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Revealing Cation Exchange Induced Phase Transformations in Multi-Elemental Chalcogenide Nanoparticles

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Abstract

To control the process of cation exchange (CE) in multi-elemental system, a detailed understanding of structural changes at microscopic level is imperative. However, the synthesis of multi-elemental system has so far relied on the CE phenomenon of binary system which does not necessarily extend to the higher order systems. Here, a direct experimental evidence supported by theoretical calculations reveal a growth model of binary Cu-S to ternary Cu-Sn-S to quaternary Cu-Zn-Sn-S which shows that cations preferentially diffuse along specific lattice plane with the preservation of sulfuric anionic framework. In addition, we also discover that unlike the commonly accepted structure ($P6_3mc$), the metastable crystal structure of Cu-Zn-Sn-S phase possesses fixed Sn occupancy sites. By revealing the preferential nature of cations diffusion and growth mechanism, our work provides insight to control the stoichiometry and phase purity of novel multi-elemental materials.

Introduction

Chalcogenides are an important class of materials consisting of cations (M) and anions (sulfides, selenides and tellurides) in the form of binary and multi-elemental (ternary and above) compounds.¹ As these materials exhibit valuable functional properties, they are widely used as light absorbing materials, ionic conductors, catalysts or phase change materials, and therefore utilized in a broad range of applications which include photovoltaic (PV), electronics, optics, and energy storage materials.²⁻¹³ The successful fabrication of functional devices often depends on the careful control of the material stoichiometry and phase purity. Unfortunately, when many elements are present, complex growth mechanisms and competing reaction kinetics hinder the formation of the desired phase.^{8, 14}

Advances in post-synthetic modification chemistry, specifically cation exchange (CE), provides pathways to previously unavailable nanomaterials including multi-elemental nanomaterials (e.g metallo-organic framework, sulfides, oxides and halides), epitaxial-core-shell and epitaxial-hetero nanostructures.¹⁵⁻²² Essentially, cation exchange enables tailoring of optical, electronic and magnetic properties through transport of dissolved cations into the extended solid.^{18, 23-29} Two factors are necessary for successful CE, firstly the Gibbs free energy of the products has to be lower than that of the reactants, and secondly the CE reaction on the solid surface and in the extended solid must be kinetically favourable. However, despite the strong interest in multi-elemental materials, especially for solar cells, more CE work has been on binary systems rather than ternary and quaternary systems. In particular, key problems to answer include non-uniform growth rates, preferential growth pathways and competitive growth kinetics.^{26, 30-31} As *ab initio* calculation remains qualitative at best, and the control of a materials formation requires a detailed understanding of events occurring during synthesis.^{22, 32-33} Further development in fundamental knowledge regarding nanomaterial formation via CE will enable further engineering of phase-pure multi-elemental materials for high performance applications.

Here, a CE growth model that accounts for the temporal changes in crystal structures, the impact on the interfacial plane alignment of the hetero-phase, and the elemental distribution of the binary host component $Cu_{52}^+Cu_6^2+S_{32}^{2-}$ ($Cu_{58}S_{32}$) nanoparticles that forms ternary $Cu_4^+Sn^{4+}S_4^{2-}$ (CTS) and quaternary $Cu_2^+Zn^{2+}Sn^{4+}S_4^{2-}$ (CZTS) will be presented sequentially. Currently, CZTS is a quaternary material explored for thin film photovoltaic (PV) application due to its high solar absorption coefficient and makeup of abundant elements.^{14, 34-37} We show direct evidence of phase transformation from binary Cu-S to ternary Cu-Sn-S and quaternary Cu-Zn-Sn-S nanoparticles via ex-situ temporal studies. High resolution transmission electron microscopy (HRTEM) images shows preferential cations diffusion in the extended solid to proceed along a specific lattice plane due to the rigid sulphur anionic framework arrangement in the crystal matrix. Furthermore, we observed two types of alloyed CE reaction mechanism; the first is a positive cooperative mechanism for the growth of binary Cu-S to ternary Cu-Sn-S phase, and the second is a classical memoryless diffusion mechanism for the growth of ternary Cu-Sn-S phase to quaternary Cu-Zn-Sn-S phase. Lastly, with Z-contrast atomic resolution TEM, the metastable crystal structure of quaternary Cu-Zn-Sn-S phase is revealed to possess fixed Sn occupancy sites, indicating that the crystal structure is $Pmn2_1$ or Pc , unlike the commonly accepted $P6_3mc$.³⁸ Our results demonstrate the complexity of multi-elemental material formation that involves multiple reaction processes in a single phase transformation. This work highlights the imperativeness of understanding the reaction kinetics and elemental distribution at nanoscale during phase formation. In addition, by using a metastable crystal structure as a growth template, it provides insight for the synthesis of novel multi-elemental materials.

Cation Exchange Phenomenon In Binary To Ternary Cu Chalcogenide

The main objective of this section is to understand the cation exchange phenomenon in binary to ternary phase transformation (Cu-S to Cu-Sn-S) (**Fig. 1a**). Firstly, binary $Cu_{58}S_{32}$ nanoparticles are synthesized via heating up method where copper(II)acetate are allowed to react with dodecanethiol at 230 °C for 60 mins (**Refer to Materials and Methods for more detailed procedure**). The binary to ternary transformation of Cu-S (**Supplementary Fig. 1-3**) to Cu-Sn-S (**Supplementary Fig. 4-6**) is proposed to occur via the following reactions, based on the XRD results (**Fig. 1vii-viii**):

where reactions (1, 2 and 3) are represented by the diffractograms collected at 0, 6 and 20 mins, respectively (**Fig 1 viii**) and EDX showing increasing Sn incorporation as reaction proceeds

(**Supplementary Fig. 7**). SERS (**Fig. 1ix**) confirms the incorporation of Sn into Cu-S as shown by the shift of the Cu-S vibration from 295 to 323 cm^{-1} as the reaction time increases.

Firstly, in the CE of binary Cu_{2-x}S nanoparticles, it was generally accepted that the free energies of formation for different Cu_{2-x}S phases are in favour of higher stoichiometry ($\text{Cu}_{64}\text{S}_{32}$ is more preferred than $\text{Cu}_{62}\text{S}_{32}$).³⁹ However, our experiment does not agree with this suggestion as we found that a higher temperature is required to form $\text{Cu}_{64}\text{S}_{32}$ (~200 °C) as compared to $\text{Cu}_{62}\text{S}_{32}$ (~180 °C) (**Supplementary Fig. 8-11**). Such discrepancy may arise because cation exchange is a localized solid-state reaction whereas the previous report by Potter et al. used electrochemical cells.³⁹ In addition, our experimental data is in good agreement with our DFT calculation which indicates that $\text{Cu}_{62}\text{S}_{32}$ is more favoured because the calculated minimum $\Delta\mu_{\text{Sn},\text{equation 1}}$ is the smallest among the 3 equations (**Table 1 and Supplementary Table 2, Refer to Materials and Methods for more detailed procedure**).

Following, Prashant *et al.* reported a rare CE exchange mechanism behaving similarly to the positive cooperatively binding of O_2 in blood haemoglobin.³¹ In a positive cooperatively CE reaction, successful cation displacement in nanoparticles increases the affinity for subsequent cation exchange. This encourages subsequent displacement to be in close proximity to the previous displaced site or an increase in rate of successive displacement. To capture the CE of Sn into $\text{Cu}_{58}\text{S}_{32}$, we intentionally reduced the amount of Sn (Sn-poor condition). The elemental mapping by EDX indicates the positive cooperatively CE reaction during the phase transformation of $\text{Cu}_{58}\text{S}_{32}$ to Cu_4SnS_4 (**Fig. 2a**) with the phases identified by XRD (**Fig. 2ai and 2aii**). We observe that Sn prefers to diffuse into heterostructure Cu-S/Cu-Sn-S NPs to form two different nanoparticles species (Cu_4SnS_4 and $\text{Cu}_{64}\text{S}_{32}$) as final product (**Supplementary Fig. 12**). When the amount of Sn to Cu ratio increases from (Cu:Sn 8:1 to 4:1), the percentage of Cu_4SnS_4 phase increases (**Fig. 2ai and 2aii**), and elemental mapping by EDX still shows two different nanoparticles species (Cu_4SnS_4 and $\text{Cu}_{64}\text{S}_{32}$) as final product. In both Cu:Sn ratio, we did not observe heterostructure Cu-S/Cu-Sn-S NPs as the final product. The incomplete reaction under Sn-poor condition can be explained by

$$\Delta\mu_{\text{Sn}} = RT \cdot \ln\Delta c_{\text{Sn}} \quad (4)$$

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. From **equation 4**, when the concentration of Sn^{4+} decreases, the value of μ_{Sn} decreases as well, hence the reaction will stop once μ_{Sn} decrease below the minimum chemical potential therefore hindering complete reaction. The continuous depletion of Sn in the solution may also explain why DFT calculations cannot accurately predict the actual $\Delta\mu_{\text{Sn}}$ as a function of time.

To conclude, we proposed that the binary ($\text{Cu}_{58}\text{S}_{32}$) to ternary (Cu_4SnS_4) transformation occurs through positive cooperative CE reaction.

Cation Exchange Phenomenon In Ternary To Quaternary Cu Chalcogenide

Next, from the XRD analysis, the cation exchange reaction of Cu_4SnS_4 to $\text{Cu}_2\text{ZnSnS}_4$ can be expressed as (**Supplementary Fig. 13-15**):

where Zn displaces Cu to form CZTS and $\text{Cu}_{64}\text{S}_{32}$ phases.

Two reactions under Zn poor and equal Zn:Sn are carried out to understand how this cation exchange reaction proceeds. Under Zn poor conditions, uniformly distributed Cu-S, Cu-Sn-S and heterostructured $\text{Cu}_3\text{SnS}_4/\text{Cu}_2\text{ZnSnS}_4$ nanoparticles can be observed (**Fig. 2biii, iv**). When equal Zn:Sn ratio is used, two different nanoparticles species ($\text{Cu}_{64}\text{S}_{32}$ and $\text{Cu}_2\text{ZnSnS}_4$) is observed (**Supplementary Fig. 16-17**). This observation shows that the CE reaction of Cu_4SnS_4 to $\text{Cu}_2\text{ZnSnS}_4$ follows the classical memoryless, diffusion limited CE process (i.e. as long as the cation can diffuse to a lattice site, exchange can take place at that site).³¹ It is noted that in both cases, there is no observable Zn-S rich phase from the elemental mapping. This can be easily understood for the Zn poor case because there is insufficient Zn to form ZnS. However, when the ratio of Zn:Sn is about 1, there is a possibility of forming ZnS phase. This prompted the need to investigate the reaction kinetics of Cu-Sn-S phase to CZTS phase formation under stoichiometric condition.

As the reaction coefficient (k_n) in the rate equation ($r_n = k_a[A]^x k_b[B]^y$) is affected by the activation energy (E_a) in the Arrhenius equation; $k_n = Ae^{-\frac{E_a}{RT}}$,⁴⁰⁻⁴¹ the temperature at which the reaction occurs depends on the activation energy. Using ex-situ XRD study, it is 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 Cu-Sn-S ($\sim 230^\circ\text{C}$), while the Cu-Sn-S to CZTS transformation is kinetically the fastest reaction process ($\sim 160^\circ\text{C}$) (**Fig. 3** and **Supplementary Fig. 18-19**). The relative reaction rates are hence ranked as: **r₃**: Cu-Zn-Sn-S (160°C) > **r₄**: Zn-S (200°C) > **r₁**: Cu-S (230°C) ~ **r₂**: Cu-Sn-S (230°C). Therefore, the absence of ZnS can be explained because of the preferential formation of Cu-Zn-Sn-S.

To conclude, we showed that the ternary (Cu_4SnS_4) to quaternary ($\text{Cu}_2\text{ZnSnS}_4$) transformation occurs through classical CE mechanism (**Supplementary Fig. 20**). In addition, we also propose that a pure phase $\text{Cu}_2\text{ZnSnS}_4$ can be obtained if the reaction is carried out at the temperature lower than the formation of the other secondary phases.

After revealing the thermodynamic growth processes of Cu-S to Cu-Sn-S and to Cu-Zn-Sn-S, we perform further HRTEM analysis to identify the preferential diffusion pathways of the cations during the CE reaction.

Sulfuric Anionic Framework Directed Cation Exchange

Alivisatos *et al.* showed that the anionic framework is preserved during CE for binary system, while Lesnyak *et al.* showed for binary to ternary and quaternary systems.^{12, 42} However, growth mechanisms are not reported in greater details. In our study, direct imaging and characterization of Cu₅₈S₃₂ to Cu₄SnS₄ and Cu₂ZnSnS₄ phase growth using TEM revealed a preferential lattice transformation growth mechanism. By quenching the growth of Cu₅₈S₃₂ to Cu₄SnS₄ after 2 mins of reaction, it freezes the transformation to reveal the lattice planes through which Sn⁴⁺ diffuses into Cu₅₈S₃₂. Firstly, a homogenous contrast at the interface of heterostructure Cu-S/Cu-Sn-S NPs using C_{3v} symmetry diffraction pattern masked on the HR-BFTEM FFT image (**Fig. 4a** and **Supplementary Fig. 21**) confirms the growth of Cu₅₈S₃₂ to Cu₄SnS₄ to follow the sulphuric anionic framework. Secondly, it is noted that the preferential diffusion of Sn⁴⁺ atoms is along the [012] plane of Cu₅₈S₃₂. The preferential diffusion along a longer pathway (across the NPs) instead of a shorter pathway (along the short axis) can be explained by the conservation of anionic framework and nanoplates morphology during the growth. Sulfur always arranges in hexagonal C_{3v} symmetry at the centre of the S-M₄ (M= Sn, Cu) tetrahedral (**Supplementary Fig. S22**). It is therefore kinetically less favourable for Sn to displace Cu with an S atom in the path.

Following on, TEM imaging revealed the growth of Cu-Sn-S to Cu-Zn-Sn-S phase to follow a preferential lattice transformation growth mechanism (**Fig. 4b** and **Supplementary Fig. 23**). Firstly, as CTS phase and CZTS phase have similar FFT patterns (**Supplementary Fig. 4, 13 and 20**), we are not able to differentiate the two phases from FFT. Therefore, by referring to the EDX data and HR-HAADF imaging, the interfacial plane alignment between hetero CTS/CZTS involved [010] plane of Cu₄SnS₄ and [100] plane of Cu₂ZnSnS₄ (**Fig. 4vii**) as Zn²⁺ diffuses along [010] plane of Cu₄SnS₄ to form Cu₂ZnSnS₄ phase. In addition, during the growth of CZTS phase via CE, displacement of Cu by Zn resulted in the formation of hetero Cu-S/Cu-Zn-Sn-S particles intermediate. Using C_{3v} symmetry diffraction pattern masked on the HR-BFTEM FFT image (**Supplementary Fig. S24-S25**) shows a homogenous contrast at the interface of hetero (Cu-S/Cu-Zn-Sn-S), indicating the growth of Cu₄SnS₄ to Cu₂ZnSnS₄ to involve epitaxial displacement of Cu.

Fixed Sn position in Cu₂ZnSnS₄ metastable crystal structure

The generally accepted metastable structure of CZTS has $P6_3mc$ symmetry. This crystal structure can be summarized as: 1) the 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 (**Supplementary Fig. S26**). However, HR-STEM characterization of the CZTS nanoparticles indicates a fixed Sn occupancy (Fig. 5a). By viewing the nanoparticles along three zone axes, two possible structures are identified to 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, a monoclinic Pc crystal phase is obtained (**Fig. 5b and Supplementary Fig. S27-S28**). Theoretical simulation of both WZ-KS and WZ-S shows non distinguishable XRD patterns while DFT calculation showed a difference of only 0.011 eV between Pc CZTS (-3.673 eV) and $Pmn2_1$ CZTS (-3.663 eV). This is therefore indicative of equal possibility of either crystal structure, or both being present (**Supplementary Table 3**).

Conclusion

This work presents a model study to highlight the complexity of phase transition via cation exchange to form multi-component sulfide nanomaterials ($Cu_{58}S_{32}$ to Cu_4SnS_4 to Cu_2ZnSnS_4). Ex situ temporal growth studies revealed that the phase transformation of binary $Cu_{58}S_{32}$ to ternary Cu_4SnS_4 to quaternary Cu_2ZnSnS_4 occurs via alloyed cation exchange in a fixed anionic framework. Tracing the structural changes of binary $Cu_{58}S_{32}$ growth to ternary Cu_4SnS_4 revealed a sequential three steps reaction involving two intermediate phases ($P2_1/n$ $Cu_{62}S_{32}$ and $P2_1/c$ $Cu_{64}S_{32}$) while preserving the anionic framework of $Cu_{58}S_{32}$. In our ex-situ studies, we observed two types of alloyed CE reaction mechanism; the first is a positive cooperative mechanism for the growth of binary Cu-S to ternary Cu-Sn-S phase, and secondly is a classical memoryless diffusion mechanism for the growth of ternary Cu-Sn-S phase to quaternary Cu-Sn-Sn-S phase.

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 $P6_3mc$ symmetry. 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 in energy (0.011 eV), hinting at an equal possibility in structural formation. This observation posed a potential challenge in future characterization of multi-component material with conflicting crystal structures but similar X-ray diffraction patterns. The importance of accurate characterization of crystal structures 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 the engineering of complex materials.

By understanding the growth dynamics, we can effectively pinpoint conflicting growth kinetics allowing the planning of plausible solutions. This allows phase-pure nanoparticles to be synthesis. The advantage of phase-pure nanoparticle (nanoink) approach include bypassing random phase formation during thin film fabrication as phase (e.g CZTS) are “preformed” during nanoparticles synthesis. As a result, it is desirable to develop a robust solution-based process for nanoparticles for the fabrication of nanoink-based devices.

Methods

Synthesis of $\text{Cu}_{58}\text{S}_{32}$ nanoparticles. 0.455mmole of $\text{Cu}(\text{OCH}_3)_2 \cdot \text{H}_2\text{O}$ (Sigma-Aldrich $\geq 98\%$) was added to 0.5 mL of Oleylamine (Oam, Acros Organics 80-90%) and 9 mL of 1-Octadecene (Sigma-Aldrich 90%) in a three-neck round bottom flask (RBF) and allowed to heat to 130°C under vacuum before adding 0.5 mL of Dodecanethiol (DDT, Sigma-Aldrich $\geq 98\%$) followed by further heating to 150°C for 10 minutes under vacuum. The solution was then rapidly heated ($10^\circ\text{C}/\text{min}$) to 230°C and reacted for 60 minutes under 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 $\text{Cu}_{32}\text{Sn}_8\text{S}_{32}$ nanoparticles) or room temperature (for characterization). Nanoparticles for characterization were washed via addition of 20 mL of hexane to the reaction solution and centrifuge at 10000 rpm for 3 minutes for 3 times and allowed to dry in a self-built N_2 box.

Synthesis of Cu_4SnS_4 nanoparticles. A solution of Sn^{4+} salt (0.225mmole of $\text{Sn}(\text{Oac})_4$ (Sigma-Aldrich) dissolved in 1mL DDT and 1mL Oam) was added to $\text{Cu}_{58}\text{S}_{32}$ nanoparticles solution when it cooled to 80°C . The reaction mixture was then heated rapidly ($10^\circ\text{C}/\text{min}$) to 150°C under vacuum and followed by heating ($10^\circ\text{C}/\text{min}$) to 230°C and allowed to react for 60 minutes 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 100°C (for synthesis of $\text{Cu}_{16}\text{Zn}_8\text{Sn}_8\text{S}_{32}$ 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 minutes and allowed to dry in a self-built N_2 box.

Synthesis of Sn-poor Cu_4SnS_4 nanoparticles. A solution of Sn^{4+} salt (0.113 mmole (halved) and 0.056 mmole (quartered) of $\text{Sn}(\text{Oac})_4$ (Sigma-Aldrich) dissolved in 1mL DDT and 1mL Oam) was added to $\text{Cu}_{58}\text{S}_{32}$ nanoparticles solution when it cooled to 80°C . The reaction mixture was then heated rapidly ($10^\circ\text{C}/\text{min}$) to 150°C under vacuum and followed by heating ($10^\circ\text{C}/\text{min}$) to 230°C and allowed to react

for 60 minutes under N₂ 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 100°C (for synthesis of Cu₁₆Zn₈Sn₈S₃₂ 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 minutes and allowed to dry in a self-built N₂ box.

Synthesis of Cu₂ZnSnS₄ nanoparticles. 0.225mmole of Zn(acac)₂.xH₂O (assuming 1 part H₂O, Sigma-Aldrich powder) is added to Cu₃₂Sn₈S₃₂ nanoparticles solution when it cooled to 80°C. The reaction mixture is then heated rapidly (10°C/min) to 150°C under vacuum and followed by heating (10°C/min) to 240°C and allowed to react for 90 minutes under N₂ 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 addition of 20 mL of hexane to the reaction solution and centrifuged at 10000 rpm for 3 minutes for 3 times and allowed to dry in a self-built N₂ box.

Synthesis of Zn poor Cu₂ZnSnS₄ nanoparticles. 0.056 mmole of Zn(acac)₂.xH₂O (assuming 1 part H₂O, Sigma-Aldrich powder) is added to Sn poor (0.113 mmole Sn⁴⁺) nanoparticles dispersion when it cooled to 80°C. The reaction mixture is then heated rapidly (10°C/min) to 150°C under vacuum and followed by heating (10°C/min) to 240°C and allowed to react for 90 minutes under N₂ 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 addition of 20 mL of hexane to the reaction solution and centrifuged at 10000 rpm for 3 minutes for 3 times and allowed to dry in a self-built N₂ box.

Synthesis of Zn:Sn equal Cu₂ZnSnS₄ nanoparticles. 0.056 mmole of Zn(acac)₂.xH₂O (assuming 1 part H₂O, Sigma-Aldrich powder) is added to Sn poor (0.056 mmole Sn⁴⁺) nanoparticles dispersion when it cooled to 80°C. The reaction mixture is then heated rapidly (10°C/min) to 150°C under vacuum and followed by heating (10°C/min) to 240°C and allowed to react for 90 minutes under N₂ 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 addition of 20 mL of hexane to the reaction solution and centrifuged at 10000 rpm for 3 minutes for 3 times and allowed to dry in a self-built N₂ box.

X-ray diffraction. XRD samples were prepared by drop casting a concentrated amount of nanoparticles solution on a Si wafer (1.5 x 1.5 cm) to form a thick and dense film. Patterns are recorded using Bruker D8 diffractometers running on Cu-K α radiation source ($\lambda_1 = 1.54056 \text{ \AA}$, $\lambda_2 = 1.54439 \text{ \AA}$) with a LynxEye detector and operated at 40 kV and 40 mA. All scan range were from 10° to 70°, with 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 (5-term Chebyshev polynomial, zero error and ‘crystallite size’ to model the microstructure-controlled line broadening).

Surface Enhanced Raman Scattering. 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. Diluted nanoparticle solution in hexane were then drop-casted (5 μ L, 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 the 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 $\times$ NA 0.9). The excitation laser power is 0.04 mW with exposure time for each line and slit width of the spectrometer are 30 s and 50 μ m respectively. The final SERS spectrum is an average of all the spectra collected (300 spectra).

TEM analysis. TEM sample preparation involved dripping 1 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 is 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 80kx magnification, 0.68nA beam current, 2068x2068 pixel resolution, with a dwell time of 15mins and an average signal count of >1000 per pixel. Fast Fourier Transform (FFT) and inverse FFT are carried out using Gatan Microscope Suite and ES Vision.

Density Functional Theory (DFT) Calculations. First-principle modelling to calculate the formation energies of each process using the Vienna *ab initio* simulation package (VASP) is employed. The projector augmented wave (PAW) method is 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 [need reference]. We used a cutoff energy of 350 eV for the plane-wave basis set. For different compounds, different *k*-mesh settings within the Monkhorst–Pack scheme are used. Lattice relaxation was continued until the forces on all the atoms are converged to less than 10^{-2} eV Å⁻¹. The volume of the supercell was fixed but all the internal freedoms are fully relaxed. The lattice constants reproduced from GGA-PBE computations, as well as the theoretical and experimental values from the literatures are listed in **Supplementary Table 1**. From the table, we found out that our calculated lattice parameters agree well with the experimental values. After relaxed the geometric structures, the formation enthalpy energies of different compounds can be calculated as:

$$\Delta H_f = E_{solid} - n_a \sum_{\alpha} E_{\alpha}^{bulk}$$

where E_{solid} is the total energy of a given bulk compound, n_a is the number of an element in compound, and E_{α}^{bulk} is the energy per atom of pure α in its standard elemental phase. In this study, the standard phase of the Cu, Zn, Sn and S elements are FCC-Cu, FCC-Zn, alpha-Sn and alpha-S (S₈), respectively. The calculated results are also listed in **Supplementary Table 1**.

ASSOCIATED CONTENT

Supporting Information.

Additional TEM images, XRD, Rietveld refinements, crystal structure parameters, XPS, SERS spectra, and EDX measurements of as-synthesized CS, CTS and CZTS nanoparticles. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Competing financial interests

The authors declare no competing financial interests.

Authors Contributions

JMR Tan and LH Wong conceived and designed this project. JMR Tan carried out material synthesis and material phase characterization using XRD and Raman spectroscopy. JMR Tan, CT Nelson, MC Scott and RZ Tao carried out TEM experiments. S Pedireddy carried out XPS characterization. W Hao carried out DFT calculation. JMR Tan and T Baikie carried out Rietveld refinement. All authors discussed and analysed the data. JMR Tan, MC Scott, T Baikie, W Hao, S. Magdassi, T White and LH Wong wrote the manuscript.

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Table of Content (ToC Image)

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 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).

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

b Linear growth rate of Cu_4SnS_4 to $\text{Cu}_2\text{ZnSnS}_4$

Figure 2| Linear and non-linear growth rate **a.** XRD and STEM-EDX imaging of nanoparticles synthesized of Cu_4SnS_4 from $\text{Cu}_{29}\text{S}_{16}$ with Cu:Sn ratio 8:1 (i) and 4:1 (ii) showing positive-cooperatively growth phenomena. **b.** XRD and STEM-EDX imaging of nanoparticles synthesized of $\text{Cu}_2\text{ZnSnS}_4$ with 0.057 mmole of Zn^{2+} with nanoparticles from 8:1 (i) and 4:1 (ii).

Multi-reaction competition during phase transformation of Cu_4SnS_4 to $\text{Cu}_2\text{ZnSnS}_4$

Figure 3| 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; EDX, Energy-dispersive X-ray Spectroscopy.

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

b Selective template-epitaxial transformation of Cu_4SnS_4 to $\text{Cu}_2\text{ZnSnS}_4$

Figure 4| Preferential growth pathway of $\text{Cu}_{29}\text{S}_{16}$ to Cu_4SnS_4 to $\text{Cu}_2\text{ZnSnS}_4$ 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 (v). **b.** Growth study of $\text{Cu}_2\text{ZnSnS}_4$ (Cu:Sn:Zn 4:1:0.5) quenched at 230°C at 90mins with elemental mapping (vi), high-resolution TEM image and schematic illustration of growth direction showing phase separation during growth of Cu_4SnS_4 to $\text{Cu}_2\text{ZnSnS}_4$ (vii).

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| 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 structure of orthorhombic WZ-S $Pmn2_1$ and monoclinic WZ-KS Pc are proposed to be the crystal structure of metastable CZTS;

Table 1. 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

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