and a LynxEye detector and operated at 40 kV and 40 mA. All scan range are from 10° to 70° 2θ , with a scan speed at 0.01° s^{-1} . All powder patterns were refined using the Topas. Quantitative Rietveld refinement is carried out using the Fundamental parameters approach, using accepted structural models obtained from the ICSD database of the respective components with just instrumental parameters refined i.e. background (5th-term Chebyshev polynomial, zero error and 'crystallite size' to model the microstructure-controlled line broadening.

5.2.3.2 Surface Enhanced Raman Scattering (SERS) spectroscopy

A 50nm thick Ag film on Si (10nm Cr coating) was prepared using thermal evaporation to serve as substrate for SERS spectroscopy characterization of as-synthesized nanoparticles. A diluted nanoparticles solution in hexane was then drop-cast (5 μL , 4mg/mL) onto an Ag coated Cr/Si wafer (5 mm x 5mm) to form a

thin film for SERS measurements. SERS spectra were obtained with the sample mounted on the Ramantouch microspectrometer (Nanophoton Inc, Osaka, Japan). A 532 nm laser was used as an excitation laser. The excitation laser light was focused into a line (x-y axis line scan mode) on a sample through a cylindrical lens and an air objective lens (LU Plan Fluor 100× NA 0.9). The excitation laser power was 0.04 mW with exposure time for each line and the slit widths of the spectrometer were 30 secs and 50 μ m. Each final SERS spectrum presented is an average of all the spectra (300 spectra) collected for each sample.

5.2.3.3 TEM analysis

TEM sample preparation involved dropping a single drop of diluted nanoparticles solution (4mg/mL) on a pure carbon Ni grid (Ted Pella) and allowing it to dry before drip-wise washing it with 1 mL of toluene. High resolution bright field (HR-BF) transmission electron microscopy (TEM) was carried out on a TECNAI F20 operating at an accelerating voltage of 200 kV. High resolution high annular angular dark field (HR-HAADF) scanning TEM image was carried out on TEAM 0.5 (a modified FEI Titan 80-300 microscope equipped with a high-brightness Schottky-field emission electron source with two CEOS hexapole-type spherical aberration correctors) operating at an acceleration voltage of 300 kV. X-ray dispersion energy spectrum (EDS) mapping was carried out on Titanx (FEI TitanX 60-300 microscope equipped with Bruker windowless EDS detector with a solid angle of 0.7 steradians enables high count rates with minimal dead time) operating at 200 kV at 80 kx magnification, 0.68 nA beam current, 2068x2068 pixel resolution, with a dwell time of 15 mins and an average signal count of >1000 per pixel. Fast Fourier Transform (FFT) and inverse FFT were carried out on a Gatan Microscope Suite.

5.2.3.4 Density Functional Theory (DFT) Calculation

First-principle modelling to calculate the formation energies of each process using the Vienna Ab-initio Simulation Package (VASP) was employed. The projector augmented wave (PAW) method was used to describe the electron-ion

interaction and the exchange correlation between electrons is described by the generalized gradient approximation (GGA) in the Perdew–Burke–Ernzerhof (PBE) form. Although the PBE functional cannot correctly describe the band structures of CZTS, the energy differences between different phases are precise enough. A cutoff energy of 350 eV for the plane-wave basis set was used. For different compounds, different k -mesh settings within the Monkhorst–Pack scheme were used. Lattice relaxation was continued until the forces on all the atoms were converged to less than 10^{-2} eV Å⁻¹. The volume of the supercell was fixed but all the internal freedoms were fully relaxed. The lattice constants reproduced from GGA-PBE computations, as well as the theoretical and experimental values from the literatures are listed in **Table 5.1**. From the table, it can be determined that the calculation results agree well with the experimental values. The formation energy is calculated as:

$$\Delta E = E(\text{products}) - E(\text{reactants})$$

where the $E(\text{products})$ and $E(\text{reactants})$ are the total energies of products and reactants, respectively.

Table 5.1 DFT: k -mesh setting and calculated lattice parameters for different compounds.

Compounds	Atoms in supercell	k -mesh setting	Lattice parameters			Total energy(eV)
			$a(\text{\AA})$	$b(\text{\AA})$	$c(\text{\AA})$	
			Calculated (Literature)	Calculated (Literature)	Calculated (Literature)	
Cu ₂₉ S ₁₆ (<i>P1</i>)	180	2×2×2	13.341(13.409)	13.530(13.405)	15.617(15.485)	-719.9440
Cu ₃₁ S ₁₆ (<i>P2₁/n</i>)	376	1×1×1	26.731(26.897)	15.930(15.745)	13.519(13.565)	-1507.5852
Cu ₃₂ S ₁₆ (<i>P2₁/c</i>)	144	1×1×1	14.996(15.246)	12.163(11.884)	13.412(13.494)	-574.1400
Cu ₄ SnS ₄ (<i>Pnma</i>)	36	2×4×4	13.622(13.558)	7.702(7.681)	6.492(6.412)	-150.0604

Table 5.2. Calculated lattice constant and energy difference by PDE functional

	Zinc-blende derived			Wurtzite derived	
	ZB-KS	ZB-ST	PMCA	WZ-ST	WZ-KS
Energy differences (eV)	0	0.046	0.060	0.135	0.114
Theoretical lattice parameters (Å)	$a=b=5.468$ $c=10.939$	$a=b=5.462$ $c=10.962$	$a=b=5.464$ $c=10.956$	$a=7.693$ $b=6.685$ $c=6.362$	$a=7.720$ $b=6.672$ $c=6.360$
Experimental lattice parameters (Å)	$a=b=5.428^{[1]}$ $c=10.856^{[1]}$	$a=b=5.436^{[2]}$ $c=10.872^{[2]}$	--	$a=7.539^{[3]}$, $7.637^{[4]}$ $b=6.430^{[3]}$, $6.614^{[4]}$ $c=6.204^{[3]}$, $6.298^{[4]}$	

ZB= Zinc-blende, KS=Kesterite, ST=Stannite, PMCA=Primitive-mixed CuAu-like, WZ=wurtzite

5.3 Principal outcomes

5.3.1 Thermodynamic growth study of binary Cu-S to ternary Cu-Sn-S phase

a TEM characterization of $\text{Cu}_{29}\text{S}_{16}$ and Cu_4SnS_4 nanoparticles

b Ex-situ temporal studies of crystal and phases changes.

Figure 5.1 Ex-situ temporal studies of $\text{Cu}_{29}\text{S}_{16}$ growth to Cu_4SnS_4 . **a.** TEM characterization of binary $\text{Cu}_{29}\text{S}_{16}$ nanoparticles and ternary Cu_4SnS_4 nanoparticles. Low magnification TEM (**i,iv**), STEM-EDX (**ii, v**) and HR-STEM (**iii, vi**) of $\text{Cu}_{29}\text{S}_{16}$ and Cu_4SnS_4 nanoparticles respectively. **b.** Pictorial illustration (**vii**) of ex-situ temporal studies of crystal and phases changes characterized using XRD (**viii**) and SERS (**ix**).

Binary Cu-S nanoparticles are synthesized via heating up method. Stoichiometry estimation of as-synthesized nanoparticles by ultra-sensitive windowless STEM-EDX detector gives a Cu:S ratio of 1.8:1 (**Figure 5.1i-iii**). XPS characterization of the oxidation states shows the presence of $\text{Cu}^{2+}/\text{Cu}^+$ and S^{2-} ,

powder XRD characterization and Rietveld refinement of as-synthesized Cu-S nanoparticles crystal structure is consistent with triclinic (*P1*) Cu₂₉S₁₆ (ICSD 185807) with a lattice parameter of $a=13.40(9)$, $b=13.41(5)$, $c=15.51(6)$, $\alpha=90.02(2)$, $\beta=90.02(1)$, $\gamma=90.02(0)$ (**Figure 5.2 and 5.3**).²⁶ SERS spectroscopy shows a characteristic absorption at $\sim 298\text{ cm}^{-1}$ assigned to the crystal lattice vibration of Cu₂₉S₁₆ phase (**Figures 5.1ix and 5.4i**). Cu₂₉S₁₆ nanoparticles are imaged by STEM to be nanoplates due to their circular shape and flat surfaces on the short axis. Fast Fourier transforms (FFTs) of the HR-STEM and HR-TEM images of Cu₂₉S₁₆ nanoplates show that the short axis of the nanoparticle is consistent with the $\langle 100 \rangle$ zone axis of *P1* Cu₂₉S₁₆ crystal structure (**Figure 5.1iii**). The equation of the reaction can be expressed as

where C₁₂S⁻ is the deprotonated ion of DDT. DDT serve as both sulphur source and reduction agent in this reaction.^{27,28} Firstly, thiol-ether (C₁₂-S-C₁₂) compound is formed after DDT ligand donates a sulphur atom and reacts with another DDT. Secondly, dodecanethiol disulphide ether (C₁₂S-SC₁₂) compound is formed after C₁₂S⁻ reduces Cu²⁺ to Cu⁺. Firstly, C₁₂S⁻ reduced Cu²⁺ to Cu⁺ by donating an electron to form C₁₂S[•] radical which dimerizes to form dodecanethiol disulphide ether (C₁₂-S-S-C₁₂) as described below

Secondly, the formation of thiol-ether (C₁₂-S-C₁₂) compound is via a disproportionation reaction as described below

Figure 5.2 (i) Elemental mapping of as-synthesized Cu-S nanoparticles on various TEM carbon grid spots. Scale bar is 30 nm. (ii) HR-BF imaging, (iii) HR-HAADF imaging, (iv) FFT image of (iii), (v) JEMS simulated TEM diffraction pattern along $\langle 100 \rangle$ zone axis. (vi) CRISP-treated HR-HAADF image, (vii) JEMS simulated HR-HAADF image along $\langle 100 \rangle$ zone axis, and (viii) JEMS simulated crystal potential along $\langle 100 \rangle$ zone axis.

Rietveld refinement of as-synthesized Cu-S nanoparticles

Figure 5.3 Rietveld refinement of XRD pattern of as-synthesized Cu₅₈S₃₂ nanoparticles.

Figure 5.4 (i) peak fitting of SERS spectrum and (ii) XPS characterization of Cu-S nanoparticles.

Elemental mapping: Time-growth study of $\text{Cu}_{29}\text{S}_{16}$ to Cu_4SnS_4 0.22 mmole Sn^{4+}

	(atom %)		
	Cu	Sn	S
10 mins	52.7 ± 4.9	7.8 ± 2.4	39.5 ± 3.8
20 mins	42.5 ± 3.9	13.1 ± 4.0	44.4 ± 4.2
40 mins	42.1 ± 3.9	13.8 ± 4.2	44.1 ± 4.1
60 mins	43.3 ± 4.0	12.7 ± 3.7	44.0 ± 4.1

Figure 5.5 Elemental mapping of nanoparticles obtained during ex-situ study during the growth of Cu_4SnS_4 from $\text{Cu}_{29}\text{S}_{16}$ at 10, 20, 40 and 60 mins.

To investigate the growth mechanism of ternary alloy Cu-Sn-S from $\text{Cu}_{29}\text{S}_{16}$, an ex-situ analysis of $\text{Cu}_{29}\text{S}_{16}$ CE with Sn^{4+} as a function of time was performed using STEM-EDX, SERS, XRD and Rietveld analysis (**Figures 5.1vii-ix** and **5.5-5.7**). Sn^{4+} solution was added to a solution of $\text{Cu}_{29}\text{S}_{16}$ nanoparticles in a ratio of 2:1 (Cu:Sn) and heated, with samples quenched rapidly by immersing the round bottom flask (RBF) in water (~25 °C) at fixed interval.

Figure 5.6 (i) SERS spectrum and (ii) XRD characterization of as-synthesized $\text{Cu}_{29}\text{S}_{16}$ nanoparticles (Black line), addition of $0.22 \text{ mmol Sn}^{4+}$ to $\text{Cu}_{29}\text{S}_{16}$ nanoparticle solution and react at 200°C for 0 min (Cu_4SnS_4 200°C for 0 min Red line), 230°C for 6 mins (Cu_4SnS_4 230°C for 6 mins Blue line) and 230°C for 60 mins (Cu_4SnS_4 Green line), addition of $0.22 \text{ mmol Zn}^{2+}$ to Cu_4SnS_4 nanoparticle solution and react at 180°C for 0 min ($\text{Cu}_2\text{ZnSnS}_4$ 180°C for 0 min Magenta line) and 230°C for 90 mins ($\text{Cu}_2\text{ZnSnS}_4$ Brown line); Quenching of reaction immediately (0 min).

Figure 5.7 Rietveld refinement of XRD diffraction patterns of (i) 200°C for 0 mins and (ii) 230°C for 6 mins after addition of Sn^{4+} into $\text{Cu}_{29}\text{S}_{16}$ nanoparticles solution

Upon quenching of the samples immediately (0 min) at 200 °C, Rietveld refinement estimates the sample to contain 81% $\text{Cu}_{30}^+\text{Cu}_{16}^{2+}\text{S}_{16}^{2-}$ ($\text{Cu}_{31}\text{S}_{16}$, $P2_1/n$, ICSD 100334) and 19% $\text{Cu}_4^+\text{Sn}^{4+}\text{S}_4^{2-}$ (Cu_4SnS_4 , $Pnma$, ICSD 628881).^{29,30} The two SERS peaks at ~295 to ~315 cm^{-1} are consistent with Cu_4SnS_4 phases (**Figures 5.5-5.6**).

Characterization data from XRD and SERS are used to propose the chemical reaction and can be expressed as:

Further heating to 230 °C for 6 mins gives a mixture of 75% $\text{Cu}_{32}^+\text{S}_{16}^{2-}$ (Cu_2S , $P2_1/c$, ICSD 100333) and 25% Cu_4SnS_4 ($Pnma$) as estimated by Rietveld refinement and verified by SERS, with the characteristic Raman peaks for Cu_4SnS_4 phase at 315 cm^{-1} and 322 cm^{-1} (**Figures 5.5-5.7**).²⁹

The formation of Cu_4SnS_4 and $\text{Cu}_{32}\text{S}_{16}$ phases at 230 °C is proposed to occur via the following reaction:

Finally, after the reaction proceeds for 60 mins at 230 °C, stoichiometric estimation of as-synthesized nanoparticles by ultra-sensitive windowless STEM-EDX detector gives a Cu:Sn:S ratio of 3.5:1:3.5. XPS characterization of the oxidation states shows the presence of $\text{Cu}^{2+}/\text{Cu}^+$, $\text{Sn}^{4+}/\text{Sn}^{2+}$ and S^{2-} , Rietveld refinement shows the crystal structure is consistent with orthorhombic ($Pnma$) Cu_4SnS_4 and Raman shows 2 SERS peaks at ~315 and ~325 cm^{-1} assigned to Cu-Sn-S crystal lattice vibrations (**Figures 5.1ix, 5.8-5.10**). Cu_4SnS_4 nanoparticles are imaged by STEM to be nanoplates due to their hexagonal shape and flat surfaces on the short axis (**Figure 5.8**). Fast Fourier transforms (FFTs) of the HR-STEM and HR-TEM images of Cu_4SnS_4 nanoplates show that the short axis of the

nanoparticle is consistent with the $\langle 001 \rangle$ zone axis of *Pnma* Cu_4SnS_4 crystal structure (**Figures 5.8**).

Figure 5.8 (i) Elemental mapping of as-synthesized Cu-Sn-S nanoparticles on various TEM carbon grid spots. Scale bar is 30 nm. (ii) HR-BF imaging, (iii) HR-HAADF imaging, (iv) FFT image of (iii), and (v) JEMS simulated TEM diffraction pattern along $\langle 100 \rangle$ zone axis. (vi) CRISP-treated HR-HAADF image, (vii) JEMS simulated HR-HAADF image along $\langle 001 \rangle$ zone axis, (viii) JEMS simulated crystal potential along $\langle 001 \rangle$ zone axis.

Figure 5.9 Rietveld refinement of XRD pattern of as-synthesized Cu-Sn-S nanoparticles.

Figure 5.10 (i) Peak fitting of SERS spectrum and (ii) XPS characterization of as-synthesized Cu-Sn-S nanoparticles.

Figure 5.11 Phases presence at fixed temperature interval. XRD spectrum of as-synthesized CTS nanoparticles after addition of Sn^{4+} into $\text{Cu}_{29}\text{S}_{16}$ nanoparticles solution, heated and immediately quenched upon reaching targeted temperature. (i) As-synthesized $\text{Cu}_{29}\text{S}_{16}$ nanoparticles showing crystal phase of Pc $\text{Cu}_{29}\text{S}_{16}$. Solution quenched at (ii) 160 °C showing crystal phase of Pc $\text{Cu}_{29}\text{S}_{16}$ + $Pnma$ Cu_4SnS_4 , (iii) 180 °C showing crystal phase Pc $\text{Cu}_{29}\text{S}_{16}$ + $P12_1c1$ $\text{Cu}_{31}\text{S}_{16}$ + $Pnma$ Cu_4SnS_4 , (iv) 200 °C showing crystal phase of $P12_1c1$ $\text{Cu}_{31}\text{S}_{16}$ + $Pmna$ Cu_4SnS_4 , (v) 230 °C showing crystal phase $P12_1n1$ $\text{Cu}_{32}\text{S}_{16}$ + $Pmna$ Cu_4SnS_4 . Standard XRD of (vi) $Pnma$ Cu_4SnS_4 , (vii) Pc $\text{Cu}_{29}\text{S}_{16}$, (viii) $P12_1c1$ $\text{Cu}_{31}\text{S}_{16}$ and (ix) $P12_1n1$ $\text{Cu}_{32}\text{S}_{16}$.

Table 5.3 DFT calculated enthalpy* of phase formation

Phase	$\text{Cu}_{29}\text{S}_{16}$	$\text{Cu}_{31}\text{S}_{16}$	Cu_2S	Cu_4SnS_4	$\text{Cu}_2\text{ZnSnS}_4$	
Space group	$P1$	$P12_1n1$	$P12_1c1$	$Pnma$	Pc	$Pmn2_1$
ΔH_f^* (eV)	-5.666	-6.656	-0.366	-2.242	-3.673	-3.663

* $\Delta H_f = E_{\text{solid}} - n_\alpha \sum_\alpha E_\alpha^{\text{bulk}} \leq n_\alpha \Delta\mu_\alpha \leq 0$, where μ_α is the chemical potential of element α during reaction, μ_α^0 is the reference chemical potential of element α in its standard elemental phase (e.g fcc-Cu_(s), fcc-Zn_(s)), $\Delta\mu_\alpha$ is the change in free energy due to the state and chemical environment of element α during reaction.

The formation of Cu_4SnS_4 phase from $\text{Cu}_{32}\text{S}_{16}$ involves the reaction:

To determine the chemical potential and thermodynamics of the above proposed chemical reactions (**equations 5.2-5.4**), first-principles calculations using Vienna Ab initio Simulation Package (VASP), and temperature dependent growth studies using XRD are carried out (**Figures 5.6 and 5.11**).³¹ The theoretical enthalpy of formation of intermediate phases ($\text{Cu}_{29}\text{S}_{16}$, $\text{Cu}_{31}\text{S}_{16}$ and Cu_2S) and Cu_4SnS_4 phase are shown in **Table 5.3**. As Sn^{4+} is the reactant promoting cationic exchange in these reactions, we focus on the chemical potential of Sn^{4+} ($\Delta\mu_{\text{Sn}}$) to predict the thermodynamic feasibility of the proposed reaction equation. For the proposed reactions (**equations 5.2-5.4**) to be thermodynamically feasible, the minimum $\Delta\mu_{\text{Sn}}$ required must be lower than the lowest theoretical calculated chemical potential of Sn^{4+} available. Under equilibrium conditions, the summation of the chemical potentials ($\Delta\mu_\alpha$) of the constituent elements (e.g Cu, Sn, S) in a phase equals that of the theoretical calculated enthalpy of formation.

$$\Delta H_f (\text{Cu}_4\text{SnS}_4) = 4\Delta\mu_{\text{Cu}} + \Delta\mu_{\text{Sn}} + 4\Delta\mu_{\text{S}} = -2.242 \text{ eV} \quad (5.5)$$

Table 5.4 Calculated chemical potential energy* of Sn and Zn

Reaction equation	$\text{Cu}_{29}\text{S}_{16} + \text{Sn}$ (2)	$\text{Cu}_{31}\text{S}_{16} + \text{Sn}$ (3)	$\text{Cu}_2\text{S} + \text{Sn}$ (4)	$\text{Cu}_4\text{SnS}_4 + \text{Zn}$ (8)	Theoretical minimum chemical potential at equilibrium
$\Delta\mu_{\text{Sn}}$ (eV)	> -2.434	> 2.422	> -0.778	-	-2.242
$\Delta\mu_{\text{Zn}}$ (eV)	-	-	-	> -1.797	-3.673

* $\Delta H_{\text{equation 2}} = \sum \Delta H_{\text{product}} - \sum \Delta H_{\text{reactant}}$

Therefore, based on the theoretical calculated enthalpy formation of Cu_4SnS_4 (**equation 5.5 and Table 5.3**), the chemical potential of Sn^{4+} in the reaction solution follows the lowest possible chemical potential energy of Sn (Sn in Cu_4SnS_4 crystal matrix) available, which is -2.242 eV (assuming $\Delta\mu_{\text{Cu}}$ and $\Delta\mu_{\text{S}}$ to be 0).

Following on, the chemical potential of Sn^{4+} required for the spontaneous reaction of the three proposed reactions (**equations 5.2 to 5.4**) is summarized in **Table 5.4**. In a typical enthalpy of reaction calculation, the enthalpy of reaction can be written as

$$\begin{aligned}\Delta H_{\text{equation 2}} &= \sum \Delta H_{\text{product}} - \sum \Delta H_{\text{reactant}} & (5.6) \\ &= (\Delta H_{\text{Cu}_4\text{SnS}_4} + \frac{13}{8} \Delta H_{\text{Cu}_3\text{S}_{16}}) - (\Delta\mu_{\text{Sn}} + \frac{15}{8} \Delta H_{\text{Cu}_2\text{S}_{16}}) \\ &= -2.434 \text{ eV} - \Delta\mu_{\text{Sn}}\end{aligned}$$

For $\Delta H_{\text{equation 2}}$ to be thermodynamically spontaneous ($\Delta H_{\text{equation 2}} < 0$), the minimum chemical potential energy of Sn^{4+} ($\Delta\mu_{\text{Sn},\text{equation 2}}$) is calculated to be -2.434 eV. As the minimum $\Delta\mu_{\text{Sn},\text{equation 2}}$ required is lower than theoretical calculated chemical potential available of -2.242 eV, **equation 5.2** is thermodynamically spontaneous. In addition, temperature dependent studies show that the reaction will occur once temperature reaches 160-180 °C, thereby explaining the observation of Cu_3S_{16} and Cu_4SnS_4 phases at 200 °C (**Figures 5.11-5.12**).

Figure 5.12 Rietveld refinement of XRD pattern obtained from nanoparticles after reacting $\text{Cu}_{29}\text{S}_{16}$ nanoparticles with Sn^{4+} at **a.** 180 °C for 2 hrs and **b.** 200 °C for 2 hrs.

Next, the calculated minimum chemical potential of Sn^{4+} required for the second reaction (**equation 5.3**) is 2.422 eV ($\Delta\mu_{\text{Sn},\text{equation 3}}$). As the $\Delta\mu_{\text{Sn},\text{equation 3}}$ of the reaction is much higher than the minimum theoretical calculated chemical potential available of -2.242 eV, **equation 3** is therefore thermodynamically not spontaneous. In addition, further studies done also show **equation 3** to be incomplete even after prolonged reaction (2 hrs) at lower temperature (180 °C). It requires higher temperature (~200 °C) for a complete reaction (**Figures 5.11-5.12**). The need for higher temperature is explained by the following thermodynamic equation

$$\Delta\mu_{Sn} = \Delta\mu_{Sn, equilibrium} + \Delta H \quad (5.7)$$

$$\Delta H = C_p \Delta T + V(1 - \alpha T)\Delta p \quad (5.8)$$

where ΔH is the change in internal energy, C_p is the heat capacity constant of the solvent, ΔT is the change in temperature, V is the volume of the reaction solution, α is the coefficient of thermal expansion, Δp is the change in pressure. As the temperature increases, the thermal energy rises $\Delta\mu_{Sn}$. When $\Delta\mu_{Sn}$ exceeds the minimum required chemical potential of $\Delta\mu_{Sn, equation 3}$ (2.422 eV), the reaction then becomes spontaneous.

Next, the calculated minimum chemical potential of Sn^{4+} required for the third reaction (**equation 5.4**) is -0.778 eV ($\Delta\mu_{Sn, equation 4}$). As the $\Delta\mu_{Sn, equation 4}$ of the reaction is much higher than the minimum theoretical calculated chemical potential available of -2.242 eV, **equation 5.4** is therefore thermodynamically not spontaneous. However as $\Delta\mu_{Sn}$ is > 2.422 eV at 200 °C, further increase of reaction temperature to 230 °C would have increased the chemical potential energy of Sn, therefore explaining the complete reaction formation of Cu_4SnS_4 from Cu_2S at 230 °C (**Figures 5.7-5.8**). From this study, Cu_4SnS_4 nanocrystals have been shown to form via an alloyed-cation exchange mechanism at 230 °C. A single phase transition ($\text{Cu}_{29}\text{S}_{16} + \text{Sn} \rightarrow \text{Cu}_4\text{SnS}_4$) has been involving three kinetically controlled domino-effect reaction processes (**equation 5.2-5.4**), with the rate-limiting step identified as being the intermediate step (**equation 5.3**).

5.3.2 Ex-situ temporal crystal structure studies of binary Cu-S to ternary Cu-Sn-S phase growth

a Preferential growth pathway of $\text{Cu}_{29}\text{S}_{16}$ to Cu_4SnS_4

b Positive co-operative growth mechanism of $\text{Cu}_{29}\text{S}_{16}$ to Cu_4SnS_4

Figure 5.13 Preferential growth pathway of $\text{Cu}_{29}\text{S}_{16}$ to Cu_4SnS_4 phase. a. TEM imaging (i) and STEM-EDX mapping (ii) of hetero-nanoparticles ($\text{Cu}_{31}\text{S}_{16}/\text{Cu}_4\text{SnS}_4$), HR-TEM (iii, iv) showing the growth direction along the phase boundary and pictorial illustration of sulphur anionic template influencing Sn^{4+} diffusion pathway. **b.** XRD and STEM-EDX (vi) imaging to nanoparticles synthesized from Cu:Sn 4:1 and 8:1 showing positive-cooperatively growth phenomena.

Next, the direct imaging of structural growth and characterization of crystal growth were carried out to investigate the preferential lattice transformation during growth of $\text{Cu}_{29}\text{S}_{16}$ to CTS. As the ternary phase is Cu_4SnS_4 , the amount of Sn consumed (Cu:Sn 4:1) was half of that available (Cu:Sn 2:1), therefore the amount of Sn used was halved. Quenching the reaction of 0.057 mmol Sn with $\text{Cu}_{29}\text{S}_{16}$ (Cu:Sn 4:1) at 2 mins froze the transformation to reveal the growth pathway (lattice planes) of Sn^{4+} taken during its diffusion into $\text{Cu}_{29}\text{S}_{16}$. STEM-EDX mapping of the nanoparticles showed elemental distribution characteristic of a hetero-phase (Cu-S/Cu-Sn-S). XRD and FFT of the HR BFTEM imaging revealed the top flat surface of the hetero-phase to be the $\langle 100 \rangle$ zone-axis of $\text{Cu}_{31}\text{S}_{16}$ ($P12_1n1$) and $\langle 001 \rangle$ zone axis of Cu_4SnS_4 ($Pnma$) (**Figures 5.13i-iv** and **5.14**). As the symmetry of S^{2-} framework along $\langle 100 \rangle_{\text{Cu}_{31}\text{S}_{16}}$ and $\langle 001 \rangle_{\text{Cu}_4\text{SnS}_4}$ is C_{3v} , the observed homogenous contrast using C_{3v} symmetry diffraction pattern masked on the HR-BFTEM FFT image (**Figure 5.15**) confirmed the growth of $\text{Cu}_{29}\text{S}_{16}$ to Cu_4SnS_4 to be an epitaxial growth process. In addition to Cu-S/Cu-Sn-S hetero-nanoparticle, it was also observed that there are nanoparticles composed with only Cu and S elements (Cu_xS nanoparticles). As the reaction was allowed to proceed further, ex-situ STEM-EDX mapping of aliquots drawn at fixed time interval showed a growth in Cu-Sn-S phase and increase in Cu-S nanoparticles size (**Figure 5.16**). The increase in Cu-Sn-S phase is indicative of Sn^{4+} incorporation into Cu-S phase, while the growth in Cu_xS nanoparticle size is due to the reaction of displaced Cu^+ and DDT with Cu-S nanoparticles via reconstructive dissolution process. In addition, the preferential growth of $\text{Cu}_{29}\text{S}_{16}$ to Cu_4SnS_4 to proceed along the flat surface instead of the short axis can be addressed (**Figure 5.13v**). Due to the conservation of anionic framework and nanoplates morphology during the growth, S always arranges in hexagonal C_{3v} symmetry with it at in the centre of the S-M_4 ($\text{M} = \text{Sn, Cu}$) tetrahedral. As the atoms in the crystal lattices involved in the displacement reaction were behind the S atoms down the atomic column of the short axis, it will be kinetically less favourable to proceed down the short axis. Therefore, the preferential diffusion of Sn^{4+} atoms along $[012]$ plane of $\text{Cu}_{29}\text{S}_{16}$ can be explained

by the lack of hindrance from S^{2-} of the anionic framework hence kinetically more favourable.

a Proposed epitaxial growth of $P1\ Cu_{29}S_{16}$ into $Pnma\ Cu_4SnS_4$ using Sulfur as growth template

b Proposed epitaxial growth of $P12_1n1\ Cu_{31}S_{16}$ into $Pnma\ Cu_4SnS_4$ using Sulfur as growth template

c Proposed epitaxial growth of $P12_1c1\ Cu_{32}S_{16}$ into $Pnma\ Cu_4SnS_4$ using Sulfur as growth template

Figure 5.14 Crystal illustration of hetero-nanoparticle interface lattice alignment during growth of $Cu_{29}S_{16}$ to Cu_4SnS_4 . **a.** $Cu_{29}S_{16}/Cu_4SnS_4$, **b.** $Cu_{31}S_{16}/Cu_4SnS_4$ and **c.** $Cu_{32}S_{16}/Cu_4SnS_4$.

a. BF-HRTEM of phase boundary between $\text{Cu}_{31}\text{S}_{16}$ and **b. HR HAADF imaging of CTS nanoparticles**

Figure 5.15 a. HR-TEM of focus image (i) showing the phase boundary between Cu_4SnS_4 and Cu_2S , out-of-focus (iv) image showing the intermediate phase during transformation of Cu_2S to Cu_4SnS_4 . Inverse FFT (ii) of (i) and false colouration (v) emphasizing on Cu_4SnS_4 phase (red contrast) from Cu_2S (blue contrast). Inverse FFT of C_{3v} symmetry hexagonal diffraction pattern (iii) of (i) and false colouration (vi) showing epitaxial hexagonal lattice arrangement between Cu_4SnS_4 and Cu_2S phase. **b.** High resolution HAADF imaging of Cu_4SnS_4 nanoparticles showing lattice plane along the side of the nanoparticle (vii), and image at higher magnification (viii, ix).

Figure 5.16 a. Elemental mapping and HR-TEM of nanoparticles obtained during ex-situ study of Cu_4SnS_4 nanoparticles grown from $\text{Cu}_{29}\text{S}_{16}$ using 0.057 mmol Sn^{4+} (**quarter**). Elemental distribution change occurring across time 2, 4, 6 and 60 mins with pictorial illustration.

Following on, the as-synthesized nanoparticles obtained after 60 mins of reaction were bifurcated into Cu-Sn-S and Cu-S phases despite sufficient Sn^{4+} to convert all $\text{Cu}_{29}\text{S}_{16}$ nanoparticles to Cu_4SnS_4 nanoparticles (**Figure 5.13vi and 5.17**). This observation can be explained from **equation 5.9**

$$\Delta\mu_{\text{Sn}} = RT \cdot \ln\Delta c_{\text{Sn}} \quad (5.9)$$

where R is ideal gas constant, T is temperature and Δc_{Sn} is the change in concentration of Sn^{4+} in the solution during reaction. Decreasing the concentration of Sn^{4+} has lowered μ_{Sn} below the minimum chemical potential hence hindering complete reaction. On the other hand, formation of bifurcated phases instead of a mono-population of incompletely reacted hetero-nanoparticles (Cu-S/Cu-Sn-S) suggests the possibility that the growth of $\text{Cu}_{29}\text{S}_{16}$ nanoparticles to Cu_4SnS_4 nanoparticles follows a positive co-operative CE pathway (**Figure 5.13vi**). Recently, Prashant et al reported a rare CE exchange mechanism behaving similarly to the positive cooperatively binding of O_2 in blood haemoglobin.²³ In positive co-operative CE reactions, successful cation displacement in a nanoparticles increases the affinity for subsequent cation exchange. The formation of bifurcated Cu-Sn-S

and Cu-S phases as a result of positive co-operation is further verified by the lower amount of Sn^{4+} (Cu:Sn 8:1) where STEM-EDX and Rietveld refinement confirmed the formation of $\text{Cu}_{32}\text{S}_{16}$ and Cu_4SnS_4 phases (**Figures 5.17-5.18**). Due to the difference in cation affinity, Sn^{4+} will react faster with reacted nanoparticles ($\text{Cu}_{29}\text{S}_{16}:\text{Sn}^{4+}$) instead of unreacted $\text{Cu}_{29}\text{S}_{16}$ nanoparticles therefore giving rise to bifurcated Cu-Sn-S and Cu-S phases.

Figure 5.17 Elemental mapping of as-synthesized CTS_{half} , $\text{CZTS}_{\text{half-quarter}}$, $\text{CTS}_{\text{quarter}}$ and $\text{CZTS}_{\text{quarter-quarter}}$ nanoparticles.

Figure 5.18 Rietveld refinement of $\text{CTS}_{\text{quarter}}$

5.3.3 Thermodynamic growth study of ternary Cu-Sn-S to quaternary Cu-Zn-Sn-S phase

Figure 5.19 Conflicting reaction kinetics involved in a single phase transformation process. **a**, HEDX mapping and schematic representation of multi-reaction competition occurring during conversion of Cu_4SnS_4 to $\text{Cu}_2\text{ZnSnS}_4$. The reaction kinetics of $\text{Cu}_{29}\text{S}_{16}$ to Cu_4SnS_4 conversion is shown to be limiting step due to higher reaction temperature as compared to conversion of Cu_4SnS_4 to $\text{Cu}_2\text{ZnSnS}_4$. The “wastage” of Zn^{2+} as a reaction kinetics r_4 is faster than r_2 therefore in the long run there the shortage of free Zn^{2+} prevents complete conversion of CTS to CZTS. As a result, multi-phase nanomaterial is obtained at the end of reaction. See the Supplementary Information for details. Cu-S, Copper-sulfide derivatives; HEDX, Hyper Energy-dispersive X-ray Spectroscopy. **b**, (**quarter**) 0.057 mmol Zn^{2+} is added into “half” and “quarter” Cu_4SnS_4 nanoparticles and allowed to react for 90 mins at 230 °C to formed “quarter-quarter” (iii) and “half-quarter” (iv) $\text{Cu}_2\text{ZnSnS}_4$. **c**, Growth study of “half-quarter” $\text{Cu}_2\text{ZnSnS}_4$ quenched at 230 °C at 90 mins with elemental mapping (v), high-resolution, (vi) zoom-in image (vii), IFFT (viii) and schematic illustration of growth direction showing phase separation during growth of Cu_4SnS_4 to $\text{Cu}_2\text{ZnSnS}_4$.

Following on from this, an investigation on the elemental distribution during the growth of ternary CTS to quaternary CZTS via CE was carried out. Initially, when the reaction was heated to 230 °C for 10 mins, Cu-Zn-Sn-S and Cu-S phases were observed (**Figures 5.19**). The reaction can be expressed as

where Cu is displaced in Cu_4SnS_4 by Zn to form $\text{Cu}_2\text{ZnSnS}_4$ phase and Cu_2S which is verified by ex-situ STEM-EDX and XRD (**Figures 5.20-5.21**). During the displacement process, multiple tiny Cu-S phases were first seen forming heterogeneously around a Cu-Zn-Sn-S phase which later fused to become one larger Cu-S phase forming a hetero-nanoparticle (Cu-S/Cu-Zn-Sn-S), which also highlights the high mobility of Cu^+ in the crystal lattice. HRTEM imaging of this hetero-nanoparticle showed epitaxial crystal alignment between Cu-S and Cu-Zn-Sn-S phase before dissolving to form soluble Cu^+ (**Figures 5.22-5.23**) for sequential reaction ($2\text{Cu} + \text{S} \rightarrow \text{Cu}_2\text{S}$).

Elemental mapping: Time-growth study of Cu_4SnS_4 to $\text{Cu}_2\text{ZnSnS}_4$, 0.22 mmole Zn^{2+}

Figure 5.20 Elemental mapping of nanoparticles obtained during ex-situ study during the growth of $\text{Cu}_2\text{ZnSnS}_4$ from Cu_4SnS_4 at 10, 20, 40, 60 and 90 mins.

Figure 5.21 XRD spectrum of as-synthesized CZTS nanoparticles after addition of Zn^{2+} into Cu_4SnS_4 nanoparticles solution, heated and immediately quenched upon reaching targeted temperature. (i) as-synthesized Cu_4SnS_4 nanoparticles showing crystal phase of $Pnma \text{ Cu}_4\text{SnS}_4$. Solution quenched at (ii) 140 °C showing crystal phase of $P2_1/c \text{ Cu}_{32}\text{S}_{16}$ + $Pnma \text{ Cu}_4\text{SnS}_4$, (iii) 160 °C showing crystal phase of $P2_1/c \text{ Cu}_{32}\text{S}_{16}$ + $Pnma \text{ Cu}_4\text{SnS}_4$ + wurtzite $\text{Cu}_2\text{ZnSnS}_4$, (iv) 180 °C showing crystal phase of $P2_1/c \text{ Cu}_{32}\text{S}_{16}$ + $Pnma \text{ Cu}_4\text{SnS}_4$ + wurtzite $\text{Cu}_2\text{ZnSnS}_4$, (v) 200 °C showing crystal phase of $P2_1/c \text{ Cu}_{32}\text{S}_{16}$ + wurtzite $\text{Cu}_2\text{ZnSnS}_4$. Standard XRD of (vi) $Pnma \text{ Cu}_4\text{SnS}_4$, (vii) $P2_1/c \text{ Cu}_{32}\text{S}_{16}$.

After 40 mins of reaction, formation of Cu-S/Cu-Sn-S hetero-phase indicated the reaction of solvated Sn^{4+} with Cu-S phase had taken place (equations 5.2-5.4). As the reaction reacts for 60 to 90 mins, a mixture of Cu-Zn-Sn-S, Cu-Sn-S/Cu-Zn-Sn-S (CTS/CZTS), Zn-S and Cu-S rich nanoparticles was observed, which were confirmed by SERS and XRD to be $\text{Cu}_2\text{ZnSnS}_4$, Cu_4SnS_4 , ZnS and $\text{Cu}_{32}\text{S}_{16}$ phases (Figure 5.24-5.26). Therefore to explain the sequential observations, the thermodynamics of the various reaction processes have to be verified. As Zn^{2+} is the reactant promoting cationic exchange in the reaction (5.10), the focus was on the chemical potential of Zn^{4+} ($\Delta\mu_{\text{Zn}}$) to predict the thermodynamic feasibility of the proposed reaction equation. In equilibrium conditions, the chemical potentials of the constituent elements in $\text{Cu}_2\text{ZnSnS}_4$ phase must satisfy the following to form the desired crystal.

$$\Delta H_f (\text{Cu}_2\text{ZnSnS}_4) = 2\Delta\mu_{\text{Cu}} + \Delta\mu_{\text{Zn}} + \Delta\mu_{\text{Sn}} + 4\Delta\mu_{\text{S}} = -3.673 \text{ eV} \quad (5.11)$$

Therefore, based on the theoretical calculated enthalpy formation of $\text{Cu}_2\text{ZnSnS}_4$ (equation 5.11), the chemical potential of Zn^{2+} in the reaction solution follows the lowest possible chemical potential energy of Zn (Zn in $\text{Cu}_2\text{ZnSnS}_4$ crystal matrix) available, which is -3.673 eV (assuming $\Delta\mu_{\text{Cu}}$, $\Delta\mu_{\text{S}}$ and $\Delta\mu_{\text{Sn}}$ to be 0).

Time-growth study of Cu_4SnS_4 (quarter) to $\text{Cu}_2\text{ZnSnS}_4$ 0.057 mmole Zn^{2+}

Figure 5.22 Elemental mapping and HR-TEM of nanoparticles obtained during ex-situ study of $\text{Cu}_2\text{ZnSnS}_4$ nanoparticles grown from Cu_4SnS_4 (quarter) using 0.057 mmol Zn^{2+} (quarter). Elemental distribution change occurring across time 2, 4, 6 and 60 mins.

For $\Delta H_{\text{equation } 10}$ to be thermodynamically spontaneous ($\Delta H_{\text{equation } 8} < 0$), the minimum chemical potential energy of Zn^{2+} ($\Delta\mu_{\text{Zn}, \text{equation } 10}$) was calculated to be -1.797 eV (Table 5.3). As the minimum $\Delta\mu_{\text{Zn}, \text{equation } 8}$ required is higher than the theoretical calculated chemical potential available of -3.673 eV (Table 5.4), equation 5.10 is thermodynamically nonspontaneous. Additional studies carried out showed the displacement reaction of Cu in Cu_4SnS_4 by Zn begins at an elevated temperature of $\sim 160^\circ\text{C}$ (Figure 5.27). However, to explain the phenomena of multiple phases formation at the later stage of the reaction, the reaction kinetics of competing reaction processes and preferential growth pathway have to be compared.

Figure 5.23 (i,ii) HR-TEM image showing the phase boundary between $\text{Cu}_2\text{ZnSnS}_4$ and $\text{Cu}_{32}\text{S}_{16}$ at 2 different corners. (iii, iv) Inverse FFT and false colouration of (i) emphasizing on $\text{Cu}_2\text{ZnSnS}_4$ phase (red contrast) from $\text{Cu}_{32}\text{S}_{16}$ (green contrast). (v, vi) Inverse FFT of C_{3v} symmetry hexagonal diffraction pattern masking and false colouration of (i) showing epitaxial hexagonal lattice arrangement between $\text{Cu}_2\text{ZnSnS}_4$ and $\text{Cu}_{32}\text{S}_{16}$ phase.

Firstly, to determine the reaction kinetics of the competing reaction processes occurring during the growth of CTS to CZTS, the relative activation energy has to be understood. The order of reactions can be estimated via the rate equation; $r_n = k_a[A]^x k_b[B]^y$, which in turn is affected by the activation energy (E_a) in the Arrhenius equation; $k_n = Ae^{-\frac{E_a}{RT}}$.^{32,33} It can be assumed that the temperature required for complete phase transformation/formation to occur to be proportional to the E_a of the reaction process. Using an ex-situ XRD study, it was verified that the formation of Cu-S/Zn-S phase occurs at $\sim 200^\circ\text{C}$, which is kinetically faster than the transformation of Cu-S to CTS ($\sim 230^\circ\text{C}$), while the CTS to CZTS transformation is kinetically the fastest reaction process ($\sim 160^\circ\text{C}$) (**Figures 5.11, 5.21 and 5.27**).

Figure 5.24 (i) Elemental mapping of as-synthesized Cu-Zn-Sn-S nanoparticles on various TEM carbon grid spots. Scale bar is 30 nm. (ii) HR-BF imaging, (iii) HR-HAADF imaging, (iv) FFT image of (iii), and (v) JEMS simulated TEM diffraction pattern along $\langle 100 \rangle$ zone axis. (vi) CRISP-treated HR-HAADF image, (vi) JEMS simulated HR-HAADF image along $\langle 001 \rangle$ zone axis, (vii) JEMS simulated crystal potential along $\langle 001 \rangle$ zone axis.

Figure 5.25 Rietveld refinement of XRD pattern of as-synthesized Cu₂ZnSnS₄ nanoparticles.

Figure 5.26. (i) Peak fitting of SERS spectrum and (ii) XPS characterization of Cu-Sn-S nanoparticles.

The relative reaction rates are hence ranked as: **r**₃: Cu-Zn-Sn-S (160 °C) > **r**₄: Zn-S (200 °C) > **r**₁: Cu-S (230 °C) ~ **r**₂: Cu-Sn-S (230 °C), due to displaced Cu⁺ reacting with dodecanethiol (**r**₁) to form Cu-S nanoparticles (**Figures 5.22-5.23**). These Cu-S nanoparticles will react with Sn⁴⁺ to form CTS phase (**r**₂), which will then react with Zn²⁺ to form CZTS phase (**r**₃). As the formation kinetics of CTS (**r**₂) is smaller than the formation kinetics of ZnS (**r**₄), **r**₄ reaction is more favourable and therefore results in the presence of ZnS in the final product. These observations agree with a recent kinetics report on multiple phase segregation, which results from unbalanced reaction kinetics.

Figure 5.27 XRD of as-synthesized Cu₃₁S₁₆/ZnS nanoparticles after reacting Cu₂₉S₁₆ with Zn²⁺ at 200 °C for 60 mins.

5.3.4 Ex-situ temporal crystal structure studies of ternary Cu-Sn-S to quaternary Cu-Zn-Sn-S phase growth

a. EDX mapping of phase boundary between Cu_2SnS_4 and $\text{Cu}_2\text{ZnSnS}_4$ of $\text{CZTS}_{\text{half-quarter}}$ nanoparticle

b. HR HAADF imaging of $\text{CZTS}_{\text{half-quarter}}$ nanoparticle

Figure 5.28 a. EDX mapping of $\text{CZTS}_{\text{half-quarter}}$ nanoparticles showing the phase boundary of Cu-Sn-S rich phase and Cu-Zn-Sn-S rich phase. b. High resolution HAADF imaging of CTS nanoparticles showing lattice plane along the side of the nanoparticle (i), and image at higher magnification (ii, iii, iv).

Next, to investigate the growth selectivity of CTS to CZTS, reactions were carried out using the two CTS nanoparticles suspensions (Cu:Sn 4:1 and 8:1) shown in **Figure 5.17** with stoichiometric amounts of Zn (Sn:Zn 1:1) and with reduced amounts (Sn:Zn 1:0.5). Firstly, STEM-EDX mapping of as-synthesized nanoparticles from Sn:Zn 1:0.5 reaction shows bifurcated Cu-S phase and Cu-Sn-S/Cu-Zn-Sn-S hetero-phase (**Figure 5.19b**). As the symmetry of S^{2-} framework

along $\langle 001 \rangle_{\text{Cu}_4\text{SnS}_4}$ is C_{3v} , the observed homogenous contrast using C_{3v} symmetry diffraction pattern masked on the HR-TEM FFT image confirmed the growth of Cu-Sn-S to Cu-Zn-Sn-S phase to be an epitaxial growth process. As CTS phase and CZTS phase have similar FFT patterns, it was impossible to differentiate the two phases by FFT. Therefore, by referring to the EDX data and HR HAADF imaging, Sn^{4+} is proposed to be propagating along [010] plane of Cu_4SnS_4 , while $\text{Cu}_2\text{ZnSnS}_4$ is growing in [100] direction (**Figure 5.28**). Secondly, STEM-EDX mapping of as-synthesized nanoparticles from Sn:Zn 1:1 reactions showed bifurcated Cu-S and Cu-Zn-Sn-S phases. Estimation by Rietveld analysis showed the sample to consist of a mixture of wurtzite $\text{Cu}_2\text{ZnSnS}_4$ and $\text{Cu}_{32}\text{S}_{16}$ ($P2_1/c$) phases (**Figure 5.29**). It was noted that in both cases, there was no observable Zn-S rich phase from the elemental mapping. This phenomenon was coherent with the observation described above (**Figure 5.19a** and **5.28**). The fast kinetics of Zn^{2+} diffusion into Cu_4SnS_4 to form $\text{Cu}_2\text{ZnSnS}_4$ reveals the strong tendency for the transformation of CTS to CZTS over the formation of a ZnS phase.

Figure 5.29 Rietveld refinement of CZTS quarter

5.3.5 High resolution Z-Contrast TEM study of metastable CZTS crystal structure

a Addressing crystal structure ambiguity of metastable $\text{Cu}_2\text{ZnSnS}_4$ phase

b Hexagonal wurtzite derived Orthorhombic and Monoclinic metastable CZTS crystal structure

Figure 5.30 Determination of crystal structure via verification of 3-zone axis HR-HAADF image. a. Verification of metastable CZTS crystal structure was carried out by taking HR-HAADF images of 3 zone- axis. Due to the difference in Z-number contrast, Sn atom will appear the brightest. **b.** Due to the inability to differential Cu to Zn, 2 crystal structures of orthorhombic WZ-S $Pmn2_1$ and monoclinic WZ-KS Pc are proposed to be the crystal structure of metastable CZTS;

During the HR-STEM characterization of CZTS nanoparticles, disparity between our experimental and generally accepted metastable CZTS crystal structure is observed.³⁴ This disparity arose because HR-STEM is more sensitive than HR-TEM in distinguishing atoms by Z-contrast (**Figure 5.30**). Verification of the crystal structure by HR-STEM imaging involves cross-examination of three zone-axis images of CZTS nanoparticles. The crystal structure of the commonly

accepted $P6_3mc$ CZTS crystal can be summarized as: 1) crystal structure is assumed to follow $P6_3mc$ wurtzite ZnS crystal structure and 2) cations (Cu, Zn and Sn) randomly occupy the cation site of $P6_3mc$ ZnS crystal structure (**Annex 5**). In the first experimental HR-HAADF zone-axis image of hexagonal-arranged atoms, ordered bright spots in “kite” arrangement is observed, indicating fixed Sn ion (Figure 5.24) position along this direction. In the second HR-HAADF zone-axis image of atoms in “cubic-like” arrangement, repetitive bright spots in a diamond arrangement provides further visual confirmation that the Sn ions have a fixed lattice coordinate in the crystal structure. In the third HR-HAADF zone-axis image, alternating rows of bright (cationic sites) and dull (sulfide sites) spots indicates the presence of Sn ions down each atomic columns (into plane). All three observations are not fulfilled by the three ($\langle 100 \rangle$, $\langle 210 \rangle$ and $\langle 100 \rangle$) zone axis of wurtzite crystal structure. Therefore, HR-HAADF verified that Sn^{4+} has fixed occupancy, unlike the reported random cations occupation model (Wurtzite $P6_3mc$). As it was impossible to differentiate Zn from Cu by using HR-HAADF Z-contrast, two possible crystal structures have been identified which fit all three HR-HAADF zone-axis images. When Zn and Cu are assumed to follow Wurtzite-Stannite (WZ-S) arrangement, an orthorhombic ($Pmn2_1$) crystal phase is obtained; whereas when Zn and Cu are assumed to follow Wurtzite-Kesterite (WZ-KS) arrangement, Monoclinic Pc crystal phase is obtained (**Annex 6-7**). Theoretical simulation shows similarity in the XRD patterns while DFT calculation showed a difference of only 0.011 eV between the two crystal structures. This is therefore indicative of the equal possibility of either crystal structure, or of both being present (**Table. 5.2**).

Conclusion

This work presents a model study to highlight the complexity of phase transition via cation exchange to form multi-component sulfide nanomaterials ($\text{Cu}_{29}\text{S}_{16}$ to Cu_4SnS_4 to $\text{Cu}_2\text{ZnSnS}_4$). This is the first time direct evidence has been shown on the phase transformation of binary $\text{Cu}_{29}\text{S}_{16}$ to ternary Cu_4SnS_4 to quaternary $\text{Cu}_2\text{ZnSnS}_4$ occurring via alloyed cationic exchange in a fixed anionic framework. Tracing the structural changes of binary $\text{Cu}_{29}\text{S}_{16}$ growth to ternary Cu_4SnS_4 revealed a sequential three steps reaction processes involving two intermediate phases ($P12_1n1$ $\text{Cu}_{31}\text{S}_{16}$ and $P12_1c1$ $\text{Cu}_{32}\text{S}_{16}$) while preserving the anionic framework of $\text{Cu}_{29}\text{S}_{16}$. In addition, the ex-situ growth study of CZTS from CTS reveals a negative domino CE growth effect resulting in precipitation of parasitic phases. Furthermore, the use of HR-HAADF imaging with Z-contrast capability enables the visualization of Sn fixed occupancy sites in our as-synthesized quaternary CZTS nanoparticles. This confirms that the crystal does not follow the commonly accepted $P6_3mc$. However, due to the inability to distinguish Zn from Cu under Z-contrast, two crystal structures (WZ-KS, WZ-S) have been proposed with a small difference of 0.011eV in energy level, hinting equal possibility in structural formation. This observation posed a potential challenge in future characterization of multi-component material with conflicting crystal structure but similar X-ray diffraction patterns. The importance of accurate characterization of crystal structure and understanding the complex chemistry behind growth of multi-component materials will aid in future theoretical calculation, material design and control of phase formation during engineering of complex materials.

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Chapter 6

Understanding The Growth Mechanism of $\text{Cu}_2(\text{M})\text{SnS}_4$ ($\text{M}=\text{Mn}$, Co and Fe) Nanoparticles

Understanding critical growth parameters of $\text{Cu}_2(\text{M})\text{SnS}_4$ nanoparticles formation is an essential prerequisite for achieving a high yielding reproducible reaction protocol. Surface-enhanced Raman scattering (SERS) spectroscopy is utilized to differentiate mixed compositional phase (e.g CZTS, CTS and ZnS). It is revealed that $\text{Cu}_2(\text{M})\text{SnS}_4$ nanoparticles proceed via two different reaction pathways. Growth of $\text{Cu}_2(\text{Mn})\text{SnS}_4$ nanoparticles is similar to $\text{Cu}_2(\text{Zn})\text{SnS}_4$ nanoparticles where ternary Cu-Sn-S phase is the intermediate phase. On the other hand, the growth of $\text{Cu}_2(\text{Co})\text{SnS}_4$ and $\text{Cu}_2(\text{Fe})\text{SnS}_4$ proceed via intermediate ternary Cu-(M)-S phase. XRD characterization of as-synthesized $\text{Cu}_2(\text{M})\text{SnS}_4$ nanoparticles revealed CZTS and CMTS to crystallize in hexagonal crystal structure while CFTS and CCTS crystallize in zinc blende crystal structure preferentially. In addition, it is demonstrated that there is a large change in reaction thermodynamics and growth pathways, despite the substituted elements being next to one another in the periodic table.

6.1 Introduction

The quaternary semiconductor $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) has attracted a lot of attention in the past decade. Due to its suitable bandgap and high absorption coefficient, CZTS has been actively studied as a solar harvesting material.¹⁻³ Currently the efficiency of CZTS thin film has been improved to 12.6% by IBM.^{4,5} In an attempt to improve the efficiency further, efforts have been made to address the intrinsic defects of CZTS that is proposed to be limiting the device performance. Recently, Wong *et al* reported a pure sulfide CZTS solar cell device with a record efficiency of 9.7% without the use of selenium.⁶ In their report, Zn is partially substituted by larger Cd atoms which caused an increase in lattice parameters. It is proposed that the increase in lattice parameters reduces the hybridization energy of the defects states hence improving the device efficiency. Besides substitution by Cd, other elements such as Mn, Co and Fe ($\text{Cu}_2(\text{M})\text{SnS}_4$ (M=Mn, Co and Fe)) have attracted much attention in recent years.⁷⁻¹²

The strong interest in $\text{Cu}_2(\text{M})\text{SnS}_4$ (M=Mn, Co and Fe) semiconductors arises from their various functional properties. Firstly, due to their suitable energy bandgaps and high absorption coefficients, $\text{Cu}_2(\text{M})\text{SnS}_4$ semiconductors possess the potential to be solar harvesting materials.¹² In addition, $\text{Cu}_2(\text{M})\text{SnS}_4$ semiconductors crystallize in a stannite crystal structure with each element having its own fixed position in the unit cell.¹³⁻¹⁵ On the other hand, CZTS crystallizes in a kesterite crystal structure with Cu and Zn randomly exchanging positions in the unit cell, creating intrinsic Zn_{Cu} and Cu_{Zn} defect states.^{16,17} Having all atoms to be in fixed positions in the crystal lattice eliminates the intrinsic substitution defects (e.g A_B , B_A) seen in CZTS, so produces the potential for these materials to be better solar harvesting materials. Secondly, the presence of a catalytic active (M=Co) element may give the quaternary semiconductors catalytic properties needed for the hydrogen evolution reaction (HER).¹⁰ Lastly, when the divalent cation is Mn, Co or Fe, it gives the resulting quaternary $\text{Cu}_2(\text{M})\text{SnS}_4$ compounds magnetic properties (dilute magnetic semiconductors).^{12,18} However, despite the strong interest in $\text{Cu}_2(\text{M})\text{SnS}_4$ semiconductors, there has been no growth study carried out to explain their growth mechanism.

A fundamental growth mechanism study is crucial in determining critical reaction thermodynamics so as to design a reproducible reaction protocol that allows the synthesis of pure phase $\text{Cu}_2(\text{M})\text{SnS}_4$ nanoparticles. In **Chapter 4**, it has been reported a reproducible high yield synthesis of pure phase CZTS nanoparticles by utilizing growth thermodynamics learnt from the fundamental growth study of CZTS nanoparticles. In this chapter, using highly-sensitive surface enhanced Raman scattering (SERS) spectroscopy, the aim is to understand the formation mechanism of $\text{Cu}_2(\text{M})\text{SnS}_4$ nanoparticles by carrying out ex-situ temporal studies of $\text{Cu}_2(\text{M})\text{SnS}_4$ nanoparticles. On the basis of these findings, the preferential growth pathway and crystal structure formation of $\text{Cu}_2(\text{M})\text{SnS}_4$ nanoparticles were established. These mechanistic growth studies provide crucial growth parameters of $\text{Cu}_2(\text{M})\text{SnS}_4$ phase formation, and hence allow the development of reaction protocols to achieve high yield pure phase $\text{Cu}_2(\text{M})\text{SnS}_4$ nanoparticles.

6.2 Experimental Methods

6.2.2 Chemicals and materials.

Copper(II) acetate monohydrate ($\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$, Aldrich, >98%), copper(II) acetylacetonate ($\text{Cu}(\text{acac})_2$, Aldrich, 97%), zinc acetate dihydrate ($\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, Aldrich, >98%), zinc acetylacetonate ($\text{Zn}(\text{acac})_2$, Aldrich, 97%), tin(IV) bis(acetylacetonate) dichloride ($\text{Sn}(\text{acac})_2\text{Cl}_2$, Aldrich, 98%), tin(IV) acetate ($\text{Sn}(\text{OAc})_4$, Aldrich), cobalt(II) acetate tetrahydrate ($\text{Co}(\text{OAc})_4 \cdot 4\text{H}_2\text{O}$, Aldrich, 98%), manganese(II) acetate ($\text{Mn}(\text{OAc})_2$, Aldrich 98%), iron(II) acetate ($\text{Fe}(\text{OAc})_2$, Aldrich, 95%), trioctylphosphine oxide (TOPO, Aldrich, 90%), 1-octadecene (ODE, Aldrich, 90%), 1-dodecanethiol (DDT, Aldrich, 98%) and oleylamine (OAm, Acros, 97%) were used without further purification.

6.2.2 Synthesis of CMTS nanoparticles

In a typical reaction, stoichiometric amounts of 0.442 mmol $\text{Cu}(\text{OAc})_2$, 0.234 mmol $\text{M}(\text{OAc})_2$ and 0.221 mmol $\text{Sn}(\text{OAc})_4$ were added into a 50 mL three-necked round bottom flask containing 10 mL of ODE. 1 mL of DDT and 1 mL of Oam (DDT:Oam, 1:1) were injected at 150 °C and heated to 240 °C at a rate of

10 °C/min. During the heating process, reaction mixtures were allowed to react for 90 mins once the temperature exceeded 200 °C. After 90 mins, the solution was cooled naturally to room temperature by removing the reaction flask from the heating mantle. 2 mL of toluene was added to quench the reaction at 80 °C as discussed by Singh *et al.*¹⁹ The Cu₂(M)SnS₄ nanoparticles that formed were then washed with 1% v/v dodecanethiol/hexane and ethanol in a ratio of 1:5 and centrifuged twice at 7500 rpm for 3 mins to separate the excess ligands from the Cu₂(M)SnS₄ nanoparticles. The nanoparticles were collected and dried in a N₂ box before storage. Dried nanoparticles can be dispersed in either hexane/chloroform or toluene.

6.2.3 Photovoltaic device fabrication

A stock solution (1 mg/mL in water) of nanoparticles (CZTS and CMTS) was prepared after ligand exchange has been carried out with NaSH. Based on the density of CZTS and CMTS material, an appropriate volume was dripped onto a Molybdenum substrate to obtain a thin film thickness of approximately 2 µm. After drying the thin film at 50 °C, thin films were annealed above 580 °C in sulfur atmosphere to obtain more crystalline thin films. CdS buffer layer with ≈60 nm thickness was deposited on (CZTS, CMTS) thin film by chemical bath deposition (CBD). Then 50 nm i-ZnO followed by 600 nm ZnO:Al layer were deposited by RF and DC magnetron sputtering. Finally, silver glue was printed onto the AZO layer to form top contact fingers.

6.2.4 Characterization

Transmission electron microscopy (TEM) images were obtained using a JEOL-JEM-1400 electron microscope at an accelerating voltage of 100 kV. X-ray diffraction (XRD) patterns were obtained using a Bruker D8 Advance with Cu K α radiation (1.5406 Å) at 0.02°/s scan rate, 2 s accumulation time, and in 2 θ ranging from 20° to 70° and analyzed using Topas.

For Surface-enhanced Raman scattering (SERS) spectroscopy, a 50 nm thick Ag film on Si was prepared using thermal evaporation to serve as a substrate

for SERS measurements. The thickness of the Ag film was monitored by quartz crystal microbalance, and the deposition rate was 0.5 Å/s. Diluted CZTS nanoparticles solution in hexane was then drop-casted (20 µL, 4 mg/mL) onto Au coated Si wafer (5 × 5 mm) to form a thin film ($\sim 10 \pm 5$ nm) for SERS measurements. Measurements were performed using x-y imaging mode of the Ramantouch microspectrometer (Nanophoton Inc., Osaka, Japan) with an excitation wavelength of 532 nm (power = 23 µW). A 20 x (N.A. 0.45) objective lens with 1 s accumulation time was used for data collection between 200 cm⁻¹ and 1800 cm⁻¹. All SERS spectra were obtained by averaging at least 25 baseline-corrected individual spectra.

For PV measurements, Current density–voltage (*J*–*V*) curves for solar cells were performed using Xe-based light source solar simulator (VS-0852 and KEITHLEY 2612A) to provide simulated one Sun (AM 1.5G) illumination which was calibrated with a standard Si reference cell.

6.3 Principal outcomes

6.3.1 Growth mechanism of Cu₂(Mn)SnS₄

Firstly, ex-situ growth study of Cu₂MnSnS₄ nanoparticle was carried out using SERS spectroscopy. In a typical reaction, stoichiometric amounts of 0.442 mmol Cu(Oac)₂, 0.234 mmol, Mn(Oac)₂ and 0.221 mmol Sn(Oac)₄ were added into a 50 mL three-necked round bottom flask containing 10 mL of ODE at room temperature and heated to 150 °C under vacuum to eliminate water and air. After 15 mins at 150 °C, 1 mL of DDT and 1 mL of Oam were injected into the reaction mixture and heated to 240 °C at a rate of 10 °C/min under N₂ atmosphere. Aliquots were extracted from the reaction mixture at regular temperature intervals, and the compositional phases present in the as-synthesized nanoparticles were examined by SERS (**Figure 6.1**).

Figure 6.1 Raman spectra of phases formed during growth of $\text{Cu}_2\text{MnSnS}_4$ nanoparticles.

The start of the reaction was indicated by the change in the colour of the reaction mixture. During the heating up process, the colour of the reaction changed from clear yellow (150 °C) to clear red (190 °C) and became opaque (black) at 230 °C. The transition from clear to cloudy indicated the formation of nanoparticle nuclei. SERS spectroscopy characterization of aliquots extracted at 200 °C showed a broad peak at $\sim 298 \text{ cm}^{-1}$ indicative of a Cu_{2-x}S ($\text{Cu}_{(2-x)}^+ \text{Cu}_x^{2+} \text{S}^-$) phase being present (**Figure 6.1**).²⁰⁻²² As the temperature of the reaction increased to 240 °C and held for 10 mins, SERS spectra showed one Raman peak at 318 cm^{-1} indicative of Cu_3SnS_4 (CTS). The equation of the reaction is proposed as

Nucleation of Cu_{2-x}S phase

Formation of Cu_3SnS_4 phase (unbalanced)

where $\text{Cu}_{(2-x)}^+ \text{Cu}_x^{2+} \text{S}$ is the stoichiometry formula for the Cu_{2-x}S phase, C_{12}S^- is the deprotonated ion of dodecanethiol, $\text{Cu}_2^+ \text{Cu}^{2+} \text{Sn}^{4+} \text{S}_4$ is the Cu_3SnS_4 phase.²³⁻
²⁷ As dodecanethiol is the sulphur source in this reaction, C_{12}S^- reduced Cu^{2+} to Cu^+ by donating an electron to form $\text{C}_{12}\text{S}^\bullet$ radical which dimerizes to form dodecanethiol disulphide ether ($\text{C}_{12}\text{-S-S-C}_{12}$). Secondly, the formation of thiol-ether ($\text{C}_{12}\text{-S-C}_{12}$) compound is via a disproportionation reaction. As the reaction is allowed to proceed longer, a red shift in the Raman peak at 318 cm^{-1} is observed. At the end of 90 mins reaction, SERS spectra shows a Raman peak at 329 cm^{-1} which was assigned to the $\text{Cu}_2\text{MnSnS}_4$ phase.²⁸ The red shifting of Raman peak from 10 mins to 90 mins is due to the incorporation of Mn^{2+} into Cu_3SnS_4 via displacement of Cu^{2+} ions. The reaction equation can be written as

Formation of $\text{Cu}_2\text{MnSnS}_4$ phase

where the displaced Cu^{2+} is proposed to undergo reaction with dodecanethiol to form $\text{Cu}_{(2-x)}\text{S}$ phase which then reacts with Sn^{4+} to form Cu_3SnS_4 and lastly reacts with Mn^{2+} to form $\text{Cu}_2\text{MnSnS}_4$ following the growth of $\text{Cu}_2\text{ZnSnS}_4$ phase as described in **Chapter 5**. Therefore, at the end of the reaction, the oxidation state of the copper in $\text{Cu}_2\text{MnSnS}_4$ is in monovalent. The red shift in Raman peak is due to the incorporation of Mn^{2+} into Cu_3SnS_4 crystal lattice to form $\text{Cu}_2\text{MnSnS}_4$. As Mn^{2+} is incorporated into the crystal lattice, the energy level of the crystal lattice vibration changes, therefore a shift in Raman peak is observed.^{29,30}

From this growth study, it is possible to determine that the formation of $\text{Cu}_2\text{MnSnS}_4$ nanoparticles originates via CTS. The growth mechanism of $\text{Cu}_2\text{MnSnS}_4$ is similar to that of CZTS, with the initial formation of a Cu_{2-x}S phase, followed by the reaction of Sn^{4+} with Cu_{2-x}S nanoparticles to form a CTS phase, and lastly the reaction of Mn^{2+} with CTS to give CMTS nanoparticles.

6.3.2 Growth mechanism of $\text{Cu}_2(\text{Fe})\text{SnS}_4$

Figure 6.2 Raman spectra of phases formed during growth of $\text{Cu}_2\text{FeSnS}_4$ nanoparticles.

Next, the growth study of $\text{Cu}_2\text{FeSnS}_4$ nanoparticle was carried out using SERS spectroscopy. In a typical reaction, stoichiometric amounts of 0.442 mmol $\text{Cu}(\text{Oac})_2$, 0.234 mmol $\text{Fe}(\text{Oac})_2$ and 0.221 mmol $\text{Sn}(\text{Oac})_4$ were used. Aliquots were extracted from the reaction mixture at regular temperature intervals, and the compositional phases present in the as-synthesized nanoparticles were examined by SERS (**Figure 6.2**). During the heating up process, the colour of the reaction changed from clear dark brownish-orange (150 °C) to opaque (black) at 200 °C. SERS spectra of the aliquots extracted at 200 °C shows a broad Raman peak at 302 cm^{-1} and assigned to Cu_{2-x}S ($\text{Cu}_{(2-x)}^+ \text{Cu}_x^{2+} \text{S}$) phase. When this reaction was heated up to 210 °C, the peak at 302 cm^{-1} was red shifted to $\sim 310 \text{ cm}^{-1}$ and an addition broad peak at $\sim 329 \text{ cm}^{-1}$ was observed, which cannot be assigned to any of the well-studied ternary Cu-Sn-S phases (Cu_2SnS_3 , Cu_3SnS_4 and Cu_4SnS_4).^{31,32} In addition, a recent growth study of $\text{Cu}_2\text{FeSnS}_4$ thin film using XRD suggests that the growth proceeds via a Cu-Fe-S ternary intermediate phase.⁷ Therefore, it is

proposed that the broad peak at $\sim 329 \text{ cm}^{-1}$ is due to the presence of a Cu-Fe-S ternary phase. However, due to the lack of Raman spectroscopic studies of Cu-Fe-S ternary compounds, it is not possible to definitely identify the exact compositional phase (e.g. CuFeS_2 , Cu_2FeS_2). Assuming the intermediate phase (Cu-Fe-S) to be Cu_2FeS_2 the overall reaction equation can be written as

Formation of Cu_2FeS_2 phase (unbalanced)

where C_{12}S^- reduces Cu^{2+} to Cu^+ . $\text{C}_{12}\text{S-SC}_{12}$ is the structural formula of the disulphide compound formed between two dodecanethiols after the reduction reaction. As dodecanethiol is the sulphur source in this reaction, the donation of sulfur and formation of thiol-ether ($\text{C}_{12}\text{-S-C}_{12}$) compound is via a disproportionation reaction. As the temperature was increased to 230°C , a Raman peak at 319 cm^{-1} was observed, and the Raman peak at $\sim 329 \text{ cm}^{-1}$ blue shifted to $\sim 324 \text{ cm}^{-1}$. The Raman peak at $\sim 319 \text{ cm}^{-1}$ is assigned to $\text{Cu}_2\text{FeSnS}_4$ while the blue shifting of the Raman peak from 329 to 324 cm^{-1} is proposed to arise from the incorporation of Sn^{4+} into Cu-Fe-S ternary phase which causes the lattice energy to change.²⁸ The equation of the formation of $\text{Cu}_2\text{FeSnS}_4$ can be written as:

Formation of $\text{Cu}_2\text{FeSnS}_4$ phase

As the reaction was allowed to proceed for another 90 mins at 240°C , Raman spectra shows only one distinct peak at 319 cm^{-1} , which is indicative of pure-phase $\text{Cu}_2\text{FeSnS}_4$ nanoparticles. From this ex-situ SERS study, it is proposed that the synthesis pathway of CFTS is as follows; firstly, Cu_{2-x}S phase nucleates out, followed by the reaction of Fe^{2+} with Cu_{2-x}S phase to give a Cu-Fe-S ternary phase. Lastly, Sn^{4+} reacts with Cu-Fe-S to form CFTS. This proposed mechanism for CFTS formation is consistent with the observations from the experiments carried out by Yan *et al.*⁷

6.3.3 Growth mechanism of $\text{Cu}_2(\text{Co})\text{SnS}_4$

Figure 6.3 Raman spectra of phases formed during growth of $\text{Cu}_2\text{CoSnS}_4$ nanoparticles.

Following on, the growth study of $\text{Cu}_2\text{CoSnS}_4$ nanoparticle was carried out using SERS spectroscopy. In a typical reaction, stoichiometric amounts of 0.442 mmol $\text{Cu}(\text{Oac})_2$, 0.234 mmol $\text{Co}(\text{Oac})_2$ and 0.221 mmol $\text{Sn}(\text{Oac})_4$ are used. Aliquots were extracted from the reaction mixture at regular temperature intervals, and the compositional phases present in the as-synthesized nanoparticles were examined by SERS (**Figure 6.3**). During the heating up process, the colour of the reaction changes from clear dark red (150 °C) to opaque (black) at 200 °C. The SERS spectra of the aliquots extracted at 200 °C shows two main peaks at 285 and 330 cm^{-1} , but it is not possible to assign these Raman peaks to known phases. As the temperature was increased to 240 °C and allowed to proceed for 90 minutes, a blue shift in Raman peak from 330 to 322 cm^{-1} was observed. The single Raman peak at 322 cm^{-1} indicates pure phase CCTS nanoparticles were obtained.²⁸ Based on previous observations, it is proposed that the growth mechanism of CCTS should follow that for CFTS. Firstly, it was observed that there was a red shift in the Raman

peak of intermediate phase to final phase when the element involved in the last phase transformation is M^{2+} (Zn^{2+} & Mn^{2+}) (**Chapters 5 and 6**). In comparison, when the element involved in the last phase transformation is Sn^{4+} , as seen in the growth pathway of the Cu_2FeSnS_4 phase, there was a blue shift in the Raman peak (**Figure 6.3**). Since a blue shift of Raman peak from 330 to 322 cm^{-1} was observed, we proposed the growth path of CCTS is similar to that of CFTS. The formation of CCTS proceeds first through nucleation of $Cu_{2-x}S$ phase, followed by rapid diffusion of Co^{2+} into $Cu_{2-x}S$ phase giving Cu-Co-S ternary phase and finally by diffusion of Sn^{4+} into Cu-Co-S ternary phase to give CCTS nanoparticles.

6.3.4 Growth mechanism of $Cu_2(Zn)SnS_4$

Figure 6.4 Raman spectra of phases formed during growth of Cu_2ZnSnS_4 nanoparticles.

Lastly, an ex-situ growth study of CZTS was carried out to compare the differences between the growth mechanism of CZTS and other $Cu_2(M)SnS_4$ nanoparticles. In a typical reaction, stoichiometric amounts of 0.442 mmol $Cu(Oac)_2$, 0.234 mmol $Zn(acac)_2$ and 0.221 mmol $Sn(Oac)_4$ were used. Aliquots were extracted from the reaction mixture at regular temperature intervals, and the

compositional phases present in the as-synthesized nanoparticles were examined by SERS (**Figure 6.4**). During the heating up process, the colour of the reaction changed from clear yellow (150 °C) to dark red at 180 °C. When the reaction mixture was heated further to 200 °C, the solution turned brownish black indicative of the formation of nuclei nanoparticles. The SERS spectra of the aliquots extracted at 210 °C showed a broad peak at $\sim 297 \text{ cm}^{-1}$ corresponding to Cu_{2-x}S phase. As the temperature of the reaction was increased to 210 °C, three Raman peaks were observed at 289 cm^{-1} corresponding to Cu_{2-x}S phase, 318 cm^{-1} corresponding to CTS phase and 336 cm^{-1} corresponding to CZTS phase.^{22,28} The presence of CTS phase indicates the reaction of Sn^{4+} with Cu_{2-x}S nanoparticles, while the formation of CZTS phase indicates the reaction of Zn^{2+} with CTS phase. From reaction equation (2), the formation of CZTS phase can be written as

Formation of $\text{Cu}_2\text{ZnSnS}_4$ phase

where the displaced Cu^{2+} is proposed to undergo reaction with dodecanethiol to form $\text{Cu}_{(2-x)}\text{S}$ phase which then reacts with Sn^{4+} to form Cu_3SnS_4 and lastly reacts with Zn^{2+} to form $\text{Cu}_2\text{ZnSnS}_4$. As the reaction was allowed to proceed at 240 °C, a red shift in the Raman peak was observed. This is due to the incorporation of Zn^{2+} into Cu_3SnS_4 crystal lattice to form $\text{Cu}_2\text{ZnSnS}_4$. As Zn^{2+} is incorporated into the crystal lattice, the energy level of the crystal lattice vibration changes, therefore a shift in Raman peak was observed. Finally after 90 mins of reaction, three Raman peaks (**Figure 6.5**) at 292, 336 and 372 cm^{-1} corresponding to pure phase CZTS nanoparticles were observed. From this experiment, it is verified that the growth mechanism of CMTS phase is the same as for CZTS.

6.3.5 XRD characterization of as-synthesized nanoparticles

Figure 6.5 X-ray diffraction (XRD) patterns were obtained using a Bruker D8 Advance with Cu K α radiation (1.5406 Å) at 0.02°/s scan rate, 1 s accumulation time, and in 2θ ranging from 20° to 70°.

The crystal structures of $\text{Cu}_2(\text{Zn})\text{SnS}_4$ and $\text{Cu}_2(\text{Mn})\text{SnS}_4$ nanoparticles are wurtzite, while $\text{Cu}_2(\text{Fe})\text{SnS}_4$ and $\text{Cu}_2(\text{Co})\text{SnS}_4$ nanoparticles are zinc-blende (**Figure 6.5**). It is noted that the growth of both CZTS and CMTS follows the same growth pathway. Initially, there is Cu_{2-x}S nuclei formation, followed by formation of CTS and finally the formation of CZTS/CMTS phase. However, the growth mechanism of CFTS nanoparticles is different. Initially there is Cu_{2-x}S nuclei formation, followed by Cu-Fe-S ternary intermediate formation and finally the formation of CFTS phase.^{33,34} From the XRD (Figure 6.5), it was noted that wurtzite is formed preferentially when the intermediate phase is wurtzite ternary Cu-Sn-S.^{32,35} However, zinc-blende crystal structure is formed preferentially when the intermediate phase is cubic ternary Cu-Fe-S. Since the crystal structure of CCTS nanoparticles is zinc blende, this further supports the SERS observation that the growth mechanism of CCTS nanoparticles is similar to that of CFTS.

6.3.6 Effect of dodecanethiol amount on nanoparticle formation

As discussed in **Chapter 4**, the amount of dodecanethiol used in the reactions will affect the reaction kinetics, and in turn affect the purity of as-synthesized nanoparticles. Therefore, the effect of the amount of sulfur source on the formation of $\text{Cu}_2(\text{M})\text{SnS}_4$ nanoparticles was investigated. Initially, all syntheses were carried out with 1 mL DDT and 1 mL of Oam to understand the purity of Cu_2MSnS_4 (M=Mn, Fe, Co and Zn) nanoparticles at low DDT amount. SERS spectrum (**Figure 6.6b**) of CFTS nanoparticles shows 1 main peak at 319 cm^{-1} . A TEM image of CFTS nanoparticles shows spheroidal nanoparticles (**Figure 6.6a**) with a narrower size distribution of $\sim 4\text{-}6\text{ nm}$. SERS spectrum (**Figure 6.6d**) of CCTS nanoparticles shows 1 main peak at 322 cm^{-1} . TEM image of CCTS nanoparticles shows prism-like nanoparticles (**Figure 6.6c**) with a wide size distribution of $\sim 4\text{-}10\text{ nm}$. The observation of prism-like nanoparticles with zinc blende crystal structure is agreeable to recent reports.³⁶ Next, the SERS spectrum (**Figure 6.6e**) of CMTS nanoparticles shows 1 main peak at 329 cm^{-1} . The nanoparticles obtained from CMTS reaction gives random nanoparticles (**Figure 6.6f**) with a wide size distribution of $\sim 5\text{-}11\text{ nm}$. Lastly, the SERS spectrum (**Figure 6.6g**) of CZTS nanoparticles shows 1 main peak at 335 cm^{-1} which is assigned to pure CZTS. A TEM image of CZTS nanoparticles shows a brick-like morphology (**Figure 10h**) with a narrower size distribution of $\sim 11\text{-}14\text{ nm}$. From the TEM images, only CZTS nanoparticles show both size and morphology control while CCTS nanoparticles show only morphology control and CFTS and CMTS show no control over morphology or size. The difference in the ability to control morphology and sizes could be due to the higher reactivity of the cations (Mn, Fe, Co) as compared to Zn. Therefore the growth of CFTS, CCTS and CMTS nanoparticles are not influenced by the ligands (Oam and DDT) to give uniform shapes and sizes.

Figure 6.6 TEM images (top row) and SERS spectra (bottom row) of CMTS nanoparticles synthesized using different reaction setup at 1 mL dodecanethiol amount: a and b) $\text{Cu}_2\text{FeSnS}_4$, c and d) $\text{Cu}_2\text{CoSnS}_4$, e and f) $\text{Cu}_2\text{MnSnS}_4$, g and h) $\text{Cu}_2\text{ZnSnS}_4$.

Figure 6.7 TEM images (top row) and SERS spectra (bottom row) of CMTS nanoparticles synthesized using different reaction setup at 5 mL dodecanethiol amount: a and b) $\text{Cu}_2\text{FeSnS}_4$, c and d) $\text{Cu}_2\text{CoSnS}_4$, e and f) $\text{Cu}_2\text{MnSnS}_4$, g and h) $\text{Cu}_2\text{ZnSnS}_4$.

Next, the volume of DDT and Oam used was increased from 1 mL to 5 mL. In the SERS spectra of CFTS, CCTS and CMTS nanoparticles (**Figure 6.7b, d and f**), only a single peak was observed at 319, 322, and 328 cm^{-1} respectively indicating pure phase nanoparticles were obtained. On the other hand, upon using 5 mL of DDT, the SERS spectrum of CZTS (**Figure 6.7h**) shows four peaks at 318 cm^{-1} indicating CTS phase, 336 and 372 cm^{-1} indicating CZTS phase and 354 cm^{-1} indicating ZnS phase. This highlights the sensitivity of CZTS nanoparticles

formation to the presence of different amounts of DDT used. The observation of mixed compositional phases can be ascribed to mismatched reactivity, which leads to sequential phase segregation and non-uniform elemental distribution.^{22,37} As reported in **Chapter 4**, the purity of CZTS nanoparticles is controlled by the relative rates of formation of CTS, and Zn^{2+} doping into CTS.²² From the TEM images, it is observed that there are no morphology and size distribution changes for both CFTS (**Figure 6.7a**) and CMTS (**Figure 6.7e**) from use of 5 mL DDT when compared to using 1 mL DDT. On the other hand, CCTS nanoparticles lose their prism-like morphology to give random-shaped morphology and an increased in size distribution to ~5-16 nm when the amount of DDT is increased to 5 mL. In addition, for 5 mL of DDT, nanorods are observed for CZTS nanoparticles with a size distribution of ~20-25 nm.

6.3.7 PV measurements

Figure 6.8 PV performance of thin film solar cell fabricated using CZTS and CMTS nanoink. Red line shows the best PV performance out of 6 PV cells while the black line shows the worse PV performance out of 6 PV cells.

Finally, to demonstrate the photovoltaic response of $\text{Cu}_2(\text{M})\text{SnS}_4$ nanoparticles, photovoltaic devices were fabricated and measured. The advantage of using nanoparticles is the capability of producing nanoink for large scale solution-based fabrication approach (drip casting, ink-jet printing). As a proof of concept, CZTS and CMTS nanoink were used to fabricate thin film solar cells via drop casting.

Table 7.1 Average PV performance of CZTS and CMTS cells.

	CZTS	CMTS
η (%)	1.16 ± 0.16	0.078 ± 0.011
V_{oc} (V)	0.30 ± 0.05	0.028 ± 0.004
J_{sc} (mA/cm ²)	8.77 ± 0.011	10.68 ± 1.32
FF (%)	43.97 ± 6.13	25.46 ± 0.34
R_{sh} (ohm)	2597 ± 622.0	65.48 ± 2.34
R_s (ohm)	614.8 ± 202.0	46.00 ± 1.40

It has been shown that PV solar cell fabricated with CZTS and CMTS nanoink can achieve average device efficiencies of 1.16% (CZTS) and 0.078% (CMTS). However, the device efficiency is still some distance from the recorded highest value of ~8.4% for CZTS and 0.73% for CMTS.⁶ Currently, one of the main factors affecting device efficiency is the uneven absorber layer (**Figure 6.9**). Therefore, in order to achieve higher efficiency, the quality of the thin film has to be optimized. This can be done via optimizing the formulation of the nanoink and the drying temperature during thin film formation.

Figure 6.9 Light microscopic image of thin film absorber layer.

It is worth noting that despite a strong interest in $Cu_2(M)SnS_4$ ($M = Mn, Co, Fe$) materials as a solar harvesting, there has not been a single report on using $Cu_2(M)SnS_4$ as a solar harvesting layer in a solar cell by other research groups. The difference between CZTS and other $Cu_2(M)SnS_4$ materials is their thermostable

crystal structure. After heat annealing at 550 °C, CZTS crystallizes in a kesterite while the $\text{Cu}_2(\text{M})\text{SnS}_4$ (M= Mn, Co, Fe) crystallize in a stannite crystal structure. Some recent reports suggest that the electrical properties of pure stannite $\text{Cu}_2(\text{M})\text{SnS}_4$ materials may be too conductive to be an efficient solar harvesting layer.^{9,38} This may pose a challenge in achieving high efficiency solar cells. However, recent work on crystal engineering of stannite $\text{Cu}_2\text{CdSnS}_4$ to Kesterite $\text{Cu}_2(\text{Cd,Zn})\text{SnS}_4$ solar cells via partial substituting of Cd with Zn, has shown it is possible to improve the device efficiency from 1.2% ($\text{Cu}_2\text{CdSnS}_4$) to 9.24% ($\text{Cu}_2(\text{Zn,Cd})\text{SnS}_4$).⁶ In addition, this efficiency is much higher than pure phase CZTS solar cell, hence hinting the need for further in-depth study of $\text{Cu}_2(\text{M})\text{SnS}_4$ materials on how their intrinsic electrical properties is related to their elemental compositional and corresponding crystal structure.

6.4 Conclusion

The mechanistic growth pathway of $\text{Cu}_2(\text{M})\text{SnS}_4$ (M=Mn, Co and Fe) are established for the first time. It was possible to deduce that the formation of $\text{Cu}_2\text{MnSnS}_4$ phase is similar to that of $\text{Cu}_2\text{ZnSnS}_4$ phase formation where the growth starts with the formation of Cu_{2-x}S nuclei, followed by formation of ternary CTS phase and lastly the formation of CMTS quaternary phase. On the other hand, the growth mechanism of CFTS nanoparticles starts with the initial formation of Cu_{2-x}S nuclei, followed by the formation of ternary Cu-Fe-S intermediate phase and lastly the formation of quaternary CFTS phase. However, due to the lack in prior Raman studies on ternary Cu-Co-S phase, it was impossible to assign any phase to the Raman peak observed from SERS spectrum for CCTS. Nevertheless, as both CFTS and CCTS nanoparticles form zinc blende crystal structure preferentially, it is proposed that both growth mechanisms could be similar.

As discussed in **Chapter 5**, due to templated-assisted (anionic framework) growth of quaternary phase from the intermediate ternary phase, the final crystal structure of the quaternary semiconductor follows that of the intermediate phase. In **Chapter 5**, the intermediate ternary Cu-Sn-S phase is shown to be orthorhombic, with the S^{2-} anion arranged in hexagonal arrangement. During the incorporation of

Zn^{2+} into orthorhombic Cu-Sn-S phase, S^{2-} anionic framework is conserved therefore the final quaternary phase crystallizes in wurtzite crystal structure. In this chapter, the growth of quaternary Cu-Mn-Sn-S phase is observed to proceed similarly with Cu-Zn-Sn-S (Cu-S to Cu-Sn-S to Cu-(M)-Sn-S) and the final quaternary phase (CMTS) crystallizes in wurtzite crystal structure too. This observation is in good agreement with the observation reported in **Chapter 5**.

Following on, the formation of quaternary Cu-Fe-Sn-S phase is also observed to be strongly influenced by the intermediate ternary phase (Cu-Fe-S). Immediate ternary Cu-Fe-S phase is reported to crystallize in cubic crystal structure, and the final quaternary Cu-Fe-Sn-S crystallizes in zinc blende crystal structure. This further highlights the strict relationship between the crystal structure of final product and the intermediate phase. It is therefore proposed that the intermediate phase of CCTS and CFTS should be the same since the intermediate ternary Cu-Co-S is reported to crystallize in cubic crystal structure as well.

In addition, it is observed that the usable range of DDT volume in the formation of pure phase $\text{Cu}_2(\text{M})\text{SnS}_4$ (M=Mn, Co and Fe) nanoparticles is larger than formation of CZTS nanoparticles, hence highlighting the difference in reaction kinetics involved. Not only can this study provides the fundamental growth parameters for the formation of CMTS nanoparticles, it highlights the need for fundamental thermodynamic studies during cationic substitution experiment. Lastly, as a proof of concept, solar cell are fabricated using CZTS and CMTS nanoparticles with encouraging efficiency of up to 1.3% and 0.1% respectively.

6.5 References

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Chapter 7

Conclusion and Future Work

In this chapter, the threads of this dissertation are drawn together. The implications and impacts of the findings, and outstanding questions will be presented. In the implications and impacts section, the extent of the hypotheses proven and the degree of design target fulfilled will be addressed. In the outstanding questions section, opportunities and strategies for future work will be highlighted. Lastly, the extent to which the outcomes of this dissertation have confirmed the original hypotheses will be addressed.

7.1 Implications and impacts of the findings

The driving factor behind nanoparticle approach over other solution-based approaches lies on the potential of pre-formation of ideal nanoparticle properties (phase purity and stoichiometry). The underlying key to this success is the formation of nanocrystals in a carefully controlled environment, and hence allows the precursors to interact more homogeneously with greater diffusivity to reach thermodynamically stable phase. However, in order to achieve a synthetic protocol that enables reproducible production of these pure phase nanoparticles, the following areas have to be answered: **i)** unambiguous differentiation of phases present in nanoparticles, **ii)** growth pathways of $\text{Cu}_2(\text{M})\text{SnS}_4$ ($\text{M}=\text{Zn}, \text{Mn}, \text{Co}, \text{Fe}$) phases, and **iii)** thermodynamics of $\text{Cu}_2(\text{M})\text{SnS}_4$ ($\text{M}=\text{Zn}, \text{Mn}, \text{Co}, \text{Fe}$) nanoparticles formation.

Ex-situ temporal studies have been carried to provide insides to the three areas as mentioned above. Our detailed findings in this thesis are summarized and presented below.

7.1.1 Outcome of hypothesis #1 [It is plausible to increase Raman signal and resolution of nanoparticles with Surface Enhanced Raman Scattering spectroscopy (SERS)]

SERS spectroscopy is proposed to possess the capability to resolve the problem of inability to differentiate secondary phases from CZTS phase due to indistinguishable XRD patterns and poor Raman signals (**Chapter 1**). A detailed working principle of SERS has been reported in **Chapter 2**. In summary, under laser irradiation, a SERS substrate (surface coated with Au, Ag) is used to generate an electromagnetic field (Surface Plasmonic Resonance (SPR)) to enhance the Raman signals. In our work, a 50 nm thick Au or Ag film is used as the SERS substrate and scanned using 633 nm and 532 nm laser respectively. The depth of space above the SERS substrate experiencing SPR is less than 10 nm, therefore a very thin film of nanoparticles (<10 nm) is required for maximum SERS enhancement.

In our findings (**Chapter 4**), XRD characterization of as-synthesized nanoparticles revealed it to be of wurtzite crystal structure. However, due to overlapping diffraction peaks of the possible phases, the standard XRD patterns of ZnS (w), CTS (k), CZTS (k), and CZTS (w) show that it is not possible to determine the purity and identities of the compositional phases present using XRD. Only the other hand, conventional Raman measurements show an ambiguous peak at $\sim 326\text{ cm}^{-1}$, hinting possible multiple phases present. This is resolved by SERS spectroscopy measurement. SERS measurements are carried out on a thin film ($\sim 10 \pm 5\text{ nm}$) of the same as-synthesized CZTS nanoparticles drop-casted on a 50 nm thick gold film. Five distinct peaks could be observed, which can be unambiguously assigned to CZTS ($293, 335\text{ and }372\text{ cm}^{-1}$), CTS (320 cm^{-1}) and ZnS phases (351 cm^{-1}). SERS spectroscopy has been demonstrated for the first time to be a sensitive tool for the characterization of phases in nanomaterials. SERS spectroscopy improves the intensity of Raman signals of nanomaterials, and hence allows the differentiation of parasitic secondary phases from CZTS phase.

The first hypothesis on SERS having the capability to characterize nanomaterials unambiguously is proven to be true.

7.1.2 Outcome of hypothesis #2 [The reaction pathway to form CZTS should start with binary Cu-S, followed by diffusion of Sn^{4+} into Cu-S to form ternary Cu-Sn-S, and finally diffusion of Zn^{2+} into ternary Cu-Sn-S to form quaternary Cu-Zn-Sn-S]

Knowledge on the growth thermodynamics and microscopic mechanism of structural transformation is the key to explain and understand the growth pathway of multi-component semiconductor nanomaterials. It is therefore vital to carry out higher-order structural transitions and kinetics studies to highlight the complexity during multi-component nanomaterial growth.

It is proposed that the growth of $\text{Cu}_2\text{ZnSnS}_4$ nanoparticle proceed via formation of Cu-S binary nanoparticle, which acts as the seed for the diffusion of Sn^{4+} ions to form ternary Cu-Sn-S. This in turn acts as the intermediate phase for the diffusion of Zn^{2+} to obtain quaternary Cu-Zn-Sn-S nanoparticle (**Chapter 1**).

In the first part of our study (**Chapter 4**), ex-situ temporal studies of CZTS nanoparticles formation confirmed the hypothesis of the growth pathway of CZTS nanoparticles to be correct. In addition, the growth of the intermediate CTS phase has been observed to be the critical growth step in ensuring pure CZTS phase formation. With the help of ex-situ studies using CE approach and first principle calculation (**Chapter 5**), the growth of binary Cu-S phase to ternary Cu-Sn-S is observed to proceed via an alloyed-cation exchange mechanism involving two intermediate phases ($\text{Cu}_{31}\text{S}_{16}$ and $\text{Cu}_{32}\text{S}_{16}$). In the CE study approach, three reaction processes are proposed as follows

with the rate-limiting step identified to be the intermediate step (5.3).

Characterization of aliquots drawn at fixed time interval during growth of binary Cu-S to ternary Cu-Sn-S phase by STEM-EDX, HRTEM and HR-STEM revealed two preferential growth phenomena (**Chapter 5**). Firstly, the growth of ternary Cu-Sn-S phase proceeds via conversion of anionic framework (S^{2-}) of binary Cu-S phase. In our HRTEM study, as the symmetry of S^{2-} framework along $\langle 100 \rangle_{\text{Cu}_{31}\text{S}_{16}}$ and $\langle 001 \rangle_{\text{Cu}_4\text{SnS}_4}$ is C_{3v} , the observation of homogenous contrast using C_{3v} symmetry diffraction pattern masked on the HR-BFTEM FFT image confirms the growth of $\text{Cu}_{29}\text{S}_{16}$ to Cu_4SnS_4 to be an epitaxial growth process. From HRTEM image, the diffusion of Sn^{4+} is proposed to be propagating along the [031] lattice plane of $\text{Cu}_{31}\text{S}_{16}$ phase, while Cu_4SnS_4 phase is growing along the [110] lattice plane. Secondly, when the amount of Sn^{4+} available for reaction is decreased, the formation of bifurcated phases (Cu-S and Cu-Sn-S) instead of mono-population of incomplete reacted hetero-nanoparticles (Cu-S/Cu-Sn-S) prompted the growth of $\text{Cu}_{29}\text{S}_{16}$ nanoparticles to Cu_4SnS_4 nanoparticles to follow positive co-operatively CE pathway.

Following on, growth studies of ternary CTS to quaternary CZTS have been revealed to follow a preferential growth pathway. By carefully maintaining the rate of CTS phase formation to be similar to the rate of Zn^{2+} ion diffusion via controlling the coordinating strengths of the chelating ligands of metal precursors, the selective formation of CZTS phase over CTS phase has been achieved (**Chapter 4**). It is also found that CTS formation is very sensitive to the reactivity of Sn precursor and the amount of sulfur source. After a systematic study, the most optimized reaction conditions to form pure CZTS nanoparticles are found to be at low DDT volume of 1 mL and using $\text{Cu}(\text{Oac})_2$, $\text{Zn}(\text{acac})_2$, and $\text{Sn}(\text{oac})_4$ as the metal precursors.

Using CE approach (**Chapter 5**), the growth mechanism of Cu-Sn-S to Cu-Zn-Sn-S can be expressed as

In addition, thermodynamics studies revealed the formation of three competing parasitic phases (Zn-S, Cu-S and Cu-Sn-S). By estimating the order of the reactions via the rate equation; $r_n = k_a[A]^x k_b[B]^y$, which in turn is affected by the activation energy (E_a) in the Arrhenius equation; $k_n = A e^{-\frac{E_a}{RT}}$, and by assuming that the temperature required for complete phase transformation/formation to occur to be the E_a of the reaction process, the ranking of the relative rates of phase formation are as follow: **r**₃: Cu-Zn-Sn-S (160°C) > **r**₄: Zn-S (200°C) > **r**₁: Cu-S (230°C) ~ **r**₂: Cu-Sn-S (230°C). The displaced Cu^+ reacts with dodecanethiol (**r**₁) to form Cu-S nanoparticles, which in turn will react with Sn^{4+} to form CTS phase (**r**₂). This CTS phase (**r**₂) will then react with Zn^{2+} to form CZTS phase (**r**₃). As the formation kinetics of CTS (**r**₂) is smaller than the formation kinetics of ZnS (**r**₄), **r**₄ reaction is more favourable and therefore results in the presence of ZnS in the final product.

Following on, characterization of aliquots drawn at fixed time interval during the growth of ternary Cu-Sn-S phase to quaternary Cu-Zn-Sn-S by STEM-

EDX, HRTEM and HR-STEM reveal a preferential growth phenomena and a crystal structure ambiguity (**Chapter 5**). Firstly, the growth of quaternary Cu-Zn-Sn-S phase proceeds via conversion of anionic framework (S^{2-}) of ternary Cu-Sn-S phase. It is proposed that during the growth of CZTS phase, Zn^{2+} propagates along the [010] plane of Cu_4SnS_4 , while Cu_2ZnSnS_4 grows in the [100] direction. Secondly, cross referencing of three different zone-axis HR-STEM images confirms that Sn^{4+} has fixed occupancy in the crystal lattice, unlike the reported random cations occupation model (Wurtzite $P6_3mc$). As it is impossible to differentiate Zn from Cu by using HR-HAADF Z-contrast, two possible crystal structures are proposed. When Zn and Cu are assumed to follow Wurtzite-Stannite (WZ-S) arrangement, an orthorhombic ($Pmn2_1$) crystal phase is obtained; whereas when Zn and Cu are assumed to follow Wurtzite-Kesterite (WZ-KS) arrangement, Monoclinic Pc crystal phase is obtained. Theoretical simulation shows similarity in the XRD patterns and DFT calculation shows a difference of only 0.011 eV between the two crystal structures. This is therefore indicative of equal possibility of either crystal structure, or both being present.

These observations highlight the possibility of unbalanced reaction kinetics that leads to multiple phase segregation. Therefore, there is a need for further fundamental studies. In addition, the importance of accurate characterization of crystal structures and the ability to understand the complex chemistry behind the growth of multi-component materials will aid in future theoretical calculation, material design and control in phase formation during engineering of complex materials.

The second hypothesis, the growth of CZTS nanoparticle to proceed via nucleation of Cu-S phase, followed by formation of ternary Cu-Sn-S phase is proven to be accurate.

7.1.3 Outcome of hypothesis #3 [It is still plausible to obtain pure-phase wurtzite nanoparticles by substitution of Zn^{2+} with Co^{2+} , Mn^{2+} and Fe^{2+}]

The strong interest in $\text{Cu}_2(\text{M})\text{SnS}_4$ ($\text{M}=\text{Mn}$, Co and Fe) semiconductors arises from their various functional properties (e.g magnetic, catalytic, PV). Due to their suitable energy bandgaps and high solar absorption coefficients, $\text{Cu}_2(\text{M})\text{SnS}_4$ semiconductors possess the potential to be solar harvesting materials. However, despite the strong interest in $\text{Cu}_2(\text{M})\text{SnS}_4$ semiconductors, there has been no growth study carried out to explain the growth mechanism.

It is proposed that since Mn^{2+} , Co^{2+} , and Fe^{2+} are isovalent to Zn^{2+} , the formation of $\text{Cu}_2(\text{M})\text{SnS}_4$ ($\text{M}=\text{Mn}^{2+}$, Co^{2+} and Fe^{2+}) nanoparticles should follow the same mechanism as that of CZTS nanoparticle (**Chapter 1**). In the XRD study, it is observed that $\text{Cu}_2\text{MnSnS}_4$ crystallizes in wurtzite crystal structure while $\text{Cu}_2\text{FeSnS}_4$ and $\text{Cu}_2\text{CoSnS}_4$ crystallize in zinc blende crystal structure. In the SERS studies (**Chapter 6**) of $\text{Cu}_2(\text{M})\text{SnS}_4$ nanoparticles formation, it is deduced that the formation of $\text{Cu}_2\text{MnSnS}_4$ phase follows $\text{Cu}_2\text{ZnSnS}_4$ phase formation where the growth starts with the formation of Cu_{2-x}S nuclei, followed by the formation of ternary CTS phase and lastly the formation of C(M)TS quaternary phase. However, the growth mechanism of CFTS nanoparticles starts with the initial formation of Cu_{2-x}S nuclei, followed by the formation of ternary Cu-Fe-S intermediate phase and lastly the formation of quaternary CFTS phase. On the other hand, due to the lack in prior Raman studies on ternary Cu-Co-S phase, it is impossible to assign any phase to the Raman peak observed from SERS spectrum for CCTS. Nevertheless, as both CFTS and CCTS nanoparticles form zinc blende crystal structure preferentially, it is proposed that both growth mechanism could be similar.

As discussed in **Chapter 5**, due to templated-assisted (anionic framework) growth of quaternary phase from the intermediate ternary phase, the crystal structure of the final quaternary semiconductor follows that of the intermediate phase. In **Chapter 5**, the intermediate ternary Cu-Sn-S phase is shown to be orthorhombic, with the S^{2-} anion arranged in hexagonal arrangement. During the incorporation of Zn^{2+} into orthorhombic Cu-Sn-S phase, S^{2-} anionic framework is

conserved therefore the final quaternary phase crystallizes in wurtzite crystal structure. In this chapter, the growth of quaternary Cu-Mn-Sn-S phase is observed to proceed in a similar way with that of Cu-Zn-Sn-S (Cu-S to Cu-Sn-S to Cu-(M)-Sn-S) and the final quaternary phase (CMTS) crystallizes in wurtzite crystal structure too. This observation is in good agreement with the observation reported in **Chapter 5**.

Following on, the formation of quaternary Cu-Fe-Sn-S phase is also observed to be strongly influenced by the intermediate ternary phase (Cu-Fe-S). Immediate ternary Cu-Fe-S phase is reported to crystallize in cubic crystal structure, and the final quaternary Cu-Fe-Sn-S crystallizes in zinc blende crystal structure. This further highlights the strict relationship between the crystal structure of final product and the intermediate phase. It is therefore proposed that the intermediate phase of CCTS and CFTS should be the same. The intermediate ternary Cu-Co-S is reported to crystallize in cubic crystal structure as well. Hence, the formation of CCTS should follow the following pathway: initial nucleation of Cu_{2-x}S phase, followed by the formation of ternary Cu-Co-S intermediate phase and lastly the formation of quaternary CCTS phase.

In addition, it is observed that the formation of pure phase $\text{Cu}_2(\text{M})\text{SnS}_4$ (M=Mn, Co and Fe) nanoparticles is less sensitive to the amount of sulphur source (DDT) available as compared to the formation of CZTS nanoparticles. This again highlights the difference in reaction kinetics involved. This study provides the fundamental growth parameters for the formation of $\text{Cu}_2(\text{M})\text{SnS}_4$ (M=Mn, Co and Fe) nanoparticles. It highlights the need for fundamental thermodynamic studies during cationic substitution experiment as the growth pathway may be different as shown in **Chapter 6**.

The third hypothesis on the growth of $\text{Cu}_2(\text{M})\text{SnS}_4$ (M= Mn, Co and Fe) nanoparticles to follow the growth of CZTS nanoparticles is proven to be partially true.

7.2 Outstanding questions

As mentioned in **Chapter 6**, the strong interest in $\text{Cu}_2(\text{M})\text{SnS}_4$ ($\text{M}=\text{Mn}$, Co and Fe) semiconductors arises from their various functional properties. Firstly, due to their suitable energy bandgaps and high absorption coefficients, $\text{Cu}_2(\text{M})\text{SnS}_4$ semiconductors have the potential to be solar harvesting materials.¹ Secondly, since the atoms in $\text{Cu}_2(\text{M})\text{SnS}_4$ ($\text{M}=\text{Mn}$, Co and Fe) materials occupy fixed positions in the crystal lattice, the formation of intrinsic substitution defects (e.g A_B , B_A) which is found in CZTS, could be minimized and hence they can potentially be a better solar harvesting material.²⁻⁴ Thirdly, the presence of catalytic active ($\text{M}=\text{Co}$) element may give the quaternary semiconductors the catalytic properties needed for hydrogen evolution reaction (HER). Lastly, when the divalent cation is either Mn , Co or Fe , it gives quaternary $\text{Cu}_2(\text{M})\text{SnS}_4$ compounds magnetic property (dilute magnetic semiconductors).^{1,5} However, despite the strong interest in $\text{Cu}_2(\text{M})\text{SnS}_4$ semiconductors, there have been few if any fundamental studies carried out on their growth mechanisms, electrical properties and catalytic activities (**Chapter 2**).

7.2.1 Establishing Raman spectra database for ternary compounds for growth mechanism studies

From the detailed fundamental growth studies of $\text{Cu}_2(\text{M})\text{SnS}_4$ ($\text{M}=\text{Zn}$, Mn , Co and Fe) nanoparticles in **Chapters 4** and **6**, the growth parameters leading to pure-phase nanoparticles formation have been established. In addition, qualitative analysis of $\text{Cu}_2(\text{M})\text{SnS}_4$ ($\text{M}=\text{Zn}$, Mn , Co and Fe) nanoparticles can be achieved with SERS spectroscopy. However, there are still some remaining questions and issues unanswered.

To fully utilize SERS spectroscopy, the characteristic Raman spectra of possible ternary phases should be established. As shown in **Chapter 6**, it is not able to obtain direct growth evidence of $\text{Cu}_2\text{CoSnS}_4$ nanoparticles due to the lack of Raman information on the ternary phases. Hence, nanoparticles of ternary phases (Cu-Co-S , Cu-Fe-S , Fe-Sn-S , Cu-Mn-S) should be synthesized and Raman spectra should be obtained.

With the establishment of Raman database of ternary intermediate phase, one can better explain and identify the formation of secondary and intermediate phases during the formation $\text{Cu}_2(\text{M})\text{SnS}_4$ ($\text{M}=\text{Zn}$, Mn , Co and Fe) quaternary phases. With the capability in identifying phase present, one can trace the formation kinetics and learn the thermodynamics of the phase formation. By gaining clearer and deeper insights into the phase formation, better control over the purity of the synthesized materials can be achieved.

7.2.2 Investigation on catalytic properties

Due to the presence of elements with catalytic activities, there have been a strong interest in using $\text{Cu}_2(\text{M})\text{SnS}_4$ ($\text{M}=\text{Mn}$, Co and Fe) materials in artificial photosynthesis, waste treatment catalyst and replacement of Pt in Dye-sensitized solar cells (DSSCs).⁶⁻⁸

As a proof of concept, Pt has been replaced with CFTS thin film as the counter electrode in DSSCs and an encouraging efficiency of 8.03% was obtained.⁹ Via a cyclic voltammetry study, it was observed that CFTS is stable during the iodine/iodide (I_2)/ I_3^-) redox reaction. In addition, the reduction potential peak of (I_2)/ I_3^-) electrolyte is observed to be lower than Pt , hence improving the V_{oc} of the DSSCs solar cell with CFTS as the counter electrode. In addition, Mokurala et al recently reported on using CCTS as the counter electrode in DSSCs and achieved an efficiency of 7.4%.⁷ In his report, DSSCs with CCTS as the counter electrode gives a higher J_{sc} than CFTS hence highlighting a great potential in exploring $\text{Cu}_2(\text{M})\text{SnS}_4$ as counter electrode in DSSCs solar cells.

Next, Ozel *et al* recently reported on using CCTS as a catalyst for hydrogen evolution reaction (HER).⁸ In this report, electrospun CCTS nanofibers exhibited catalytic H_2 evolution comparable to Pt . As a highly efficient, inexpensive, and abundant catalyst offers new opportunities and greater flexible by avoiding expensive noble metals. Lastly, Zhong *et al* recently reported on fabrication of 3D (3 Dimensional) CFTS hierarchical microspheres for photo-catalytic activity.⁶ In this report, CFTS exhibits enhanced photo-catalytic activity on the photo-catalytic degradation of organic waste (Rhodamine B) in water.

Therefore, in order to further tap on the catalytic activities of $\text{Cu}_2(\text{M})\text{SnS}_4$ quaternary materials, experiments such as systematic doping studies to increase the catalytic activities and stability could be carried out.

7.2.3 General reaction protocol for large scale synthesis of $\text{Cu}_2(\text{M})\text{SnS}_4$ ($\text{M}=\text{Zn}, \text{Mn}, \text{Co}$ and Fe) nanoparticles

To establish a general protocol for large scale synthesis of $\text{Cu}_2(\text{M})\text{SnS}_4$ nanoparticles, CE approach method is a good candidate (**Chapters 3 and 5**). From the studies carried out in **Chapters 4 and 6**, it is understood that the growth pathway of $\text{Cu}_2\text{MnSnS}_4$ and $\text{Cu}_2\text{ZnSnS}_4$ nanoparticles proceed via the formation of intermediate Cu-Sn-S phase whereas $\text{Cu}_2\text{FeSnS}_4$ (CFTS) and $\text{Cu}_2\text{CoSnS}_4$ (CCTS) go through the intermediate Cu-(M)-S phase. Due to the difference in preferential growth pathway, preliminary studies were carried out to investigate if both CFTS and CCTS can be grown from ternary Cu-Sn-S phase. SERS and XRD characterization were carried out on the $\text{Cu}_2(\text{M})\text{SnS}_4$ nanoparticles synthesized using CE approach (**Figure 7.1**).

Figure 7.1 Schematic illustration of reaction setup showing two possible reaction pathway. Fe^{2+} as used as an example.

In a preliminary experiment, a pot of nanoparticles consisting of 50% $\text{Cu}_{32}\text{S}_{16}$ and 50% Cu_4SnS_4 was used as the starting materials for reaction (**Figure 7.1**). By adding $\text{M}=\text{Fe}, \text{Co}, \text{Zn}$ and Mn into the nanoparticles solution for reaction

it was possible to study the preferential growth pathway of the CMTS material's formation.

Figure 7.2 XRD and SERS characterization of as-synthesized $\text{Cu}_2(\text{M})\text{SnS}_4$ nanoparticles using CE approach.

It was observed that only CMTS and CZTS nanoparticles crystallize in wurtzite crystal structure while CCTS and CFTS still show preferential zinc blende crystal structure formation (**Figure 7.2**). It is understood in **Chapter 5** that if the reaction uses wurtzite Cu-Sn-S ternary phase as intermediate growth template, the final quaternary compound should be wurtzite crystal structure as well. Therefore, the formation of zinc blende crystal structure suggests that the both CCTS and CFTS did not use the wurtzite Cu-Sn-S ternary phase as the growth template (**Figure 7.1 pathway 2**). Instead it is propose that the reaction should proceed via Pathway 1 (**Figure 7.1**) and later react with Sn^{4+} to form CMTS quaternary phase instead. In addition, both SERS spectrum of CCTS and CFTS show the presence of secondary phases while SERS spectrum of CZTS and CMTS show phase pure nanoparticles.

Therefore, in order to optimize CE approach for large scale synthesis of phase pure nanoparticles, further investigation should be carried out with Cu-(M)-S (M=Co, Fe) ternary phase as the intermediate phase.

7.2.4 Optimization of thin film solar cell fabrication using $\text{Cu}_2(\text{M})\text{SnS}_4$ (M=Zn, Mn, Co and Fe) nanoink

Figure 7.3 Schematic of coffee stain formation for an evaporating drop with pinned contact lines (a) and with mobile contact lines (b) leading to solute concentration in a single spot. Contact line mobilization is achieved by applying an AC voltage between the interdigitated electrodes (short red and blue lines) in (b). Reproduced with permission from Reference 10. Copyright 2012, Royal Society Chemistry.

As discussed in **Chapter 6**, strong coffee ring effect during the drying of CZTS and CMTS nanoink on Molybdenum substrate restricts homogeneous deposition of nanoparticles on the substrate. In return, this uneven nanoparticle thin film hinders the performance of the PV solar cell. As shown in **Figure 7.3**, there are two main types of coffee ring effect, the first (Figure 7.3a) shows pinned solvent contact lines and the second (**Figure 7.3b**) shows mobile solvent contact line.¹⁰

In the case of pinned solvent contact lines, due to interaction between substrate surface and solvent, the contact line of an evaporating solvent is prevented from receding. In order to sustain the evaporation of the solvents, there is a constant convective flow from the centre of the solvent droplet towards the edge of the drop. This drying process leaves behind a concentrated ring of nanoparticles around the substrate with a poor coverage of nanoparticles in the centre of the substrate. On the other hand, in the case of a mobile contact lines, due to the poor interaction between substrate surface and the receding contact line of an evaporating solvent,

the solvent line resides as the solvent droplets decrease in size due to evaporation. This drying process leaves behind a concentrated spot of nanoparticles in the centre of the substrate with occasional multiple coffee ring stain around it. In both cases, the drying of the nanoink leaves behind a nonhomogeneous film of nanoparticles. Therefore in order to achieve a homogenous dried droplet, the surface energy of the substrate and the solvent wettability has to be balance.

Figure 7.4 Zoom out and zoom in bright field light microscopic image of thin film formed from varying in the concentration (v/v %) of hexanol and IPA in CZTS nanoink.

One common approach in minimizing coffee stain effect is by increasing the wettability of the nanoink. Commonly, co-solvent (e.g alcohol) with lower surface energy is added into the nanoink to improve the wettability. In our preliminary studies (**Figure 7.4**), CZTS nanoink (1 mg/mL in H₂O) with varying amount of iso-propyl alcohol and hexanol are dried on glass slides to form thin films. From our studies, it is observed that by incorporation of alcohol, the coverage of the nanoink improves, and there is a slight improvement in the coffee ring effect. From the bright field light microscopy images, it is observed that 10 %v/v hexanol and IPA gives the best thin film formation.

Therefore, further studies should be carried out on formulating the best nanoink for inkjet printing so as to facilitate fabrication of homogenous thin film at a large scale. Possible directions may include addition of wetting agents, co-solvents and even drying temperature of nanoink.

7.2.5 Opto-electronics studies of $\text{Cu}_2(\text{M})\text{SnS}_4$ (M=Mn, Co and Fe) material

Charge carrier density denotes the number of charge carriers per volume, which in turns affects the electrical conductivity of the material. Ideally, the carrier density of a solar harvesting material should be approximately 10^{16} . In initial studies, the carrier density of CFTS has been measured to be 10^{14} - 10^{16} , CMTS to be 10^{19} while Krishnaiah et al recently reported CCTS to be 10^{16} .^{9,11} In addition, Mott-Schottky (MS) plot of all three materials is measured to be p-type conductivity. Due to the highly metallic nature of CMTS (carrier density of 10^{19}), recent studies shows the CMTS solar cell experiences light dependent shunt conductance. This greatly affects the carrier lifetime of the electron-hole pairs and hence results in low V_{oc} and causes low device performance efficiency. Further studies should be carried out with our self-built AC hall measurements to identify the source of the high conductivity in CMTS materials and at the same time investigate the effect of secondary phases on the lifetime of electron-hole pair in all $\text{Cu}_2(\text{M})\text{SnS}_4$ materials.

In addition, the bandgap of $\text{Cu}_2(\text{M})\text{SnS}_4$ materials have been reported to vary greatly with dopants. For an example, in $\text{Cu}_2(\text{Zn,Fe})\text{SnS}_4$, substituting of Fe with Zn increases the bandgap from ~1.35 to 1.53 eV, and for $\text{Cu}_2(\text{Zn,Mn})\text{SnS}_4$, substitution of Mn with Zn increases the bandgap from ~1.23 to 1.51 eV.^{12,13} Due to the ease of tuning the bandgap of $\text{Cu}_2(\text{M})\text{SnS}_4$ materials, one can match the band alignment of $\text{Cu}_2(\text{M})\text{SnS}_4$ materials with other materials (e.g metallic back contact, n-type buffer) better. This allows one to design a wider variety of devices and match materials better to achieve better solar cell performance.

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Appendix

Annex 1. Rietveld refinement of **OAc** reaction setup for 1 and 5 mL DDT.

Refined lattice parameters of **OAc** reaction setup for 1 and 5 mL DDT.

Sample	Lattice parameters		Unit cell vol (Å ³)	ParticleSize (nm)	R_B (%)
	a (Å)	b (Å)			
OAc 1mL					
w. Cu ₂ ZnSnS ₄	3.8260(6)	6.3092(1)	79.995(3)	11.37(2)	0.670
OAc 5mL					
w. Cu ₂ ZnSnS ₄	3.8216(4)	6.3049(6)	79.745(2)	23.42(5)	1.155
s. Cu ₃ SnS ₄	5.4640(1)	10.8384(4)	323.59(2)	-	4.856

Annex 2. Rietveld refinement of **Cu-acac** reaction setup for 1 and 5 mL DDT.

Refined lattice parameters of **Cu-acac** reaction setup for 1 and 5 mL DDT.

Sample	Lattice parameters		Unit cell vol (Å ³)	ParticleSize (nm)	<i>R</i> _B (%)
	<i>a</i> (Å)	<i>b</i> (Å)			
Cuacac 1mL					
w. Cu ₂ ZnSnS ₄	3.8263(5)	6.3071(9)	79.968(2)	13.37(3)	0.837
Cuacac 5mL					
w. Cu ₂ ZnSnS ₄	3.8197(4)	6.3000(6)	79.604(2)	24.35(5)	1.153
s. Cu ₃ SnS ₄	5.4259(9)	10.8235(3)	322.54(2)	-	6.220

Annex 3. Rietveld refinement of **Zn-acac** reaction setup for 1 and 5 mL DDT.

Refined lattice parameters of **Zn-acac** reaction setup for 1 and 5 mL DDT.

Sample	Lattice parameters		Unit cell vol ($\text{\AA}^3$)	ParticleSize (nm)	R_B (%)
	a ($\text{\AA}$)	b ($\text{\AA}$)			
Znacac 1mL w. $\text{Cu}_2\text{ZnSnS}_4$	3.8266(5)	6.3099(9)	80.017(2)	11.38(2)	0.565
Znacac 5mL w. $\text{Cu}_2\text{ZnSnS}_4$	3.8233(4)	6.3055(6)	79.882(2)	22.09(4)	0.545
s. Cu_3SnS_4	5.4633(1)	10.8290(4)	323.22(2)	-	2.676

Annex 4. Rietveld refinement of **Sn-acac** reaction setup for 1 and 5 mL DDT.

Refined lattice parameters of **Sn-acac** reaction setup for 1 and 5 mL DDT.

Sample	Lattice parameters		Unit cell vol (Å ³)	ParticleSize (nm)	<i>R</i> _B (%)
	<i>a</i> (Å)	<i>b</i> (Å)			
Snacac 1mL					
w. Cu ₂ ZnSnS ₄	3.8306(1)	6.3213(2)	80.330 (5)	15.69(8)	1.015
s. Cu ₃ SnS ₄	5.4377(4)	10.8000(2)	319.33(7)	-	0.538
Snacac 5mL					
w. Cu ₂ ZnSnS ₄	3.8237(6)	6.3128(7)	79.930(2)	19.66(5)	0.513
s. Cu ₃ SnS ₄	5.4545(2)	10.7581(7)	320.07(3)	-	0.745

Annex 5. 3D crystal illustration of accepted hexagonal wurtzite $\text{Cu}_2\text{ZnSnS}_4$ showing the atom arrangements in their respective atomic rows and columns.

Annex 6. 3D crystal illustration of simulated orthorhombic $\text{Cu}_2\text{ZnSnS}_4$ showing the atoms arrangement in their atomic rows and columns.

Annex 7. 3D crystal illustration of simulated monoclinic $\text{Cu}_2\text{ZnSnS}_4$ showing the atom arrangements in their respective atomic rows and columns.

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