SYNTHESIS, INTERCONVERSION, CATION INCORPORATION, AND APPLICATIONS OF PLASMONIC COPPER SULFIDE-BASED NANOMATERIALS

by

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Dedicated to my beloved mother, father and girlfriend
ABSTRACT

A diverse array of colloidal semiconductor nanomaterials has been synthesized and studied over the past few decades. They are being explored or employed in many emerging applications based on their unique physical, chemical, and biological properties. Among these nanomaterials, copper chalcogenides have been the subject of much recent research in colloidal semiconductor nanocrystals (NCs) that exhibit localized surface plasmon resonance (LSPR) which can produce strong absorbance and scattering of light. This optical phenomenon is useful in several rapidly growing applications in theranostics, nanophotonics, and nanoelectronics.

This dissertation focuses on synthesis, interconversion, heterocation incorporation and applications of plasmonic copper sulfide-based nanomaterials. Chapter 1 provides an introduction to copper sulfide NCs and describes methods for synthesizing them. It includes our recent progress on developing a chemical method for synthesis of high-quality plasmonic covellite CuS nanoplatelets (NPLs), with useful absorbance at near-infrared wavelengths. LSPR was observed in these NCs and tuning of their LSPR was achieved by controlling their diameter while keeping their thickness constant (tuning their aspect ratio). We further generalized the method for preparation of CuS NPLs to achieve rapid, room-temperature synthesis of various metal sulfides, including Ag₂S, PbS, and CdS, with tunable optical properties.

In Chapter 2, we describe and demonstrate reversible interconversion between copper sulfide NCs of different composition and crystal phase. The copper sulfide class of materials is known for its many possible crystal phases and morphologies. We
studied the reversible interconversion by reducing disulfide bonds in covellite CuS and adding an organo-sulfur complex. We also revealed that covellite CuS NCs have a preferential plate-like morphology, due to the layered structure of covellite CuS.

Chapter 3 mainly involves the outcomes, mechanisms, and related shape and composition evolution of incorporation of foreign cations into copper sulfide NCs. Ternary copper tin sulfide (CTS) NPLs were prepared by using binary CuS NPLs as the template. Two distinct CTS crystal phases were obtained using different combinations of Sn sources (Sn(II) or Sn(IV) precursors) and reducing agents. In addition, copper indium sulfide (CIS) NPLs were prepared by a similar method. Then CIS NPLs were further converted to biconcave (red blood cell-like) djurleite Cu$_{1.94}$S NCs via cation exchange. The formation of biconcave structures is attributed to aggregation of defects produced by rapid In$^{3+}$ out-diffusion. These defects migrate to the center of NPLs to trigger the local collapse of the NPLs. Finally, we further prepared a variety biconcave metal sulfide NPLs (CdS, ZnS, MnS and CuInS$_2$) using the biconcave Cu$_{1.94}$S NPLs as a template. We demonstrated that the compatibility of anion sublattice (hcp vs. fcc) plays a decisive role in controlling morphology preservation or evolution before and after cation exchange (CE) reactions. Again starting from the covellite CuS NPL templates, we incorporated monovalent Ag$^+$ into them to produce heterogeneous copper sulfide-based nanostructures. The outcome of the incorporation process strongly depended on the initial amount of Ag$^+$ provided. Plate-satellite CuS-Ag$_2$S heterostructures were produced when using a small (0.1 mmol, insufficient to fully convert CuS to Ag$_2$S) amount of Ag$^+$, while biconcave-particle Ag$_2$S-Ag heterodimers were produced when
applying high (0.5 mmol, in excess of the amount required to fully convert CuS to Ag₂S) amount of Ag⁺.

Through this series of studies, we conclusively demonstrated that trivalent and tetravalent cations can be incorporated into reduced CuS NPs to produce homogeneous ternary alloy NPs, while the monovalent and divalent cations cannot coexist with Cu⁺ ions in the Cu₂₋ₓS phase. In turn, the incorporation of them leads to formation of heterogeneous NPs and finally produces copper-free metal sulfide NPs. The cation valence selectivity arises from conflicts between charge balance and coordination between Cu⁺ and divalent cations. Last but not least, we incorporated indium and tin into Cu₁₋ₓ₁S-ZnS heterostructures. We demonstrate that the outcomes of cation incorporation are strongly influenced by heterocation identity and valence and by the presence of a Cu-extracting agent. The selectivity of cation incorporation depends upon both the cation itself and the hetero-domains in which CE reactions take place. The final nanocrystals (NCs) emerge in many forms including homogeneous NCs, heterodimers, core@shell nanoheterostructures (NHs) and NHs with three different domains.

Chapter 4 mainly contains two examples of applications of copper chalcogenide nanomaterials, for electrocatalysis and photothermal therapy. The CuS NPs were tested for electrocatalytic activity for oxygen reduction reaction (ORR) in alkaline solution. ORR activity increased with increasing diameter of the CuS NPs, due to anisotropy of electron mobility and electrochemical activity of 2-dimensional NPs. Size-tunable Cu₂₋ₓSe nanoparticles (NPs) were used as photothermal agent in the second biological window of transparency, taking advantage of their tunable LSPR absorbance at near-
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A summary and outlook for future work in this field are presented in Chapter 5.
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Figure 3-29. Low magnification TEM images of covellite CuS NPls (a) before and (b) after Ag$^+$ incorporation. (c) TEM image of a single CuS-Ag$_2$S plate-satellite nanostructure (d) HR-STEM image of CuS-Ag$_2$S plate-satellite nanostructure. (e) HAADF-STEM image and corresponding elemental maps of Ag, S, and Cu. (f) XRD patterns of CuS template NPls (red curve), 0.1 mmol of Ag$^+$ treated CuS NPls with 10 min (orange) and 120 min (blue).

Figure 3-30. Top panels show the top-view and side-view TEM images of Ag$^+$ incorporation into covellite CuS NPls process at different reaction times. The scale bars in top panels are 20 nm. Bottom panel shows the schematic illustration of Ag$^+$ incorporation-induced shape evolution of covellite CuS NPls.

Figure 3-31. TEM images of Ag$_2$S NCs before and (b) after Cu$^{2+}$ treatment. (c) XRD patterns of Ag$_2$S NCs before and (b) after Cu$^{2+}$ treatment. (d-e) HRTEM image of single NC from panel (a) and (b), respectively.

Figure 3-32. (a) TEM image of djurleite Cu$_{1.94}$S template NPls. Panels (b)-(d) are low magnification TEM images of Cu$_{1.94}$S treated with 0.05, 0.1, and 0.5 mmol Ag$^+$, respectively. Panel (e)-(g) are top-view HRTEM images of samples in panels (b)-(d), respectively. The insets are corresponding side-view HRTEM images, sharing the same magnification with the corresponding TEM image. Right panel presents HAADF-STEM image and corresponding elemental maps for Ag, Cu and S of djurleite Cu$_{1.94}$S NPls after treatment with 0.05, 0.1 and 0.5 mmol of Ag$^+$, respectively.

Figure 3-33. XRD patterns of djurleite NPls treated with 0.05 mmol (red), 0.1 mmol (orange), and 0.5 mmol (blue) of Ag$^+$.

Figure 3-34. Sulfur sub lattice projection of covellite CuS (a) viewed along [001] direction and (b) its (110) planes. Sulfur sub lattice projection of reduced covellite CuS (c) viewed along [001] direction and (d) its (110) planes. Sulfur sub lattice projection of acanthite Ag$_2$S (e) viewed along [221] direction and (f) its (112) planes. The black lines show the boundaries of crystal unit cells.

Figure 3-35. TEM image of NPls obtained by treating covellite CuS NPls with (a) 0.1, (b) 0.2, (c) 0.3, (d) 0.4, and (e) 0.5 mmol of Ag$^+$. (f) Typical HRTEM image of Ag$_2$S (satellite) domain of plate-satellite structure.
Figure 3-36. Low magnification of Ag₂S-Ag biconcave-particle heterostructures. (b) HR-STEM image of a single heterostructure with Ag NPs grown on the edge. (c) Typical side-view HR-STEM image of the heterostructures. (d) HR-STEM image of a single heterostructure with Ag NPs grown in the center of concave. Panels (e) and (f) are HAADF-STEM image and corresponding elemental maps for Ag, S, and Cu of a single heterostructure from panel (d) and (b), respectively.

Figure 3-37. TEM image of covellite CuS template NPs after treatment with 0.5 mmol of Ag⁺ for 30 sec.

Figure 3-38. Schematic illustration of overall shape evolution.

Figure 3-39. Schematic illustration of valence selectivity of cation incorporation into covellite CuS NPs.

Figure 3-40. (a) Top view and (b) side view TEM images of covellite CuS NP templates. (c) Top-view HR-STEM (d) Side-view HRTEM image of CuS NPs.

Figure 3-41. TEM characterization of CIS and CTS NPs. (a) TEM image, (b) HAADF-STEM image, (c) top-view HRTEM, (d) side-view HRTEM, and (e) STEM-EDS elemental mapping for CIS NPs; (f) TEM image, (g) HAADF-STEM image, (h) top-view HRTEM, (i) side-view HRTEM, and (j) STEM-EDS elemental mapping for CTS NPs. The insets in (c), (d), (h), and (i) show FFT of the regions of the corresponding HRTEM images outlined by red squares.

Figure 3-42. XRD pattern of covellite CuS NPs treated with (a, red) 0.1 mmol In³⁺ precursors (a, blue) 0.5 mmol In³⁺ precursors, (b) 0.5 mmol In³⁺ precursors without DDT, (c) 0.5 mmol Cd²⁺ and (d) 0.5 mmol Zn²⁺. XRD patterns showing the conversion (e) from CIS to CZIS NPs and (f) from CTS to CZTS NPs.

Figure 3-43. (a) Schematic illustration of transformation from covellite CuS to roquesite CIS and wurtzite CIS.

Figure 3-44. (a) TEM image of In³⁺ treated CuS NPs, showing star-like NCs of a secondary phase that are isolated from NPs. HRTEM image of (b) star-like structures and (c) In³⁺ treated CuS NPs. (d) HAADF-STEM image and corresponding element maps for In³⁺ treated CuS NPs. (e) TEM image, (f) top view and (g) side view HRTEM images of CIS NPs synthesized using insufficient In³⁺ precursor. The red dashed lines highlight the boundary of a NP. (h) HAADF-STEM image and corresponding element maps of (a).

Figure 3-45. (a-d) TEM images of NPs produced by In³⁺ incorporation into CuS NPs at different temperatures. (e) XRD patterns of CuS NP templates and transformed NPs. (f) Photograph of dispersion of the NPs (~1 mM cation concentration).

Figure 3-46. (a) TEM image, (b,c) HRTEM images, (d) XRD pattern and (e) HAADF image and corresponding elemental maps of CuFeS₂ NPs.

Figure 3-47. (a) TEM image, (b,c) HRTEM images, (d) XRD pattern and (e) HAADF image and corresponding elemental maps of CuGaS₂ NPs.

Figure 3-48. (a) TEM image, (b,c) HRTEM images, (d) HAADF image and corresponding elemental maps and (e) XRD pattern of CuGeS₂ NPs.

Figure 3-49. (a) TEM image of Cd²⁺ treated CuS NPs, (b) HRTEM image of a single Cu₂S-CdS heterogeneous NP, the green area shows the CdS domain, while the red area shows the Cu₂S domain. (c) HR-STEM image of a heterogeneous NP at the boundary between...
Cu₂S and CdS domains, highlighted by dashed line. (d) HAADF-STEM image and corresponding elemental maps of a Cu₂S-CdS heterogeneous NPl. (e) TEM image of Zn²⁺ treated CuS NPls, (f) HR-STEM image of the Cu₂S-ZnS heterogeneous NPls at the boundary between Cu₂S and ZnS, highlighted by dashed line. (g) Top view and (h) side view HAADF-STEM images and corresponding elemental maps of a Cu₂S-ZnS heterogeneous nanoparticle.

Figure 3-50. (a) TEM image, (b,c) HRTEM images. (d) XRD pattern and (e) HAADF image and corresponding elemental maps of excess (2 mmol) Cd²⁺-treated covellite CuS NPls.

Figure 3-51. (a) TEM image and (b) EDS analysis of excess (2 mmol) Zn²⁺-treated covellite CuS NPls.

Figure 3-52. (a) TEM image, (b) HAADF image and corresponding elemental maps, (c,d) HRTEM images. (e) XRD pattern of covellite CuS NPls treated with 0.5 mmol Pb²⁺.

Figure 3-53. Panels (a), (b), (e) and (f), (g), (j) are TEM images, corresponding HAADF-STEM images and elemental maps for CZIS and CZTS NPls, respectively. Panels (c) and (d) are a top view HRTEM image of CZIS NPls and the corresponding FFT of the indicated region; panels (h) and (i) are a top view HRTEM image of CZTS NPls and corresponding FFT of the indicated region.

Figure 3-54. Side view (top row) and top view (bottom row) of structural models of ternary and quaternary phases.

Figure 3-55. (a) projection of (-1,-3,1) planes of CTS NPls, (b) projection of (112) planes of CZTS, (c) structure model of CTS NPls showing the interplanar spacing of (-1,-3,1) planes, (d) structure model of CZTS NPls showing the interplanar spacing of (112) planes.

Figure 3-56. (a) Low magnification STEM-HAADF and (b) HR-STEM image of Cu₁₈₁S-ZnS NHs. (c) STEM-HAADF image and corresponding elemental maps of a single NC from panel (a). The red area shows the Cu₁₈₁S domain and green area shows the ZnS domain.

Figure 3-57. Size distribution histograms of all samples.

Figure 3-58. XRD patterns of Cu₁₈₁S template NCs (orange) and Cu₁₈₁S-ZnS NHs (blue). TEM, HAADF-STEM image and corresponding elemental maps of Cu₁₈₁S-ZnS NHs.

Figure 3-59. (a) Low magnification TEM image of NHs after treatment with In³⁺ and TOP. (b) HR-STEM image of a single NC. The arrows indicate boundaries between different domains. (c) HAADF-STEM image and corresponding elemental maps for Cu, In, and Zn. (d) Schematic illustration of mechanisms of formation of ZnS-CuInS₂ sandwich NCs.

Figure 3-60. XRD patterns of all samples.

Figure 3-61. Additional TEM and HR-STEM image, and corresponding elemental maps of Cu₁₈₁S-ZnS NHs after In³⁺ and TOP treatment.

Figure 3-62. (a) Low magnification TEM image of NCs after treatment with excess In³⁺ and TOP. (b) HR-STEM image of a single NC and (c) corresponding elemental maps for Cu, In, and Zn.

Figure 3-63. (a) Low magnification TEM (b) HRTEM image of NHs after Sn⁴⁺ and TOP.
treatment. (c) HR-STEM image of individual ZnS cap. (d),(e) TEM images of NCs during the transformation at reaction times of 1 min and 5 min. (f) STEM-HAADF image and corresponding elemental maps for Zn and S. (g) Schematic illustration of the transformation from Cu_{1.81}S-ZnS NHs to ZnS NCs.

Figure 3-65. (a) Low magnification TEM image, (b) HR-STEM image and (c) corresponding elemental maps of In^{3+}-treated NHs. (d) Low magnification HAADF-STEM image, (e) HR-STEM image and (f) corresponding elemental maps of the NHs during the In^{3+} treatment at reaction time of 1 min. (g) Schematic illustration of the transformation from Cu_{1.81}S-ZnS NHs to CuInS_{2} NCs.

Figure 3-66. (a) TEM, (b) HR-STEM, (c) HAADF-STEM image of Sn^{4+}-treated NHs, and corresponding elemental maps for Cu and S. TEM images of aliquots extracted during the reaction times of (d) 1 min, (e) 10 min, and (f) 20 min. (g) Schematic illustration of the transformation from Cu_{1.81}S-ZnS NHs to CuInS_{2} NCs.

Figure 3-67. (a) Low magnification STEM-HAADF and (b) HR-STEM image of NHs after treatment with Sn^{2+} and TOP, and (c) corresponding elemental maps for Zn and Sn. The scale bar in panel c is 10 nm.

Figure 3-68. (a) TEM, (b) HR-STEM, (c) HAADF-STEM image of Sn^{2+}-treated NHs, and corresponding elemental maps for Cu and S. The scale bar in panel c is 10 nm.

Figure 3-69. Low magnification STEM-HAADF image and corresponding elemental maps of Sn^{2+} treated NHs. The Zn content is negligible, compared to Cu, Sn and S.

Figure 3-70. Schematic illustration of overall selective cation incorporation into Cu_{1.81}S-ZnS NHs.

Figure 3-71. (a) Low magnification TEM image and (b) HRTEM image of roxbyite Cu_{1.81}S NCs after treatment with In^{3+} and TOP. (c) Low magnification TEM image, (d) HR-STEM image, (e) HAADF image and corresponding elemental maps of roxbyite Cu_{1.81}S NCs after treatment with Sn^{2+} and TOP.

Figure 3-72. (a) Comparison of XRD patterns of In^{3+} and TOP treated Cu_{1.81}S NCs (blue) and excess In^{3+} and TOP treated Cu_{1.81}S-ZnS NHs (red). (b) Low magnification HAADF image and corresponding elemental maps for In^{3+} and TOP treated Cu_{1.81}S NCs (blue). The scale bar in panel b is 100 nm.

Figure 3-73. TEM image of (a) TOP and (b) oleylamine treated Cu_{1.81}S-ZnS NHs.

Figure 4-1. Size distribution histograms of covellite CuS NPs.

Figure 4-2. (a) Top view and (b) side view HR-STEM images of covellite CuS NPs. (c) HAADF image and corresponding elemental mapping for CuS NPs, with a scale bar of 20 nm.

Figure 4-3. TEM images of covellite CuS NPs with different diameters. The top-view and side-view are shown for each size of NPs. In panel b, I and II are HRTEM images of 25 nm CuS NPs, III and IV show the FFT of the regions of the corresponding HRTEM images in the outlined squares.

Figure 4-4. (a-g) TEM image of NPI growth at different reaction times. (h) Schematic illustration of mechanism of NPI growth. All panels share a same magnification with a scale bar of 100 nm.

Figure 4-5. XRD patterns of covellite CuS NPs with different sizes.

Figure 4-6. (a) ORR steady-state polarization curves of covellite CuS NPs with different size.
(b) ORR steady-state polarization curves for CuS-105 NPs with varying electrode rotation rates. (c) Koutecky–Levich plots of the ORR for CuS-105 NPs. (d) Tafel plots for ORR on CuS-105 NPs.

Figure 4-8. The TEM images of (a) CuS-25 NPs and (b) CuS-105 NPs deposited on carbon substrate.

Figure 4-9. Low magnification TEM images of (a) CuS-25 NPs and (b) CuS-105 NPs deposited on carbon substrate.

Figure 4-10. Schematic illustration of different electron transfer mechanisms on different CuS NPs.

Figure 4-11. (a) Structural model of covellite CuS. Potential ORR surfaces: (b) (110) planes with mixed Cu1 and Cu2 atoms, (c) Cu2 terminated and (d) Cu1 terminated (001) planes. The arrows indicate the cleavage planes.

Figure 4-12: Optimized surface structures for intermediates in ORR reaction and DFT study on different CuS surfaces.

Figure 4-13. (a-d) TEM images of Cu1.8Se NPs with different diameters, (e) typical HRTEM image of Cu1.8Se NPs, (f) HAADF-STEM image and corresponding elemental maps for Cu and Se.

Figure 4-14. Size distribution histograms for all samples.

Figure 4-15. (a) XRD patterns of Cu2-x Se NPs with different sizes. (b) UV-vis-NIR absorbance of Cu2-x Se NPs with different sizes.

Figure 4-16. (a) Schematic illustration of the preparation of the hydrophilic Cu2-x Se NCs with Tween 20 surface functionalization. (b) UV-Vis-NIR absorbance spectra of pure water and the aqueous solution containing different concentrations of hydrophilic Cu2-x Se NCs. (c-e) Temperature elevation of pure water and the aqueous solution containing different concentrations of hydrophilic Cu2-x Se NPs under 808 nm, 980 nm, and 1210 nm laser irradiation, respectively.

Figure 4-17. Absorbance spectra of Cu2-x Se NPs before and after Tween 20 surface functionalization. TEM images indicate that the NPs are well dispersed before and after Tween 20 surface functionalization.

Figure 4-18. (a) Plot of temperature elevation of pure water and aqueous solution containing different concentrations of hydrophilic Cu2-x Se NPs over a period of 600 s versus the wavelength of laser irradiation. (b) The photothermal profile of hydrophilic Cu2-x Se NPs aqueous solution (1 mL, 200 µg/mL) irradiated with 808, 980, and 1210 nm lasers for 10 min at a power density of 1.5W/cm², followed by natural cooling to room temperature. (c) Linear time data versus −Ln(θ) obtained from the cooling period of (b). The time constant (rs) for heat transfer from the system is determined to be 198 s, 137 s and 119 s for 808, 980, and 1210 nm lasers, respectively.
Chapter 1. Synthesis of Copper Sulfide Nanocrystal with Tunable Size and Localized Surface Plasmon Resonance

1.1 Recent Advances on Synthesis, Interconversion, Incorporation and Applications of Copper Sulfide Nanomaterials

The composition, crystal structure, and size- and shape-dependent properties of colloidal Cu$_{2-x}$S nanostructures have attracted considerable attention recently.$^{1-5}$ A suitable band gap, low toxicity, and high absorbance coefficient make some copper sulfides promising absorbers material for future photovoltaics.$^{6,7}$ They have also proven useful in electrodes for lithium batteries and in thermoelectrics.$^{8-10}$ Moreover, copper sulfides are parent compounds of many copper-based ternary and quaternary semiconductors being explored for photovoltaics, including CuInS$_2$ (CIS),$^{11-14}$ Cu$_2$SnS$_3$ (CTS),$^{8,15}$ and Cu$_2$ZnSnS$_4$ (CZTS).$^{16}$ Recently, copper sulfide nanocrystals (NCs) have been shown to possess strong NIR absorbance due to localized surface plasmon resonance (LSPR), arising from oscillation of free holes in the valence band of this material.$^{17-21}$ This property has sparked extensive research on employing copper sulfide in photoacoustic imaging, photothermal therapy, and other applications where strong NIR absorbance is required.$^{22-25}$ Copper sulfide is composed of inexpensive earth-abundant elements, and can serve as a lower-cost alternative to plasmonic noble metal nanostructures in biomedical applications.

Generally, we classify the thermodynamically stable copper sulfides into three categories: CuS, Cu$_{2-x}$S ($0 < x < 1$), and Cu$_2$S. Covellite CuS has recently attracted considerable attention because it has the highest concentration of free carriers in the
copper sulfide class of materials.\textsuperscript{26-28} Among thermally and air-stable copper-sulfur phases, CuS has the lowest Cu to S ratio. In the covellite crystal lattice, disulfide bonds are formed to balance the coordination and occupancy of lattice sites at this low Cu to S ratio.\textsuperscript{29, 30} The resulting electronic structure gives covellite its $p$-type metallic character. At the other extreme, pure high chalcocite (Cu$_2$S) has the highest Cu to S ratio.\textsuperscript{31-33} Because the free holes in Cu$_{2-x}$S materials arise from copper deficiency, Cu$_2$S (with $x = 0$) has few free carriers and does not exhibit LSPR at NIR wavelengths. However, upon air exposure, Cu$_2$S can transform to the djurleite (Cu$_{1.94}$S) phase, which has sufficient free holes to exhibit NIR LSPR.\textsuperscript{34, 35} Covellite CuS NCs adopt a plate-like morphology due to the intrinsic layered structure of covellite.\textsuperscript{36} Covellite NCs have been limited to a fixed thickness (only one or a few unit cells), despite the ability to produce a wide range of diameters. In contrast, colloidal Cu$_{2-x}$S NCs exhibit various sizes and morphologies due to many possible phases, use of capping ligands that stabilize different crystal facets, and other reaction conditions. Cu$_{2-x}$S NCs zero-dimensional (0D) nanodots, 1D nanowires and nanorods, 2D nanoplatelets and nanosheets, and 3D polyhedrons.\textsuperscript{37-42} Moreover, recent discoveries have revealed the possibility of producing Cu$_{2-x}$S NCs with complex, assembled and asymmetric morphologies via elaborate nanochemistry methodologies.\textsuperscript{41-43}

Along with many separate studies of CuS and Cu$_{2-x}$S NCs, the relationship (e.g. interconversion) between them has also been investigated, providing new insights into their colloidal synthesis and optical properties. CuS can be converted into Cu$_2$S by adding a Cu(I) complex at room temperature or heating at 220 °C alone.\textsuperscript{44, 45} Roxbyite
Cu$_{1.91}$S was transformed to djurleite Cu$_{1.94}$S through tributylphosphine etching, producing a ~200 nm red shift in the LSPR peak absorbance. However, further studies providing general pathways for, and understanding of, reversible transformations between the limiting CuS and Cu$_2$S stoichiometries are needed.

The free carrier concentration, and therefore LSPR wavelength, of Cu$_{2-x}$S NCs can be tuned not only by adjusting the copper deficiency, $x$, but also through addition of other cations. The process of introducing of heterocations can be classified as doping (at low level of heterocation concentration), cation exchange (CE, which mainly refers to replacement of cations with preservation of the anion sublattice), and cation incorporation (addition of heterocations that can co-exist with the existing cation in one unit cell, sometimes with re-organization of the anion sublattice).

Extrinsically alloyed copper sulfide NCs have been the subject of numerous recent studies, producing ternary and quaternary copper sulfide-based nanomaterials through addition of monovalent (Au$^+$, Ag$^+$), divalent (Zn$^{2+}$, Cd$^{2+}$, Hg$^{2+}$, Pb$^{2+}$, Mn$^{2+}$ and Co$^{2+}$), trivalent (In$^{3+}$, Fe$^{3+}$, Ga$^{3+}$, Sb$^{3+}$ and As$^{3+}$), and tetravalent (Sn$^{4+}$, Ge$^{4+}$) cations. Incorporation of a heterocation (M) into Cu$_{2-x}$S may produce heterogeneous Cu$_{2-x}$S-MS NCs or homogeneous Cu-M-S alloys. However, the factors determining whether heterogeneous NCs or homogeneous alloy NCs are produced have not previously been fully elucidated.

A diverse array of copper sulfide-based nanomaterials has been developed in recent years, especially following the discovery of LSPR in Cu$_{2-x}$S NCs. Applications of copper sulfide-based nanomaterials, particularly ternary and quaternary compounds, in
photovoltaics, bioimaging, and other areas have been explored extensively. However, there are still emerging applications of such materials in electrocatalysis, photothermal therapy, and optoelectronic devices.\textsuperscript{64, 65} Most of these applications will eventually require scalable production of high quality, monodisperse, and well-controlled materials, and meeting these requirements is essential for long-term practical application of copper sulfide nanostructures.

Building on the recent advances described above, many intriguing ideas remain to be pursued, and many unknowns still wait to be discovered. Rather than traditional hot-injection methods of colloidal synthesis, we have mainly focused on developing and advancing rapid, low-temperature methods to prepare copper sulfide NCs with well-controlled size and morphology. In the work reported in this dissertation, we extend and generalize this method to produce various metal sulfide NCs with tunable size, shape, composition, and therefore controllable optical properties. We also developed processes for reversible morphology and composition interconversion between many possible phases in the copper sulfide class of nanomaterials. Moreover, we have explored the process of cation incorporation (or exchange) in Cu\(_{2-x}\)S using different heterocations, different capping ligands and Cu-extracting agents. Prior to the work presented here, very few processes starting from covellite CuS templates had been reported. The unique layered structure and reducible disulfide bonds in covellite could strongly influence the cation incorporation process. From these studies, we also draw general conclusions about the valency selectivity of cation incorporation into copper sulfide NCs, revealing the factors governing the outcome of the process (homogeneous vs. heterogeneous...
product NCs). Finally, we synthesize high quality, monodisperse and well-controlled copper sulfide-based NCs for applications such as electrocatalysis, photovoltaics and photothermal therapy.
1.2 Room-Temperature Synthesis of Covellite Nanoplatelets with Broadly Tunable Localized Surface Plasmon Resonance

1.2.1 Synthesis of Covellite CuS Nanoplatelets at Ambient Conditions

In this section, we present a new method of fabricating covellite copper sulfide nanocrystals by reacting ammonium sulfide (AS) with an oleylamine-Cu (OAm-Cu) precursor in toluene at ambient conditions. Results are shown in Figure 1-1, in which we used stepwise injections of 450 µL of AS each, with 1.5 mmol of Cu precursor. The first injection produced monodisperse 4.3 nm NCs (Figure 1-la). A second injection resulted only in slight growth of the NCs to 5-7 nm in diameter (Figure 1-1b). A third injection produced a broadening of the NC size distribution (Figure 1-1c), ultimately producing NCs with a bimodal size distribution, consisting of a mixture of monodisperse 21 nm NCs and nearly monodisperse 5-7 nm nanocrystals (Figure 1-1d). This size distribution did not change further (Figure 1-1e). Size-selective centrifugation was performed to obtain pure 21 nm NCs (Figure 1-1f) at an overall yield of ~25% relative to the amount of Cu precursor provided.

The importance of AS-induced growth is further demonstrated by the formation of 34 nm NPls from a mixture of 4.3 nm NCs and 21 nm NPls. As shown in Figure 1-2a, we mixed the purified 4.3 nm NCs and 21 nm NPls. If no AS was added to this mixture, the size of the NCs and NPls did not change. They could be separated by size-selective centrifugation to recover the original populations, as shown in Figure 1-2d,e. However, when AS was added to this mixture, all of the NCs grew. This produced the larger 34
nm diameter platelets shown in Figure 1-2b and the smaller 5-7 nm NCs shown in Figure 1-2c.

**Figure 1-1.** TEM images following the evolution of NCs produced using 1.5 mmol of Cu with 4.05 mmol of AS provided in 3 injections. (a) 1 min after the first injection, 4.3 ± 0.6 nm NCs were formed. The size did not change without further addition of AS. (b) 1 min after the second injection, 5-7 nm particles were observed with no sign of smaller NCs. (c) 1 min after third injection. Some NCs are irregular in shape, and some have grown to ~11 nm in diameter. (d) 10 min after third injection, 21 nm and 5-7 nm NCs appeared in the solution. (e) This situation was maintained after an additional 10 min. (f) After size-selective centrifugation, monodisperse 21.0 ± 1.2 nm NCs were obtained.

**Figure 1-2.** TEM images illustrating growth of 34 nm NPs. (a) Mixture of freshly prepared 21.0 nm
NPs and 4.3 nm NCs. (b) 34.0 ± 3.0 nm NPs after growth in the presence of AS, followed by size-selective centrifugation. (c) NCs from supernatant after size-selective centrifugation. Without AS, no size change was observed. The 21.0 nm NPs in (d) and 4.3 nm NCs in (e) remained unchanged from (a).

XRD analysis clearly showed that all NCs synthesized using the Cu\(^{2+}\) precursor were phase-pure covellite, as shown in Figures 1-3. The crystal phase of copper sulfide is closely related to its stoichiometry. HRTEM images of NPs are shown in Figures 1-3b,c. Images with the platelets lying flat on the substrate, as in Figures 1-3b, clearly showed the two most prominent lattice fringes for covellite. The spacing of 0.19 nm corresponds to (110) and 0.33 nm corresponds to (100) planes of covellite. The edge-on view in Figures 1-3c shows a 0.27 nm lattice spacing assigned to the (006) planes. Therefore, the NCs grew perpendicular to the c-axis of covellite. Except for 4.3 nm NCs, all NCs reported here are platelets with a constant thickness of ~4 nm. As the size increased, the basal plane evolved from circular to hexagonal. The anisotropic growth can be related to the energy difference between (001) and (110) facets.\(^{66}\) OAm may bind more strongly to the basal planes and less strongly to the facets perpendicular to the c-axis. Previous reports of covellite NCs prepared by high-temperature methods also obtained platelets with suppressed growth in the c-axis direction. However, the thickness of NPs in those prior studies was generally much greater than that observed here. In our synthesis, the platelet thickness is only ~4.0 nm. The ultrathin NPs are only ~2.5 unit cells thick, comparable to the 2 unit cell thickness previously reported for covellite sheets.\(^{39}\) Our synthetic protocol carried out at ambient conditions provides a new pathway for colloidal synthesis of such anisotropic NCs.
Figure 1-3. Characterization of covellite CuS NCs. (a) XRD patterns from NCs synthesized with Cu\(^{2+}\) (Cu:S = ~1, top panel) and with Cu\(^+\) (Cu:S = ~1.75, bottom panel). The middle panel shows the standard covellite PDF card, which matches the top panel and not the bottom panel. (b) HRTEM of NPI with basal plane sitting on the substrate (inset) and (c) with an edge-on view. S2p XPS spectra of NCs synthesized with (d) Cu\(^{2+}\) and (e) Cu\(^+\). The red curves in both (d) and (e) are the experimental results. The arrow in (d) indicates the peak assigned to persulfide.

X-ray photoemission spectroscopy (XPS) was performed to further clarify the state of sulfur. The spectra showed clearly that, when Cu\(^{2+}\) is used, the sulfur 2p peak contains a shoulder doublet from persulfide at a lower binding energy (Figures 1-3d). The arrow indicates the fitted peak for persulfide. The spectra of NCs synthesized with Cu\(^+\), however, could be well fit by one peak around 160.0 eV. Covellite is a hexagonal crystal with sulfide and persulfide ions stacked along the c-axis. The persulfide ions are generally absent in other copper sulfide phases.\(^6\)\(^7\) Therefore, the persulfide signal in Figures 1-3d should be due to covellite. In the synthesis using AS, the only sulfur sources (S\(^2-\) or HS\(^-\)) contribute sulfur as S\(^2-\). Thus, oxidation of S by Cu\(^{2+}\) to create persulfide is needed for forming covellite. Cu\(^+\), however, could directly react with S\(^2-\)
without occurrence of such a redox reaction. It should be noted that samples prepared for XPS, with both Cu$^{2+}$ and Cu$^+$, were prepared in an argon atmosphere. Cu$^+$ can be easily oxidized into Cu$^{2+}$ under air. These samples also eliminate interference by reaction with oxygen, which is known to oxidize Cu$_{2-x}$S ($x < 1$) into covellite.$^{68}$
1.2.2 Covellite CuS Nanoplatelets with tunable Localized Surface Plasmonic Resonance

Covellite has an inherently high concentration of free holes in its valence band. It has strong NIR absorbance due to LSPR oscillation. Similar to the case of noble metal nanostructures, the LSPR energy for copper sulfide is dependent upon charge carrier density and shape parameters (e.g., aspect ratio). Typically, separating these two factors in plasmonic semiconductor NCs like copper sulfide has been exceedingly difficult because the carrier density (related to the stoichiometry and phase) and the aspect ratio can both change. Only a relatively narrow range of aspect ratios has been accessible at fixed composition and carrier density.\textsuperscript{69-71} The phase purity and large range of aspect ratio of covellite CuS NPs allowed us to explore this shift in optical absorbance quantitatively. UV-vis-NIR extinction spectra showed that the NCs exhibit pronounced LSPR absorbance in the near-IR. The LSPR wavelength was size-dependent, red-shifting with increasing NPl diameter. We attribute this red-shift to the changing aspect ratio (AR) of the NPs, as they maintain a constant thickness of approximately 4 nm. The experimental extinction spectra are shown in Figure 1-4a. In an anisotropic plate-like structure, both in-plane and out-of-plane LSPR modes can be excited. However, the out-of-plane mode is difficult to observe because of its overlap with the stronger in-plane mode.
Figure 1-4. Comparison of smoothed experimental (a) and simulated (in-plane (b) and out-of-plane (c)) spectra for four NC sizes. (d) Illustration of in-plane and out-of-plane modes.
1.2.3 Experimental Section

**Chemicals.** All chemicals were used as received. Oleylamine (70%, OAm) was purchased from Sigma-Aldrich. CuCl₂·2H₂O, toluene, and ammonium sulfide (21.2%) were purchased from Fisher Scientific.

As described in detail below, the size and shape of the product NCs depended upon the manner in which AS was injected into the Cu precursor solution. In a typical experiment, an appropriate amount (0.5 or 1.5 mmol) of CuCl₂·2H₂O was dissolved in 10 mL of OAm via sonication, followed by addition of toluene to give a total volume of 20 mL. AS solution, in excess of the amount needed to react stoichiometrically with copper, was then added in a series of injections. The number of injections, amount of AS per injection, and time interval between injections were varied to control product formation. After a desired reaction time, the reaction was quenched via addition of 10-20 mL of ethanol, which induces flocculation of the product particles. Centrifugation was used to retrieve the particles for further characterization. A summary of synthetic conditions and results is provided in Table 1-1.

**Table 1-1. Summary of reaction conditions and resulting nanoplatelet size**

<table>
<thead>
<tr>
<th>Cu²⁺</th>
<th>Injection/Interval/Total/Waiting Time</th>
<th>Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 mmol</td>
<td>50/30s/800/30s</td>
<td>7.5 nm</td>
</tr>
<tr>
<td></td>
<td>400/30s/800/30s</td>
<td>&gt;100 nm</td>
</tr>
<tr>
<td>1.5 mmol</td>
<td>450/1 min/450/1 min</td>
<td>4.3 nm</td>
</tr>
<tr>
<td></td>
<td>450/1 min/900/1 min</td>
<td>5-7 nm</td>
</tr>
<tr>
<td></td>
<td>450/1 min/1350/10-20 min +Size Selective Centrifugation</td>
<td>21.0 nm</td>
</tr>
</tbody>
</table>

**Characterization.** Transmission electron microscopy (TEM) images were obtained
using a JEOL-2010 or an FEI Tecnai F20 G2, in both cases at an accelerating voltage of 200 kV. TEM grids were prepared by dropping a dilute NC dispersion onto the carbon-coated grid and allowing the sample to dry under air. Powder X-ray diffraction measurements were carried out using a Rigaku Ultima IV diffractometer with a Cu Kα X-ray source. Samples were prepared by drop-casting concentrated NC dispersions onto glass slides. Elemental analysis of NCs by energy-dispersive X-ray spectroscopy (EDX) was obtained using an Oxford Instruments X-Max 20 mm² EDX detector within a Zeiss Auriga scanning electron microscope (SEM). Thermogravimetric analysis (TGA) was performed on a NETZSCH TGA 209 F1 thermal analyzer at a heating rate of 5 °C/min under an argon flow. UV-vis-NIR spectra of NC dispersions in chloroform were taken on a Shimadzu UV-3600. X-ray photoelectron spectra (XPS) were acquired on a Phi VersaProbe 5000 with an Al kα X-ray source.
1.3 Rapid Room-Temperature Synthesis of Metal Sulfide Nanocrystals with Tunable Properties

1.3.1 Introduction

In Section 1.2, we showed that CuS NPs can be synthesized by mixing ammonium sulfide (AS) solution with Cu-OAm complex at ambient condition. Moreover, providing additional AS can produce larger CuS NPs with corresponding red-shifts of their NIR LSPR absorbance. In this section, we expand this room-temperature synthetic method to many different metal sulfide (MS) NCs. Although several reports focused on generic methods to synthesize binary MS NCs have been published, preparing ternary and quaternary MS NCs using a simple and generalized synthetic route remains a formidable challenge. Therefore, developing a general solution method for the direct fabrication of a variety of binary, ternary and quaternary MS NCs is still of great significance.

Traditional approaches to synthesis of colloidal metal sulfide NCs usually suffer from difficulty in achieving and controlling a desired level of precursor reactivity. Utilizing a highly-reactive sulfur precursor is one means of increasing the conversion of less reactive cations. Robinson’s group previously reported a generic method for scalable synthesis of monodisperse metal sulfide NCs by using OAm-AS (dried using molecular sieves) and aqueous AS solutions as the sulfur precursors. However, most of the reactions were carried out at temperatures above 250°C. Postsynthetic modification of MS NCs using AS has not been studied, and doing so is necessary to understand the effect of additional AS on determining the shape of NCs. Therefore, we
aimed to develop a rapid room-temperature method to synthesize MS NCs with well-controlled morphology by combining OAm, metal precursors, AS, and toluene (as a solvent to dilute the system).

In this section, we present a novel and general method to synthesize a variety of binary, ternary, and quaternary MS NCs. Compared to traditional colloidal synthesis, which requires external heating, this approach enables a rapid, low temperature synthesis, by directly mixing metal-OAm complexes with AS solution. The MS crystallization process occurs immediately, as indicated by a rapid color change upon introducing the AS solution. This is illustrated Figure 1-5, in which the vials in the top row contain metal precursors in OAm and those in the bottom row are diluted dispersions of MS NCs in hexane with a cation concentration of ~2.5 mM. Furthermore, these MS NCs behaved differently when additional AS was added after the initial particle formation. We observed additional growth upon introducing more AS to the CuS, Ag2S, and CdS NCs. However, further growth of PbS and SnS NCs upon AS addition was minimal. Ternary and quaternary NCs can be prepared by the same method, but in some cases with low crystallinity. This general method provides an opportunity to study the properties of distinct MS NCs using a consistent fabrication process.
Figure 1-5. Images of metal cation solutions and product NC dispersions with a schematic illustration of the reaction leading to NC formation. The vials above the schematic contain the metal precursors in OAm, while the vials below the schematic contain the corresponding MS NCs dispersed in hexane at a cation concentration of ~2.5 mM.
1.3.2 Reaction Kinetics

All MS NCs were prepared by injecting aqueous AS into a solution of cation precursor(s) (metal-OAm complex(es)) in toluene at ambient conditions. Organosulfur precursors are often prepared by dissolving sulfur powder in organic ligands (neat or diluted in solvent). Other commercially-available sulfur-containing organic compounds (e.g. di-t-butyl disulfide, dodecanethiol), which thermally decompose to release a reactive sulfur component at elevated temperature can also be used.\(^{15,75-77}\) In contrast to traditional organic and some other inorganic sulfur sources (e.g. Na\(_2\)S), AS can not only be readily dissolved in organic solvents containing ligands but can also release highly reactive S\(^{2-}\) at low temperature.\(^{73}\) Common commercially available AS solution (~20 wt.% AS in water), contains ~3.1 mmol of S\(^{2-}\) per mL solution. High reactivity of AS, and the use of excess AS drive rapid formation of MS NCs. In the case of CuS NPls, as shown in Figure 1-5, the dark blue color of the Cu-OAm solution shows the presence of Cu\(^{2+}\). After adding AS solution, the color of the solution changed to dark green instantly, indicating formation of covellite CuS. Similarly, homogeneous solutions were obtained by mixing other metal salts with OAm and toluene via sonication. When AS was introduced, the various solutions exhibited different colors such as bright yellow, dark brown and reddish brown, due to formation of NCs with specific absorbances at visible wavelengths.
1.3.3 Morphology of MS NCs

The MS NCs synthesized using this general room temperature method are typically quite monodisperse. Here, we present typical TEM and HRTEM image of MS NCs, with corresponding fast Fourier transforms (FFT). Figure 1-6a shows a TEM image of 19.2 ± 1.5 nm covellite CuS NPls. The side-view high-resolution TEM (HRTEM) image of a covellite CuS NPl with lattice fringes in the inset of Figure 1-6a shows the product CuS is single crystalline, with an interplanar spacing of 0.27 nm, corresponding to the (006) planes of covellite. The TEM and HRTEM images shows that the (100) and (010) directions lie within the plane of the CuS NPls, while the (001) direction corresponds to the NPl thickness.

Figure 1-6b shows a typical TEM image of spherical Ag₂S NCs of 11.6 ± 0.5 nm diameter. HRTEM of Ag₂S nanoparticles (NPs) shows an interplanar spacing of 0.29 nm, which matches the (311) lattice spacing the monoclinic Ag₂S phase. The TEM image in Figure 1-6c shows that the CdS NCs produced by this method have a truncated triangular morphology, due to the fast growth rate of (001) planes in wurtzite CdS phase as well as Ostwald ripening. The HRTEM image in the inset indicates that CdS NCs exhibit an interplanar spacing of 0.34 nm, which matches the spacing of (111) planes in wurtzite CdS. TEM and HRTEM images of SnS NCs are shown in Figure 1-6d. The interplanar spacing of 0.29 nm matches the (200) planes of SnS phase. A typical TEM image of AgInS₂ quantum dots (QDs) is displayed in Figure 1-6e. The lattice fringe spacing of 0.21 nm in the corresponding HRTEM image matches the (204) planes of AgInS₂.
PbS NPls exhibit a square plate-like shape with dimension of $7.7 \pm 0.6 \times 2.7 \pm 0.3$ nm, as shown in Figure 1-6f. This is, to the best of our knowledge, the first report of monodisperse square PbS NPls. The side-view HRTEM image of PbS NPl indicates an interplanar spacing of 0.15 nm, corresponds to (400) planes in the galena PbS phase. According to the previous reports, PbS nanocubes can be synthesized at precursor ratios of Pb:S < 1, otherwise produces PbS NCs adopt a cuboctahedral shape. The Pb:S ratio in this rapid reaction is -0.1, leading to the formation of the truncated cuboid morphology. To investigate the formation of PbS NPls, we then studied the Pb-OAm precursor, which appears to be a dispersion, rather than a true solution. The Pb-OAm complex was centrifuged to collect Pb-OAm species, then the Pb-OAm was redispersed in toluene to form a suspension. TEM imaging of the diluted suspension revealed that the Pb-OAm is in chain-like assemblies in which Pb-based chelates were linked by OAm (Figure 1-7a). PbS nanocubes have isotropic growth rates on six facets of a cube, producing a cubic shape. However, the chain-like template of Pb-OAm suppresses growth on a pair of equivalent facets, due to passivation by OAm. Thus, when $S^{2-}$ ions
are reacting with Pb$^{2+}$ on the surface of growing nanoparticles, the other two pairs of equivalent facets possess higher reaction rates, leading to anisotropic growth with the shape of a NPI (Figure 1-7b).

![TEM image of Pb-OAm complex and schematic illustration of template-assistant growth of PbS NPs.](image)

**Figure 1-7.** (a) TEM image of Pb-OAm complex. (b) A schematic illustration of template-assistant growth of PbS NPs.
1.3.4 Crystal Phase and Optical Properties of MS NCs.

The study of crystal phase and optical properties of these MS NCs further helps us to understand the capabilities and potential of this synthetic method. Figure 1-S(a-f) present XRD patterns of MS NCs prepared using this method. Figure 1-8a shows that the crystal phase of the NPls is covellite CuS (ICDD PDF 04-007-1392). Similarly, the crystal phases of other MS NCs are confirmed by the close correspondence of their XRD patterns to standard references. The XRD study clearly reveals that these MS NCs exhibit good crystallinity when synthesized at room temperature within a short growth time.

The UV-vis-NIR absorbance spectrum shows that the ~19 nm CuS NPls have strong absorbance at NIR wavelengths, peaking at ~1100 nm. This LSPR absorbance arises because CuS is p-type semiconductor with intrinsically high carrier concentration. The absorbance spectra and corresponding calculated band gaps of other binary MS NCs are presented in Figure 1-S(h,i). The differences in absorbance and band gaps of these MS NCs arise from their morphology, size, crystal structure, and electronic structure.
Figure 1-8. (a)-(f) XRD patterns of MS NCs, (g) UV-vis-NIR spectra of covellite CuS NPls. (h) Absorbance spectrum of MS NCs. (i) Calculated direct band gaps of MS NCs.
1.3.5 Tuning Size and Properties of MS NCs.

Most of the MS NCs are known for their tunable size- and shape-dependent properties. The ability to control the size and morphology of MS NCs is of great interest. In Section 1.2, we discussed the growth mechanism of CuS NPs by adjusting the ratio of Cu:S and AS injection manner. Covellite NPs exhibit LSPR absorbance that depends upon their aspect ratio (diameter over thickness), with their dominant in-plane dipolar resonance red-shifting as the aspect ratio increases.\(^{18,36}\) Similarly, we find that small Ag\(_2\)S NPs can be prepared by reducing the amount of AS solution (10 µl) and the reaction time (10 sec) for Ag\(_2\)S synthesis. As shown in Figure 1-9a, this method produced monodispersed Ag\(_2\)S NPs of 4.1 ± 0.5 nm diameter. Figure 1-9(b-c) reveal the Ag\(_2\)S NPs have a lattice spacing of 0.22 nm, corresponding to (130) planes of the acanthite Ag\(_2\)S phase. When the radius of a NC approaches the exciton Bohr radius, the motions of electron-hole pairs are confined. For some semiconductors such as Ag\(_2\)S, CdS and ZnS, they can be excited by specific incident light producing emission light over a wide spectral range due to quantum confinement. The Bohr radius in Ag\(_2\)S is 2.2 nm.\(^{81}\) However, we could not detect any PL from these small Ag\(_2\)S NPs, most likely due to surface defects that provide non-radiative recombination pathways.

Ag\(_2\)S is a potential candidate for NIR QDs for in vivo photoacoustic imaging and diagnostics, due to negligible toxicity and ideal band gap.\(^{82}\) Note that photoacoustic imaging only requires strong absorbance of light, and not PL, so NPs with surface defects that reduce PL may not be a problem. In order to study the growth mechanism of Ag\(_2\)S NPs, we carried out more systematic synthesis of them. The room-temperature
growth of Ag$_2$S NCs depends upon at least three factors: reaction time, concentration of S$^{2-}$, and concentration of Ag$^+$. As shown in Figure 1-9d, the results related to reaction time indicate the size of the Ag$_2$S NPs changes very little with increasing reaction time from 10 s to 600 s (first row). This implies that reactions were accomplished rapidly. On the other hand, continuously increasing the concentration of Ag$^+$ and S$^{2-}$ can facilitate NP growth. In addition, we observed aggregation of Ag$_2$S NPs when employing a larger excess of S$^{2-}$ (second row). This is consistent with our previous discussion that excess S$^{2-}$ can partially remove ligands from the surface of the NP, leading to additional growth and ultimately aggregation of metal sulfide NPs. In order to assess this growth mechanism, we carefully analyzed TEM images of Ag$_2$S NPs during growth. As shown in Figure 1-9f, instead of Ostwald ripening, the growth of Ag$_2$S NPs follows an aggregative growth process. The newly-nucleated small NPs possess high surface energy, which prompts two or more NPs to diffuse into each other upon contact. The formation of dumbbell-like structures clearly illustrates this sintering of small NPs. Finally, dumbbell-like structures experience a shape evolution to spheres in order to minimize their surface energy. Figure 1-9g provides a schematic illustration of the mechanism of the aggregative growth.

CdS QDs have attracted much attention due to their direct band gap at visible wavelengths, high PL quantum yield, and long-term photostability.$^{83-86}$ Thus, CdS QDs have been explored widely for use in light emitting diodes, sensors, lasers and biomedical imaging and labeling. Here, we produced CdS NCs with reduced size to test their photoluminescence. The small CdS QDs were prepared by adding 10 µl of AS
solution into Cd-OAm complex containing 0.1 mmol of Cd$^{2+}$. Knowing that CdS QDs can emit light at wide range of wavelength by tailoring their size, we employed different amounts of AS solution to obtain CdS QDs with tunable emission wavelengths. The UV-vis and PL spectra of CdS QDs prepared with different S$^{2-}$ concentrations are recorded in Figure 1-10(a-b). In the UV-vis spectra, a red shift in absorbance from 370 to 430 nm was observed due to reduced quantum confinement with increasing amount of AS solution (from 10 to 200 µl). The PL emission peaks of CdS QDs in hexane solution were tuned from 500-675 nm, red-shifting with increasing amount of S$^{2-}$, due to increasing size of the CdS QDs. The PL QY of CdS QDs was estimated to be 4.9%. Figure 1-10c shows the dispersion of CdS QDs in hexane solution under room light (left) and UV light (right).
Figure 1-9. (a) TEM image, (b) HRTEM image and (c) corresponding FFT of 4.1 nm Ag₂S NPs. (d) Integrated study on growth of Ag₂S NPs: panels (1-3), (4-6) and (7-9) focus on factors of reaction time, concentration of S²⁻, and concentration of Ag⁺, respectively. (e) The parameters of integrated study on Ag₂S growth mechanism. (f) TEM image for aggregative growth of Ag₂S NPs. (g) Schematic illustration of aggregative growth of Ag₂S NPs. The scale bars in panel (b) and (f) are 2 nm and 50 nm, respectively.
PbS NCs have great potential for use in thermoelectric, photocatalytic and photovoltaic devices. There have been some reports focused on shape evolution of PbS NCs by changing the molar ratio between Pb$^{2+}$ and S$^{2-}$ precursors, reaction time, ligands, and temperature in the colloidal system. However, post-synthetic modification of PbS NCs using AS has not been studied. Here we introduce AS solution to cuboctahedral PbS NCs. AS solution is a highly reactive sulfur precursor with potential to trigger shape evolution at room temperature. Cuboctahedral PbS NCs were synthesized according to Cademartiri’s work. The TEM image in Figure 1-10d
reveals that the monodisperse PbS NCs have a diameter of 8.2 ± 0.6 nm. The HRTEM image in Figure 1-10f shows the NCs are single crystalline, with an interplanar spacing of 0.36 nm, matching the (111) planes of galena PbS. We added 0.5 mL of AS solution into a toluene dispersion of these PbS NCs, at a concentration of ~0.5 mmol Pb²⁺ at room temperature. Interestingly, the cuboctahedral PbS NCs were converted into PbS nanocubes (NCbs), with side length of 7.7 ± 0.4 nm. Consistent with prior reports of PbS shape evolution at higher temperatures, the shape evolution observed here can be generally described as follows.⁷⁹, ⁸⁸, ⁹¹ The surface energy of the (111) facets of cuboctahedral PbS NCs is much higher than the (100) facets and the atom occupancy of (111) can be considered as alternating Pb and S layers. Prior to AS addition, OAm can effectively stabilize the (111) facets. However, the (111) facets would finally disappear in the presence of AS because of the high reactivity of AS and its ability to displace OAm from Pb-terminated (111) facets. A schematic illustration of this process is displayed in Figure 1-10h. XRD analysis also provides evidence of shape evolution. Both cuboctahedral and NCbs PbS are in the galena phase. However, for the nanocubes, the corresponding to (111) planes is depressed compared to the peak corresponding to (200) planes, indicating (111) facets of PbS NCbs are diminished after the shape evolution.
1.3.6 Experimental Section.

Chemicals. Oleylamine (70%, OAm), oleic acid (technical grade, OA 90%), silver nitrate (AgNO₃), tin (II) chloride (SnCl₂), tin (IV) chloride (SnCl₄), cadmium sulfide (CdCl₂), lead chloride (PbCl₂), indium acetate (In(ac)₃), zinc chloride (ZnCl₂) and hexane were purchased from Sigma-Aldrich. CuCl₂·2H₂O, toluene, and ammonium sulfide (21.2% wt% in water) were purchased from Fisher Scientific. All chemicals were used as received.

Cation Precursor Preparation. The cation precursor can be generally prepared by sonicinging metal salt(s) with 5 mL of OAm and 5 mL of toluene for about 3-5 min in a 20 mL vial. All the mixtures formed uniform solutions or suspensions of various colors without precipitation. In contrast to the other metal salts, PbCl₂ in OAm takes over 30 min to dissolve or disperse. Heating can be used to accelerate dissolution of PbCl₂.

Synthesis of metal sulfide NCs. The general method of synthesizing MS NCs is to inject AS solution into the solution or suspension of cation precursor(s) at room temperature. The volume of OAm and toluene remain the same in all cases, while reaction parameters including the volume of AS solution and moles of metal salts were varied as listed in Table 1-2. To purify the MS NCs, 10 mL ethanol was added to destabilize the NC dispersion, followed by centrifugation at 5000 rpm for 1 min. Then the NCs were redispersed in hexane and washed with ethanol to remove excess sulfur and ligands. The MS NCs could be redispersed in organic solvents including chloroform, hexane and toluene for further characterization.
Table 1-2. Parameters for synthesis of all metal sulfides mentioned.

<table>
<thead>
<tr>
<th>Metal Sulfide</th>
<th>Cation Precursor Amount (mmol)</th>
<th>AS Solution Amount (ml)</th>
<th>Reaction Time (sec)</th>
<th>AS Solution Addition Manner</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuS</td>
<td>0.25</td>
<td>0.75</td>
<td>60</td>
<td>0.25 mL x 3 times with interval of 1 min</td>
</tr>
<tr>
<td>Ag₂S NPs</td>
<td>0.25</td>
<td>0.25</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>small Ag₂S</td>
<td>0.25</td>
<td>0.01</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>CdS NCs</td>
<td>0.5</td>
<td>0.5</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>CdS QDs</td>
<td>0.1</td>
<td>0.01-0.2</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>SnS</td>
<td>0.5</td>
<td>0.5</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>PbS</td>
<td>0.1</td>
<td>0.1</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>AgInS₂</td>
<td>0.25/0.25</td>
<td>0.25</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>CuInS₂</td>
<td>0.25/0.5</td>
<td>0.05</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>Cu₂Sn₂S₇</td>
<td>0.5/1</td>
<td>0.2</td>
<td>60</td>
<td>dropwise</td>
</tr>
<tr>
<td>Cu₂ZnSnS₄</td>
<td>0.25/1/0.5</td>
<td>0.06</td>
<td>60</td>
<td></td>
</tr>
</tbody>
</table>

**Synthesis of PbS NPs.** The synthesis of PbS NPs was based on Cademartiri’s method with some modifications. First, 9.6 mmol PbCl₂ was dissolved in 16 mL OAm and the mixture was heated to 120 °C under argon and held at this temperature for 30 min to remove dissolved oxygen. Simultaneously, 1 mmol sulfur powder was dissolved in 8 mL OAm. The 8 mL OAm-S was then injected into the Pb-OAm complex and the reaction vessel was kept at 120 °C for 15 min before quenching by adding 20 mL of ethanol. To remove impurities, the dispersion was centrifuged and the precipitate was redispersed in 3 mL hexane to which 6 mL of OA was added before centrifuging a second time. The precipitate was redispersed in hexane then destabilized with ethanol before centrifuging a third time. The precipitate was redispersed in 5 mL toluene for further characterization and for studying PbS shape evolution.

**Shape Evolution of PbS NCs.** To investigate shape evolution of PbS NCs, 0.5 mL of
PbS NPs in toluene was added to a mixture of 5 mL OAm and 5 mL toluene at room temperature. Then, 0.5 mL of AS solution was added and the reaction vessel was stirred for 5 min. To purify the PbS NCs, 10 mL ethanol was added into the solution followed by centrifugation at 5000 rpm for 1 min. The precipitate was collected and redispersed in toluene.

**Characterization.** Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-2010 or an FEI Tecnai F20 G2, in both cases at an accelerating voltage of 200 kV. TEM grids were prepared by dropping a dilute NC dispersion onto a carbon-coated copper or nickel TEM grid and allowing the sample to dry under air. Size distributions were obtained from TEM images by measuring at least 150 NCs from multiple TEM images from different areas of the grid, using Nanomeasurer v. 1.2. STEM imaging was carried out on a FEI Tecnai F20 200KV STEM with a Fischione HAADF STEM detector using samples prepared on Ni TEM grids. Powder X-ray diffraction (XRD) measurements were carried out using a Rigaku Ultima IV diffractometer with a Cu Kα X-ray source. Samples were prepared by drop-casting concentrated NC dispersions onto glass slides. UV-vis-NIR spectra of NC dispersions in hexane were taken on a Shimadzu UV-3600. PL emission spectra were recorded by a Fluorolog-3.11 Jobin Yvon-Horiba spectrofluorometer.
Chapter 2. Reversible Crystal Phase Interconversion between Different Copper Sulfide Nanocrystals.

2.1 Reversible Crystal Phase Interconversion between Covellite CuS and High Chalcocite Cu2S Nanocrystals

2.1.1 Introduction

As we discussed in the previous sections (Section 1.2 and 1.3), copper sulfide NCs, especially covellite CuS NPs, can be prepared by a rapid room-temperature method. The LSPR absorbance of CuS NPs is tunable over a wide range. This is attributed to precisely controlled synthesis of covellite CuS NPs with different aspect ratios.\(^\text{18}\) Solid-solid phase transformations in NCs are of great importance not only for providing an understanding of nanostructures themselves but also as novel pathways to produce new nanostructures.\(^\text{92}\) Pressure-induced phase transformation of NCs can occur by single nucleation events. Other parameters, including temperature and magnetic field, have been shown to play key roles in phase transformations of NCs.\(^\text{31, 93}\) Reports of reversible transformations of NCs between crystal phases containing the same elements at different stoichiometries are relatively rare. The copper-sulfide system, by virtue of the many possible binary phases of different stoichiometries, provides unique opportunities to investigate such transitions. While transformations that require adding or removing atoms from a solid are likely to be kinetically limited by solid-state diffusion in bulk samples, they are more easily observed in discrete NCs where the length scale for diffusion is very small.

Methods of obtaining NCs of Cu\(_{2-x}\)S (0 ≤ x ≤ 1) with a specific targeted
stoichiometry and crystal phase are well-known. However, understanding of the transformation between these copper sulfides is still lacking. Understanding the mechanism of transformation starting from arbitrary Cu$_{2-x}$S has been a challenge because most reported Cu$_{2-x}$S NCs contain a mixture of crystal phases of $x$ value from 0 to 1. Moreover, the positions of copper and sulfur ions in these crystal phases are not well-defined. Therefore, reports of obtaining a controlled pure phase via the transformation of another copper sulfide phase are limited. In consideration of these challenges, the two stoichiometric limits (CuS and Cu$_2$S) are the ideal initial templates to obtain other compositions.  

The transformation from CuS to Cu$_2$S by adding Cu precursors into a system containing CuS NCs has been reported, leading to an increased Cu/S atomic ratio, crystal phase transformation, LSPR damping, and changes in the oxidation states of Cu and S. However, this approach may introduce foreign ions like F$^-$ and Cl$. Although many studies have demonstrated the ability to preserve the morphology of NCs during changes in composition, composition-induced morphology evolution is also of great interest, especially if it can be controlled. There are few reports demonstrating the production of thicker (> 10 nm) Cu$_2$S NPs, and these all relied on processes carried out at high temperature (> 180 °C). Therefore, the idea of intrinsic shape evolution emerges to describe the transformations between nanostructures without introducing extrinsic elements into the system.

On the other hand, the transformation from Cu$_2$S to CuS has rarely been considered. On the basis of Section 1.2, covellite CuS can be prepared by mixing CuCl$_2$ with AS
solution at ambient conditions. The sulfur precursor and ligand should be carefully chosen for the synthesis of covellite CuS; other sulfur donors and ligands would lead to Cu_{2-x}S with non-uniform NC size or shape. In addition, most covellite NPls have been limited to a fixed thickness (<6 nm), despite the ability to produce a wide range of diameters. Covellite CuS NPls tend to have limited growth along their c-axis. This arises from strong ligand binding on the basal planes (perpendicular to the c-axis), while the facets parallel to the c-axis remain available for growth. Moreover, anisotropic covellite can be considered as a collection of 2-D layers stacked perpendicular to the c-axis and cleaved preferentially across the interlayer of Cu2-S1 bonds (where Cu2 is a tetrahedrally coordinated Cu atom, and S1 is a trigonal bipyramidally coordinated S atom that does not participate in disulfide bonds). Thus, a reliable method of increasing the thickness of covellite NPls, without introducing foreign ions, while maintaining the hexagonal NPl morphology would be of significant value.
**2.1.2 Preparation of Covellite CuS template NPs**

CuS NPs were synthesized according to our previously reported method with minor modifications.\(^{18}\) Synthesis at 70°C produced 55.5 ± 2.8 nm NPs with a thickness of 4 nm in the c-axis direction. Diameters of hexagons are reported as the mean ± one standard deviation, according to their excircles. Size-distribution histograms for this and subsequent samples are presented in Figure 2-10. Larger covellite CuS NPs were obtained by the addition of AS solution and mild heating. Figure 2-1 shows TEM images, HRTEM images, and fast Fourier transforms (FFT) of ~55 nm covellite CuS NPs. The lattice fringes with a measured interplanar spacing of 0.19 nm correspond to the (110) planes of CuS, while 0.33 and 0.27 nm spacings correspond to (100) and (006) planes, respectively.

![Figure 2-1](image)

**Figure 2-1.** (a) TEM image of covellite CuS NPs with an average diameter of ~55 nm. The inset shows a side view of the CuS NPs. (b) Top view and side view (inset) HRTEM images of covellite CuS NPs with a thickness of ~4.0 nm. The insets are each at the same magnification as the corresponding main panel. Panels c and d show FFT of the regions of the corresponding HRTEM images in the outlined squares.
2.1.3 Forward Transformation (from CuS to Cu$_2$S)

Starting from the $\sim 55$ nm diameter covellite NPls, we studied both forward (from CuS to Cu$_2$S) and reverse (Cu$_2$S to CuS) transformation to understand the NPl shape evolution. We first discuss the forward transformation. Typically, 2 mL of DDT was introduced as a mild reducing agent to drive disulfide bond reduction in covellite. Note that DDT does not thermally decompose below 200 °C on chalcocite, so we do not expect DDT to release sulfur during the transformation. The results of the transformation were analyzed by TEM, XRD and vis-NIR absorbance spectroscopy. Figure 2-2a shows the typical transformed Cu$_2$S NCs, which have a round shape. The diameter of the Cu$_2$S NCs is $29.2 \pm 2.0$ nm and their thickness is $10.8 \pm 0.7$ nm. The hexagonal CuS NPls are converted into relatively thicker and smaller-diameter disc-shaped Cu$_2$S NPls. The Cu$_2$S NPls are monodispersed with no secondary phases, which suggests that each CuS NPl evolves into a Cu$_2$S NPl. The total volume of the round Cu$_2$S NPls is very close to that of the starting CuS NPls (8% lower based upon the nominal dimensions obtained from TEM images). Similar nanostructures have been observed by others. Compared to the CuS NPls, the Cu$_2$S NPls have a strong tendency to self-assemble via face-to-face stacking. This phenomenon can be driven by dipole-dipole interactions of ferroelectric Cu$_2$S NPls, minimization of surface energy, and the strong capillary force during the drying process when preparing the TEM sample. Moreover, edge-to-edge interactions are weaker in round NPls, compared to those in hexagonal NPls, simply because of the geometric effect of greater average edge-to-edge distance in close-packed circles compared to that in hexagons.
Figure 2-2. (a) TEM image of typical transformed Cu$_2$S NPls. (b) XRD patterns of covellite CuS NPls, NPs after 1 min of transformation and completely transformed high chalcocite Cu$_2$S NPls. HRTEM images showing the (c) top view and (d) side view of Cu$_2$S NPls. Panels e and f show FFT of the regions of the corresponding HRTEM images in the outlined squares. The scale bars for panels c and d are 10 and 5 nm, respectively.

HRTEM images in Figure 2-2c,d show the top and side views of Cu$_2$S NPls. Figure 2-2e,f shows the corresponding FFT patterns generated from the crystalline regions outlined by the squares. The HRTEM images indicated that the Cu$_2$S NPls are single-crystalline with lattice spacings of 0.20, 0.19, and 0.34 nm. These distances match (110), (103), and (102) lattice fringes in hexagonal high chalcocite Cu$_2$S. XRD confirmed that the CuS template NPls were in the covellite phase (ICDD PDF 04-007-1392, Figure 2-2b, black curve), while the Cu$_2$S NCs are in the high chalcocite phase (ICDD PDF 04-010-5153, Figure 2-2b, blue curve). Clearly, the primary peaks for covellite, corresponding to (100), (101), (006), and (110) planes, are suppressed after
DDT reduction. Simultaneously, all major peaks expected for high chalcocite Cu$_2$S NCs [(002), (110), (103), and (112)] appear, indicating the transformation of Cu$_2$S.

To understand the ability of DDT to promote the shape evolution, we first consider the covellite crystal structure. Covellite can be described as being composed of layers of triangular CuS$_3$ units, each sandwiched between two layers of CuS$_4$ tetrahedra. Each triple layer is then linked to the triple layers above and below it via disulfide bonds. The disulfide bonds are aligned with the c-axis and arranged in a plane perpendicular to the c-axis. Breaking of the disulfide bonds and removal of sulfur from the lattice drives expansion along the c-axis direction, as the (006) planes with a lattice spacing of 0.27 nm in CuS become the (002) planes with a lattice spacing of 0.34 nm in Cu$_2$S. This is accompanied by a contraction in the lateral direction, as Cu atoms move to new lattice positions. Thus, the transformation of stoichiometry and crystal phase is accompanied by a shape transformation, as well as rearrangement of Cu and S lattice positions and bonding.

TEM images in Figure 2-3(a-f) show the morphology evolution during the forward transformation. The thickness (nm) is plotted vs time (s) in Figure 2-3g. Starting from NPLs with thickness of 4 nm, the thickness of the NPLs grows with increasing reaction time. Initially, the thickness increases very rapidly, reaching ~6 nm after 1 min. This rapid increase may reflect the increase in lattice spacing along the c-axis that accompanies the phase change. The thickness then increases more slowly, reaching 9.6 nm after 20 min and ~11 nm after 30 min. This suggests that the transformation is a two-step process of rapid phase transition during the first minute, followed by a slower
shape evolution (“ripening”) process. To test this hypothesis, we also recorded the XRD pattern of NCs extracted after 1 min of the transformation process (Figure 2-2b, red curve). The XRD pattern showed the NCs are already in the high chalcocite phase. However, the NCs have limited growth on crystal planes such as (002) and (103), indicated by low diffracted intensities. Note that the formation of round discs of high chalcocite NPls is uncommon but not unprecedented.\textsuperscript{100} The shape of NCs is governed by minimization of surface energy (thermodynamic driving force) and kinetics of shape evolution. Here, because the shape does evolve, the structure should not be kinetically trapped. We conclude that in the presence of the particular combination of ligands and solvent used here, minimization of surface energy provides a thermodynamic driving force for the transition from hexagonal to round shape upon conversion from CuS to Cu\textsubscript{2}S. The formation of Cu\textsubscript{2}S is promoted by the low occupancy of Cu in CuS and the nominal partial occupancy of the Cu lattice positions in Cu\textsubscript{2}S, both of which promote the high mobility of Cu atoms within the relatively fixed S sublattice.\textsuperscript{45}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2-3.png}
\caption{TEM images of aliquots extracted during the CuS to Cu2S transformation after times of (a) 15 s, (b) 30 s, (c) 1 min, (d) 5 min, (e) 10 min, and (f) 20 min. (g) Plot of the thickness (nm) vs growth time.}
\end{figure}
Visible to NIR absorbance observed in cation deficient Cu$_{2-x}$S NCs originates from LSPR of free holes in the valence band. In isotropic particles, the LSPR energy is mainly determined by the $x$ value, which corresponds to the concentration of free holes arising from copper deficiency in the Cu$_{2-x}$S NCs.\textsuperscript{101} For covellite CuS, the disulfide bonds provide two free holes in the valence band per unit cell and thus can be viewed as responsible for the LSPR in CuS. The copper deficiency and free hole concentration are fixed in covellite CuS, but the LSPR energy can be tuned by varying the aspect ratio of anisotropic nanostructures, such as NPls. We discuss the LSPR of covellite further below. The Cu$_{2}$S NPls are not expected to exhibit LSPR because they lack free holes generated by copper deficiency ($x = 0$). Figure 2-4 shows that the LSPR absorbance of the CuS NPl templates peaks at $\sim$1400 nm (blue curve) and that the LSPR absorbance peak disappears after conversion to Cu$_{2}$S (orange curve). As shown in Figure 2-5, after 2 days of exposure to air, the Cu$_{2}$S NCs are oxidized to yield plasmonic Cu$_{2-x}$S NCs that exhibit NIR LSPR. This is consistent with other recent reports. Thus, all evidence indicates complete forward transformation from CuS NPls to Cu$_{2}$S NPls.
Figure 2-4. Vis-NIR absorbance spectra of original CuS NPls template (blue), forward-transformed Cu$_2$S NPls (orange), and reverse transformed CuS NPls (green). Measured absorbance was combined with measured Cu concentration to obtain the absolute absorbance cross-section per Cu atom.

Figure 2-5. UV-vis-NIR spectrum of Cu$_2$S without NIR absorbance and Cu$_{2-x}$S with NIR absorbance due to LSPR, produced by air exposure of Cu$_2$S NPls.
2.1.4 Reverse Transformation (from Cu$_2$S to CuS)

To further understand the mechanism of transformation of copper sulfides, we also conducted experiments on the reverse transformation starting from Cu$_2$S NPs. To produce sulfur-rich CuS from copper-rich Cu$_2$S, we added sulfur ions into the system rather than partially removing copper ions. An appropriate sulfur source would not only promote the transformation from Cu$_2$S to CuS but also help restore the hexagonal shape of original covellite NP. Our group previously demonstrated that Cu$_{2-x}$S NCs synthesized using S-OA precursors prepared by simply dissolving sulfur powder in pure OA had the covellite crystal structure ($x = 1$).$^{101}$ Other recent studies also suggest that OA facilitates the formation of covellite instead of other Cu$_{2-x}$S phases.$^{67,102}$ Thus, we chose OA-S as the sulfur source to accomplish reverse transformation. OA-S was prepared by heating sulfur powder and OA to 120 °C. Then, 0.5 mmol of OA-S was injected into the Cu$_2$S NP dispersion at 160 °C. The results of reverse transformation were again characterized by TEM, XRD and vis-NIR absorption. **Figure 2-6a** shows a typical TEM image of CuS NPs transformed using OA-S. The CuS NPs are hexagonal, with a thickness of 11.2 ± 0.9 nm, nearly equal to the thickness of the Cu$_2$S NPs. Compared to the original covellite CuS template with a diameter of ~55 nm, the diameter of the new CuS NPs was reduced to 43.1 ± 2.0 nm. HRTEM analysis also revealed that the reverse-transformed CuS NPs have a hexagonal phase similar to that of the covellite CuS template but show different relative diffraction intensities.

The XRD pattern results of new CuS NPs show that they are in the covellite phase. Further, the intensities of characteristic peaks in the XRD patterns (**Figure 2-6b**) also...
provide evidence of aspect ratio changes. As mentioned above, (006) planes define the faces of each platelet (peak at ~32° in XRD), while the (110) planes (~48° peak in XRD) are in the hexagonal basal plane, perpendicular to the c-axis. The intensity ratio of the (006) to (110) peaks increased from 0.33 in the initial NPls to 0.65 after the reverse transformation. This is consistent with the increased thickness and decreased diameter of the NPls.

**Figure 2-6.** (a) TEM image of reverse-transformed CuS NPls with a diameter of ~43 nm. (b) XRD patterns of original covellite NPls and transformed covellite NPls. (c) HRTEM images showing the (c) top view and (d) side view of reverse-transformed CuS NPls. Panels e and f show FFT of the regions of the corresponding HRTEM images in the outlined squares. The scale bars for panels c and d are 5 nm.

Covellite NPls exhibit LSPR absorbance that depends upon their aspect ratio, with their dominant in-plane dipolar resonance red-shifting as the aspect ratio increases. The vis–NIR spectra in **Figure 2-4** show that the LSPR absorbance of the original CuS NPls
peaked at 1400 nm, while that of the NPls after reverse transformation peaked at 1000 nm. This blue shift of the LSPR is consistent with the observed decrease in aspect ratio. Thus, this approach provides a new route to thicker CuS NPls that can provide a combination of size and LSPR energy that was not previously accessible. To the best of our knowledge, the ~11 nm CuS NPls reported here are thicker than any previously reported CuS NPls. The reversible transformation process (Figure 2-7) provides a means of breaking the intrinsic growth limit of 2.5, 3, or 3.5 unit cell thickness that has been widely observed in CuS NPls.

![Figure 2-7. Schematic illustration of reversible interconversion between CuS and CuS NPls](image)

2.1.5 Structural Perspective of Reversible Interconversion between CuS and Cu$_2$S

Considering the crystal structures of covellite CuS and high chalcocite Cu$_2$S can provide further insight into the transformation mechanism. Figure 2-8a shows a side-view comparison of the covellite and high chalcocite structures. For clarity, we show Cu-S bonds but do not explicitly show the Cu atoms. On the one hand, reduction of disulfide bonds accompanied by insertion of Cu atoms increases the distance between sulfur layers, producing an expansion in the c-axis direction (thickness) of the NPl. On the other hand, considering the stoichiometry of CuS and Cu$_2$S, half of the sulfur atoms are removed during the transformation. As a result, the volume per copper atom is smaller for Cu$_2$S than that for CuS, and the overall volume of each NPl must decrease during the transformation. The thickness of the starting covellite CuS NPls is 4 nm, containing ~2.5 unit cells with 16 layers of sulfur atoms along the c-axis (16.27 Å per unit cell). After the initial phase transformation (~1 min after the injection of CuS NPls), the high chalcocite Cu$_2$S NPl has ~8.5 unit cells along the c-axis (6.88 Å per unit cell, thickness of ~6 nm) and therefore contains about 17 layers of sulfur atoms. Thus, this initial transition can be envisioned as expansion in the c-axis (NPl thickness) direction and contraction in the perpendicular directions, while maintaining a nearly fixed number of layers of sulfur atoms. In covellite CuS, the distance between two different S layers is 3.01 Å and the length of a disulfide bond is 2.15 Å. In contrast, the distance between S layers in high chalcocite is 3.44 Å, producing 14.3% and 66.2% expansion, respectively, in the distance between these layers. This expansion produces the 25.9% increase in lattice spacing for the (100) planes in going from covellite (0.27 nm spacing...
of (006) planes) to high chalcocite (0.34 nm spacing of (002) planes), as observed in HRTEM. However, the final thickness reached after 20 min heating, ~11 nm, corresponds to about 32 layers of S atoms. Thus, the transformation from the initial hexagonal covellite NPLs to round high chalcocite NPLs can be considered to occur in two steps: a rapid phase transformation that maintains a fixed number of S layers and a slower thickening or ripening process in which the number of S layers in the NPL increases.

Figure 2-8. (a) Schematic illustration of forward and reverse transformation for sulfur atoms when viewed down the c-zone axis. (b) Top view of the (001) planes of covellite CuS NPLs (left) and high Cu2S (001)
As shown in Figure 2-8b, the initial hexagonal CuS with (001) basal plane transformed into hexagonal Cu$_2$S with (001) basal plane. Both phases exhibit the same P6$_3$/mmc hexagonal crystal symmetry. Viewed along the [001] axis, all Cu and S atoms are arranged hexagonally in both of the crystal structures. The distance between S atoms in the (001) plane of high chalcocite Cu$_2$S is 3.89 Å, which is only 3.2% larger than that in covellite CuS (3.77 Å). This allows the transformation to take place with minimal changes for some S1 atoms in the sulfur sublattice.

The reverse transformation occurs by further S addition, so it does not strictly follow the same mechanism as the forward transformation. We speculate that upon sulfur addition, sulfur layers are inserted to reform the disulfide bonds, as illustrated schematically in Figure 2-8. The ~11 nm thickness of the high chalcocite NPIs contains ~16 unit cells and ~32 layers of S atoms along the c-axis. The reverse transformation preserved the thickness, which corresponds to ~41 layers of S atoms along the covellite c-axis. The increase from ~32 to ~41 layers corresponds roughly to the increase from 6 to 8 sulfur layers illustrated in Figure 2-8, which produces very little change in thickness along the c-axis. Although ~10 layers of sulfur atoms were inserted, the thickness remained nearly constant because the distance between sulfur layers was reduced from 3.44 to 3.01 Å (S1-S2) or 2.15 Å (disulfide bonds). While the increase in the number of layers and decrease in layer spacing offset one another, the total volume of the NPIs increases during the reverse transformation, as reflected by the increased diameter. The shape evolution from round to hexagonal NPIs indicates additional
rearrangement beyond that hypothesized here, presumably driven by surface energy minimization.

To further address the question of whether the preferential plate-like shape for covellite CuS is formed due to its crystal structure or simply preserves the shape from the previous step, we also used spherical roxbyite Cu$_{1.78}$S NPs as a template to produce covellite CuS. The roxbyite NCs were prepared by reacting Cu(II) with di-tert-butyl disulfide. The transformation to covellite was then conducted by adding OA-S to roxbyite Cu$_{1.78}$S NCs. Figure 2-Sa,b show the typical TEM images of spherical roxbyite Cu$_{1.78}$S template particles and transformed CuS NCs. The monodispersed roxbyite Cu$_{1.78}$S NCs are 22.8 ± 0.8 nm in diameter, while the transformed CuS NPs have a diameter of 36.4 ± 2.3 nm and thickness of 9.2 ± 0.8 nm. The many CuS platelets with edge-on orientation in Figure 2-Sb clearly indicate the shape evolution from sphere to platelet. HRTEM analysis proved that the transformed CuS NPs have similar lattice spacings with the CuS template, indicating the formation of a covellite phase. The XRD pattern of NCs after OA-S treatment (Figure 2-9), also confirmed the expected covellite phase. This result suggests that covellite NCs preferentially adopt a hexagonal platelet morphology due to their intrinsic crystal structure and associated surface energies of different facets, and are not simply maintained from the initial template. We attribute the formation of plate-like shape to the unique layered structure of covellite, in which layers are linked by S-S bonds, and (006) facets are particularly stable.
Figure 2-8. (a) TEM image of roxbyite \( \text{Cu}_{1.76} \) S NCs and (b) TEM image of transformed NCs after OA-S treatment. (c) HRTEM images of (c) roxbyite \( \text{Cu}_{1.76} \) S NCs and the (d) top view and (e) side view of transformed NCs after OA-S treatment. (f-h) FFT of the regions of the corresponding HRTEM images in the outlined squares. The scale bars for panels c-e are 5 nm.

Figure 2-9. XRD patterns of \( \text{Cu}_{1.76} \) S NCs and CuS NPs synthesized by treating \( \text{Cu}_{1.76} \) S NCs with OA-S.
Figure 2-10. (a) Size distribution of covellite CuS NPs template. Size distribution of NPs after (b) forward transformation and (c) reverse transformation. Size distribution of roxbyite nanocrystals before (d) and after (e) OA-S treatment. Thickness distribution of NPs before (f) and after (g) reverse transformation. (h) Thickness distribution of roxbyite nanocrystals after OA-S treatment. Diameters and thicknesses are reported as mean ± one standard deviation. Diameters of hexagons in (a)-(c) and (e) are according their excircles. (i) Schematic illustration of excircle of a hexagon.
2.1.6 Conversion from djurleite Cu$_{1.94}$S to Covellite CuS

Based on the previous section (Section 2.1.5), when Cu$_{2-x}$S NCs are converted to covellite CuS NCs, their morphology should be transformed into a plate-like shape, regardless of the morphology of initial Cu$_{2-x}$S template.\textsuperscript{36} We attributed this shape evolution to the unique layered structure of covellite, in which layers are linked by S-S bonds, and (006) facets are particularly stable. Here, the biconcave djurleite NPls were converted to covellite CuS by treatment with an OA-S complex (the preparation of biconcave NPls is provided in Section 3.2.2). Figure 2-11 shows TEM and HRTEM images of the NPls before and after OA-S treatment, starting from the products of 1 and 60 min of CE reaction. The OA-S treated NPls both exhibited hexagonal NPl morphology, with lattice spacings of 0.33 nm [(100) planes] and 0.27 nm [(006) planes] in top-view and edge-view images, respectively. The change of thickness can be explained by the increased number of layers of sulfur atoms and decreased average distance between sulfur layers in the covellite sublattice, which is consistent with our previous discussion.

In an attempt to preserve the biconcave morphology during the OA-S treatment, less OA-S (0.1 mmol) was allowed to react with biconcave NPls obtained after 60 min of CE. As shown in Figure 2-12, the djurleite Cu$_{1.94}$S biconcave NPls were converted into a mixture of digenite Cu$_{1.8}$S and roxbyite Cu$_{1.75}$S NPls. Compared to the results using 0.5 mmol of OA-S, it is obvious that 0.1 mmol of OA-S is not enough to convert the Cu$_{2-x}$S from nearly one stoichiometric extreme (Cu$_2$S) to another (CuS). However, the formation of flat surfaces on the resulting NPls after even a moderate change in
stoichiometry indicates the strong tendency of Cu_{2-x}S NCs to form flat NPls, which in turn, highlights the novelty of biconcave NPls.

Figure 2-11. (a,d) TEM, (b,e) top-view and (c,f) side-view HRTEM images of NPls before and after OA-S treatment, starting from the products of 1 and 60 min of CE reaction, respectively. The OA-S treated NPls both exhibited hexagonal NPl morphology.

Figure 2-12. (a) TEM image and (b-c) XRD patterns of the NPls obtained from 60 min of CE reaction after treatment of biconcave Cu_{1.5}S NPls with 0.1 mmol of OA-S. Panels (b) and (c) compare XRD patterns of biconcave NPls before (violet) and after (pink) 0.1 mmol of OA-S treatment, indicating the transformation from djurleite Cu_{31}S_{16} to a mixture of digenite Cu_{9}S_{5} and roxbyite Cu_{8}S_{4}.
2.1.7 Experimental Section

Chemicals. All chemicals were used as received. Di-tert-butyl disulfide (97%), oleylamine (70%, OAm), oleic acid (technical grade, OA 90%), 1-octadecene (ODE, technical grade, 90%), and 1-dodecanethiol (DDT, ≥ 98%) were purchased from Sigma-Aldrich. CuCl₂·2H₂O, toluene, and ammonium sulfide (21.2 wt % in water) were purchased from Fisher Scientific. The synthesis and transformations were carried out in three-necked flasks under argon, using Schlenk line techniques, within a fume hood. Some steps could conceivably produce H₂S as a byproduct. Appropriate precautions should be taken to avoid exposure to any such gases produced.

Preparing CuS Templates. For the synthesis of 55 nm hexagonal CuS NPs, 1.5 mmol of CuCl₂·2H₂O was dissolved in a mixture of 10 mL of OAm and 10 mL of toluene, then heated to 70 °C. 1.5 mL of AS solution (21.2% in water) was injected into the Cu-OAm to form CuS NPs. After 2 h, 10 mL of ethanol was added to destabilize the NP dispersion, followed by centrifugation at 4000 rpm for 1 min. To remove excess AS and OAm, the precipitate was redispersed in chloroform, then, once again, ethanol was added followed by centrifugation at 4000 rpm for 1 min. This purification process was applied to all of the NPs described in the following sections. The NPs could be redispersed in organic solvents including chloroform, hexane, and toluene. We used toluene in subsequent steps.

Conversion of CuS NPs to Cu₂S NPs. In a typical synthesis, a mixture of 8 mL of OAm and 2 mL of DDT was degassed at room temperature under argon protection followed by heating to 160 °C. Then, a CuS NP dispersion containing 0.5 mmol of Cu was injected into the mixture, and the solution was held at this temperature for 30 min.
To collect the NPIls, 10 mL of ethanol was added, followed by centrifuging at 4000 rpm for 1 min.

**Preparing Organo-sulfur Precursors.** OA-S was prepared by mixing 1 mmol of sulfur powder with 10 mL of OA and heating to 120 °C for 20-30 min until a clear homogeneous solution was formed.

**Conversion of Cu2S NPIls Back to CuS NPIls.** For the conversion of Cu2S NPIls to CuS NPIls using OA-S, 10 mL of OAm was degassed at room temperature under argon protection followed by heating to 160 °C. A Cu2S dispersion containing 0.5 mmol Cu was then injected. When the temperature returned to 160 °C, 0.5 mmol of OA-S was injected, and the mixture was held at 160 °C for 30 min. To collect the NPIls, 10 mL of ethanol was added to the reaction product, followed by centrifuging at 4000 rpm for about 1 min.

**Synthesis of Roxbyite Cu1.7sS NCs.** The method for preparing roxbyite Cu1.7sS NCs was adapted from Li and co-workers’ report. In a typical synthesis, 0.5 mmol of CuCl2·2H2O was dissolved in 10 mL of OAm, and the solution was degassed under flowing argon to remove oxygen. Then, the mixture was heated to 220 °C and cooled to 180 °C before adding 2 mL of di-tert-butyl disulfide. The reaction proceeded for 40 min at 180 °C. NCs were collected by adding ethanol followed by 1 min of centrifugation at 4000 rpm.

**Characterization.** Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-2010 or an FEI Tecnai F20 G2, in both cases at an accelerating voltage of 200 kV. TEM grids were prepared by dropping a dilute NC dispersion onto
a carbon coated copper or nickel TEM grid and allowing the sample to dry under air. Size distributions were obtained from TEM images by measuring at least 100 NCs from multiple TEM images from different areas of the grid, using Nanomeasurer v. 1.2. STEM imaging was carried out on a FEI Tecnai F20 200 kV STEM using samples prepared on nickel TEM grids. Powder X-ray diffraction (XRD) measurements were carried out using a Rigaku Ultima IV diffractometer with a Cu Kα X-ray source. Samples were prepared by drop-casting concentrated NC dispersions onto glass slides. Elemental analysis of NCs by energy-dispersive X-ray spectroscopy (EDS) was obtained using an Oxford Instruments X-Max 20 mm² EDS detector within a Zeiss Auriga scanning electron microscope (SEM). UV-vis-NIR spectra of NC dispersions in chloroform were taken on a Shimadzu UV-3600. Inductively coupled plasma optical emission spectrometry (ICP-OES), using a iCAP 6000 spectrometer (Thermo Scientific), was used to quantify the amount of Cu in the NPls to normalize absorbance spectra based on Cu concentration. For ICP-OES analysis, the NPls were digested in aqua regia (3:1 (v/v) HCl/HNO₃) for 48 h.
Chapter 3. Cation Incorporation into Copper Sulfide Nanocrystals

3.1 Synthesis Copper Tin Sulfide Nanoplatelets Using Sn(II) and Sn(IV) Sources

3.1.1 Introduction

The family of copper chalcogenide-based semiconductors, which includes copper indium sulfide/selenide (CIS),\textsuperscript{48} copper tin sulfide (CTS),\textsuperscript{15, 103, 104} copper indium gallium sulfide/selenide (CIGS),\textsuperscript{105, 106} and copper zinc tin sulfide/selenide (CZTS)\textsuperscript{75, 107-109} is of great interest for use in thin-film solar cells. Preparation of these materials as colloidal inks can allow low-cost fabrication by solution-phase printing and coating processes. CTS is an intermediate crystal that can be further incorporated with zinc to produce CZTS. CTS nanocrystals (NCs) can, themselves, serve as an absorber for thin-film photovoltaics, with a near-optimal band gap around 1.43 eV.\textsuperscript{110} Further, CTS, is composed of relatively low-cost, naturally abundant, and nontoxic elements. Thus, it is of great interest both as an intermediate to formation of CZTS and for its own potential applications in solar cells and related optoelectronic devices.

Properties of compound semiconductors, including the copper chalcogenides, can be tuned by varying the cation fraction in mixed cation materials such as CTS. Two alternatives are available for preparation of such materials: (1) direct synthesis of ternary materials using multiple cation precursors simultaneously;\textsuperscript{15, 48} and (2) multistep synthesis in which NCs of a binary material are first prepared, and then a cation exchange process is used to introduce the second cation.\textsuperscript{1, 103} In some cases, copper chalcogenides have been used as templates for complete cation exchange to produce an entirely different metal chalcogenide from which all copper cations have been
Direct synthesis of ternary or quaternary materials from multiple precursors in one pot often suffers from stoichiometric imbalance and formation of secondary phases due to differences in precursor reactivities. Cation exchange can circumvent this by stepwise replacement of cations. Adjustment of reactivity of one reagent is much easier than managing the reactivity of multiple precursors simultaneously. The cation ratio in the product can also be easily manipulated by the amount of substitutive cation provided. For copper sulfide, the process can also be tuned through use of copper-extracting agents such as trioctylphosphine (TOP) and dodecanethiol (DDT). The strong affinity of such reagents for Cu\(^{+}\), combined with the modest stability of the copper-chalcogenide bond, facilitates exchange of Cu for metals that form stronger bonds with chalcogenides and/or are more weakly complexed by these agents. This has been demonstrated for making CdS from Cu\(_{2-x}\)S. Choosing appropriate copper-extracting ligands is crucial in cation exchange.

Although Sn incorporation into copper sulfide has been previously studied, valence selectivity has been greatly debated for converting copper chalcogenides into copper tin chalcogenides. Recent research suggested Sn\(^{4+}\) can more effectively insert into the Cu\(_{2-x}\)Se substrate, due to its smaller size relative to Sn\(^{2+}\). Starting from berzelianite Cu\(_{2}\)Se, use of Sn\(^{4+}\) precursors allowed production of CTSe NCs, while use of Sn\(^{2+}\) produced heterostructures of Cu\(_{2-x}\)Se and SnSe. The effectiveness of Sn incorporation, however, may vary with the stoichiometry and crystal phase of the starting copper chalcogenide nanostructures. Starting from NCs of different crystal phase may also produce final alloyed NCs of different crystal phases.
3.1.2 Reaction without DDT: Incorporation of Sn$^{2+}$ into Covellite.

Here we focus on using covellite CuS as the host lattice, because few examples of cation insertion or exchange starting from covellite CuS have been reported, and because covellite has the unique structural feature of potentially reactive disulfide bonds in its crystal structure. Stabilizing ligands with a variety of functional groups have been employed to promote cation insertion and exchange. We selected DDT for its low toxicity, stability in air, and good performance in other cation exchange reactions.

Covellite CuS NPs were synthesized according to the similar method we described in Section 1.2. Figure 3-la shows a TEM image of 55.5 ± 2.8 nm covellite CuS NPs. X-ray diffraction showed that the crystal phase of the CuS NPs is covellite (ICDD PDF 04-007-1392, Figure 3-1b). The lattice fringes in top-view HRTEM images (Figure 3-1c) have interplanar spacings of 0.19 and 0.33 nm, corresponding to the (110) and (100) planes of covellite, respectively. Side-view HRTEM images (Figure 3-1d) show a lattice spacing of 0.27 nm, corresponding to (006) planes. The TEM and HRTEM images show that the (100) and (010) directions lie within the plane of the CuS NPs, while the (001) direction corresponds to the NP thickness. This is consistent with the sharp (110) peak in the XRD pattern (Figure 3-1b). As shown previously, this synthetic approach constrains growth in the (001) direction while allowing control of the size in the perpendicular directions.
Figure 3-1. (a) TEM image of covellite CuS NPs with diameter of \( \sim 55.5 \pm 2.8 \) nm. (b) XRD pattern of covellite CuS NPs. (c) Top-view and (d) side-view HRTEM images of covellite CuS NPs with thickness of \( \sim 4.0 \) nm.

We tested the incorporation of Sn into the CuS NPs using precursors with each of the stable Sn oxidation states (Sn\(^{4+}\) and Sn\(^{2+}\)) to deduce the dependence of Sn incorporation on valency. We first discuss results obtained using Sn\(^{2+}\) ions. Figure 3-2 shows typical TEM images of Cu\(_3\)Sn\(_x\)S\(_{3+x}\) NCs \((x \leq 1)\). Sn\(^{2+}\) was supplied in amounts corresponding to Cu:Sn ratios of 7:1, 5:1, and 3:1, using \( \sim 55 \) nm NPs as templates. The size and shape of the CuS NPs were preserved as Sn was incorporated. Use of appropriate temperature and low concentrations of the OAm-Sn complex ensured complete preservation of the morphology of the initial NPs. Starting from the CuS NP templates, Cu\(_3\)Sn\(_x\)S\(_{3+x}\) NCs \((x \leq 1)\) gradually changed from the covellite (CuS) crystal structure to kuramite (Cu\(_3\)SnS\(_4\)). The excess sulfur required for this conversion was presumably provided by residual \( S^{2-} \) remaining from the CuS NP synthesis. As shown in Figure 3-3, both crystal phases have a major peak at \( 2\theta \approx 48^\circ \), which changes little with Sn incorporation. The shift of the covellite peak near \( 31^\circ \) to \( \sim 34^\circ \) provides the
clearest evidence of the phase transformation.

**Figure 3-2.** TEM images of CTS NPs produced using (a) 7:1, (b) 5:1, and (c) 3:1 ratios of Cu:Sn. Insets show side-view images from the same samples and are at the same scale as the corresponding main panel.

![TEM images of CTS NPs](image)

**Figure 3-3.** X-ray diffraction patterns of Cu$_3$Sn$_x$S$_4$ (0 < x < 1), from covellite to kuramite NPs. Magenta, red, and blue curves are from NPs produced using 3:1, 5:1, and 7:1 Cu:Sn$^{2+}$ ratios, respectively.

We employed STEM-HAADF EDX mapping to characterize the composition of individual NPs. Panels a and b of **Figure 3-4** show an STEM-HAADF image and an EDX line-scan analysis of kuramite CTS NPs (prepared using a 3:1 Cu:Sn ratio), while panels c and d of **Figure 3-4** show the results obtained using an excess of OAm-Sn$^{2+}$ (1:1 Cu:Sn ratio), which results in formation of a secondary phase, visible as flower-like structures. We first discuss the 3:1 case. The EDX line scan of **Figure 3-4b** shows that Cu, Sn, and S are uniformly distributed across the NPI. The signals decay on both
sides, which suggests that the region outside the platelet is free of these elements. The chlorine signals are due to trace residues of the metal-Cl salts used as precursors. When excess Sn\(^{2+}\) was supplied, beyond the stoichiometric 3:1 Cu:Sn ratio for kuramite, a secondary phase appeared. A sharp new peak near 21.7° appears in the XRD pattern shown in Figure 3-4e. This phase appears as the nanoflowers shown in Figure 3-4f and Figure 3-4c. There are multiple reports of flower-like tin sulfide NCs, which all agree that SnS NCs tend to form flower-like morphology.\(^{115,116}\) An EDX line scan (Figure 3-4d) across the nanoflower in Figure 3-4c shows that the Sn content is much higher than that of CTS NPs. However, the significant Cu signal detected implies that CTS NPs may be attached on or beneath the nanoflower. While the single new XRD peak and limited composition data do not allow unambiguous identification of this new phase, clearly a new Sn-rich phase is formed when excess Sn is added.

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![Figure 3-4](image)

**Figure 3-4.** STEM HAADF TEM images (a, c) and STEM-EDX line scans (b, d) along the indicated lines, for (a, b) Cu\(_3\)SnS\(_4\) NPs prepared using a 3:1 Cu:Sn ratio and (c, d) NCs prepared using a 1:1 Cu:Sn ratio, which results in formation of a Sn-rich secondary phase. (e) XRD pattern and (f) TEM image of CTS NCs produced using a 1:1 Cu:Sn ratio.
The covellite NPls exhibit strong NIR LSPR absorbance from 1000 to 2000 nm depending on their aspect ratio. As the Sn content of the NPls increased, the LSPR shifted to longer wavelength (red-shifted) and decreased in intensity, an important indication of successful Sn incorporation, accompanied by a reduced cation deficiency and corresponding reduced free carrier concentration. Figure 3-5a shows that starting from covellite NCs, with an absorbance peak at 1400 nm, the addition of increasing amounts of Sn induced a red shift of the near-IR absorbance band to around 1600 nm. The red shift of the LSPR is attributed to a decrease in the free carrier concentration with increased Sn content. This change in LSPR absorbance is consistent with the transformation from covellite to kuramite. However, the fact that the LSPR absorbance persists even after conversion to kuramite suggests that the NPls remain cation deficient. Kuramite nanoparticles prepared directly in solution were reported not to exhibit LSPR, but thin films of copper-deficient kuramite have shown free carrier concentrations of $3 \times 10^{21} \text{cm}^{-3}$. A similar free carrier concentration would produce near-IR LSPR in the NPls. In addition, the UV-vis absorbance band of absorbance of these NPls are recorded in the inset of Figure 3-5a. The absorbance minimum (trough) between the UV-vis band-to-band absorbance and the LSPR absorbance also red-shifted with increased Sn incorporation, reflecting a decrease in band gap energy accompanying the conversion from covellite CuS to kuramite Cu$_3$SnS$_4$. However, the overlap between the band-to-band and LSPR absorbances prevented us from quantitatively extracting the optical band gap from these absorbance spectra. The indirect band gaps of these CTS NPls were estimated by extrapolating the linear portion
of plots of \((ahv)^2\) vs \(h\nu\), the photon energy, to \(a = 0\) (Figure 3-5b). Based on this estimation, the band gap energy of covellite CuS NPls is nearly 2.40 eV. The indirect band gap of CTS NPls estimated in this manner increased from 2.46 to 2.90 eV with increasing incorporation of Sn into covellite CuS. Although overlap between the tails of band gap absorbance and LSPR absorbance, along with possible defect-related absorbance, produce substantial ambiguity and uncertainty in the determination of bandgaps from such optical absorbance measurements, we believe the trend of increasing bandgap with increasing Sn incorporation is genuine.

![Figure 3-5](image.png)

**Figure 3-5.** (a) NIR absorbance spectra of NPls before Sn\(^{2+}\) incorporation and after incorporation at 7:1, 5:1, and 3:1 Cu:Sn ratios. Sharp peaks superimposed on the smooth absorbance curves are due to solvent absorbance. The inset is the UV-vis absorbance of these nanocrystals, labels indicating the troughs of the curves. (b) Plots of \((ahv)^2\) vs photon energy (eV) for above Cu-Sn-S NPls. The dotted lines represent the fits of individual spectra with the \(x\)-axis intercepts.
3.1.3 Reaction without DDT: Incorporation of Sn$^{4+}$ into Covellite.

In contrast to Sn$^{2+}$, we found that Sn$^{4+}$ could not be incorporated into the CuS NPls under conditions similar to those used for Sn$^{2+}$ incorporation. Figure 3-6a shows representative TEM image of the product of attempts to incorporate Sn$^{4+}$ into covellite CuS. As shown there, the NPls were etched and separate nanoparticles of a secondary phase are evident. Comparison of XRD patterns of samples before and after the attempted Sn$^{4+}$ incorporation confirm the presence of a second phase (Figure 3-6b). The primary diffraction peaks of covellite, corresponding to the (110) and (102) planes, remain clearly present after the Sn$^{4+}$ addition. Simultaneously, all major peaks expected for berndtite SnS$_2$ NCs [(110), (101), (003) and (103)] appear, clearly indicating the formation of a separate SnS$_2$ phase. The coexistence of covellite CuS and berndtite SnS$_2$ further confirms that Sn$^{4+}$ cannot be incorporated into CuS without the use of additional reagents that promote Cu extraction or disulfide bond reduction.

![Figure 3-6. (a) TEM image and (b) XRD pattern of CuS NCs treated with Sn$^{4+}$.](image-url)
3.1.4 Reaction with DDT: Incorporation of Sn\(^{2+}/Sn^{4+}\) into Covellite.

DDT has been used as a capping ligand for many nanoparticle synthesis processes and, as discussed above, can enhance cation exchange in copper chalcogenides by extracting copper from the lattice. Here, we performed the same experiments described above, using either Sn\(^{2+}\) or Sn\(^{4+}\), with the addition of DDT to test the hypothesis that DDT drives cation exchange in this system. **Figure 3-7** shows a representative TEM image and XRD pattern of the product of treating covellite NPls with Sn\(^{4+}\) in the presence of DDT. The TEM image shows that the original size and shape of the NPls was well-preserved, and no separate phases can be found. The corresponding XRD pattern shows that the NPls have been converted to the mohite phase of CTS (ICDD PDF 04-010-5719), for which the standard stoichiometry is Cu\(_2\)SnS\(_3\). This demonstrates that the initial covellite NPls can be converted to two different CTS materials using different combinations of Sn sources and additives. Without DDT, Sn\(^{2+}\) addition produced kuramite, and with DDT, Sn\(^{4+}\) produced mohite, while in both cases the NPl size and morphology were preserved. When Sn\(^{2+}\) was used with DDT, as shown in the TEM image of **Figure 3-8a**, NPs of a secondary phase were formed, and the corresponding XRD pattern (**Figure 3-8b**) showed the presence of both covellite and herzenbergite SnS. This may be explained by greater reactivity of the thiol with the metal cations, compared to the amine, and the ability of DDT to reduce disulfide bonds. The combined ability of DDT to extract Cu and to reduce disulfide bonds reversed the dependence of Sn incorporation on the valency of the Sn source.
Figure 3-7. (a) TEM image and (b) XRD pattern of CTS NCs prepared using Sn$^{4+}$ in the presence of DDT.

Figure 3-8. TEM image of (a) CuS NPs treated with Sn$^{2+}$ in the presence of DDT and (b) corresponding XRD patterns.
3.1.5 Mechanisms of Conversion from Covellite CuS to Copper Tin Sulfide Nanocrystals

The results presented above show that Sn ions of different valences can incorporate into copper sulfide of different stoichiometry and crystal structure and that this incorporation is influenced by the addition of ligands that can extract Cu from Cu$_{2-x}$S and that can reduce disulfide bonds in covellite. The impact of Sn incorporation on the free carrier concentration can be tracked by observing the red shift and decreased intensity of LSPR absorbance. The covellite structure can be described by a repeat unit composed of a layer of triangular CuS$_3$ units, sandwiched between two layers of CuS$_4$ tetrahedra. Each triple layer is then linked to a top and bottom triple layer by disulfide bonds. The disulfide bonds not only link the CuS triple layers but also provide two free holes in the valence band per unit cell. Covellite thus behaves as a semimetal with the highest hole concentration among the family of stable Cu$_{2-x}$S ($0 \leq x \leq 1$) materials. The disulfide bonds also appear to play a key role in the transformation from CuS to CTS. We propose that Sn$^{2+}$ can reduce the disulfide bonds and can thus be simultaneously oxidized and incorporated into the covellite structure. Reduction of disulfide bonds decreases the concentration of free holes in the NPls. With the NPl geometry and other parameters fixed, the LSPR energy is approximately proportional to the square root of the free hole concentration. Thus, reduction of the disulfide bonds produces a red shift of the LSPR absorbance peak of the NPls. In contrast to Sn$^{2+}$, Sn$^{4+}$ ions cannot be further oxidized and therefore cannot reduce disulfide bonds. Addition of Sn$^{4+}$ to the CuS dispersion, which contains excess sulfur, thus leads to formation of
SnS₂ as a separate secondary phase rather than incorporation of Sn into the covellite host lattice. Conversely, when Sn²⁺ is used in the presence of DDT, the Sn²⁺ is not oxidized to Sn⁴⁺ and is not incorporated into the covellite lattice. Instead, it remains in its Sn²⁺ oxidation state and forms SnS.

Covellite can be described as Cu₆S₆, in which four of the Cu ions have tetrahedral coordination and two have triangular coordination, while four of the S atoms form two disulfide bonds and two S atoms are present as sulfide ions. The product of CuS treatment with Sn²⁺ is kuramite, with a tetragonal structure (space group I4m2). If the cations are fully ordered, then the 2a and 4d positions are occupied by Cu, while Sn is at the 2b position and S is at the 8i position (Figure 3-9). In this structure, all of the atoms are tetrahedrally coordinated. To convert covellite to kuramite, each entering Sn²⁺ ion must break a disulfide bond and migrate to a suitable position. Breaking all of the disulfide bonds leads to formation of kuramite CTS NCs. The observed upper limit of tin incorporation of one Sn for every three Cu atoms (two Sn per unit cell) corresponds to the amount required to break the two disulfide bonds per unit cell. Manna’s group has similarly reported that S-S bonds are ruptured by electron donors and foreign metal cations.⁵⁹ Note that conversion of covellite to kuramite requires incorporation of two additional S atoms per unit cell, along with the addition of two Sn atoms per unit cell, transforming the Cu₆S₆ unit cell to Cu₆Sn₂S₈.

XPS analysis of the kuramite NPls produced by addition of Sn²⁺ to covellite NPls revealed that copper was present solely as Cu⁺; no Cu²⁺ satellites were observed (Figure 3-10). The Sn valency is predominantly Sn⁴⁺. This is consistent with the
hypothesis that each Sn\(^{2+}\) provides two electrons to reduce a disulfide bond, while the Sn\(^{2+}\) itself is oxidized to Sn\(^{4+}\). The determination of the valence state of sulfur is more difficult than for copper and tin. The valency of sulfur in covellite remains the subject of debate. Comparing the XPS of kuramite NPIs to that of the covellite NPIs in our previous study suggests that the S is present entirely as S\(^{2-}\) in the kuramite NPIs, in contrast to its mixed valence in covellite. The observed oxidation states would imply a formula of \((\text{Cu}^{+})(\text{Sn}^{4+})(S^{2-})_4\), which does not reflect a balance between the cation and anion valences. The ambiguity of the oxidation states is similar to that of the parent covellite structure, and simply reflects the fact that the description of bonding in these structures, in which the bonds have substantial covalent character, is not perfectly described by strict oxidation states.

**Figure 3-9.** Schematic illustration of the structural transformation from covellite to kuramite.

**Figure 3-10.** (a)-(c) High-resolution XPS scans of kuramite CTS NPIs in energy ranges corresponding
to (a) Cu, (b) S and (c) Sn signals.

When DDT was present, it could either reduce disulfide bonds directly or could extract Cu$^+$ and then the Cu$^+$ could reduce the disulfide bonds. EDX and XRD showed that CTS synthesized from covellite using a combination of DDT and Sn$^{4+}$ adopted a different crystal phase than that prepared using Sn$^{2+}$. These results not only show that this approach to producing CTS NPls is flexible and controllable but also suggests that the transformation mechanisms in the two cases are significantly different. To investigate the effect of DDT, we consider the change of crystal structure upon Sn incorporation. Mohite Cu$_2$SnS$_3$ (with nominal oxidation states (Cu$^+$)$_2$(Sn$^{4+}$)(S$^{2-}$)$_3$ can be described as Cu$_{2.667}$Sn$_{1.333}$S$_4$.$^{117}$ For comparison with covellite (Cu$_6$S$_6$), we can consider mohite as Cu$_8$Sn$_4$S$_{12}$ and covellite as Cu$_{12}$S$_{12}$. Stoichiometrically, the transformation consists of replacing four Cu$^+$ cations with four Sn$^{4+}$ cations. In contrast with kuramite formation, in which breaking of disulfide bonds makes space for entering Sn, the formation of mohite involves replacement of Cu with Sn in the covellite framework. In the covellite lattice, one-third of the Cu has planar trigonal coordination, and the remaining two-thirds of the Cu has tetrahedral coordination. The more weakly bound trigonally coordinated copper is presumably more easily extracted and therefore is most likely to be replaced by Sn.
3.1.6 Experimental Section

**Chemicals.** Oleylamine (OAm; 70%), tin(II) chloride (SnCl$_2$; reagent grade, 98%), tin(IV) chloride pentahydrate (SnCl$_4$; reagent grade, 98%), oleic acid (OA; technical grade, 90%), and 1-dodecanethiol (DDT; ≥98%) were purchased from Sigma-Aldrich. CuCl$_2$·2H$_2$O, CuCl, sulfur powder, toluene, and ammonium sulfide (21.2 wt % in water) were purchased from Fisher Scientific.

**Preparing CuS Nanoplatelets.** For the synthesis of ~55 nm hexagonal CuS nanoplatelets (NPls), 1.5 mmol of CuCl$_2$·2H$_2$O was dissolved in a mixture of 10 mL of OAm and 10 mL of toluene and then heated to 70 °C. A 1.5 mL aliquot of ammonium sulfide solution (21.2% in water) was injected into the Cu-OAm to form CuS NPls. After 120 min, 10 mL of ethanol was added to destabilize the NPl dispersion, followed by centrifugation at 4000 rpm for 1 min. The NPls could be re-dispersed in organic solvents including chloroform, hexane, and toluene. Toluene dispersions were used in subsequent experiments reported here.

**Incorporation of Sn into CuS NPls.** In a typical synthesis of kuramite NPls using Sn$^{2+}$ precursor without DDT, 0.167 mmol (31.67 mg) of SnCl$_2$ was dissolved in 10 mL of OAm and then heated to 160 °C. A 0.5 mL aliquot of CuS NPl dispersion containing 0.5 mmol of Cu was injected into Sn-OAm and aged for 20 min. To purify the NPls, 10 mL of ethanol was added, followed by centrifuging at 4000 rpm for about 1 min. Different SnCl$_2$ amounts were used to synthesize Cu$_{3}S_{x}S_{3-x}$ NCs (x ≤ 1) with different compositions. To test the incorporation of Sn$^{4+}$ into CuS, in a typical synthesis, 0.167 mmol (58.3 mg) of SnCl$_4$ was used to replace SnCl$_2$, the other experimental conditions
and procedures were kept the same as those for the synthesis of kuramite NPIs.

For synthesis of mohite Cu$_2$SnS$_3$ NPIs, 0.167 mmol (58.3 mg) of SnCl$_4$ was added to a mixture of 8 mL of OAm and 2 mL of DDT and then heated to 160 °C, followed by injecting 0.5 mL of CuS NPI dispersion into Sn-OAm-DDT and aging for 20 min. To purify the NPIs, 10 mL of ethanol was added, followed by centrifuging at 4000 rpm for about 1 min. To test the incorporation of Sn$^{2+}$ in the presence of DDT, 0.167 mmol (31.67 mg) of SnCl$_2$ was used to replace SnCl$_4$, while the other experimental conditions and procedures were kept the same as those for the synthesis of mohite NPIs.

**Characterization.** Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-2010 or an FEI Tecnai F20 G2, in both cases at an accelerating voltage of 200 kV. TEM grids were prepared by dropping a dilute NC dispersion onto a carbon-coated copper or nickel TEM grid and drying in air. Size distributions were obtained from TEM images by measuring at least 100 (in most cases at least 150) NCs from multiple TEM images from different areas of the grid, using Nanomeasurer v. 1.2. STEM imaging was carried out on a FEI Tecnai F20 200 kV STEM with a Fischione HAADF STEM detector using samples prepared on Ni TEM grids. Powder X-ray diffraction (XRD) measurements were carried out using a Rigaku Ultima IV diffractometer with a Cu Kα X-ray source. Samples were prepared by drop-casting concentrated NC dispersions onto glass slides. UV-vis-near-IR spectra of NC dispersions in chloroform were taken on a Shimadzu UV-3600. X-ray photoelectron spectra (XPS) were acquired on a Phi Versa Probe 5000 with an Al Kα X-ray source.
3.2 Shape Evolution of Biconcave Djurleite Cu$_{1.94}$S Nanoplatelets Produced from CuInS$_2$ Nanoplatelets by Cation Exchange

3.2.1 Introduction

Post-synthesis modification of nanocrystals (NCs) has emerged as a promising general approach to design and produce complex nanomaterials with controlled structures, morphologies, compositions, and crystal phases that cannot be achieved in a single step. Cation exchange (CE) is a central strategy for post-synthesis modification of NCs, which has attracted considerable attention because it provides a predictable means to design crystalline nanostructures with controlled size, shape, and composition. Often, this involves synthesizing a template material whose shape can be well controlled during synthesis, then changing both its composition and crystal phase to produce a new material that maintains the shape of the template. In some approaches, further controlled shape evolution occurs during the CE process. Cu$_{2-x}$S (0 ≤ x ≤ 1) NCs are an ideal template for CE reactions, because the Cu atoms are highly mobile. Copper vacancies allow rapid copper diffusion, and multiple phases within the Cu$_{2-x}$S family share a similar anion sublattice with different arrangements and occupancies of Cu sites. Use of Cu$_{2-x}$S templates also allows the insertion of a new cation without removal of Cu, or with only partial removal of Cu. This can involve filling of Cu vacancies, and changes in the valence of Cu and S atoms to accommodate new cations. Thus, introduction of a second cation can trigger partial or complete CE, or formation of an alloy. Binary metal sulfides (ZnS, CdS, CoS, and PbS), heterogeneous nanostructures (Cu$_{2-x}$S-ZnS, Cu$_{2-x}$S-PbS, and Cu$_{2-x}$S-CdS),
and ternary alloys (CuInS₂, Cu₃SnS₄, CuFeS₂, and CuGaS₂), can be obtained using different cations, ligands, and reaction conditions. Controllable synthesis of these metal sulfides nanostructures not only sheds light upon the growth mechanism of these NCs, but also allows production of new nanostructures with promising applications in photovoltaic devices, bioimaging, and photocatalysis.

In most cases, the final NCs after CE reaction preserve the overall morphology of the template NCs. To promote shape preservation, CE reactions are carried out at mild reaction temperatures, at which the diffusion rate of the incoming cation can be controlled, without disrupting sublattice structure. However, use of conditions at which controlled shape evolution can occur during CE has been less explored. Similarly, while binary-to-binary (e.g., Cu₂₋ₓS to CdS) and binary-to-ternary (e.g., Cu₂₋ₓS to CuInS₂) CE processes are well-explored, transformations from ternary Cu-M-S to binary Cu₂₋ₓS have rarely been considered. Homogeneous or heterogeneous Cu-M-S NCs can be prepared by CE starting from Cu₂₋ₓS NCs. With subsequent exposure of these ternary NCs to Cu⁺ ions under appropriate conditions, the incoming Cu⁺ may diffuse into Cu₂₋ₓS domain to form Cu₂S, or replace the M⁺⁺ in the MS domain, or trigger morphology evolution of the entire NC. The overall process of conversion from Cu₂₋ₓS to a ternary system and back to a different Cu₂₋ₓS phase provides a powerful means of accessing new combinations of composition, crystal phase, and morphology and can provide valuable insights into mechanisms of NC shape and phase evolution.
3.2.2 Preparation and Characterization of Biconcave Djurleite Cu$_{1.94}$S NPLs.

In Section 3.1, we demonstrated the synthesis of copper tin sulfide (kuramite Cu$_3$SnS$_4$ and mohite Cu$_2$SnS$_3$) NPLs using covellite CuS NPL templates under reducing conditions that favor breaking of disulfide bonds in covellite. The Sn$^{4+}$ ions insert into the lattice of the reduced CuS phase. Here, we prepared CIS NPLs by the same strategy and at similar conditions by simply replacing the Sn$^{4+}$ cation with In$^{3+}$. The XRD pattern of the CIS NPLs (Figure 3-13, pink pattern) matches well with that expected for roquesite CuInS$_2$ (ICDD PDF 01-075-0106). Figure 3-11a shows a TEM image of the CIS NPLs, which reveals uniform hexagonal platelets with thicknesses and diameters of 3.7 ± 0.4 and 68.1 ± 3.3 nm, respectively. Size- and thickness-distribution histograms for this and subsequent samples are presented in Figure 3-23. HRTEM imaging of CIS NPLs (Figure 3-11b) shows that the edge and basal planes have lattice spacings of 0.19 and 0.31 nm, corresponding to (220) and (112) planes, respectively. In Figure 3-11c, co-localization of the Cu, In, and S signals of the CIS NPLs in STEM-EDS element mappings is evident by comparing with the corresponding HAADF-STEM image.
Figure 3-11. (a) Representative TEM image of CIS NPls. (b) Top-view and side-view (inset) HRTEM images of CIS NPls. (c) HAADF-STEM image and corresponding STEM-EDS elemental maps for Cu, In, and S, confirming the incorporation of In^{3+} into the product NPls. All elemental maps share the same scale bar of 50 nm.

Next, the CIS NPls were used as a CE template for synthesis of Cu_{2-x}S NCs. Synthesis of a copper sulfide-based ternary metal sulfide from a binary Cu_{2-x}S generally requires a copper-extracting agent. Here, to avoid other factors that affect the CE reactions, we only use OAm, which was already present in the system, as solvent and capping ligand, Cu^{+} to replace In^{3+}, and a mild heating temperature of 160 °C. TEM images shown in Figure 3-12 illustrate the morphology evolution during the transformation. After the CE reaction was initiated, the thin, flat CIS NPls were gradually transformed to a biconcave shape. After the center of the biconcave NPls reached a minimum thickness below 2 nm, the biconcave NPls gradually evolved back to flat NPls. By carefully studying side-view TEM images of these NPls at different reaction times, we divided the shape evolution of NPls into three stages. Initially, from the beginning to 10 min (panels a-d), the thickness of the NPls rapidly grows to 5.0 ±
0.3 nm, while maintaining flat top and bottom surfaces. Near the end of this stage, the edge of the NPs begins to contract in the lateral direction and expand perpendicular to the plates, producing a thickened ring around the edge of the NPs. Then, from 10 to 60 min (panels d-g), the center of the NPs gradually shrinks to a thickness of 1.7 ± 0.4 nm. Meanwhile, the edges of the NPs continue to contract laterally, finally producing a biconcave shape reminiscent of a red blood cell. From 60 to 120 min (panels g-m), the thickness of the NPs gradually expands to 17.8 ± 1.2 nm, and the concave regions are filled, restoring flat lateral surfaces of the NPs. Compared to the template, the NPs are converted into much thicker NPs with smaller diameter. XRD patterns and STEM-EDS results show that, starting from 30 s after Cu⁺ addition, all the NPs have been converted to the djurleite phase with negligible residual In content (<0.3%), which indicates that In³⁺ was removed prior to any significant shape evolution (Figures 3-13). The crystal phase and composition remain the same through the end of the experiment (120 min). These results indicate that the CE process occurs very rapidly, prior to the shape evolution process.
Figure 3-12. Schematic illustration (top panel) of the three-step shape evolution process. Panels a−m show side-view TEM images of NPls during shape evolution. All the panels are at the same magnification with a 50 nm scale bar shown in (a). The CIS NPls rapidly transformed into Cu1.94S NPls, followed by a slower shape evolution from flat NPls to biconcave NPls, then back to thicker NPls with flat surfaces.

Figure 3-13. (a) XRD patterns of NPls undergoing shape evolution after different CE reaction times, and of the CIS template NPls. (b) A typical STEM-EDS spectrum of djurleite biconcave NPls. The inset is the atomic percentage from the spectrum.

We further investigated the novel biconcave NPls using HAADF-STEM imaging. The low-magnification TEM image in Figure 3-14a of selected (30 min) biconcave NPls reveals that the transformed biconcave NPls do not preserve the hexagonal shape of the CIS templates, possibly due to crystal transformation from the highly symmetric tetragonal CIS to less symmetric monoclinic Cu1.94S. Figure 3-14b shows a top view high-resolution HAADF-STEM image of a single biconcave NPl. Compared to the edges, the center of the biconcave NPl has low contrast and less obvious crystallinity, due to limited layers of Cu atoms and less contribution to the 2D projection for imaging. Although djurleite Cu1.94S has a low symmetry crystal structure (structural view in panel c and e), groups of neighboring copper atoms produce bright dots in the HR-
STEM images. The top view of the NPl (Figure 3-14c) reveals that the copper atoms are hexagonally packed (highlighted by red dots), with an interatomic spacing of ~2.4 Å, which is close to the side length of the hexagon highlighted in the djurleite unit cell (Figure 3-14c, below TEM image). Therefore, the top and bottom surfaces of the NPls, which become concave, are perpendicular to the α-axis of the unit cell. From analysis of many TEM images during the transformation, we find that the biconcave NPls tend to preserve their thin centers, rather than breaking to form toroidal structures with a hole in the center. Figure 3-14d exhibits a side view of a typical thin center of a biconcave NPl with a minimum thickness of ~1.78 nm, which is less than a single unit cell along the a direction (lattice constants for djurleite are \( a = 26.90 \text{ Å} \), \( b = 15.75 \text{ Å} \), and \( c = 13.57 \text{ Å} \)). The HR-STEM image of a side view of the NPls (Figure 3-14e) indicates that the distance between two groups of parallel row of three dots is ~6.8 Å, which is nearly consistent with double the interplanar spacing of (800) planes of 3.3 Å, as illustrated in the accompanying unit cell image.
Figure 3-14. (a) Low-magnification TEM image of biconcave NPls after 30 min of shape evolution. HAADF-STEM top-view (b) and side-view (d) images of biconcave NPls after 60 min. (c,e) HR-STEM images from (b) and (d), with scale bars of 1 and 2 nm, respectively. In the schematic crystal structures accompanying (c) and (e), the orange lines indicate the unit cell boundary. Combining the crystallographic data and the HR-STEM image, the thickness direction of biconcave NPls is along the $a$-axis of the djurleite Cu$_{1.64}$S unit cell.
3.2.3 Mechanism of Formation of Biconcave Djurleite $\text{Cu}_{1.94}\text{S}$ NPls.

To investigate the mechanism of formation of biconcave NPls, we carefully examined the NPls early in the transition process, 1 min after injection of the CIS NPls into the $\text{Cu}^+$ solution. Figure 3-15a presents a typical HAADF-STEM image of the NPls extracted at this time. The NPls are monodispersed and smooth. However, as shown in Figure 3-15b,c, each NPl contains numerous randomly distributed defects. Figure 3-15e also provides evidence that atoms are partially missing in some regions, as indicated by the green arrows. Assembly and migration of defects have been observed extensively in other contexts.$^{132, 133}$ These defects may assemble and migrate to the central region of NPls, and then collapse or be expelled at the NPl top and bottom surfaces to produce thinning of the central region of each plate. Figure 3-15d reveals that, in edge-on view, the NPls have a lattice spacing of 0.33 nm, corresponding to $(800)$ planes of the djurleite phase. We also observe some defects on the surface of the NPl in Figure 3-15f, with apparent surface roughness and reduced crystallinity compared to the central planes of the NPl. The central layers in the edge-on view exhibit few visible defects compared to the top-view image, but the thickness of the material being viewed in edge-on view is also much greater than that in the top view. The element mapping in panels (g)-(j) shows Cu and S uniformly distributed across the thickness of the djurleite NPls, while the In signal has dropped to the background level.

When the shape evolution is allowed to continue past 60 min, the concave surfaces are gradually transformed to flat surfaces. This reduces the total surface area, and therefore surface energy, of the NPl. Initially, both the convex and concave portions of
the top and bottom surfaces of the NPIs are symmetric about the central plane of the NPI. However, as shown in Figure 3-16a, when atoms from the convex edge migrate toward the concave center of the NPIs, indicated by the red arrows on the NPIs and schematic illustration, this symmetry may be broken. Interestingly, the thinnest center portion of the NPI, which corresponds to a partial djurleite unit cell (thickness is along the a-axis), occasionally breaks, producing nanorings and nanohorseshoes. Figure 3-16b,c show HRTEM images of these two types of atypical NCs. Both of the NCs have lattice spacings of 0.19 nm, corresponding to the (080) planes of the djurleite phase. Apparently, the nanorings and nanohorseshoes evolved from biconcave NPIs. They were only observed at the later stages of shape evolution, 60 or more minutes after initiation of CE. However, beyond 60 min reaction time, most of the biconcave NPIs were evolving into flat disks, and the formation of nanorings and nanohorseshoes was limited to a few percent of the total NPI population.

Figure 3-15. (a) Low-magnification HAADF-STEM image of NPIs after 1 min of shape evolution. (b,c) TEM and corresponding HAADF-STEM image of a single NPI from (a). (d) Side view HRTEM image
of NPs from (a). (e,f) HR-STEM images of the NPs from (b) and (d). Green arrows indicate regions of defects. (g-i) TEM image and corresponding STEM-EDS elemental maps for Cu and S, with overlaid Cu and S maps in (j), sharing the same magnification with a scale bar of 20 nm. During this early stage of the shape evolution process, the NPs are highly defective, and indium has already been removed from the NPs very rapidly.

**Figure 3-16.** (a) HRTEM image of biconcave NPs evolving to restore flat surfaces. The inset shows the atom migration direction. (b,c) Representative HRTEM images of nanorings and nanohorseshoes.

The mechanism of formation of biconcave NPs has been proposed, however, the mechanism of formation of defects is unclear. The formation of biconcave structures is not unprecedented, however, it is very rare in copper sulfide-based nanostructures. Although some of the studies attributed the formation of concave surface to chemical etching, such etching processes produced sharp corners on NCs’ surfaces. In contrast, our biconcave NPs have rounded corners, which suggesting a mild shape evolution instead of chemical etching. Moreover, none of the ions or functional groups present are known to participate in a surface etching process. We carried out additional
experiments to study the driving force for formation of the defects. Given that the In$^{3+}$ ions are removed instantly, and the crystal phase is converted to djurleite when CE is initiated, one might expect that directly synthesized djurleite NPs would react with Cu$^+$ and additional In$^{3+}$ to form biconcave NPs under conditions matching the CE reaction conditions. To test this possibility, djurleite NPs were directly prepared, using a reported method, by mixing CuCl$_2$, DDT, and OAm at elevated temperature. The TEM image in Figure 3-17a and the XRD pattern in Figure 3-17h (red pattern) reveal that the directly synthesized NPs are in the djurleite phase with hexagonal shape. Upon exposure to In$^{3+}$ and Cu$^+$ under conditions matching the CE reaction conditions, the NPs maintained the hexagonal NP morphology of the template, with only a limited expansion of their thickness (Figure 3-17b). HRTEM images (Figure 3-17c,d) of the treated NPs show interplanar spacing of 0.19 nm in top-view and 0.24 nm in edge-on view, corresponding to (080) and (804) planes of the djurleite phase. The HAADF-STEM image and corresponding elemental maps in Figure 3-17g show uniform distribution of Cu and S in the NPs, and minimal In content. The change of relative diffraction intensity between (080) and (804) planes is due to the thickness expansion. Compared to the CE reaction that led to formation of biconcave NPs, the only difference is that, initially, the In$^{3+}$ ions were present in the surrounding solution instead of inside of the NPs. Therefore, we conclude that the In$^{3+}$ out-diffusion process is essential for evolution to biconcave structures.
Mu et al. showed that CuInS$_2$ nanorings (NPls with a central region removed) can be prepared from template Cu$_{2-x}$S NPls by a CE reaction with In$^{3+}$. This is, in a sense, the opposite of the present study, in that shape evolution resulted from In$^{3+}$ insertion, rather than removal. The formation of a hole in the center of these NPls during CE with In$^{3+}$ was attributed to the nanoscale Kirkendall effect, first reported by Alivisatos and coworkers. According to this mechanism of shape evolution, the basal planes of the
NPiIs are well passivated by the ligands. Therefore, the edge planes are relatively active, which allows In$^{3+}$ ions to diffuse into the NPi. Indiscriminate ion exchange through the broad top and bottom surfaces would lead to erosion of the NPi, destroying the morphology and symmetry of the NPiIs. In contrast, the edges of the NPiIs generally tend to be ragged and defective, and less-well protected by ligand. Thus, CE through the edges apparently has a lower barrier. The presence of a Cu extracting agent such as trioctylphosphine can facilitate removal of Cu$^+$ from the NPiIs. Formation of center-hollowed NPiIs can be attributed to the faster diffusion rate of Cu$^+$ compared to In$^{3+}$ in that system. Similarly, in our study, when In$^{3+}$ ions are replaced by Cu$^+$ due to a high concentration of Cu$^+$ in the environment, the edges of the NPi provide a more accessible pathway for in- and out-diffusion compared to the top and bottom surfaces. Combined with all the results and discussion above, we propose that formation of biconcave NPiIs occurs by a similar nanoscale Kirkendall effect, but that in this case, removal of In$^{3+}$ is much faster than uptake of Cu$^+$. Note that transformation from CuInS$_2$ to Cu$_{1.9}$S requires uptake of multiple Cu$^+$ cations for each In$^{3+}$ that is removed. Initially, In$^{3+}$ rapidly diffuses from the center to the edges of the NPiIs, where CE between Cu$^+$ and In$^{3+}$ occurs, producing the swollen edges of the NPiIs. Transformation of the crystal phase to djurleite appears to occur very rapidly, prior to any shape evolution. The incoming Cu$^+$ ions migrate toward the center of the NPiIs much more slowly, leaving extensive cation defects in the djurleite NPiIs (Stage 1). These defects then assemble and migrate to the center of the NPiIs. The metastable center then collapses and donates its Cu$^+$ and S$^{2-}$ to the well-crystallized edge regions, producing concave surfaces at the
center (Stage 2). However, the biconcave NPs are not a thermodynamically stable structure. Compared to flat NPs, they have higher surface area and more step edges or exposed high-index facets. Thus, the biconcave NPs further transform back to flat NPs that are thicker than the starting NPs (Stage 3). The whole process is illustrated in Figure 3-18. The last step of shape evolution is also considered as a surface area minimization process. Therefore, we consider the whole transformation process to be a combination of both kinetically and thermodynamically controlled processes.

![Figure 3-18. Schematic illustration of overall shape evolution.](image)

Additionally, we found that the rate of the shape evolution process can be governed by the initial concentration of Cu⁺ and by the reaction temperature. By decreasing (120 °C) or increasing (200 °C) the temperature during the CE process, the reaction can be dramatically decelerated or accelerated but still follows the same overall shape evolution process. As shown in Figure 3-19a, after 30 min of reaction at 120 °C, the NPs nearly preserved the morphology of the CIS template, with only a thickness expansion, which is similar to the NPs shown in Figure 3-12b (1 min case). When the CE reaction time was extended to 75 min, the NPs had a thickened ring around the
edge, as shown in Figure 3-19b. The minimum thickness of NPls was observed at 180 min, and their flat surfaces had been restored after 5 h (Figure 3-19c,d). On the other hand, as shown in Figure 3-19e,f, the NPls treated at higher temperature required only 15 min to form biconcave NPls, then grew to thicker NPls with nearly flat surfaces (similar to Figure 3-12m, 120 min case), after 30 min of CE, implying an accelerated reaction compared to the standard conditions.

![Figure 3-19. TEM images of djurleite NPls transformed using a decreased (120 °C) and increased (200 °C) temperature. The temperature and reaction time are labeled on each panel. The inset in (a) shows a side view of the NPls, sharing the same magnification with the main panel.](image)

To investigate the Cu⁺ concentration dependence of NPl evolution of crystal phase and shape, we treated the CIS NPls (prepared by adding 0.5 mmol In³⁺ to CuS nominally prepared from 0.5 mmol Cu⁺) with 0.1 mmol of Cu⁺. As shown in Figure 3-20a, the resulting NPls retained the flat surfaces of the template NPls, with only a slight increase in thickness. Both HRTEM images and XRD pattern confirmed the preservation of CIS NPls, indicating that 0.1 mmol of Cu⁺ is insufficient to trigger either shape or crystal evolution. When the CE reaction was initiated with 0.4 mmol of Cu⁺,
the transformed NPls started exhibiting a slightly biconcave shape and had transformed to the djurleite crystal phase. Such incomplete shape evolution is consistent with our previous observation that CE reactions occur prior to the shape evolution process. In this case, the supernatant remained slightly blue in color, suggesting the presence of a small excess of Cu$^+$ that was not incorporated. When 0.7 and 1.0 mmol (standard condition) of Cu$^+$ were used, an accelerated overall process was observed with increasing initial Cu$^+$ concentrations. Both shape and crystal structure evolution are sensitive to the concentration of Cu$^+$, and ~0.4 mmol is the critical amount required to trigger the both processes at this scale.

The biconcave NPls can be also produced using other ternary copper sulfide NPl templates. As shown in Figure 3-21, the products of Cu$^+$ treated mohite copper tin sulfide NPls were a mixture of biconcave NPls and striped NPls in which the crystal phase was converted from mohite Cu$_2$SnS$_3$ to djurleite Cu$_{1.94}$S. Similar results were observed using chalcopyrite CuFeS$_2$ NPls. These observations imply that the synthesis of biconcave NPls can be applied to different stoichiometric and crystal systems of ternary NPls. Although differences in diffusion rates, cation radii and valences between In$^{3+}$, Sn$^{4+}$, and Fe$^{3+}$ produce variations in reaction rate and formation of a mixture of biconcave and striped NPls, we believe the overall phase and shape evolution process starting from these other ternary NPls follows the same general mechanism as proposed for CIS templates.
Figure 3-20. (a-d) TEM image, top and side view HRTEM images, HAADF image and corresponding elemental maps of djurleite NPls produced using 0.1 mmol of Cu⁺, respectively. Panel (e-h) and panel (i-)
show the corresponding results obtained using 0.4 mmol and 0.7 mmol of Cu⁺, respectively. Scale bars
in panels (d), (h), (l) are 200 nm. (m) TEM image of djurleite NPls produced using 1.0 mmol of Cu⁺
(standard conditions used elsewhere in the manuscript). Insets in panels (e) and (i) show the edges of the
NPls, at the same magnification as the main panel. Insets in panels (a), (e) and (i) show photographs of
the supernatant after the CE reaction, suggesting that excess Cu⁺ is required to trigger the shape evolution.
(n) XRD patterns of CIS template and NPls produced using different amount of Cu⁺. In panel (d) the
indium signal is collocated with the other elements, while in panels (h) and (l), for NPls treated with
increased amount of Cu⁺, the detectable residual indium signal is randomly dispersed. Top-view HRTEM
images in panels (f) and (j) indicate that the center of NPls is less crystalline, compared to the edges, which is consistent with our proposed mechanism.

**Figure 3-21.** (a) TEM, (b) HRTEM image and (c) XRD pattern of biconcave NPls produced using copper tin sulfide NPl templates. (d) TEM, (e) HRTEM image and (f) XRD pattern of biconcave NPls produced using copper iron sulfide NPl templates.
3.2.4 Synthesis and Mechanism of Striped, Flat and Thick Djurleite Cu$_{1.94}$S NPs.

When the flat surface of the NPs has been restored, most of the final NPs exhibit a stripe across their center, in edge-on view. However, both ends of the edges are smooth, so that the possibility of etching on the edge is excluded. Figure 3-22a clearly shows a stripe on each NPl when viewed from the edge. The thickness of the stripe is not strictly fixed, but is usually between 1 to 2 nm, similar to the minimum thickness in the center of the biconcave NPs. As shown in Figure 3-22b, the interplanar spacing was found to be 0.33 nm [(800) planes], indicating that the stripe is perpendicular to $a$-axis of the djurleite unit cell. As shown in Figure 3-22d, the light blue area is the intact djurleite unit cell, growing along the direction of the green arrows ($a$-axis). The light yellow region is the stripe on the edge. Stacking faults are visible at the interfaces between the stripe and edge regions (inside of red dashed lines). The atoms are well-organized in both parts. STEM-EDS mapping in Figure 3-22f-h confirms that the Cu and S distributions are uniform across the striped region. Therefore, we propose a mechanism of stripe formation as follows (Figure 3-22i). Initially, the NPs collapse and reach a minimum thickness of 1-2 nm, which is only a partial unit cell along the $a$-axis. The ripening process in Stage 3 requires the migration of atoms from the edge to the center. The new layers of atoms are deposited on the residual layers, in order to grow djurleite unit cells. However, they are bounded by stacking faults. After that, the defect-free djurleite unit cells grow along the direction of the green arrows. Finally, the stripe reaches the edge of the NPl as the diameter decreases during the ripening process.
Figure 3-22. (a) TEM and (b) HRTEM image of NPs with a stripe. (c,d) HAADF-STEM images for striped NPs at different magnifications. The light blue area shows defect-free djurleite unit cells, while the light yellow area shows the residual layers that we suggest were present during formation of biconcave NPs. The two areas are bounded by stacking faults, indicated by red dashed lines. The green arrows show the direction of thickness expansion. (e-h) TEM image and corresponding STEM-EDS elemental maps for Cu and S. The scale bar for panel (d) is 2 nm, while the scale bar for other panels is 10 nm. (i) A schematic illustration of the formation of striped NPs. The copper atoms are distributed in chevron-like arrangements when viewed along the b-axis, and the pattern can be matched with the red dashed lines in panel (i). The black line in both panels (d) and (i) represents the boundary of a djurleite unit cell.

Figure 3-22. Size distribution (a) and thickness distribution (b) of CIS NPs. Thickness distribution of center of NPs at reaction times of 10 min (c), 60 min (d), and 120 min (e), respectively.
3.2.5 Experimental Section

**Chemicals.** All chemicals were used as received. Indium chloride (InCl₃, 98%), copper(I) chloride (CuCl, ≥99.995%), tin(IV) chloride (SnCl₄, reagent grade, 98%), iron acetylacetonate [Fe(acac)₃, 99.99%], oleylamine (70%, OAm), oleic acid (technical grade, OA 90%), 1-octadecene (ODE, technical grade, 90%), tert-dodecanethiol (t-DDT, 98.5%), and 1-dodecanethiol (DDT, ≥98%) were purchased from Sigma-Aldrich. Cu(NO₃)₂·2.5H₂O, CuCl₂·2H₂O, toluene, and ammonium sulfide (21.2 wt% in water) were purchased from Fisher Scientific.

**Preparing CuS Templates.** For the synthesis of hexagonal CuS NPls, 1.5 mmol of Cu(NO₃)₂·2.5H₂O was dissolved in a mixture of 10 mL of OAm and 10 mL of toluene, then heated to 70 °C under an argon flow. 1.5 mL of ammonium sulfide (AS) solution (21.2% in water) was injected into the Cu-OAm to form CuS NPls. After 2 h, 10 mL of ethanol was added to destabilize the NPl dispersion, followed by centrifugation at 4000 rpm for 1 min. To remove excess AS and OAm, the NCs were washed by precipitation upon addition of ethanol, followed by redispersion in chloroform. This purification process was applied to all of the NPls described in the following sections. The NPls could be redispersed in organic solvents including chloroform, hexane, and toluene.

**Preparing CIS Templates.** A CuS NPl dispersion was prepared by dispersing dry CuS NPls (one batch, typically ~230 mg) in 9 mL of OAm. A mixture of 0.5 mmol InCl₃, 8 mL of OAm, and 2 mL of DDT was held under flowing argon at ambient temperature for 30 min before heating to 160 °C. Next, 3 mL of CuS NPl dispersion was injected into the mixture, and the solution was held at this temperature for 30 min. To collect
the NPLs, 10 mL of ethanol was added, followed by centrifuging at 4000 rpm for 1 min.

**Synthesis of Biconcave Djurleite NPLs.** A CIS NPl dispersion was prepared by dispersing dry CIS NPLs (one batch, typically ~70mg) in 3 mL of OAm. A mixture of 1 mmol of CuCl, and 10 mL of OAm was held under flowing argon at ambient temperature for 30min, followed by heating to 200 °C. The mixture was then cooled to 160 °C, followed by injection of 3 mL of the CIS dispersion. Aliquots were extracted via syringe at different reaction times and immediately quenched by injecting them into a mixture of toluene and methanol.

**Synthesis of djurleite NPLs.** The synthesis of djurleite NPLs was adapted from a previous report with some modifications. A mixture of 1 mmol of CuCl₂·2H₂O, 5 mmol of OAm (~1.65 mL) and 10 mL of ODE was degassed at ~80 °C for 30 min and then quickly heated to 180 °C under argon. 4 mL of t-DDT was added to the reaction mixture at 120 °C. The mixture was held at 180 °C for 5 min before being quenched with 10 mL ethanol. The NPLs were collected by centrifugation at 4000 rpm for 1 min. The NPLs were purified by precipitation upon addition of ethanol followed by redispersion in chloroform. The NPLs were dispersed in hexane for further treatment.

**Exposing djurleite NPLs to In³⁺ and Cu⁺.** The dry djurleite NPLs (one batch, typically ~27 mg) were dispersed into 3 mL OAm to obtain a djurleite NPL dispersion. A mixture of 0.5 mmol InCl₃, 1 mmol CuCl and 10 mL of OAm was degassed at room temperature under argon protection followed by heating to 200 °C. Then, the mixture was cooled to 160 °C, followed by injection of 3 mL of djurleite solution. The mixture was held at 160 °C for 30 min before being quenched with 10 mL ethanol. The NPLs were collected
by centrifugation at 4000 rpm for 1 min. The NPIs were purified by precipitation upon addition of ethanol followed by redispersion in chloroform. The NPIs were finally dispersed in hexane.

**Characterization.** Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-2010 at an accelerating voltage of 200 kV. High-resolution TEM (HRTEM) images were obtained on a FEI Tecnai G2 F30 at 300 kV. High-angle annular dark field scanning TEM (HAADF-STEM) images, HR-STEM images, and STEM energy-dispersive X-ray spectroscopy (STEM-EDS) maps were collected using a JEOL JEM-ARM200F STEM equipped with spherical aberration correctors on the image, at an accelerating voltage of 200 kV. TEM grids were prepared by dropping a dilute NC dispersion onto a carbon-coated copper or nickel TEM grid and allowing the sample to dry under air. Size distributions were obtained from TEM images by measuring at least 100 NCs from multiple TEM images from different areas of the grid, using Nanomeasurer v.1.2. Powder X-ray diffraction (XRD) measurements were carried out using a Rigaku Ultima IV diffractometer with a Cu Kα X-ray source. Samples were prepared by drop-casting concentrated NC dispersions onto glass slides.
3.3 Synthesis of Biconcave Metal Sulfide Nanoplatelets by Cation Exchange

3.3.1 Introduction

Cation exchange (CE) has emerged as an intriguing and important means to produce semiconductor nanocrystals (NCs) with complex and tunable compositions, crystal phases and morphologies. Basically, a CE process can be described as the replacement of cations of a starting NC with heterocations, while preserving the original anion sublattice, which in some cases undergoes a structural reorganization.\(^4\,126,143,144\) Cu\(_{2-x}\)S NCs have emerged as an ideal template for CE reactions, because Cu atoms are highly mobile at elevated temperatures, enabling efficient interstitial diffusion and substitution of incoming cations.\(^123,145\) Synthesis of semiconductor NCs with morphology-dependent optical, electrochemical, and magnetic properties is of great interest.\(^146-148\) However, many opportunities to develop new morphologies of various metal sulfide NCs remain, and creating these new morphologies can expand the potential properties and thereby applications of these materials. Therefore, the Cu\(_{2-x}\)S class of nanomaterials, known for its various possible morphologies and cation compatibility of the sulfur sublattice, has been used as a CE template to develop previous unavailable morphology for metal sulfide NCs.\(^36,145,149\)

Ion exchange-induced shape evolution (or shape preservation) of semiconductor NCs has attracted considerable attention.\(^47,143,150\) However, the mechanisms of morphology transformation and retention have not been fully elucidated. Quasi-spherical NCs were typically used as the template for CE reactions due to the expected isotropic ion diffusion rate.\(^47,58,150\) Those template NCs usually have low crystallinity
and simple structure, so that further shape evolution is limited and is difficult to observe. Therefore, we were inspired to perform CE reactions using templates with relatively complex anisotropic structure. Either morphology evolution or preservation from template NCs with complex morphologies not only sheds light on mechanisms of solid-solid phase transformation but also provides the ability to manipulate NCs’ size, shape, and internal structure.
3.3.2 Synthesis of Biconcave CdS, ZnS, CuInS\(_2\) and MnS Nanoplatelets via Cation Exchange

As described in Section 3.2, biconcave djurleite Cu\(_{1.94}\)S NPls were prepared by reacting Cu\(^+\) with CuInS\(_2\) NPls at 160 °C for 1 hour. Generally, we attribute the formation of the biconcave structure of these NCs to generation of defects produced by rapid In\(^{3+}\) out-diffusion. These defects then migrate to the center of the NPls to trigger the local collapse of the center of the NPls. Figure 3-23a shows transmission electron microscopy (TEM) images of the uniform biconcave NPls produced by this method. Figure 3-23b-c show top-view and side-view HR-STEM images of biconcave NPls, with observed lattice spacings of 0.19 nm [(080) planes] and 0.33 nm [(800) planes], respectively.

![Figure 3-23](image)

**Figure 3-23.** (a) TEM image of Cu\(_{1.94}\)S biconcave NPls. (b) Top-view and (c) side-view HR-STEM images of the NPls.

Copper sulfide NCs have been considered an ideal template for cation exchange to produce a variety of metal sulfide NCs products such as CdS, ZnS and PbS\(^{47,60,112}\) but most of the Cu\(_{2-x}\)S NC templates studied to date have flat surfaces and relatively simple morphologies, or are quasi-spherical, which limits the accessible morphologies of the product metal sulfide NCs. The biconcave NCs are particularly interesting templates...
because they have curved surfaces (like spherical NCs) but are strongly anisotropic (like NPls that have flat surfaces). Moreover, unlike spherical particles, these templates exhibit both convex and concave regions of surface curvature. We find that biconcave CdS NPls can be produced by reacting the biconcave Cu$_{1.94}$S template NCs with Cd$^{2+}$ and a copper-extracting agent, trioctylphosphine (TOP), at elevated temperature. The XRD pattern of the resulting NPls matches well with the wurtzite-type CdS phase (greenockite, Figure 3-24a).

![Figure 3-24](image)

**Figure 3-24.** XRD patterns of biconcave (a) CdS, (b) ZnS, (c) CuInS$_2$, and (d) MnS NPls obtained by cation exchange.

The TEM image in Figure 3-25a shows that the biconcave NPl morphology of the Cu$_{1.94}$S template is retained after the CE reaction (Cu$^+$ to Cd$^{2+}$). As revealed by top-view HR-STEM image in Figure 3-25b, the atoms are hexagonally packed in the NPls.
The (110) and (100) planes are visible in the top view of the NPls, according to the fast Fourier transform (FFT) of Figure 3-25b. Therefore, the top and bottom surfaces of the NPls, which remain concave, are perpendicular to the c-axis of the CdS unit cell. Figure 3-25c exhibits a side view of a typical thin center of a CdS biconcave NPl with a minimum thickness of ~2.5 nm. STEM-EDS mapping of the NPls confirms the colocalization of Cd and S, with negligible residual Cu. Figure 3-25e illustrates the hexagonal arrangement of S atoms in the unit cells of Cu1.94S and CdS when viewed along the c-axis. The hexagonal arrangement of sulfur atoms in Cu1.94S is slightly disordered. The distance between neighboring S atoms in CdS is 2.39 Å, which is only 5.3% larger than the corresponding distance in the Cu1.94S template (2.27 Å). This allows the transformation to take place with minimal changes in the sulfur framework. This similarity not only facilitates uptake of Cd\(^{2+}\), but also helps to preserve the biconcave structure of the templates.
Figure 3-25. (a) TEM image of transformed biconcave CdS NPls. (b) Top-view and (c) side-view HR-STEM image of the CdS NPls. The inset in panel (b) shows the corresponding FFT of top-view HR-STEM image. (d) HAADF STEM image and corresponding elemental maps for Cd, Cu, and S. The scale bars in panel d are 20 nm. (e) Sulfur atoms projections of Cu$_{1.94}$S (viewed along a-axis) and CdS (viewed along c-axis). The black lines indicate the boundaries of the unit cells.

In addition to biconcave NPl templates, flat Cu$_{1.94}$S NPls with different thicknesses can be converted into CdS with preservation of morphology. As shown in Figure 3-26, Cu$_{1.94}$S NPls with thickness of 4.5 ± 0.4 nm and 15.2 ± 0.7 nm were prepared using different CE reaction (In$^{3+}$ to Cu$^+$ exchange) time. Then, both of the ~4.5 nm (denoted as “thin”) and ~15.2 nm (denoted as “thick”) Cu$_{1.94}$S NPls were converted into CdS NPls with flat surfaces. The thickness of the obtained CdS NPls is close to that of the template NPls, suggesting the similar cation replacement process as proposed for formation of biconcave CdS NPls. These observations indicate that a variety morphologies of Cu$_{2-x}$S can be transformed into CdS NCs via CE reactions, consistent with our discussion above.
Figure 3-26. TEM images of (a) thin and (b) thick Cu$_{1.94}$S NPls; TEM images of transformed CdS NPls produced from (c) thin and (d) thick Cu$_{1.94}$S NPls. The EDS results and corresponding elemental maps of (e) thin and (f) thick CdS NPls. The scale bar in panel f is 100 nm. The thickness distribution histogram is displayed, indicating the thickness preservation before and after CE reactions.

Similar to the formation of biconcave CdS NPls, biconcave ZnS NPls can be produced via CE reactions using Zn$^{2+}$ and TOP. As shown in Figure 3-27a, Zn$^{2+}$ and TOP-treated Cu$_{1.94}$S NPls have a similar biconcave structure to the template NPls. The XRD pattern (Figure 3-24) of the transformed NPls corresponds to the wurtzite ZnS phase, indicating the complete conversion from Cu$_{1.94}$S to ZnS. Top-view and side-view
HRTEM images in Figure 3-27b-c reveal the lattice spacings of 3.3 Å, 2.9 Å and 3.1 Å, corresponding to the (100), (101) and (002) planes of wurtzite ZnS, respectively. In contrast with the product CdS and ZnS whose Cu$^+$ ions are completely replaced by Cd$^{2+}$ or Zn$^{2+}$, respectively, CE reactions using In$^{3+}$ produce ternary CuInS$_2$ alloy NPs. The TEM and HRTEM images (Figure 3-27d-f) and XRD pattern (Figure 3-24) of the obtained NPs indicate the formation of biconcave CuInS$_2$ NPs after CE reaction. In$_2$S$_3$, which is the complete CE reaction product, has a crystal structures with an fcc stacking of S$^{2-}$ anions. That anion framework is intrinsically different from hexagonal Cu$_{2-x}$S and wurtzite CIS (with hcp packing), which is an important factor in avoiding complete CE from Cu$_{1.94}$S into In$_2$S$_3$. This is consistent with a previous report that wurtzite CuInS$_2$ was obtained by In$^{3+}$ incorporation into low chalcoite (which also has hcp packing in its sulfur framework).\textsuperscript{151} The formation of CuInS$_2$ NPs, together with the process for preparation of Cu$_{1.94}$S template NPs, actualize a reversible composition and phase interconversion between CuInS$_2$ and Cu$_{1.94}$S. In addition, we observed the formation of biconcave MnS NPs under similar reaction conditions to those used above (Figure 3-27g-i). The XRD pattern (Figure 3-24) of the NPs confirms the formation of MnS phase. Zincblende, rocksalt and wurtzite are three distinct polymorphs that can be produced via colloidal synthesis for MnS NCs. Consistent with the formation of wurtzite CdS, ZnS and CuInS$_2$ NPs, the formation of wurtzite-type MnS is due to retention of the anion sublattice with hcp stacking in the Cu$_{1.94}$S template during the CE process.
Most previously reported ion exchange reactions were performed on simple nanostructures such as spheres, rods and plates. The preservation of the morphology of these structures is usually feasible because they have relatively low surface energy, which makes them relatively stable during post-synthetic modifications. More importantly, most of the facets of these nanostructures are well passivated by ligands, so the CE process can only occur on the less well-passivated facets. The limited and controllable ion diffusion rate can also facilitate the morphology preservation of template NCs. In contrast, the maintenance of the biconcave structure, which is relatively complex and thermodynamically metastable, reflects the possibility of different mechanisms when using different cations. Basically, preservation of the biconcave structure of djurleite Cu$_{1.94}$S requires similar hcp stacking of the sulfur...
sublattice of the target metal sulfide NCs. Both CdS and ZnS intrinsically have preferential wurtzite crystal structure. Compared to CdS and ZnS, the formation of CuInS₂ only requires partial cation replacement in a unit cell. Both fcc and hcp CuInS₂ can be easily produced through colloidal synthesis. However, the sulfur sublattice of djurleite Cu₁.₉₄S provides a template that drives formation of the hcp CIS phase here. Similarly, although wurtzite MnS is metastable as a bulk solid, exclusive formation of the wurtzite MnS phase here also suggests that both anion and cation sublattice features from djurleite Cu₁.₉₄S were retained during the CE process.
3.3.3 Shape Evolution of Biconcave Djurleite Cu$_{1.94}$S Nanoplatelets via Cation Exchange

We also carried out CE reactions of biconcave Cu$_{2-x}$S templates using other cations (Sn$^{2+}$, Sn$^{4+}$, Pb$^{2+}$), under similar reaction conditions to those used with Zn$^{2+}$, Cd$^{2+}$, Mn$^{2+}$ and In$^{3+}$. The HRTEM images (Figure 3-28) confirm the formation of copper-free metal sulfide NCs. However, none of the products retained the biconcave morphology from the template NPls (Figure 3-28). Instead, the obtained metal sulfide NCs exhibit relatively irregular morphologies. In contrast to those cations that can be used to produce biconcave NPls, SnS, PbS and SnS$_2$ all have fcc cation and anion sublattices. As a result, the anion atoms in these transformed NCs must undergo additional migration and reorganization to construct new NCs, producing shape evolution of the template NPls. While not the primary focus of this work, we noticed that the shape of the NCs varied when using different cations, but the overall size of the template NCs was retained. The difference in the morphology of these NCs is attributed to the nature of preferential crystal structure as well as radii of the heterocations.
Figure 3-28. (a) TEM and (b) HRTEM images of transformed SnS NPs. (c) TEM and (d) HRTEM images of transformed PbS NPs. (e) TEM and (f) HRTEM images of transformed SnS$_2$ NPs.
3.3.4 Experimental Section

Chemicals. All chemicals were used as received. Cadmium chloride (CdCl₂, 99.99%), zinc chloride (ZnCl₂, ≥ 97%), indium chloride (InCl₃, 98%), tin (II) chloride (SnCl₂, reagent grade, 98%), manganese (II) chloride (MnCl₂, 99.999%), lead chloride (PbCl₂, 98%), tin (IV) chloride (SnCl₄, reagent grade, 98%), oleylamine (OAm, 70%), trioctylphosphine (TOP, 90%) and 1-dodecanethiol (DDT, ≥ 98%) were purchased from Sigma-Aldrich. Cu(NO₃)₂·2.5H₂O, toluene, and ammonium sulfide (21.2 wt % in water) were purchased from Fisher Scientific.

Preparing CuS Templates. For the synthesis of hexagonal CuS NPls, 1.5 mmol of Cu(NO₃)₂·2.5H₂O was dissolved in a mixture of 10 mL of OAm and 10 mL of toluene, then heated to 70 °C under an argon flow. 1.5 mL of ammonium sulfide (AS) solution (21.2% in water) was injected into the Cu-OAm to form CuS NPls. After 2 h, 10 mL of ethanol was added to destabilize the NPl dispersion, followed by centrifugation at 4000 rpm for 1 min. To remove excess AS and OAm, the NCs were washed by precipitation upon addition of ethanol followed by redispersion in chloroform. This purification process was applied to all of the NPls described in the following sections. The NPls could be redispersed in organic solvents including chloroform, hexane, and toluene.

Preparing CIS Templates. The CuS NPl solution was prepared by dispersing dry CuS NPls (one batch, typically ~230 mg) in 9 mL of OAm. A mixture of 0.5 mmol InCl₃, 8 mL of OAm and 2 mL of DDT was held under flowing argon at ambient temperature for 30 min before heating to 160 °C. Then, 3 mL of CuS NPl dispersion was injected.
into the mixture and the solution was held at this temperature for 30 min. To collect the NPIs, 10 mL of ethanol was added, followed by centrifuging at 4000 rpm for 1 min.

**Synthesis of Cu$_{1.94}$S NPIs.** The CIS NPI solution was prepared by dispersing dry CIS NPIs (one batch, typically ~70 mg) in 3 mL of OAm. A mixture of 1 mmol of CuCl and 10 mL of OAm was held under flowing argon at ambient temperature for 30 min followed by heating to 200 °C. Then, the mixture was cooled to 160 °C, followed by injection of 3 mL of the CIS dispersion. To produce biconcave Cu$_{1.94}$S NPIs, the solution was held at this temperature for 60 min. The thin (~4.5 nm) and thick (~15 nm) Cu$_{1.94}$S NPIs with flat surfaces are produced using reaction time of 1 min and 120 min, respectively. To collect the NPIs, 10 mL of ethanol was added, followed by centrifuging at 4000 rpm for 1 min.

**Cation Exchange Reaction Using Biconcave Cu$_{1.94}$S NPI Templates.** The biconcave djurleite NPI solution was prepared by dispersing dry biconcave NPIs (one batch, typically ~51 mg) in 5 mL of TOP. A mixture of 0.5 mmol CdCl$_2$ (or other cation precursors as indicated) and 10 mL of OAm was held under flowing argon at ambient temperature for 30 min before heating to 160 °C. Then, 5 mL of Cu$_{1.94}$S NPI dispersion was injected into the mixture and the solution was held at this temperature for 30 min. To collect the NPIs, 10 mL of ethanol was added, followed by centrifuging at 4000 rpm for 1 min.

**Characterization.** Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-2010 at an accelerating voltage of 200 kV. High-resolution TEM (HRTEM) images were obtained using a FEI Tecnai G2 F30 at an accelerating voltage
of 300 kV. High angle annular dark field scanning TEM (HAADF-STEM) images, HR-STEM images, and STEM energy dispersive X-ray spectroscopy (STEM-EDS) maps were collected using a JEMARM200F STEM equipped with spherical aberration correctors on the image at an accelerating voltage of 200 kV. TEM grids were prepared by dropping a dilute NC dispersion onto a carbon-coated copper or nickel TEM grid and allowing the sample to dry under air. Size distributions were obtained from TEM images by measuring at least 100 NCs from multiple TEM images from different areas of the grid, using Nanomeasurer v.1.2. Powder X-ray diffraction (XRD) measurements were carried out using a Rigaku Ultima IV diffractometer with a Cu Kα X-ray source. Samples were prepared by drop-casting concentrated NC dispersions onto glass slides.
3.4 Ag⁺ Incorporation-Induced Shape Evolution of Covellite CuS Nanoplatelets

3.4.1 Introduction

Copper sulfide-based heterostructures have attracted extensive attention due to their potential for applications in catalysis, electronics, optics, and photovoltaics. These heterostructures possess advantages including tunable size, phase, and composition as well as a good compatibility for integration with other metal or semiconductor NCs. The copper sulfide class of materials is known for p-type semiconductor behavior. Integration with other heterodomains may provide a means of influencing charge carrier separation and recombination that is not available in homogeneous structures, and may also produce shifts in localized surface plasmon resonance (LSPR) energy and intensity, or promote other synergistic interactions between domains. Preparation of these heterostructures can be generally divided into one-pot mixing methods and multistep growth methods. Both of the synthetic routes involve nucleation of Cu₂₋ₓS template (seed) NCs, followed by incorporation of incoming cations.

According to the previous reports and our recent discovery, the outcome of cation incorporation into Cu₂₋ₓS NCs strongly depends on the valence of the incoming cation. Cation incorporation into Cu₂₋ₓS NCs using trivalent (e.g., In³⁺ and Sb³⁺) and tetravalent (e.g., Sn⁴⁺ and Ge⁴⁺) cations produces homogeneous ternary alloy (e.g., CulnS₂ or Cu₂SnS₃). In contrast, incorporation of divalent cations (e.g., Zn²⁺ and Cd²⁺) results in heterogeneous Cu₂₋ₓS-MS NCs, or copper-free MS NCs. The cation valence selectivity arises from conflicts between charge balance and coordination...
between Cu\(^+\) and divalent cations.\(^5\) However, general rules and mechanisms governing monovalent cation (Au\(^+\) and Ag\(^+\)) incorporation are less clear. The outcomes may depend upon the preferred coordination numbers and cation radius of the incoming cations. Similar to divalent cations, incorporation of tetragonally coordinated Au\(^+\) into Cu\(_{2-x}\)S NCs leads to a complete replacement of all Cu\(^+\) in one Cu\(_{2-x}\)S unit cell, producing Cu\(_{2-x}\)S-Au\(_2\)S heterostructures.\(^{57,111,158}\) However, because ternary Ag-Cu-S alloy and binary Ag\(_2\)S NCs are both stable and accessible \textit{via} colloidal synthesis,\(^{57,159-161}\) the results of the Ag\(^+\) incorporation process are expected to depend on the initial template and reaction conditions.

Most copper sulfide phases exhibit hcp stacking of their sulfur sublattice (e.g., high chalcocite Cu\(_2\)S, djurleite Cu\(_{1.94}\)S, and roxbyite Cu\(_{1.81}\)S).\(^{36,58,143}\) Moreover, products of cation incorporation almost always inherit the crystal structure (especially the anionic sublattice) of the template phase.\(^{151}\) As a result, the product NCs after cation incorporation are strongly influenced by the anionic framework of the template. Among many possible copper sulfide crystal phases and compositions, covellite CuS, which is one of the stoichiometric extremes, is unique in several ways. The stacking of sulfur layers in covellite CuS can be described as ABAABA, which is neither the typical hcp-type ABABAB stacking nor the fcc-type ABCABC stacking. Furthermore, rather than simple cation replacement observed in typical CE reactions, the process of cation incorporation into covellite CuS involves additional redox reactions associated with the breaking of disulfide bonds and changes in the oxidation state of sulfur.\(^{44,59}\) Colloidal synthesis of CuS nearly always produces single-crystal nanoplatelets (NPLs) with the c-
axis of the covellite crystal structure perpendicular to the large flat surfaces of the NPLs.

As a template for CE reactions, these CuS NPLs have advantages of fixed morphology, stable and pure crystal phase, and relatively easy observation of formation of heterodomains, making them ideal templates for studying cation exchange and incorporation processes. Thus, we have employed CuS NPLs in the present study.
3.4.2 Synthesis of CuS-Ag$_2$S Plate-Satellite Heterostructure via Cation Exchange

Covellite CuS NCs generally adopt a plate-like morphology due to the intrinsic layered structure of covellite. The basal planes of covellite (perpendicular to the c-axis) are well passivated by the capping ligands. The TEM image in Figure 3-29a illustrates the hexagonal plate-like morphology of the covellite CuS template NPs. CE reactions of Cu$_{2-x}$S NCs usually require a copper extracting agent (e.g. trioctylphosphine (TOP) or dodecanethiol (DDT)) to break the Cu-S bonds for subsequent cation replacement. However, covellite CuS is an exception because of existing disulfide bonds and average valence of +1 and -1 for Cu and S. This unique structural feature allows simultaneous redox reactions and cation incorporation. Due to the greater thermodynamic stability of Ag$_2$S (relative to its elemental components) compared to CuS, as well as the similar absolute hardness (in the context of hard-soft acid-base interactions) of Ag$^+$ and Cu$^+$, the Ag incorporation process occurs readily, even at ambient conditions and without the use of a copper-extracting agent.

As shown in Figure 3-29b, Ag$^+$ incorporation into covellite CuS NPs yields a uniform, plate-satellite structure. The TEM image in Figure 3-29c reveals that a single plate-satellite structure has a hexagonal plate as a core, with six quasi-spherical NPs at the six corners of the plate. In some of the hexagonal plates, not all six corners have an attached NP, but the location of the NP growth is predominantly at the corners whenever a NP is present. The XRD pattern in Figure 3-29g (orange curve) suggests that the heterostructure contains covellite CuS (ICDD PDF 04-007-1392) and acanthite Ag$_2$S (ICDD PDF 00-014-0072) phases. However, the substantial overlap between the XRD
patterns of these two materials, combined with the small size of the satellite domains make definitive assignment of the crystal structure difficult. The pattern does not show any evidence of metallic silver. Thus, the plate-satellite structures are composed of darker-contrast Ag₂S domains and lighter contrast CuS domains. The crystalline heterointerface between CuS and Ag₂S domains can be clearly seen in Figure 3-29d, with two similar lattice spacings of 1.9 Å, corresponding to the (110) planes of CuS (plate) and (212) planes of Ag₂S (satellite).

Figure 3-29e displays the FFT patterns of the CuS plate, an Ag₂S satellite and the whole area of one heterostructure. We note that the [100] zone axis projection of the CuS domains matches the [221] zone axis projection of the Ag₂S domains, with only a slight shift between the (110) spots of CuS and (212) of Ag₂S, due to very small differences between the respective d-spacings. The unindexed spots are contributed by a neighboring CuS plate visible at the top right of Figure 3-29d, and other high-index planes. STEM-EDS elemental maps show the Ag signal is located mainly on the satellite NPs, segregated from the Cu signal, which is mainly located on the plates. The overlapping Ag and Cu signals are possibly due to the limited thickness of the NPs and the presence of ions absorbed on the surfaces. We note that the Ag⁺-OAm precursors were prepared by sonicating a mixture of AgNO₃ (Ag source), OAm (capping ligand and coordinating solvent) and toluene (non-coordinating solvent in order to dilute the solution). Although heating such a solution could produce Ag NPs, nucleation of metallic Ag does not occur at the temperature and concentrations used here.
To further investigate the growth mechanism of CuS-Ag₂S plate-satellite heterostructures, we carefully studied top-view and side-view TEM images of these heterostructures at different reaction times (Figure 3-30). We divided the Ag⁺ incorporation-induced shape evolution of covellite CuS NPls into three stages. Initially, the CuS NPls have flat surfaces and sharp corners. These sharp corners of the NPls with higher surface energy provide lower reaction barriers for Ag⁺ incorporation, as discussed further below. This is because the basal planes of the NPls are well passivated by ligands, consistent with the previous discussions. This stage occurs instantly (< 30 s), producing small Ag₂S domains on the corners of a hexagon. The side-view TEM image of the heterostructure at this stage confirm the nucleated Ag₂S domains have limited size (< 4 nm, the thickness of CuS template NPls) and relatively low crystallinity. Then, from 30 s to 10 min, the size of the Ag₂S domains gradually grew larger, with an average diameter of 10.6 ± 1.4 nm. This is, to the best of our knowledge, the first report of preparation of CuS-Ag₂S plate-satellite heterostructures. Heterostructures with larger Ag₂S domains can be obtained by further extending the reaction time to 120 min (16.1 ± 1.4 nm). As mentioned above, the (110) planes are observed parallel to the thickness of CuS template NPls. The relative intensity of (110) planes in XRD patterns decreased as the size of the CuS domains shrank and that of the Ag₂S domains grew. This is also consistent with the increase in relative intensity of peaks near 34° that correspond to the (021), (121) and (002) planes of Ag₂S from 10 min to 120 min reaction time.
Figure 3-29. Low magnification TEM images of covellite CuS NPls (a) before and (b) after Ag⁺ incorporation. (c) TEM image of a single CuS-Ag₂S plate-satellite nanostructure (d) HR-STEM image of CuS-Ag₂S plate-satellite nanostructure. (e) FFT patterns of CuS in blue ([001] zone axis) and Ag₂S in red ([221] zone axis) showing the relative orientation and the similarity in crystal lattices (CuS + Ag₂S FFT pattern). (f) HAADF-STEM image and corresponding elemental maps of Ag, S, and Cu. (g) XRD patterns of CuS template NPls (red curve), 0.1 mmol of Ag⁺ treated CuS NPls with 10 min (orange) and 120 min (blue). The scale bar in panel d is 30 nm.

Figure 3-30. Top panels show the top-view and side-view TEM images of Ag⁺ incorporation into covellite CuS NPls process at different reaction times. The scale bars in top panels are 20 nm. Bottom panel shows the schematic illustration of Ag⁺ incorporation-induced shape evolution of covellite CuS NPls.
CE reactions are well known to occur in some metal chalcogenide nanostructures under mild conditions, facilitated by high cation mobilities and favorable chemical driving forces in both the NCs and in solution. Here, to avoid other factors that affect the CE reactions, we only use OAm, which was already present in the system, as solvent and capping ligand, Ag to replace Cu, and an ambient temperature. Covellite CuS can be described as layers of triangular CuS$_3$ units sandwiched between two layers of CuS$_4$ tetrahedra. Each triple layer is then linked to the triple layers above and below it via disulfide bonds. Unlike other copper sulfides in which ions are clearly present as Cu$^+$ and S$^{2-}$, the valency of ions in covellite is still debated. Many reports agree that the average oxidation states of Cu and S are +1 and -1. The formation of Ag$_2$S then requires the Ag$^+$ to participate in redox reactions (Cu$^+$ to Cu$^{2+}$ and (S$_2$)$_2$ to 2S$^{2-}$), and the overall reaction can be expressed as (considering sulfur in CuS to have an average valence of -1):

$$2Ag^+ + Cu^+S^- \rightarrow Ag_2^+S^{2-} + Cu^{2+}$$

As proposed by Rivest et al. and other prior reports, the thermodynamic equilibrium of a CE reaction can be analyzed by breaking the overall process into sub-steps for which the Gibbs energy changes are known or can be estimated. In this case, the process of CE reaction can be divided in four ideal steps: Cu-S dissociation (3481 kJ/mol), Ag$^+$ desolvation (350 kJ/mol), Ag-S association (-2677 kJ/mol), and Cu$^{2+}$ solvation (-1920 kJ/mol). Here, the dissociation and association energies include lattice energy and surface energies of the NCs. The solvation energies given here are for an aqueous environment and are thus, at best, crude estimates. The solvation en-
ergies in the mixed solvent system used here, in which the cations are complexed with OAm, are unknown and not readily measured. The surface energy component of the dissociation energies is similarly uncertain. Nonetheless, these estimates provide a qualitative basis for understanding the driving force for the reaction. The negative value of the overall Gibbs energy change calculated from the above energies (-416 kJ/mol) implies that the proposed CE reaction tends to be spontaneous, which is consistent with our observations. Though the lattice energies suggest the parent CuS is more stable than product Ag₂S crystals, the much greater solvation energy of Cu²⁺ compared to that of two Ag⁺ ions drives the reaction toward formation of Ag₂S and Cu²⁺. Because the solvation energies depend strongly on temperature, solvent, ligands, and other factors, the reaction equilibrium might be shifted toward CuS and 2Ag⁺ under other reaction conditions, but we did not observe any such conditions.

This mechanism is also consistent with the previous discussion on Cu⁺ incorporation into covellite CuS. To confirm this assumption, we carried out the reverse reaction by reacting Cu²⁺ with Ag₂S NCs. Ag₂S NCs were prepared in a manner similar to that used for CuS preparation, by reacting Ag⁺-OAm complex with ammonium sulfide solution. As shown in Figure 3-31, the size and morphology of Cu²⁺ treated Ag₂S NCs are preserved from the Ag₂S template NCs. The HRTEM images and XRD patterns of the Ag₂S NCs before and after Cu²⁺ treatment show that they are both Ag₂S NCs, indicating that the reverse reaction (from Ag₂S to CuS) did not occur in the presence of Cu²⁺ ions (Figure 3-31c,d).
Figure 3-31. TEM images of Ag\textsubscript{2}S NCs before and (b) after Cu\textsuperscript{2+} treatment. (c) XRD patterns of Ag\textsubscript{2}S NCs before and (b) after Cu\textsuperscript{2+} treatment. (d-e) HRTEM image of single NC from panel (a) and (b), respectively. The scale bars in panel (a) and (b) are 50 nm. The scale bars in panel (d) and (e) are 5 nm.
3.4.3 Mechanisms of Conversion from CuS to Ag₂S Nanocrystals

To confirm that the formation of CuS-Ag₂S plate-satellite structure is attributed to the local redox reaction, we carried out control experiments in which the template covellite CuS NPs were replaced by NPs of another typical Cu₂₋ₓS phase. Djurleite Cu₁.₉₄S NPs were prepared, as previously reported by Zhai and Shim, by mixing CuCl₂, t-DDT, and OAm at elevated temperature. The TEM image in Figure 3-32a shows that the Cu₁.₉₄S NPs have a hexagonal shape. Upon exposure to Ag⁺ under conditions matching the CE reaction conditions, the NPs maintained the hexagonal NP morphology of the template, with only a limited variation of their thickness (Figure 3-32b-g). The XRD patterns in Figure 3-33 indicate that the NPs treated with 0.05 and 0.1 mmol of Ag⁺ retained the djurleite crystal phase. However, a phase transition was triggered using an increased amount of Ag⁺ (0.5 mmol), and jalpaite Ag₃CuS₂ NPs were obtained. HRTEM images of the 0.05 and 0.1 mmol Ag⁺ treated NPs show interplanar spacings of 1.9 Å in top view and 3.3 Å in edge-on view, corresponding to (080) and (800) planes of the djurleite phase. Lattice spacings of 1.9 and 3.6 Å are observed in Ag₃CuS₂ NPs, corresponding to (332) and (103) planes of jalpaite, respectively. The HAADF-STEM images and corresponding elemental maps in Figure 3-32 confirm the very small amount of residual Ag⁺ in the 0.05 and 0.1 mmol Ag⁺ treated Cu₁.₉₄S NPs. In contrast, EDS results indicated that the transformed jalpaite Ag₃CuS₂ NPs are Ag-deficient (Ag : Cu = ~ 1.7 : 1) but clearly had substantial Ag content. Here, 0.5 mmol of Ag⁺ was enough to trigger the complete phase transition (rather than formation of heterogeneous domains), even though the product was far from the ideal stoichiometry. This observation is consistent with our previous discus-
tion that complete phase transition usually precedes complete composition transformation.55

Figure 3-32. (a) TEM image of djurleite Cu$_{1.94}$S template NPs. Panels (b)-(d) are low magnification TEM images of Cu$_{1.94}$S treated with 0.05, 0.1, and 0.5 mmol Ag$^+$, respectively. Panel (e)-(g) are top-view HRTEM images of samples in panels (b)-(d), respectively. The insets are corresponding side-view HRTEM images, sharing the same magnification with the corresponding TEM images, with the same scale bar of 2 nm. Right panel presents HAADF-STEM image and corresponding elemental maps for Ag, Cu and S of djurleite Cu$_{1.94}$S NPs after treatment with 0.05, 0.1 and 0.5 mmol of Ag$^+$, respectively.

Figure 3-33. XRD patterns of djurleite NPs treated with 0.05 mmol (red), 0.1 mmol (orange), and 0.5 mmol (blue) of Ag$^+$. 

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Compared to the CE reaction that led to formation of CuS-Ag$_2$S plate-satellite structures, the absence of disulfide bonds allows the cation replacement in djurleite to occur without an accompanying redox reaction or reconstruction of the sulfur sublattice. Therefore, we conclude that the rupture and reorganization of disulfide bonds in covellite CuS NPs is essential for both shape evolution to plate-satellite structure and formation of binary Ag$_2$S. Moreover, the process of Ag$^+$ incorporation into CuS NPs is more similar to the incorporation behavior of divalent cations, in which Cu$^+$ ions are replaced by Ag$^+$, producing heterogeneous domains. In contrast, homogeneous Ag-CuS alloy was obtained by using Cu$_{1.94}$S templates, similar to the behavior of trivalent and tetravalent cations that nearly always incorporate into copper sulfide phases to produce a ternary alloy phase, rather than completely replacing copper.$^{166}$ Incorporation of trivalent or tetravalent cations produces phases in which all cations are 4-coordinated, unlike the parent copper sulfide phases.$^{167}$ However, Ag$_3$CuS$_2$ contains both 4-coordinated and 6-coordinated Ag atoms and only 2-coordinated Cu atoms. Therefore, although incorporation of Ag$^+$ into djurleite Cu$_{1.94}$S yields a homogeneous alloy, we cannot conclude more broadly that incorporation of monovalent cations into copper sulfide produces homogenous alloys. In light of the results obtained using covellite CuS templates, we note that for CE with monovalent cations like Ag$^+$ the final outcome depends on the specific copper sulfide phase used as the template. This structure differs from the typical Cu-M-S alloys containing M$^{3+}$ or M$^{4+}$, in which all cations are 4-coordinated.
A typical CE process consists of the replacement of cations of a starting NC with new cations, with preservation of the original anion sublattice. However, Ag\textsubscript{2}S produced by Ag\textsuperscript{+} incorporation into covellite CuS requires not only cation replacement of Cu\textsuperscript{+} with Ag\textsuperscript{+}, but also extensive structural reorganization, due to elimination of disulfide bonds and additional sulfur atom migration. Although the crystal structure of covellite is hexagonal, the sulfur atoms in covellite CuS are not in a typical hcp stacking (ABABAB). The stacking of sulfur atoms in covellite CuS is more similar to ABAABA, with adjacent A anion layers linked by disulfide bonds, and no cation layer between them. On the other hand, the space group of Ag\textsubscript{2}S is monoclinic (P2\textsubscript{1}/c, with a = 4.229 Å, b = 6.931 Å, c = 8.2822 Å, and β = 110.618 °). The detailed route by which transformation between these two complex structures occurs remains unclear. Direct observation of the very rapid transition is not readily possible. Most cation incorporation processes require minimal anion sublattice migration because the radii of anions are much larger than those of cations, and the cations have relatively high mobility due to applied chemical driving forces and the presence of cation defects. Therefore, rearrangement of the anion lattice is the limiting factor in the transformation, and we proposed a mechanism of phase transformation from CuS to Ag\textsubscript{2}S in terms of evolution of the sulfur sublattice.

The lattice fringes observed on the CuS domain and Ag\textsubscript{2}S domains are parallel to each other, with a similar spacing of 1.9 Å, corresponding to the (110) planes of CuS and (212) planes of Ag\textsubscript{2}S. **Figure 3-34b** shows the sulfur atom frameworks in (110) planes of covellite CuS. Each unit cell contains 4 S\textsubscript{1} atoms (forming two disulfide
bonds) and 2 S2 atoms, with vertical planes of S1 atoms (in the (110) plane) parallel to the c-axis and S2 atoms in positions between these S1 atom layers. The interlayer spacing of S1 atoms is 3.29 Å, as indicated in Figure 3-34b. Sulfur atoms in the (212) planes of Ag2S have a similar layered stacking, with a similar interlayer spacing of 3.40 Å (Figure 3-34f). This similarity allows the structural transformation to occur with preservation of the S1 sublattice. We then view the CuS and Ag2S structures along the [001] and [221] zone axis respectively. Consistent with the results of HR-STEM images, similar lattice spacings with the same orientation are observed from the sulfur framework of both materials (1.90 Å for CuS and 1.96 Å for Ag2S). Both the S1 atoms in CuS and the sulfur atoms in Ag2S are hexagonally packed when viewed along the [001] and [221] zone axis, respectively. During the transformation, the S2 atoms in CuS should migrate to positions similar to the S1 atoms to conform to the sulfur framework in transformed Ag2S (Figure 3-34e).

Initially, the incorporated Ag+ can trigger the redox reaction in covellite CuS, producing a metastable reduced covellite structure. The redox reaction produces an expansion of the distance between S1 atoms and additional S2 atom migration. Figure 3-34d depicts the sulfur atom sublattice of (110) planes of reduced covellite CuS, with an average interlayer spacing of 2.73 Å. As a result, the sulfur framework viewed along the [001] direction is close to that of Ag2S viewed along the [221] direction, with only 3% expansion. However, the in-layer neighboring sulfur atoms in (212) planes of Ag2S have an average distance of 1.36 Å, which is nearly half of the interlayer spacing of 2.73 Å in (110) planes of reduced covellite CuS. Therefore, half of the sulfur atoms in
the reduced CuS structure migrate within the layer to produce the sulfur atom distribution in $\{212\}$ planes of Ag$_2$S. Of course the cation replacement from Cu$^+$ to Ag$^+$ requires uptake of two Ag$^+$ cations for each Cu$^+$ that is removed, which drives volume expansion along with rearrangement of the anion lattice. We note that there are 6 and 4 sulfur atoms in each CuS and Ag$_2$S unit cell respectively, with unit cell volumes of approximately 205 and 227 Å$^3$, respectively. Thus, upon transformation from CuS to Ag$_2$S, the volume per sulfur atom increases by approximately 66%. This substantial volume increase may explain why the template shape is not maintained during CE reactions. Instead, the transformed satellite particles are thicker than the NPIs.

**Figure 3-34.** Sulfur sublattice projection of covellite CuS (a) viewed along [001] direction and (b) its (110) planes. Sulfur sublattice projection of reduced covellite CuS (c) viewed along [001] direction and (d) its (110) planes. Sulfur sublattice projection of acanthite Ag$_2$S (e) viewed along [221] direction and (f) its $\{212\}$ planes. The black lines show the boundaries of crystal unit cells.
3.4.4 Synthesis and Mechanisms of Biconcave-Particle Ag₂S-Ag Heterostructure

The shape evolution of plate-satellite structure was highly Ag⁺-concentration dependent. In a typical synthesis using 0.1 mmol of Ag⁺, CuS-Ag₂S plate-satellite heterostructures were produced. When an increased amount (> 0.1 mmol) of Ag⁺ was employed, the overall plate-satellite morphology was still observed, but NCs were fully transformed into acanthite Ag₂S. As shown in Figure 3-35, the size of the satellite particle increased with increasing initial Ag⁺ concentration from 0.1 to 0.3 mmol. The increased relative contrast also indicates the increased size of satellite domains, whereas the thickness of the plate remains nearly constant. According to the HRTEM images in Figure 3-35f, the lattice spacings observed on the Ag₂S domain are assigned to the (111) and (110) planes of Ag₂S. Interestingly, when 0.4 mmol of Ag⁺ was employed, the resulting NPls exhibited a biconcave shape, without satellite particles. Further, treatment of CuS NPls with 0.5 mmol of Ag⁺ produced a particle attached to the biconcave NPl.

![Figure 3-35. TEM image of NPls obtained by treating covellite CuS NPls with (a) 0.1, (b) 0.2, (c) 0.3, (d) 0.4, and (e) 0.5 mmol of Ag⁺. All TEM images share the same magnification with a scale bar of 50 nm. (f) Typical HRTEM image of Ag₂S (satellite) domain of plate-satellite structure.](image)
Figure 3-36. Low magnification of Ag$_2$S-Ag biconcave-particle heterostructures. (b) HR-STEM image of a single heterostructure with Ag NPs grown on the edge. (c) Typical side-view HR-STEM image of the heterostructures. (d) HR-STEM image of a single heterostructure with Ag NPs grown in the center of concave. Panels (e) and (f) are HAADF-STEM image and corresponding elemental maps for Ag, S, and Cu of a single heterostructure from panel (d) and (b), respectively. The scale bars in panel (e) and (f) are both 20 nm.

We further investigated the novel biconcave-particle heterostructures using HAADF-STEM imaging. The low-magnification HAADF-STEM image in Figure 3-36a reveals that the transformed biconcave NPIs do not preserve the hexagonal shape of the CuS templates, possibly due to crystal transformation from the highly symmetric hexagonal CuS to less symmetric monoclinic Ag$_2$S. Compared to the edges, the center of the biconcave NPI has low contrast and less obvious crystallinity, due to limited layers of Ag atoms and less contribution to the 2D projection for imaging. In some cases, the attached particle is located at the center of biconcave NPI (Figure 3-36e); otherwise, the particle grows at the edge of the biconcave NPI (Figure 3-36f). Both Ag and S signals are distributed throughout the whole NC. The residual Cu content is negligible,
consistent with the XRD patterns (blue curve) in Figure 3-36g, and indicating that Cu was removed completely. We note that the Ag signal is more concentrated in the particle domain, which also has higher contrast in the TEM and HAADF-STEM images. However, the S signal is weaker at those locations, indicating that the particle domains are elemental Ag. Moreover, a pentagonally twinned structure was observed in the high contrast Ag domain. This behavior is consistent with previous reports of the propensity of pure Ag NPs to form penta-twinned structures, which further confirms that the product is a Ag2S-Ag heterostructure. Ag NPs are known for preferential formation of pentagonally twinned structure. This crystal feature was observed in the high contrast domain in Figure 3-36b, further confirming the formation of a Ag NP. The lattice spacings were found to be 2.4 Å on the Ag domain and 2.2 Å on the Ag2S domain, corresponding to (111) and (031) planes, respectively. Similar lattice spacings were observed in heterostructures with the particle at the center of the biconcave NPl. The side-view HR-STEM image in Figure 3-36c reveals the typical thin center (4.2 ± 0.9 nm) of biconcave NPs, with interplanar spacings of 2.7 Å and 3.4 Å, consistent with (120) and (012) planes of Ag2S.

To investigate the mechanism of formation of biconcave-particle heterostructures, we then examined the NPs early in the transition process, 30 sec after injection of the CuS NPs into the Ag+ solution. Figure 3-37 presents a typical TEM image of the NPs extracted at this time. Compared to product Ag2S-Ag biconcave-particle heterostructures, the NPs obtained after 30 s are less concave, and have smaller Ag domains, which is supported by the increase in relative intensity of the diffraction peak.
of (111) planes of Ag from 30 s to 10 min (Figure 3-36). Note that the phase transition from CuS to Ag$_2$S is already complete after 30 s. Side-view TEM images of the NPls reveal that, compared to the CuS template NPls, the thickness of the NPls first expands to $8.0 \pm 0.7$ nm at the start of the shape evolution. Therefore, the formation of biconcave structure is due to removal of the center of NPls instead of simply expansion of the edges. Interestingly, the thinnest center portion of the NPl occasionally breaks to produces a nanoring, which confirm the proposed shape evolution process, and consistent with our previous observations.

![Figure 3-37. TEM image of covellite CuS template NPls after treatment with 0.5 mmol of Ag$^+$ for 30 sec.](image)

The formation of biconcave structures is not unprecedented, however, it is very rare in Ag$_2$S based nanostructures. Mu et al. showed that CuInS$_2$ nanorings (NPls with a central region removed) can be prepared from template Cu$_{1.94}$S NPls by a CE reaction with In$^{3+}$. In contrast, our group previously reported that Cu$_{1.94}$S biconcave NPls could be produced by reacting flat CuInS$_2$ NPls with Cu$^+$. The formation of a hole or concave region in the center of these NPls was attributed to the nanoscale Kirkendall
According to this mechanism of shape evolution, the basal planes of the CuS template NPs are well passivated by the ligands. Therefore, the edge planes are relatively active, which allows Ag\(^+\) ions to diffuse into the NP. This is also supported by the fact that Ag\(_2\)S NPs tend to grow at the corner of CuS NPs. Thus, CE through the edges apparently has a lower barrier. The rate of cation replacement and sulfur sublattice reorganization was modest when starting with lower initial concentration (0.1 mmol) of Ag\(^+\), producing controllable growth of Ag\(_2\)S domains at the corners of the NPs.

When Cu\(^+\) ions are more rapidly replaced by Ag\(^+\) due to a high concentration of Ag\(^+\) in the environment, the edges only provide a limited pathway for in- and out-diffusion of cations. Initially, Cu\(^+\) rapidly diffuses from the center to the edges of the NPs, where CE reaction occurs, producing complete Ag\(_2\)S NPs (stage 1). However, the incoming Ag\(^+\) ions migrate toward the center of the NPs much more slowly, due to the narrow edges. Cation deficiency near the center then provides a driving force for transport of S toward the edges as well. Overall, material is transported from the center of the NP toward the edges, where formation of Ag\(_2\)S is occurring (stage 2). As discussed above, even during formation of the plate-satellite structures, with insufficient Ag\(^+\) for complete conversion of CuS to Ag\(_2\)S, we saw evidence of transport of sulfur to the growing Ag\(_2\)S domains. After the biconcave Ag\(_2\)S NPs were produced, the Ag\(^+\) ions had not been completely consumed and the colloidal system contained excess Ag\(^+\). Although the system cannot provide enough reducing potential for nucleation of Ag NPs alone, the Ag\(^+\) ions can gradually nucleate on the existing Ag\(_2\)S
domains, producing $\text{Ag}_2\text{S}$-$\text{Ag}$ heterostructures. In some cases, the Ag NPs locate at the center of biconcave NPs, which can be explained by the lower crystallinity of these centers and minimization of total surface area. The heterostructure formation was then followed by a ripening process in which the depth of the concave region was increased and the NPs grew larger (stage 3). Though $\text{Ag}_2\text{S}$-$\text{Ag}$ hybrid nanostructures have been explored and reported,$^{159,172-174}$ the biconcave-particle morphology is unprecedented. Its formation is attributed the unique crystal structure and morphology of covellite CuS template NPs, which in turn, highlights the novelty of our work. The schematic illustration of overall shape evolution is shown in Figure 3-38.

![Figure 3-38. Schematic illustration of overall shape evolution.](image-url)
3.4.5 Experimental Section

**Chemicals.** All chemicals were used as received. Silver nitrate (99.99%, AgNO₃), tert-dodecanethiol (t-DDT, 98.5%) and oleylamine (70%, OAm), were purchased from Sigma-Aldrich. Cu(NO₃)₂·2.5H₂O, CuCl₂·2H₂O, toluene, and ammonium sulfide (21.2 wt % in water) were purchased from Fisher Scientific.

**Preparing CuS Templates.** For the synthesis of hexagonal CuS NPs, 1.5 mmol of Cu(NO₃)₂·2.5H₂O was dissolved in a mixture of 10 mL of OAm and 10 mL of toluene, then heated to 70 °C under an argon flow. 1.5 mL of ammonium sulfide (AS) solution (21.2% in water) was injected into the Cu-OAm to form CuS NPs. After 2 h, 10 mL of ethanol was added to destabilize the NP dispersion, followed by centrifugation at 4000 rpm for 1 min. To remove excess AS and OAm, the NCs were washed by precipitation by addition of ethanol followed by redispersion in chloroform. This purification process was applied to all of the NPs described in the following sections. The NPs could be redispersed in organic solvents including chloroform, hexane, and toluene.

**Ag⁺ Incorporation into CuS NPs.** The CuS dispersion was prepared by dispersing dry CuS (one batch, typically ~230 mg) in 9 mL of OAm. From 0.1 mmol to 0.5 mmol of AgNO₃, as specified for different experiments, was dissolved in a mixture of 10 mL of OAm and 10 mL of toluene via sonication. Then, 3 mL of the CuS dispersion was injected into the Ag-OAm complex, and it was held at ambient conditions with magnetic stirring for 10 min. To collect the NPs, 10 mL of ethanol was added, followed by centrifuging at 4000 rpm for 1 min.
**Synthesis of Ag₂S NCs.** To prepare Ag₂S template NCs, 0.25 mmol of AgNO₃ was dissolved in a mixture of 5 mL of OAm and 5 mL of toluene via sonication. 0.25 mL of ammonium sulfide (AS) solution (21.2% in water) was injected into the Ag-OAm to form Ag₂S NCs. After 1 min, 10 mL of ethanol was added to de-stabilize the NC dispersion, followed by centrifugation at 5000 rpm for 1 min. To remove excess AS and OAm, the NCs were washed by precipitation upon addition of ethanol followed by redispersion in chloroform. The NPLs could be re-dispersed in organic solvents including chloroform, hexane, and toluene.

**Cu²⁺ Incorporation into Ag₂S NPs.** The Ag₂S dispersion was prepared by dispersing dry Ag₂S (one batch, typically ~36.3 mg) in 3 mL of OAm. 0.1 mmol Cu(NO₃)₂ was dissolved in a mixture of 10 mL of OAm and 10 mL of toluene via sonication. Then, 3 mL of the Ag₂S dispersion was injected into the Cu-OAm complex, and it was held at ambient conditions with magnetic stirring for 10 min. To collect the NPLs, 10 mL of ethanol was added, followed by centrifuging at 4000 rpm for 1 min.

**Synthesis of Djurleite Cu₁.₉₄S NPLs.** The synthesis of djurleite NPLs was adapted from a previous report with some modifications. A mixture of 1 mmol of CuCl₂·2H₂O, 5 mmol of OAm (~1.65 mL) and 10 mL of ODE was degassed at ~80 °C for 30 min and then quickly heated to 180 °C under argon. 4 mL of t-DDT was added to the reaction mixture at 120 °C. The mixture was held at 180 °C for 5 min before being quenched with 10 mL ethanol. The NPLs were collected by centrifugation at 4000 rpm for 1 min.
The NPls were purified by precipitation upon addition of ethanol followed by redispersion in chloroform. The NPls were dispersed in hexane for further treatment.

**Ag⁺ Incorporation into Cu₂.₉₄S NPls.** The CuS dispersion was prepared by dispersing dry Cu₂.₉₄S (one batch, typically ~30 mg) in 3 mL of OAm. 0.05 mmol (or as indicated) AgNO₃ was dissolved in a mixture of 10 mL of OAm and 10 mL of toluene via sonication. Then, 3 mL of the Cu₂.₉₄S dispersion was injected into the Ag-OAm complex, and it was held at ambient conditions with magnetic stirring for 10 min. To collect the NPls, 10 mL of ethanol was added, followed by centrifuging at 4000 rpm for 1 min.

**Characterization.** Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-2010 at an accelerating voltage of 200 kV. High-resolution TEM (HRTEM) images were obtained on a FEI Tecnai G2 F30 at an accelerating voltage of 300 kV. High angle annular dark field scanning TEM (HAADF-STEM) images, HR-STEM images and STEM energy dispersive X-ray spectroscopy (STEM-EDS) maps were collected using a JEOL JEM-ARM200F STEM equipped with spherical aberration correctors on the image, at an accelerating voltage of 200 kV. TEM grids were prepared by dropping a dilute NC dispersion onto a carbon-coated copper or nickel TEM grid and allowing the sample to dry in air. Size distributions were obtained from TEM images by measuring at least 100 NCs from multiple TEM images from different areas of the grid, using Nanomeasurer v. 1.2. Powder X-ray diffraction (XRD) measurements were carried out using a Rigaku Ultima IV diffractometer with a Cu Kα X-ray source. Samples for XRD were prepared by drop-casting concentrated NC
dispersions onto glass slides.
3.5 Valence Selectivity of Cation Incorporation into Covellite CuS Nanoplatelets

3.5.1 Introduction

Colloidal copper sulfide-based nanomaterials have attracted considerable attention because of their potential for use in thermoelectric, electrocatalytic, and photovoltaic applications, as well as possible biological applications. These nanomaterials possess advantages such as low cost, low toxicity, suitable band gaps for optoelectronic applications at visible and near infrared wavelengths, and strong optical absorbance, which have inspired sustained research into their synthesis and applications over the past several decades. The ability to controllably synthesize NCs of these materials is of great interest for harnessing size-dependent properties and producing nanocomposites and colloidal dispersions for low-cost processing. Fabrication of these NCs can be generally divided into one-pot mixing methods and multi-step growth methods. In general, both of the synthetic routes involve nucleation of Cu2-xS NCs, followed by incorporation of additional cations.

Under conditions used for cation incorporation, the Cu atoms, and therefore the copper vacancies, in Cu2-xS are highly mobile, which allows both out-diffusion of copper and in-diffusion of other cations. Introduction of a second cation can trigger partial or complete cation exchange (CE), or formation of a ternary alloy. Consequently, heterostructured metal sulfide NCs (Cu2-xS-ZnS and Cu2-xS-CdS), new binary metal sulfide NCs (CoS, ZnS, CdS, MnS, and PbS), and ternary alloys (CuInS2, CuGaS2, CuFeS2, CuSbS2 and Cu3SnS4) can be prepared by such routes under appropriately controlled conditions. In some cases, heterogeneous
ternary NCs are obtained by incomplete cation incorporation and diffusion (e.g. \( \text{Cu}_2\cdot\text{S-CuInS}_2 \)), under conditions that would ultimately fully convert the templates into ternary NCs.\(^{158}\) Note that these NCs are distinct from heterogeneous NCs with immiscible boundaries (e.g. \( \text{Cu}_2\cdot\text{S-PbS} \)). \( \text{Cu}_2\cdot\text{S} \) crystal structures “reject” the interstitial diffusion of some kinds of incoming cations, which are only allowed to replace Cu atoms in the \( \text{Cu}_2\cdot\text{S} \) structure. Therefore, we classify the results of cation (\( \text{M}^{\text{III}} \)) incorporation into \( \text{Cu}_2\cdot\text{S} \) into one of two outcomes: formation of ternary \( \text{Cu-M-S} \) alloy NCs (“acceptance”) or formation of heterogeneous \( \text{Cu}_2\cdot\text{S-MS} \) (“rejection”).

Cation incorporation and CE reactions leading to both of the above outcomes, starting from a variety of \( \text{Cu}_2\cdot\text{S} \) NCs have been studied extensively. However, to achieve desired morphology and composition of the final NCs, different \( \text{Cu}_2\cdot\text{S} \) templates and a variety of reaction conditions have been employed. Thus, although certain trends emerge from these prior studies, general rules and mechanisms governing the two outcomes remain unclear or unproven. In addition, the ability to control the stoichiometry and crystal phase of ternary and quaternary NCs is still a challenge because of the varying reactivity of different metal precursors as well as the complex interactions between the capping ligands and NCs, which may result in the formation of non-stoichiometric products and secondary phases.\(^1\) Utilizing stepwise synthesis can help to overcome this challenge by separating the nucleation step from the cation incorporation step.

Covellite \( \text{CuS} \) NPs are used as the template to investigate the cation incorporation process. The copper sulfide class of materials is well known for its many possible
crystal phases, compositions and morphologies. Synthesis of Cu$_{2-x}$S NCs often produces a mixture of different crystal phases with similar compositions. These similar crystal phases have relatively low interconversion barriers, producing complex multiphase systems and unexpected shape evolution during cation incorporation. Thus, the choice of covellite CuS, which is one of the stoichiometric extremes in this system, provides a practical means of avoiding formation of other Cu$_{2-x}$S byproducts. Moreover, a plate-like template with relatively large aspect ratio can provide clearer evidence of formation of heteronanostructures. Fundamentally, the same underlying anisotropy of crystal structure (in this case the layered structure of covellite) that leads to growth of anisotropic geometries can produce anisotropic cation exchange even when starting from templates with isotropic quasi-spherical shape. Thus, we choose covellite CuS NPs as the template for cation incorporation because it has advantages of fixed morphology, stable and pure crystal phase, and relatively easy observation of formation of heterodomains.

![Figure 3-39. Schematic illustration of valence selectivity of cation incorporation into covellite CuS NPs.](image)
3.5.2 Incorporation Trivalent and Tetravalent Cation into Covellite CuS Nanoplatelets

To study the valence selectivity of cation incorporation into CuS, as well as the structural properties of copper sulfide-based NCs, large covellite CuS NPls were synthesized and used as template NCs. The TEM images in Figure 3-40a,b reveal the hexagonal NPl morphology of the covellite CuS template NCs. EDS analysis also confirm the expected Cu:S ratio of nearly 1:1. The EDS results of this and subsequent samples are presented in Table 3-1. The top view HR-STEM image shows that the copper atoms of the CuS NPls are hexagonally packed, with an interatomic spacing of ~0.23 nm. This spacing matches the distance (2.3 Å) between two neighboring copper atoms in a covellite unit cell viewed along the c-axis. As shown in Figure 3-40d, lattice fringes with a measured interplanar spacing of 0.27 nm, visible in edge view HRTEM, correspond to the (0,0,6) planes of CuS.

![Figure 3-40.](image)

Table 3-1. EDS Results of All Mentioned Copper Sulfide-Based NPls (unit/%).
<table>
<thead>
<tr>
<th>NPls</th>
<th>Stoichiometrics</th>
<th>Reference</th>
<th>Cu</th>
<th>Foreign Cation(s)</th>
<th>S</th>
</tr>
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<tr>
<td>CuS</td>
<td>CuS</td>
<td>Fig. 3-40</td>
<td>48.6</td>
<td>N.A.</td>
<td>51.4</td>
</tr>
<tr>
<td>CIS, T=80 °C</td>
<td>CuInS₂/CuS</td>
<td>Fig. 3-45a</td>
<td>40.8</td>
<td>2.4</td>
<td>56.8</td>
</tr>
<tr>
<td>CIS, T=120 °C</td>
<td>CuInS₂</td>
<td>Fig. 3-45b</td>
<td>32.8</td>
<td>15.7</td>
<td>51.5</td>
</tr>
<tr>
<td>CIS, T=160 °C</td>
<td>CuInS₂</td>
<td>Fig. 3-41e</td>
<td>26.1</td>
<td>24.7</td>
<td>49.2</td>
</tr>
<tr>
<td>CIS, T=200 °C</td>
<td>CuInS₂</td>
<td>Fig. 3-45d</td>
<td>26.4</td>
<td>25.3</td>
<td>48.3</td>
</tr>
<tr>
<td>0.1 (insufficient) In, CIS</td>
<td>CuInS₂</td>
<td>Fig. 3-44h</td>
<td>43.1</td>
<td>9.1</td>
<td>47.8</td>
</tr>
<tr>
<td>CTS</td>
<td>Cu₂SnS₃</td>
<td>Fig. 3-41j</td>
<td>35.7</td>
<td>15.5</td>
<td>48.8</td>
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<tr>
<td>CFS</td>
<td>CuFeS₂</td>
<td>Fig. 3-46e</td>
<td>22.4</td>
<td>23.4</td>
<td>54.2</td>
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<tr>
<td>CGS</td>
<td>CuGaS₂</td>
<td>Fig. 3-47e</td>
<td>38.2</td>
<td>12.3</td>
<td>49.5</td>
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<tr>
<td>CGeS</td>
<td>Cu₂GeS₃</td>
<td>Fig. 3-48d</td>
<td>38.8</td>
<td>10.2</td>
<td>51.0</td>
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<tr>
<td>Cu-Cd-S</td>
<td>N.A.</td>
<td>Fig. 3-49d</td>
<td>23.4</td>
<td>29.9</td>
<td>46.7</td>
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<tr>
<td>Cu-Zn-S</td>
<td>N.A.</td>
<td>Fig. 3-49h</td>
<td>24.5</td>
<td>27.0</td>
<td>48.5</td>
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<tr>
<td>Cu-Pb-S</td>
<td>PbS</td>
<td>Fig. 3-52b</td>
<td>5.4</td>
<td>42.7</td>
<td>51.9</td>
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<td>2.0 (excess) Cd, Cu-Cd-S</td>
<td>CdS</td>
<td>Fig. 3-50e</td>
<td>6.7</td>
<td>43.8</td>
<td>49.5</td>
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Covellite CuS can be described as layers of triangular CuS$_3$ units sandwiched between two layers of CuS$_4$ tetrahedra. Each triple layer is then linked to the triple layers above and below it via disulfide bonds. Here, DDT is introduced to not only reduce the disulfide bonds (converting each S$_2^-$ moiety to 2 S$^{2-}$) but also to extract Cu$^+$ ions from the sublattice. This allows new cations to more easily diffuse into the CuS lattice and be incorporated.$^{36,126}$ The TEM image in Figure 3-41a shows that CIS NPLs produced by In incorporation nearly preserve the size and morphology of the CuS template NPLs. The overlapped NPLs exhibit platelet-wide Moiré fringes, suggesting that they are single crystalline.$^{32,128}$

<table>
<thead>
<tr>
<th>Composition</th>
<th>Structure</th>
<th>Fig.</th>
<th>Cu</th>
<th>Zn</th>
<th>S</th>
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<td>Fig. 3-51b</td>
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<td>34.5</td>
<td>46.4</td>
<td></td>
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<tr>
<td>CZIS</td>
<td>Cu$<em>{0.4}$In$</em>{0.4}$Zn$_{0.2}$S</td>
<td>Fig. 3-53e</td>
<td>18.7</td>
<td>19.5</td>
<td>10.9</td>
</tr>
<tr>
<td>CZTS</td>
<td>Cu$_2$ZnSnS$_4$</td>
<td>Fig. 3-53j</td>
<td>26.0</td>
<td>11.8</td>
<td>11.9</td>
</tr>
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</table>

Figure 3-41. TEM characterization of CIS and CTS NPLs. (a) TEM image, (b) HAADF-STEM image, (c) top-view HRTEM, (d) side-view HRTEM, and (e) STEM-EDS elemental mapping for CIS NPLs; (f) TEM image, (g) HAADF-STEM image, (h) top-view HRTEM, (i) side-view HRTEM, and (j) STEM-EDS elemental mapping for CTS NPLs; The insets in (c), (d), (h), and (i) show FFT of the regions of the
The XRD pattern of the resulting NPs most closely matched that of the tetragonal roquesite CIS phase (ICDD PDF 00-027-0159, Figure 3-42a) with an fcc-like anion lattice. However, formation of hexagonal wurtzite-type CIS is also possible, and would produce a similar diffraction pattern, with several overlapping diffraction peaks. Wurtzite and zincblende type structures are both possible forms for many kinds of semiconductor NCs.\(^{183, 184}\) The anions in wurtzite-type NCs have a hcp packing, distinguished from those of zincblende-type NCs, with fcc packing. However, the energy difference between them is often only a few meV per atom.\(^{185}\) Both wurtzite and zincblende (roquesite for CIS) CIS nanostructures have been synthesized via CE reactions in prior reports.\(^{128, 143, 151, 186}\) In general, products of CE reactions almost always inherit the crystal structure (especially the anionic sublattice) of the template phase. Thus, investigation of the crystal phase of In\(^3^+\) incorporated covellite CuS NPs can provide insights into both the crystal structure of template CuS and overall transformation process. Typical wurtzite structures (e.g., CdS and ZnS) have a well-organized hexagonal packing (ABABAB). The stacking of sulfur layers in in covellite is neither ABABAB as in the wurtzite structure, nor ABCABC as in the zincblende (fcc-related) structure. It is rather like ABAABA, with adjacent A anion layers linked by disulfide bonds, with no cation layer between them. While covellite has a mixture of 3-coordinated and 4-coordinated copper, both wurtzite and roquesite CuInS\(_2\) have only tetrahedrally-coordinated cations and no disulfide bonds. These differences imply that the mechanism of conversion from covellite CuS to CuInS\(_2\) cannot be simply explained.
by cation replacement with minimal anionic sublattice change. As shown in Figure 3-43, the sulfur atoms in both (112) planes of roquesite and (002) planes of wurtzite are hexagonally packed (though roquesite is less ordered). Both of the planes have similar interplanar distances of ~3.2 Å, which is far greater than the distances between sulfur atom layers in covellite (3.01 Å for S1-S2 and 2.15 Å for the disulfide bond). Therefore, both of the possible conversions require substantial sulfur atom migration and reorganization in addition to cation incorporation. As shown in Figure 3-41d, the (112) planes of roquesite CIS are observed in side-view images of the NPIs, indicating that these planes are perpendicular to the thickness direction of the NPIs. The limited (~4 nm) thickness of the anisotropic NPIs thus produces extreme size broadening of this reflection (near $2\theta = 28^\circ$) while the (220) planes are parallel to the thickness direction and thus are much less subject to size broadening (producing the sharp peak near 46°).

The (102) and (103) peaks from the wurtzite structure, which would have a component in the plane of the platelets, would produce peaks broader than that near 46°, but much sharper than that from planes perpendicular to the NPI thickness. Thus, the absence of diffraction peaks for (102) and (103) planes of wurtzite CIS (Figure 3-43) confirms the formation of roquesite CIS, which can be understood based on the unique stacking arrangement in covellite, which requires significant rearrangement of the anion sublattice to arrive at either the wurtzite or roquesite structure.
Figure 3-42. XRD pattern of covellite CuS NPs treated with (a, red) 0.1 mmol In$^{3+}$ precursors (a, blue) 0.5 mmol In$^{3+}$ precursors, (b) 0.5 mmol In$^{3+}$ precursors without DDT, (c) 0.5 mmol Cd$^{2+}$ and (d) 0.5 mmol Zn$^{2+}$. XRD patterns showing the conversion (e) from CIS to CZIS NPs and (f) from CTS to CZTS NPs.

Note that preferential orientation of the NPs could eliminate some reflections in XRD patterns. For example, the diffraction peaks corresponding to the crystal planes on the edge of NPs can be damped if the NPs are mainly standing on-edge. Though the anisotropic plate-like templates produce broadening of diffraction peak, the XRD patterns of the NPs consistently exhibit all diffraction peaks due to their random orientation, as shown in Figure 3-41 and the following TEM images of other NPs. We also fitted the XRD pattern using Reitveld refinement for both of the roquesite and wurtzite CIS phases (Figure S4b). The results are consistent with our above discussion that fcc CIS, instead of hcp CIS, is formed upon indium incorporation into covellite CuS.
Figure 3-43. (a) Schematic illustration of transformation from covellite CuS to roquesite CIS and wurtzite CIS. The thickness of the starting covellite CuS NPLs is 4 nm (resulting CIS NPLs nearly retained this thickness), containing ~2.5 unit cells with 16 layers of sulfur atoms and 4-5 disulfide bonds along the c-axis (16.27 Å per unit cell). After indium incorporation, the retained thickness of the NPLs contains ~6 CIS unit cells with 12 layers of sulfur atoms along the c-axis (6.44 Å per unit cell). In covellite CuS, the distance between two different S layers is 3.01 Å, and the length of a disulfide bond is 2.15 Å. In contrast, the distance between S layers in roquesite CIS is 3.20 Å, so the conversion from covellite CuS to roquesite CIS requires both expansion of the distance of neighboring layers of sulfur atoms and some lattice shrinkage induced by migration of one layer of sulfur atoms from the broken disulfide bonds. (b) Representative results of fitting of the XRD pattern by Reitveld refinement assuming anisotropic line broadening and either the roquesite (top) or wurtzite (bottom) crystal structure. The accompanying illustration shows the anisotropic disc-like shape corresponding to the typical fitting results (similar for both crystal structures).

To further explore the possibility of formation of the wurtzite structure, we fitted the XRD pattern using Reitveld refinement for both the roquesite and wurtzite CIS phases. This fitting of XRD data was
performed using the MAUD program, with the “Popa” rules for anisotropic broadening due to finite crystallite size, and assuming no strain-induced broadening. The fits obtained were not unique, in that for each phase, comparably good fits to the pattern could be obtained with different combinations of parameters (lattice parameters plus crystallite dimensions). However, the fitting results using the roquesite CIS phase were consistently better than those obtained using the wurtzite CIS phase. Figure S4 presents two representative fits, for the two possible phases, obtained for anisotropic crystallite dimensions that corresponded to a disc-like shape. Size-induced peak broadening in the wurtzite structure that was sufficient to smear the three characteristic wurtzite peaks (100, 002 and 101) into a single peak and to suppress the appearance of the (102) and (103) peaks of the wurtzite structure could not also maintain the sharp peak near 47 degrees. Thus, we believe the crystal phase resulting from indium incorporation into the covellite platelets is most similar to the roquesite crystal phase.

As revealed by HRTEM analysis in Figure 3-41c,d, the CIS NPs have interplanar spacings of 0.19 nm and 0.32 nm, corresponding to (2,2,0) and (1,1,2) planes of CuInS₂ (ICDD PDF 00-027-0159) respectively. STEM-EDS mapping was used to confirm the expected composition of the NPs. In Figure 3-41e, co-localization of the Cu, In and S signals on the CIS NPs is evident by comparing with the corresponding HAADF-STEM image (Figure 3-41b). Consistent with our previous report, incorporation of tetravalent Sn⁴⁺ into covellite CuS NPs produces similar results. The morphology preservation from the CuS NP template, consistency between lattice spacings and diffraction peaks, and co-localization of the Cu, Sn and S signals, all prove that Sn⁴⁺ has been incorporated into covellite CuS to produce CTS NPs (Figure 3-41f-j).

We also conducted control experiments to investigate the effect of DDT on the cation incorporation process. Figure 3-44a shows the results obtained by directly reacting In³⁺ with CuS NPs (without DDT), which led to formation of star-like nanostructures of a secondary phase. HRTEM analysis in Figure 3-44b,c shows that
the secondary phase is crystalline, with lattice spacings of 0.18 nm and 0.30 nm, while the isolated NPl has lattice spacing of 0.19 nm. Figure 3-44d shows the HAADF-STEM image and corresponding elemental mapping of the mixture of In\(^{3+}\)-treated NPls and secondary phases. The Cu signals are mainly located on the NPls, separate from the In\(^{3+}\) signals, which are mainly in the secondary phase. The S signals are collocated with those of Cu, indicating that the NPls are composed of Cu and S, but the secondary phase contains little sulfur. According to the XRD pattern in Figure 3-42, the mixture is composed of Cu\(_{1.8}\)S NPls and In\(_2\)O\(_3\). The lattice spacings of the In-rich phase observed in HRTEM match the spacings of the (2,2,2) and (4,4,0) planes of In\(_2\)O\(_3\). The observed lattice spacing in the NPl corresponds to (2,2,0) planes in Cu\(_{1.8}\)S. Obviously, In\(^{3+}\) ions are not incorporated into the CuS template without addition of DDT. The CuS NPls were converted into Cu\(_{1.8}\)S NPls upon heating with OAm.125 We speculate that In\(^{3+}\) ions were reduced to elemental In nanoparticles upon heating in OAm, then rapidly oxidized to In\(_2\)O\(_3\) nanoparticles during purification and storage.

The In\(^{3+}\) incorporation process was also found to be strongly governed by the reaction temperature. As shown in Figure 3-45, NPls produced by In\(^{3+}\) incorporation at different temperatures almost preserve the morphology of the covellite CuS NPl templates. The XRD patterns (Figure 3-45e) together with EDS results (Table 3-1) indicate that the CuS NPls were gradually converted into CIS NPls, while the indium content increased from negligible to nearly equal to the Cu content. The color of the dispersion of these NPls gradually changed from dark green to dark brown, consistent with the transformation from covellite CuS to roquesite CIS. In a previous study, we
treated CuS NPs with tin, as Sn$^{2+}$ or Sn$^{4+}$, with or without DDT. When Sn$^{4+}$ was employed without DDT, we observed formation of a secondary phases rather than cation incorporation into CuS template. Thus the behavior of In$^{3+}$, requiring a reagent like DDT to reduce disulfide bonds and promote cation incorporation, is consistent with the previous observation for Sn$^{4+}$.

**Figure 3-44.** (a) TEM image of In$^{3+}$ treated CuS NPs, showing star-like NCs of a secondary phase that are isolated from NPs. HRTEM image of (b) star-like structures and (c) In$^{3+}$ treated CuS NPs. (d) HAADF-STEM image and corresponding element maps for In$^{3+}$ treated CuS NPs. (e) TEM image, (f) top view and (g) side view HRTEM images of CIS NPs synthesized using insufficient In$^{3+}$ precursor. The red dashed lines highlight the boundary of a NPI. (h) HAADF-STEM image and corresponding element maps of (a). Scale bars in panels (d) and (h) are 50 nm and 100 nm, respectively.
Figure 3-45. (a-d) TEM images of NPs produced by In$^{3+}$ incorporation into CuS NPs at different temperatures. (e) XRD patterns of CuS NPs templates and transformed NPS. (f) Photograph of dispersion of the NPs (~1 mM cation concentration). The results show that the lower reaction temperature (80 °C) is not enough to trigger the crystal phase transformation. The crystal phase gradually transformed from covellite CuS to roquesite CIS by increasing the reaction temperature from 80 °C to 160 °C (consistent with the EDS results in Table S1). Further increasing the reaction temperature does not affect the In$^{3+}$ incorporation process.

In our typical ternary copper sulfide-based alloy fabrication process, 0.5 mmol of cation precursors were used to ensure that CuS NPs were fully converted to Cu-M-S NPs. We also studied the synthesis of CIS NPs using a quantity of In$^{3+}$ precursor that was not sufficient to fully convert the CuS NPs to CIS NPs. As shown in Figure 3-44e, broken NPs were obtained by using 0.1 mmol In$^{3+}$ in the presence of DDT. XRD analysis revealed that the broken NPs are the same CuInS$_2$ phase produced by complete conversion using 0.5 mmol of In$^{3+}$, without obvious change in peak width or position (Figure 3-42). Top view and side view HRTEM images of broken NPs in Figure 3-44f-g also show that these NPs have the same lattice spacings as the NPs produced by
the typical CIS synthesis, without obvious defects or stacking faults. Figure 3-44h also provides a HAADF-STEM image for a collection of these NPs. Indium signals are colocated with those of Cu and S, although the intensity of indium is lower than that of Cu (as quantified by EDS results in Table 3-1). These results indicate that DDT and insufficient $\text{In}^{3+}$ precursors have triggered the complete phase transition from CuS to CIS, but incomplete composition transformation, producing broken single-phase indium-poor NPs rather than partially transformed NPs.

Similarly, CFS NPs were synthesized using the typical conditions for synthesis of CIS NPs (Figure 3-46). The morphology preservation from the CuS template, the matching of lattice spacings in HRTEM images and the XRD pattern, and the element maps prove that the covellite CuS was fully converted into chalcopyrite CuFeS$_2$. CGS and CGeS NPs were also prepared using this approach. However, higher temperature (200 °C) was required for Ga$^{3+}$ or Ge$^{4+}$ incorporation, due to lower reactivity of Ga$^{3+}$ and Ge$^{4+}$ compared to that of In$^{3+}$, Sn$^{4+}$ and Fe$^{3+}$ (Figure 3-47 and Figure 3-48).\textsuperscript{187} Note that the XRD patterns of CGS and CGeS NPs have unexpected minor diffraction peaks $\sim$30 °. This can be attributed to incomplete cation incorporation due to lower cation reactivity, producing Cu$_{2-x}$S phases as byproducts. This observation is consistent with the lower than expected cation ratio (Cu:M) of the NPs (Table 3-1).
Figure 3-46. (a) TEM image, (b,c) HRTEM images, (d) XRD pattern and (e) HAADF image and corresponding elemental maps of CuFeS$_2$ NPs. The scale bars in panel b, c and e are 5 nm, 5 nm and 200 nm, respectively.

Figure 3-47. (a) TEM image, (b,c) HRTEM images, (d) XRD pattern and (e) HAADF image and corresponding elemental maps of CuGaS$_2$ NPs. The scale bar in panel e is 100 nm.
Combining all of the above results and observations, we can propose a mechanism of incorporation of trivalent and tetravalent cations into covellite. The absence of disulfide bonds in the Cu-M-S ternary alloys requires reduction of disulfide bonds in covellite CuS before or during trivalent or tetravalent cation incorporation. Then, the trivalent In$^{3+}$, Fe$^{3+}$, or Ga$^{3+}$, or tetravalent Sn$^{4+}$ or Ge$^{4+}$ ions are inserted into the reduced CuS lattice. In the covellite structure, the disulfide bonds are aligned with the $c$-axis and arranged in a plane perpendicular to the $c$-axis. The incoming cations must diffuse to the locations of the breaking disulfide bonds. The formation of M-S bonds at these positions can prevent the collapse of unit cells and thereby retain the overall structure of the NPls, even though the NPls are only a few unit cells in thickness. Completion of this cation insertion process produces stoichiometric Cu-M-S NPls. When insufficient cation precursor is provided, although the CuS crystal is still converted to the Cu-M-S phase, the NPls partially collapse due to lack of incoming cations. This reflects a lack
of stability of non-stoichiometric alloys in these systems. Rather than preserving the
original NPl geometry with a highly M-deficient composition, a fraction of the NPl is
converted to the Cu-M-S phase, and the remaining fraction is lost.
3.5.3 Incorporation Divalent Cation into Covellite CuS Nanoplatelets

Instead of the homogeneous phases obtained using trivalent and tetravalent cations, the incorporation of divalent cations (Zn$^{2+}$, Cd$^{2+}$ and Pb$^{2+}$) into CuS template NPls produces heterogeneous NCs with clear boundaries between domains of immiscible phases. As shown in Figure 3-49a, the NPls treated with 0.5 mmol of Cd$^{2+}$ and DDT nearly preserve the plate-like shape, but with non-uniform thicknesses. We notice that the edges of the NPls are not as smooth as those of the template NPls, but also that the NPls do not have large areas missing, like those produced when an insufficient quantity of In$^{3+}$ was employed. HRTEM analysis in Figure 3-49b reveals that a single NPl has a clear boundary between Cu$_2$S and CdS domains, with interplanar spacings of 0.19 nm [(1,1,0) planes of Cu$_2$S] and 0.36 nm [(1,0,0) planes of CdS], respectively. Because Cd$^{2+}$ does not diffuse into the covellite CuS crystal lattice, here DDT only serves to reduce the disulfide bonds in CuS, converting covellite CuS to high chalcocite Cu$_2$S, consistent with our previous report. In the presence of a copper extracting agent (here DDT), Cd$^{2+}$ can then replace Cu$^+$ in high chalcocite, but does not coexist with Cu$^+$ within the same crystalline domain. Both phases are oriented with their c-axis direction perpendicular to the plane of the NPl (pointing across the thickness of the NPl). We note that the sulfur sublattices for both Cu$_2$S and CdS are hexagonally packed. The distance between neighboring S atoms in CdS is 4.15 Å, which is only 6.6% larger than that of high chalcocite Cu$_2$S (3.89 Å). This allows the phase transition to occur with minimal changes in the sulfur sublattice. In the Cu$_2$S structure, the angle between the [100]/[100] direction and (1,1,0) planes is 60°. Thus, the growth direction of the
CdS domain is along the [100]/[100] direction of both Cu$_2$S and CdS. STEM-EDS mapping of a single NPl (Figure 3-49d) confirms that the NPls have distinct regions containing Cu$^+$ and Cd$^{2+}$. The overlay (Cu and Cd) imaging further supports that the NPls are composed of two different materials. The XRD pattern of the heterogeneous NPls in Figure 3-42 also confirm that the NPls contain both Cu$_2$S and CdS. Note that the intensity of diffraction peaks of the Cu$_2$S domain is relatively low, which indicates that the NPls are mainly composed of CdS domains (similar to the specific NPl shown in Figure 3-49d with a large CdS domain and smaller Cu$_2$S domain).

**Figure 3-49.** (a) TEM image of Cd$^{2+}$ treated CuS NPls, (b) HRTEM image of a single Cu$_2$S-CdS heterogeneous NPl, the green area shows the CdS domain, while the red area shows the Cu$_2$S domain. (c) HR-STEM image of a heterogeneous NPl at the boundary between Cu$_2$S and CdS domains, highlighted by dashed line. (d) HAADF-STEM image and corresponding elemental maps of a Cu$_2$S-CdS heterogeneous NPl. (e) TEM image of Zn$^{2+}$ treated CuS NPls, (f) HR-STEM image of the Cu$_2$S-ZnS heterogeneous NPls at the boundary between Cu$_2$S and ZnS, highlighted by dashed line. (g) Top view and (h) side view HAADF-STEM images and corresponding elemental maps of a Cu$_2$S-ZnS heterogeneous nanoparticle. Scale bars in panels (d), (g) and (h) are 20 nm, 20 nm and 10 nm, respectively.

Similarly, as shown in Figure 3-49e, treatment of the template NPls with Zn$^{2+}$ and
DDT produced heterogeneous NPLs with two different domains, with different contrast. The HR-STEM image (Figure 3-49f), top view and side view elemental maps and the XRD pattern (Figure 3-42d), show that these are Cu$_2$S-ZnS heterogeneous NPLs. When covellite CuS NPLs were exposed to an excess of Cd$^{2+}$ precursors (e.g. 2 mmol), the CuS NPLs were completely converted into CdS NPLs, as shown in Figure 3-50. However, incorporation of 2 mmol Zn$^{2+}$ precursor did not fully convert the NPLs to ZnS (Figure 3-51), due to the lower reactivity of Zn$^{2+}$ towards sulfur, compared to that of Cd$^{2+}$. In both cases of supplying excess divalent cations (Cd$^{2+}$ or Zn$^{2+}$) the NPLs maintain their overall hexagonal plate-like shape. However, the Cd$^{2+}$ treated NPLs have a more fragmented appearance than those treated with excess Zn$^{2+}$. This may reflect the fact that Cu$^+$ has similar cation radius (60 pm, tetrahedrally coordinated) to that of Zn$^{2+}$ (60 pm), which is smaller than that of Cd$^{2+}$ (78 pm). This mismatch of the cation radius can produce local lattice expansion during CE reactions with Cd$^{2+}$. Pb$^{2+}$ has also been studied for CE with Cu$_{2-x}$S NCs. In this case, because of the high reactivity of Pb$^{2+}$, the CuS NPLs were fully converted into PbS NPLs using just 0.5 mmol of Pb$^{2+}$ precursor at 120 °C for 5 min (Figure 3-52). In summary, CuS NPLs undergo a partial or complete CE process when incorporating divalent cations, producing heterogeneous Cu$_2$S/MS NPLs or new MS NPLs.
Figure 3-50. (a) TEM image, (b,c) HRTEM images. (d) XRD pattern and (e) HAADF image and corresponding elemental maps of excess (2 mmol) Cd$^{2+}$-treated covellite CuS NPs.

<table>
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Figure 3-51. (a) TEM image and (b) EDS analysis of excess (2 mmol) Zn$^{2+}$-treated covellite CuS NPs.

Figure 3-52. (a) TEM image, (b) HAADF image and corresponding elemental maps, (c,d) HRTEM images. (e) XRD pattern of covellite CuS NPs treated with 0.5 mmol Pb$^{2+}$. 
3.5.4 Synthesis of Quaternary CZIS and CZTS Nanoplatelets and Mechanism of Valence Selectively

CZTS and CZIS NCs are known as promising absorber materials for photovoltaic devices because of their optimal band-gaps, large absorption coefficients, and high photostability. Quaternary CZIS and CZTS NPs can be prepared by incorporating Zn$^{2+}$ into CIS and CTS NPs. When incorporating cations into Cu$_{2-x}$S NCs, TOP is usually applied as a copper-extracting agent during Cu$_{2-x}$S CE reactions, because TOP is a soft base that binds strongly to the Cu$^+$ cations (a soft acid). As shown in Figure 3-53a,f, Zn$^{2+}$ containing quaternary NPs almost preserve the morphology of the template CIS and CTS NPs. HRTEM images in Figure 3-53c,h reveal that the NPs both have lattice spacings of 0.19 nm, correspond to (2,2,0) planes in both CZIS and CZTS phases. The XRD patterns for comparison of CIS/CZIS and CTS/CZTS NPs are presented in Figure 3-42. Note that there is only a minor difference ($< 0.1^\circ$) of diffraction patterns between CIS (CTS) and CZIS (CZTS), owing to similarity of crystal structures and parameters. The diffraction peaks slightly shift to higher 20 angles during the conversion from ternary NCs to quaternary NCs. As shown in Figure 3-54, CIS and CZIS have similar crystal symmetry. The incorporated Zn$^{2+}$ ions (60 pm) replace both Cu$^+$ (60 pm) and In$^{3+}$ (62 pm) ions, producing a slight shrinkage of the crystal lattice ($a = 5.52 \text{ Å}$ for CIS to $a = 5.51 \text{ Å}$ for CZIS).

As shown in Figure 3-54 (e-h) the conversion from monoclinic CTS to tetragonal CZTS is relatively complex. According to the first major diffraction peak of CTS and CZTS, atoms in (-1,-3,1) planes of CTS and (1,1,2) planes of CZTS are both
hexagonally packed Figure 3-55a,b). The distance between neighboring cations in CTS (-1,-3,1) planes (2.27 Å) is slightly larger than that of neighboring cations in the (1,1,2) planes of CZTS (2.21 Å). These similarities allow the CE process to occur with minimal changes in the crystal lattice. As shown in Figure 3-55c,d, the interplanar distance between (-1,-3,1) planes of CTS (3.139 Å) shrinks to 3.136 Å between (1,1,2) planes of CZTS, shifting the corresponding diffraction peak to a slightly higher angle. STEM-EDS elemental mapping of the CZIS and CZTS NPs confirms that Cu, In (Sn), Zn and S are uniformly distributed within the NPs (Figure 3-53). Therefore, we confirm that Zn$^{2+}$ has been incorporated into ternary CIS/CTS NPs to form the corresponding CZIS/CZTS NPs.

Figure 3-53. Panels (a), (b), (e) and (f), (g), (j) are TEM images, corresponding HAADF-STEM images and elemental maps for CZIS and CZTS NPs, respectively. Panels (c) and (d) are a top view HRTEM image of CZIS NPs and the corresponding FFT of the indicated region; panels (h) and (i) are a top view HRTEM image of CZTS NPs and corresponding FFT of the indicated region. Scale bars in panel (b) and (e) are 50 nm; scale bars in panel (g) and (j) are 100 nm.

As discussed above, divalent cations cannot be incorporated directly into copper sulfide phases to form alloys; they can only replace the Cu$^+$ in the cation sublattice. Copper atoms in copper sulfide crystals occupy a mixture of 2-, 3- and 4-coordinate
sites, but in the ternary phases all copper atoms are coordinated to 4 sulfur atoms (Figure 3-54). Divalent cations such as Cd$^{2+}$ are always coordinated to four sulfur atoms, with a similar overall structural symmetry to that of the ternary crystals. Note that the numbers of cations and anions in these 4-coordinated crystals are equal. The crystal structure of covellite CuS shows that structures in which all Cu atoms in copper sulfide are 4-coordinated are not thermodynamically favorable. Rather than all Cu atoms assuming the Cu$^{2+}$ oxidation state, which would allow coordination to four sulfur atoms, the stable CuS structure incorporates disulfide bonds that allow the Cu atoms to remain in the Cu$^{+}$ oxidation state. Thus, there is an inherent conflict in copper sulfide phases between the preferred coordination (4-coordinate) and preferred oxidation state (+1) of the copper cations. In ternary phases incorporating trivalent or tetravalent cations, this conflict is relieved. Once this conflict has been relieved, divalent cations can be incorporated into a ternary phase by displacing both Cu$^{+}$ and In$^{3+}$ or Sn$^{4+}$ in a manner that allows all of the cations to maintain their most stable oxidation states while remaining tetrahedrally coordinated.
Figure 3-54. Side view (top row) and top view (bottom row) of structural models of ternary and quaternary phases.

Figure 3-55. (a) projection of (-1,-3,1) planes of CTS NPs, (b) projection of (112) planes of CZTS, (c) structure model of CTS NPs showing the interplanar spacing of (-1,-3,1) planes, (d) structure model of CZTS NPs showing the interplanar spacing of (112) planes.
3.5.5 Experimental Section

Chemicals. All chemicals were used as received. Indium chloride (InCl₃, 98%), gallium chloride (GaCl₃, 99.99%), tin (IV) chloride (SnCl₄, reagent grade, 98%), cadmium chloride (CdCl₂, 99.99%), zinc acetate [Zn(OAc)₂, 99.99%], lead chloride (PbCl₂, 99.999%), iron acetylacetonate [Fe(acac)₃, 99.99%], oleylamine (70%, OAm), trioctylphosphine (TOP, 97%), 1-octadecene (ODE; technical grade, 90%), and 1-dodecanethiol (DDT, ≥ 98%) were purchased from Sigma-Aldrich. Germanium (IV) iodide (GeI₄, 99.99%) was purchased from Strem Chemicals. Cu(NO₃)₂·2.5H₂O, toluene, and ammonium sulfide (21.2 wt % in water) were purchased from Fisher Scientific.

Preparing CuS Templates. For the synthesis of hexagonal CuS NPs, 1.5 mmol of Cu(NO₃)₂·2.5H₂O was dissolved in a mixture of 10 mL of OAm and 10 mL of toluene, then heated to 70 °C under an argon flow. 1.5 mL of ammonium sulfide (AS) solution (21.2% in water) was injected into the Cu-OAm to form CuS NPs. After 2 h, 10 mL of ethanol was added to destabilize the NP dispersion, followed by centrifugation at 4000 rpm for 1 min. To remove excess AS and OAm, the NCs were washed by precipitation upon addition of ethanol, followed by redispersion in chloroform. This purification process was applied to all of the NPs described in the following sections. The NPs could be redispersed in organic solvents including chloroform, hexane, and toluene. The CuS NPs (one batch, typically ~230 mg) were then dried and dispersed in 9 mL OAm for subsequent experiments (CuS-OAm dispersion).
Synthesis of Ternary CIS, CFS, CGS, CGeS and CTS NPls. For synthesis of ternary NPls, a mixture of 0.5 mmol cation precursor [InCl₃, Fe(acac)₃, GaCl₃, SnCl₄ or GeCl₄], 8 mL of OAm and 2 mL of DDT was held under flowing argon at ambient temperature for 30 min before heating to 160 °C (for CIS, CFS and CTS) or 200°C (for CGS and CGeS). Then, 3 mL of CuS-OAm dispersion was injected into the mixture and the solution was held at this temperature for 30 min. To collect the NPls, 10 mL of ethanol was added, followed by centrifuging at 4000 rpm for 1 min. For control experiments with a substoichiometric amount of precursor for cation incorporation, 0.1 mmol InCl₃ was used, while the other experimental conditions and procedures were kept the same as those for the synthesis of intact CIS NPls.

Synthesis of Quaternary CZIS/CZTS NPls. The CIS/CTS NPI dispersion was prepared by dispersing dry CIS/CTS NPls (one batch, typically ~70 mg for CIS NPls and ~73 mg for CTS NPls) in 2 mL of TOP. A mixture of 1 mmol of Zn(OAc)₂, 4 mL of ODE, and 8 mL of OAm was held under flowing argon at room temperature for ~30 min, followed by heating to 160 °C. Then, 2 mL of CIS/CTS dispersion was injected into the mixture and the solution was held at this temperature for 30 min. To collect the NPls, 10 mL of ethanol was added, followed by centrifuging at 4000 rpm for 1 min.

Incorporation of In³⁺ into Covellite CuS NPls without DDT. A mixture of 0.5 mmol of InCl₃ and 10 mL of OAm was degassed at room temperature under argon protection followed by heating to 160 °C, following by injection of 3 mL of CuS-OAm dispersion. The mixture was held at this temperature for 30 min. To collect the NPls, 10 mL of ethanol was added, followed by centrifuging at 4000 rpm for 1 min.
Synthesis of Heterogeneous CdS-Cu_{2-x}S, ZnS-Cu_{2-x}S, CdS and PbS NPs. For synthesis of heterogeneous CdS-Cu_{2-x}S or ZnS-Cu_{2-x}S NPs, a mixture of 0.5 mmol of cation precursor [CdCl₂ or Zn(OAc)₂], 8 mL of OAm and 2 mL of DDT was degassed under an argon flow for 30 min before heating to 160 °C. Then, 3 mL of CuS-OAm dispersion was injected into the mixture and the solution was held at this temperature for 30 min. Synthesis of CdS NPs employed 2 mmol CdCl₂, while the other experimental conditions and procedures were kept the same. For synthesis of PbS NPs, a mixture of 0.5 mmol of PbCl₂ and 8 mL of OAm was degassed under an argon flow for 30 min before heating to 120 °C. The CuS-OAm dispersion was injected at 100 °C. Then 2 mL DDT was injected and the mixture was held at 120 °C for 5 min. To collect the NPs, 10 mL of ethanol was added, followed by centrifuging at 4000 rpm for 1 min.

Characterization. Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-2010 at an accelerating voltage of 200 kV. High-resolution TEM (HRTEM) images were obtained using a FEI Tecnai G2 F30 at an accelerating voltage of 300 kV. High angle annular dark field scanning TEM (HAADF-STEM) images, HR-STEM images and STEM energy dispersive X-ray spectroscopy (STEM-EDS) maps were collected using a JEM-ARM200F STEM equipped with spherical aberration correctors on the image at an accelerating voltage of 200 kV. TEM grids were prepared by dropping a dilute NC dispersion onto a carbon-coated copper or nickel TEM grid and allowing the sample to dry under air. Powder X-ray diffraction (XRD) measurements were carried out using a Rigaku Ultima IV diffractometer with a Cu Kα X-ray source. Samples were prepared by drop-casting concentrated NC dispersions
onto glass slides. Elemental analysis of NCs by energy-dispersive X-ray spectroscopy (EDX) was obtained using an Oxford Instruments X-Max 20 mm² EDX detector within a Zeiss Auriga scanning electron microscope (SEM).
3.6 Selective Cation Incorporation into Copper Sulfide-Based Nanoheterostructures

3.6.1 Introduction

Heterogeneous metal chalcogenide nanostructures are of considerable interest for applications in solution-processed solar cells, photocatalysis, and photoacoustic imaging. Among these nanostructures, copper sulfide-based nanoheterostructures (NHs) have attracted extensive attention, due to their controllable morphology, tunable bandgaps, and large absorption coefficients. Formation of NHs not only integrates properties of two or more different materials in a single structure, but also provides a means of influencing charge carrier separation and recombination that is not available in homogeneous structures, and may promote other synergistic interactions between domains. Thus, the ability to design and synthesize targeted NHs is of great potential value. Fabrication of these NHs generally involves formation of a Cu$_{2-x}$S nanocrystal (NC) matrix, following by heterocation incorporation at appropriate conditions. Cu$_{2-x}$S NCs have emerged as an ideal template for cation incorporation, because Cu atoms are highly mobile at elevated temperatures, enabling efficient interstitial diffusion and substitution of incoming cations.

In most cases, CE reactions preserve the morphology of template NCs. Incomplete CE can produce NHs with a clear boundary between immiscible Cu$_{2-x}$S and MS domains. Less commonly, cation incorporation leads to additional shape evolution when heterogeneous NCs are formed. The synthesis of heterogeneous, ternary Cu$_{2-x}$S-MS NCs has drawn considerable attention due to their uncommon
combinations of properties. However, further cation incorporation using these NCs to produce quaternary Cu-M-N-S NCs has rarely been considered. Upon subsequent exposure of ternary Cu$_{2-x}$S-MS NCs to a third type of cation N$^{n+}$ under appropriate conditions, the incoming N$^{n+}$ may (1) diffuse into the Cu$_{2-x}$S domain to form a homogeneous Cu-N-S alloy domain; (2) replace M$^{n+}$ in the MS domain; (3) enter both domains and promote mixing of Cu and M$^{n+}$ ions, producing a homogeneous, single-phase NC; or (4) trigger morphology evolution of the entire NC. The overall process of transformation from Cu$_{2-x}$S into a ternary heterogeneous system and then further into a different multi-domain NH provides a powerful means of accessing different combinations of NH composition, crystal phase, and morphology and can provide valuable insights into mechanisms of NCs’ shape and phase evolution.

When designing and synthesizing a new combination of metal sulfide (MS-NS) NHs, two common synthetic routes are available: (1) one-pot synthesis by directly mixing multiple cation precursors simultaneously;¹⁰⁹,¹¹⁹,¹²¹ and (2) multistep synthesis by growing a new NS domain onto an existing MS domain.⁴⁷,¹⁵¹,¹⁹³ However, when neither of the alternatives can produce desired NHs, a new approach using Cu$_{2-x}$S template NCs could be the solution for preparation of previously unavailable NHs. The synthetic route can be generally described as: first synthesize Cu$_{2-x}$S-MS NHs by M incorporation into Cu$_{2-x}$S template NCs, followed by N incorporation into the rest of Cu$_{2-x}$S domain. Thus, a better understanding of cation incorporation mechanisms, especially using Cu$_{2-x}$S template NCs, is indeed intriguing and significant.
According to Section 3.5, incorporation of divalent cations into Cu$_{2-x}$S NCs exclusively produces heterogeneous Cu$_{2-x}$S-MS NCs due to conflicts between valence and coordination number of divalent cations.$^{55,118}$ Heterogeneous ternary NCs can also be obtained by incomplete trivalent and tetravalent cation incorporation and diffusion, under conditions that would ultimately fully convert the Cu$_{2-x}$S templates into homogeneous ternary NCs.$^{128,158,194}$ For example, treatment of Cu$_{2-x}$S using Zn$^{2+}$ and Cd$^{2+}$ consistently produces Cu$_{2-x}$S-ZnS/CdS heterostructures rather than homogeneous alloy NCs. In contrast, cation incorporation using trivalent In$^{3+}$ or tetravalent Sn$^{4+}$ would produce Cu-In-S or Cu-Sn-S ternary alloy NCs (possibly with Cu$_{2-x}$S-CuInS$_2$ or Cu$_{2-x}$S-Cu$_2$SnS$_3$ as an intermediate product). Thus, the heterostructures produced by divalent cation incorporation provide two clearly-defined domains of different composition, one of which (ZnS) has both the preferred cation valence (+2) and coordination satisfied, and one of which (Cu$_{1.81}$S) still suffers from a conflict between preferred cation valence (+1) and coordination. Observing the evolution of this heterostructure upon exposure to different cations can provide insights into the relative stability of the two domains, and of the interface between them. In addition, incorporation of foreign cations with cation radii much different from Cu$^+$ could lead to lattice expansion- or shrinkage-induced shape evolution of the Cu$_{2-x}$S template NCs.$^{4,55,131,195}$ Therefore, NHs produced by Zn$^{2+}$ incorporation into Cu$_{2-x}$S (here we use Cu$_{1.81}$S-ZnS), are an ideal template to investigate cation incorporation into copper sulfide-based NHs.
3.6.2 Cation Incorporation into Cu$_{1.8}$_S-ZnS with TOP

Cu$_{1.8}$_S-ZnS NHs were prepared using a previously reported procedure. Briefly, Zn$^{2+}$ was incorporated into a roxbyite Cu$_{1.8}$_S NCs template to form dual-interface heterostructured (sandwich) NCs in the presence of TOP. As shown in Figure 3-56a, the monodisperse dual-interface heterostructured NCs have a diameter of 20.3 ± 0.6 nm. Size distribution histograms for this and subsequent samples are presented in Figure 3-57. The ZnS grows epitaxially, parallel to the $a$-axis of roxbyite Cu$_{1.8}$_S ($c$-axis of ZnS) to form caps on both sides of each NH. Their XRD pattern and elemental mapping (Figure 3-58) reveal that the NCs consist of both Cu$_{1.8}$_S and ZnS phases. The STEM-EDS results suggest that Cu (red) is concentrated at the middle of the NCs, whereas Zn (green) is located in the caps. Sulfur (yellow) is distributed homogeneously throughout the entire NC. Although the thickness of the Cu$_{1.8}$_S interlayer is tunable, we choose NCs with a thickness of ~7 nm as the template for further cation incorporation experiments because they can not only provide clear evidence of any morphology evolution, but also retain enough Cu and Zn content to allow formation of different Cu- and Zn-containing crystal phases after additional cation treatment.

![Figure 3-56](image_url)

Figure 3-56. (a) Low magnification STEM-HAADF and (b) HR-STEM image of Cu$_{1.8}$_S-ZnS NHs. (c)
STEM-HAADF image and corresponding elemental maps of a single NC from panel (a). Scale bar in panel c is 5 nm. The red area shows the Cu$_{1.81}$S domain and green area shows the ZnS domain.

\[
\begin{align*}
\bar{d} &= 20.3 \pm 0.6 \ nm \\
\bar{d} &= 21.6 \pm 0.7 \ nm \\
\bar{d} &= 20.4 \pm 0.6 \ nm \\
\bar{d} &= 20.2 \pm 0.9 \ nm \\
\bar{d} &= 21.2 \pm 1.1 \ nm \\
\bar{d} &= 20.0 \pm 1.2 \ nm \\
\bar{d} &= 20.3 \pm 1.8 \ nm \\
\bar{d} &= 20.3 \pm 1.8 \ nm \\
\bar{d} &= 21.1 \pm 1.2 \ nm
\end{align*}
\]

Figure 3-57. Size distribution histograms of all samples.

Figure 3-58. XRD patterns of Cu$_{1.81}$S template NCs (orange) and Cu$_{1.81}$S-ZnS NHs (blue). TEM, HAADF-STEM image and corresponding elemental maps of Cu$_{1.81}$S-ZnS NHs.

Next, the Cu$_{1.81}$S-ZnS NHs were used as a template for cation incorporation. TOP has been widely used as a Cu-extracting agent because it has strong affinity for Cu$^+$, compared with the modest stability of the soft copper-chalcogenide bond.$^{196}$ Thus, the presence of TOP is expected to strongly affect the cation incorporation results. Note that, to ensure effective CE, we used excess TOP (5 mL) whenever TOP was used in experiments reported here. Figure 3-59 shows the results obtained using In$^{3+}$ with TOP. The low magnification TEM image in Figure 3-59a reveals that the product NCs
preserve the overall shape, size \( (d = 21.6 \pm 0.7) \) and multidomain structure of the template NHs, but with less obvious boundaries between different domains. Figure 3-59b and c show HR-STEM images of a single NH treated with \( \text{In}^{3+} \) and TOP and the corresponding elemental maps, indicating that the resulting NC consists of a Cu-In-S alloy center, with two Zn-S caps. As shown in Figure 3-60a, the XRD pattern of the resulting NCs most closely matches that of the wurtzite \( \text{CuInS}_2 \) phase (ICDD PDF 01-007-9459). However, because of overlap in the XRD patterns (< 0.7° differences in peak positions) and the similarity of crystal structures among these crystal phases of wurtzite \( \text{Cu}_{0.4}\text{Zn}_{0.2}\text{In}_{0.4}\text{S} \) and \( \text{ZnS} \), as well as obvious overlapping of elemental signals, exclusive identification of specific phases is not feasible. Products of CE reactions almost always inherit the crystal structure (especially the anion sublattice) of the template. Thus, formation of roquesite \( \text{CuInS}_2 \) is unlikely due to its fcc anion sublattice. ZnS domains tend to be preserved during CE reactions with TOP (as discussed further below). Moreover, because the \( \text{CuInS}_2 \), \( \text{ZnS} \) and \( \text{Cu}_{0.4}\text{Zn}_{0.2}\text{In}_{0.4}\text{S} \) have similar unit cell parameters, the heterointerfaces between different domains are not very obvious.
Figure 3-59. (a) Low magnification TEM image of NHs after treatment with In$^{3+}$ and TOP. (b) HR-STEM image of a single NC. The arrows indicate boundaries between different domains. (c) HAADF-STEM image and corresponding elemental maps for Cu, In, and Zn, with a scale bar of 10 nm. (d) Schematic illustration of mechanisms of formation of ZnS-CuInS$_2$ sandwich NCs.

Figure 3-60. XRD patterns of all samples.

According to a previous report, Zn$^{2+}$ ions diffuse into roxbyite Cu$_{1.81}$S NCs along the (100) direction of roxbyite, which becomes the (001) direction of the resulting wurtzite ZnS.$^{47}$ We will refer to this direction, which is roughly perpendicular to the phase boundaries in the NHs, as the $z$-direction in the NHs. In contrast, Cu atoms can
diffuse out of the NC in all directions. When In$^{3+}$ ions react with the NHs in the presence of TOP, we find that In$^{3+}$ ions diffuse into the NHs through the Cu$_{1.81}$S domain. This reflects the fact that In$^{3+}$ incorporation into the Cu$_{2-x}$S phase is more favorable than incorporation into ZnS. Meanwhile, Cu$^+$ ions are extracted from the sublattice by TOP, through both z- and xy-directions. When Cu$^+$ ions migrate to the caps of a NC, Cu$^+$ can interact with incoming In$^{3+}$ and existing Zn$^{2+}$ ions in both caps, producing a Cu-Zn-In-S quaternary alloy in the caps of NHs. In some cases, NCs with three different domains, of Cu-S, In-S, and Zn-S, were observed (Figure 3-61). We attribute this to an imbalance between the rates of Cu-out-diffusion and In-in-diffusion. The whole transformation process is illustrated schematically in Figure 3-59.

Figure 3-61. Additional TEM and HR-STEM image, and corresponding elemental maps of Cu$_{1.81}$S-ZnS NHs after In$^{3+}$ and TOP treatment. As shown in panel b and c, the NC exhibits three different domains of Cu-S, In-S, and Zn-S. The highly crystalline heterointerfaces in the NCs can be clearly observed in panel b. The preservation of ZnS domains is confirmed by an observed lattice spacing of 0.29 nm [(002) planes]. When Cu$^+$ ions migrate to the caps of a NC, Cu$^+$ can replace all or some of the Zn$^{2+}$ ions in both caps, producing uniform Cu$_{2-x}$S and ZnS caps or non-uniform Cu-rich caps. Although we cannot match the XRD pattern with any high quality standard PDF card of Cu$_{2-x}$S, and the complexity and many
possible phases of Cu$_{2x}$S, create substantial ambiguity in the determination of the Cu$_{2x}$S phase, we believe that In$^{3+}$ incorporation into the NHs through Cu$_{1.81}$S domain is genuine. The formation of separate phases of In$_2$S$_3$ and Cu$_{2x}$S implies that the rate of Cu$^+$ extraction is faster than that of In$^{3+}$ replacement. Cu$^+$ ions tend to migrate to the caps or bind with TOP before In$^{3+}$ ions diffuse in. While this triple domain NC was not produced consistently as the dominant product, the observations are consistent with our discussion on selective cation incorporation mechanisms.

To provide further insight into the cation exchange process we conducted experiments using excess In$^{3+}$ (0.5 mmol), to increase the driving force for In$^{3+}$ indiffusion. As shown in Figure 3-62a, the excess In$^{3+}$-treated NHs remain as heterogeneous NCs, with diameters of 20.4 ± 0.6 nm. Some of the NHs are Janus-like, with just two different domains, rather than sandwich-like with three domains. The elemental maps for a single NC both indicate that the In signals are colocated with those of Cu, and separate from those of Zn (Figure 3-62). This is consistent with the observations using 0.15 mmol In$^{3+}$ that the Cu$_{2x}$S domain, rather than ZnS, can offer a pathway for In$^{3+}$ incorporation. The XRD pattern (Figure 3-60) of the resulting NCs can be matched with the wurtzite CuInS$_2$ phase. Considering the results of the elemental maps, the ZnS unit cells may undergo ~3% expansion to adapt to the lattice framework of dominant CuInS$_2$ domains. As shown in Figure 3-62b, HR-STEM image analysis of a single NC shows lattice spacings of 0.33 nm and 0.30 nm are observed on the CuInS$_2$ domain, corresponding to its (100) and (002) planes, respectively, while the observed lattice spacing in the ZnS domain corresponds to the (100) planes. The transformation from three different domains to two domains indicates that the latter is more stable and the ions in the colloidal system remain highly mobile. Compared to the formation of ZnS-CuInS$_2$ sandwich NCs or Cu$_{2x}$S-In$_2$S$_3$-ZnS NCs, using a lower concentration of
In$^{3+}$, the high concentration of In$^{3+}$ facilitates the incorporation of In$^{3+}$ into Cu$_{2-x}$S phase before complete Cu$^{+}$ extraction and migration processes. The higher In$^{3+}$ concentration also drives elimination of one of the ZnS domains in many cases. Compared to the results when using excess In$^{3+}$, the NCs obtained using less initial In$^{3+}$ amount can be viewed as an intermediate stage. We note that, in the presence of TOP, treatment with In$^{3+}$ does not lead to removal of both ZnS domains, even when excess In$^{3+}$ remains in solution.

![Figure 3-62](image)

**Figure 3-62.** (a) Low magnification TEM image of NCs after treatment with excess In$^{3+}$ and TOP. (b) HR-STEM image of a single NC and (c) corresponding elemental maps for Cu, In, and Zn. The scale bar in panel c is 10 nm.

We also treated the NHs with TOP and Sn$^{4+}$ under similar reaction conditions to those used with In$^{3+}$. As shown in Figure 3-63a, the resulting NCs retained the morphology of template NHs ($d = 20.2 \pm 0.9$), while the boundaries and interfaces in the NCs disappeared. The XRD pattern in Figure 3-60 is consistent with wurtzite ZnS. As revealed by HRTEM analysis in Figure 3-63b, the transformed NCs are single crystalline, with interplanar spacings of 0.31 nm and 0.28 nm, corresponding to (002) and (101) planes of ZnS, respectively. To investigate the mechanism of transformation
from Cu$_{1.81}$S-ZnS NHs to homogeneous ZnS NCs, we analyzed the cation incorporation process at different reaction times. Figure 3-63d,e reveal that the Cu$_{1.81}$S domain of NHs was removed quickly (< 1 min), followed by a ripening of the separated ZnS caps. The removal of the Cu$_{1.81}$S domain is attributed to TOP-induced chemical etching. This observation is consistent with the previous report. The HR-STEM image in Figure 3-63c also confirms that the single ZnS cap is crystalline, without interfaces between heterodomains. The STEM-HAADF image and corresponding elemental maps of transformed NCs in Figure 3-63f confirm the co-localization of Zn and S, as well as the presence of very little residual Cu and Sn. Extending the reaction time at 120 °C eventually led to complete dissolution of the ZnS NCs, but this occurred on a longer time scale than the removal of the Cu$_{1.81}$S domain and the ripening of the ZnS caps into spheres.

The restoration of ~20 nm spherical NCs also supports the observation of high mobility of ions in this colloidal system, as the ZnS caps ripen into NCs with diameter of ~20 nm by redissolution of small ZnS NCs. When synthesizing the roxbyite Cu$_{1.81}$S template NCs, once the NCs reach a diameter of ~20 nm, further extending the reaction time produces hexagonal Cu$_{1.81}$S nanoplatelets, instead of continuously increasing the diameter (Figure S14). This also indicates that ~20 nm is a critical diameter for those NCs. 

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Figure 3-63. (a) Low magnification TEM (b) HRTEM image of NHs after Sn$^{4+}$ and TOP treatment. (c) HR-STEM image of individual ZnS cap. (d),(e) TEM images of NCs during the transformation at reaction times of 1 min and 5 min. (f) STEM-HAADF image and corresponding elemental maps for Zn and S. (g) Schematic illustration of the transformation from Cu$_{1.5}$S-ZnS NHs to ZnS NCs. The scale bars for panel d and f are 50 nm and 10 nm, respectively.

Figure 3-64. (a) TEM images of roxbyite Cu$_{1.5}$S synthesized using extended reaction time.
3.6.3 Cation Incorporation into Cu$_{1.81}$S-ZnS without TOP

To further investigate cation exchange or incorporation of In$^{3+}$/Sn$^{4+}$, we also directly reacted these cations with the NHs, without adding TOP. As shown in Figure 3-65, In$^{3+}$ treatment of the NHs produced homogeneous NCs with diameters of 20.4 ± 1.1 nm. STEM-EDS elemental maps of a single NC (Figure 3-65c) confirm the co-localization of Cu, In, and S, as well as the presence of a small amount of residual Zn. Thus, the transformation includes both In$^{3+}$ incorporation and ZnS dissolution processes. As shown in Figure 3-60, the XRD pattern of these NCs indicates the presence of both CuInS$_2$ and Cu$_{1.81}$S. The residual Cu$_{1.81}$S may be due to insufficient In$^{3+}$ incorporation along with ZnS dissolution. The HR-STEM image (Figure 3-65b) reveals that the atoms are hexagonally packed (highlighted by a red hexagon), with an interatomic spacing of ~2.4 Å, which is close to the side length of the hexagonally-arranged CuInS$_2$ unit cell. To investigate the shape, composition and crystal phase evolution process, we analyzed the NHs after 1 min of In$^{3+}$ treatment. As shown in Figure 3-65(d-f), one of the ZnS caps dissolved very quickly, producing CuInS$_2$-ZnS heterodimers upon In$^{3+}$ incorporation. Then, the remaining ZnS cap was gradually removed to produce homogeneous CuInS$_2$ NCs upon continued In$^{3+}$ incorporation and additional atom migration. The whole transformation process is illustrated in Figure 3-65g.
Figure 3-65. (a) Low magnification TEM image, (b) HR-STEM image and (c) corresponding elemental maps of In$^{3+}$-treated NHs. (d) Low magnification HAADF-STEM image, (e) HR-STEM image and (f) corresponding elemental maps of the NHs during the In$^{3+}$ treatment at reaction time of 1 min. (g) Schematic illustration of the transformation from Cu$_{1.81}$S-ZnS NHs to CuInS$_2$ NCs. The scale bars in panel c and f are 5 nm.

On the other hand, directly mixing Sn$^{4+}$ with the NHs produced homogeneous Cu$_{1.81}$S NCs. As shown in Figure 3-66a, the product NCs are homogeneous, having a diameter of 20.0 ± 1.2 nm, without obvious interfaces or internal variation in composition. The XRD pattern of the resulting NCs in Figure 3-60 confirms that they are in the roxbyite Cu$_{1.81}$S phase. As shown in Figure 3-66b, HR-STEM reveals that the resulting NCs have lattice spacings of 0.28 nm and 0.32 nm, corresponding to (18 2 1) planes and (604) planes of roxbyite Cu$_{1.81}$S, respectively. The STEM-HAADF image and corresponding elemental maps in Figure 3-66c also indicate the NCs are mainly composed of Cu and S, with minimal Sn and Zn content. The shape evolution
from Cu$_{1.81}$S-ZnS NHs to Cu$_{1.81}$S NCs is recorded in Figure 3-66(d-f). Similar to the NHs treated with In$^{3+}$, one of the ZnS caps of each Cu$_{1.81}$S-ZnS NH is removed quickly. Then, the resulting heterodimers gradually transform into homogeneous Cu$_{1.81}$S NCs upon aging.

The above results showed that, unlike In$^{3+}$, Sn$^{4+}$ is not incorporated into the Cu$_{2.8}$S domain, whether or not TOP is added as a copper extracting agent. To further address the question of whether the selectivity of cation incorporation is due to the oxidation states or the nature of the elements, we also investigated incorporation of Sn$^{2+}$ into Cu$_{1.81}$S-ZnS NHs. Treatment of the NHs with Sn$^{2+}$ and TOP produced a new type of
heterostructures (Figure 3-67a). As shown in Figure 3-60, the XRD pattern and the elemental maps of the NCs reveal that the transformed heterodimers are composed of SnS and ZnS. The crystalline heterointerface in the NCs can be clearly seen in Figure 3-67b, with lattice spacings of 0.17 nm [(212) planes] and 0.28 nm [(013) planes] in the SnS domain, and 0.29 nm [(101) planes] in the ZnS domain. The STEM-HAADF image and corresponding elemental maps of a single NC also confirm the two distinct SnS and ZnS domains, while Cu signals are negligible throughout the NH (Figure 3-67c). However, we note that the resulting NCs no longer preserved the morphology of the parent NHs. This change can be attributed to the fact that Sn$^{2+}$ has a cation radius of ~118 pm, which is much larger than that of Cu$^{+}$ (~60-77 pm), Zn$^{2+}$ (~60-74 pm), In$^{3+}$ (~62-80 pm) and Sn$^{4+}$ (~55-81 pm). The mismatch of the cation radius produces local lattice expansion and thereby shape evolution during the cation incorporation process. Although the morphology of SnS-ZnS NHs is relatively irregular, the diameter of these NHs ($d = 20.3 \pm 1.8$) is still quite close to that of the template NCs.
Figure 3-67. (a) Low magnification STEM-HAADF and (b) HR-STEM image of NHs after treatment with Sn²⁺ and TOP, and (c) corresponding elemental maps for Zn and Sn. The scale bar in panel c is 10 nm.

In addition, we treated the Cu₁.₈₁S-ZnS NHs with Sn²⁺ without adding TOP. As shown in Figure 3-68a, the Sn²⁺-treated NHs maintained the overall morphology of the template NHs \(d = 21.1 \pm 1.2\) but the internal phase boundaries of the template were gone. They appear to be homogeneous, single-phase NCs. However, the HAADF image and corresponding elemental maps of the NCs reveal that most of the transformed NCs are Cu₂₋₄S@SnS core@shell NHs (Figure 3-69). This observation is supported by the XRD pattern, indicating that the copper sulfide domain is roxbyite Cu₁.₈₁S (Figure 3-60). The HR-STEM image in Figure 3-68b shows that the Cu₁.₈₁S core has a lattice spacing of 0.18 nm, corresponding to (886) planes of Cu₁.₈₁S. Though the crystal phases and elemental distribution have been confirmed, we did not observe the heterointerface between Cu₁.₈₁S and SnS on NHs. As shown in Figure 3-68c, the SnS shell is as thin
as 1-2 nm. We attribute this thin SnS shell to the limited extent of CE that occurs without any copper extracting agent. Similar to the case using Sn⁴⁺, the ZnS caps were removed in the absence of TOP. Meanwhile, Sn²⁺ ions adsorbed onto the surface of Cu₁.₈₁S core and started replacing Cu⁺ ions. However, the CE reactions only occur on the surface of Cu₁.₈₁S core, due to lack of Cu-extracting agent, producing Cu₁.₈₁S@SnS core@shell NHs with a shell thickness of only 1-2 nm. Therefore, the blurry heterointerface on NHs may arise from the thin and less-crystalline SnS shell.

The formation of core@shell structures can occur via the following steps: The ZnS caps of the template were removed one after another in the absence of TOP, leaving behind the less-spherical Cu₁.₈₁S cores. Because the Sn²⁺ has relatively large cation radius and no TOP was present to promote Cu⁺ extraction, the Sn²⁺ ions could only adsorb on the surface of the Cu₁.₈₁S core and therefore the extent of CE reaction (Cu⁺ replacement with Sn²⁺) was very limited. Simultaneously, the S²⁻ ions released from dissolved ZnS caps (no ZnS was detected according to XRD and EDS characterization) can react with the absorbed Sn²⁺, producing thin SnS shells. This process is also limited by its higher reaction barrier, compared with the CE reaction. Therefore no individual SnS particles, free from the Cu₁.₈₁S cores were observed.
Figure 3-68. (a) TEM, (b) HR-STEM, (c) HAADF-STEM image of Sn$^{2+}$-treated NHs, and corresponding elemental maps for Cu and S. The scale bar in panel c is 10 nm.

Figure 3-69. Low magnification STEM-HAADF image and corresponding elemental maps of Sn$^{2+}$-treated NHs. The Zn content is negligible, compared to Cu, Sn and S. All panels share the same magnification with the bar of 20 nm.
### 3.6.4 Mechanism of Selective Cation Incorporation into Cu$_{1.81}$S-ZnS Nanoheterostructure

Combining all of the above results and observations, as summarized schematically in Figure 3-70, we can propose mechanisms of selective cation incorporation, extraction, and exchange in these NHs. Starting from the Cu$_{1.81}$S-ZnS NHs, direct exposure to foreign cations, without a copper extracting agent, leads to rapid dissolution of one of the ZnS caps, finally producing Zn-free NCs. This reflects the fact that the ZnS caps of the template NHs, in the absence of a copper complexing agent like TOP, are less thermodynamically stable than the Cu$_{1.81}$S interlayer. This observation is also supported by recent reports of core@shell or dimer nanostructures that are metastable and convert to other structures upon post-heating or electron beam irradiation.\(^{197-199}\)

However, in most cases, subsequent cation incorporation into the Cu$_{1.81}$S domain requires a copper complexing agent (copper extracting agent) that stabilizes Cu ions in solution, driving their removal from the NH. According to the HSAB theory, the ranking of hardness of cations is Sn$^{4+} > $In$^{3+} > $Zn$^{2+} > $Sn$^{2+} > $Cu$^{+}$.\(^{4}\) This difference in hardness of cations also strongly affects the affinity of cations toward S$^{2-}$. Therefore, In$^{3+}$ and Sn$^{2+}$, which occupy intermediate positions in this sequence, can bind to S$^{2-}$ more strongly than Sn$^{4+}$, producing a lower reaction barrier for cation incorporation. Compared to Sn$^{2+}$, incorporation of In$^{3+}$ is more favorable due to its similar cation radius to Cu$^{+}$, partial cation replacement required in a unit cell, and the slightly weaker Cu-S (274.5 $\pm$ 14.6 kJ/mol) bond in comparison with In-S (287.9 $\pm$ 14.6 kJ/mol) in CuInS$_2$.\(^{200}\) Thus, even without a Cu-extracting agent, In$^{3+}$ can partially replace Cu in the Cu$_{1.81}$S domain, producing CuInS$_2$.
On the other hand, using a Cu-extracting agent such as TOP leads to elimination of the Cu$_{1.81}$S domain while retaining the ZnS domain. Post-synthesis treatment with Sn$^{4+}$ or Sn$^{2+}$ in the presence of TOP leads to complete removal of Cu from the NHs. Sn$^{2+}$, which is a softer cation than Sn$^{4+}$ can replace part of the Cu to produce a SnS domain. However, although Sn$^{4+}$ accelerated the dissolution of the Cu$_{1.81}$S domain, its incorporation into the NHs was negligible. This is consistent with prior studies in which Sn$^{4+}$ and some other ions (e.g. Al$^{3+}$) were employed to modify the morphology during synthesis of Cu$_{2-x}$S$_{201-204}$. In those cases, Sn$^{4+}$ was not incorporated into the growing NCs, but the formation of Sn(IV)-organo-halide complexes influenced the nucleation and growth rates of specific facets, producing NCs with controlled morphology as well as decreased ensemble polydispersity.$^{202,203}$

Figure 3-70. Schematic illustration of overall selective cation incorporation into Cu$_{1.81}$S-ZnS NHs.

To investigate how the ZnS domains affect the cation incorporation results and to avoid interferences due to overlapping diffraction patterns, we treated the template roxyrite Cu$_{1.81}$S NCs (without ZnS domains) with In$^{3+}$/Sn$^{2+}$ in the presence of TOP. As
shown in Figure 3-71a,b and Figure 3-72, colocation of Cu, In and Sn signals and HRTEM imaging indicate the formation of CuInS₂. The XRD pattern further confirms the formation of wurtzite CuInS₂. These results imply that the ZnS domains do not influence the outcome of the In³⁺ incorporation. Figure 3-71(c-e) shows that Sn²⁺, in the presence of TOP, can replace all the Cu⁺ from the Cu₁.₈₁S NCs, producing homogeneous SnS NCs. The XRD pattern of these NCs (Figure 3-60) shows only the herzenbergite SnS phase. To further confirm the effect of Sn⁴⁺ on the cation incorporation process, we also treated the Cu₁.₈₁S-ZnS NHs at similar reaction conditions in the absence of Sn⁴⁺, both with (Figure 3-73a) and without (Figure 3-73b) TOP. The results indicate that Sn⁴⁺ accelerates the dissolution of the ZnS (without TOP) or Cu₁.₈₁S (with TOP) domains, even though it is not incorporated into the NCs under our reaction conditions, consistent with the studies using Sn⁴⁺ to control NC morphology during growth mentioned above.²⁰²,²⁰³
Figure 3-71. (a) Low magnification TEM image and (b) HRTEM image of roxbyite Cu$_{181}$S NCs after treatment with In$^{3+}$ and TOP. (c) Low magnification TEM image, (d) HR-STEM image, (e) HAADF image and corresponding elemental maps of roxbyite Cu$_{181}$S NCs after treatment with Sn$^{2+}$ and TOP.

Figure 3-72. (a) Comparison of XRD patterns of In$^{3+}$ and TOP treated Cu$_{181}$S NCs (blue) and excess In$^{3+}$ and TOP treated Cu$_{181}$S-ZnS NHs (red). (b) Low magnification HAADF image and corresponding elemental maps for In$^{3+}$ and TOP treated Cu$_{181}$S NCs (blue). The scale bar in panel b is 100 nm. Diffraction peaks are slightly shifted to higher angle when the template is a NH with ZnS domains. The unit cell of wurtzite ZnS is slightly smaller than that of wurtzite CuInS$_2$ (~3%). The relative intensity of diffraction peaks also changed due to removal of ZnS domains. For example, relative intensity of (002)
planes was suppressed due to ZnS caps on the CuInS\textsubscript{2} domains, and (002) planes are at the CuInS\textsubscript{2}/ZnS interfaces.

**Figure 3-73.** TEM image of (a) TOP and (b) oleylamine treated Cu\textsubscript{1,8}S\textsubscript{2}-ZnS NH\textsubscripts{5}. As shown in panel a, the obtained NH\textsubscript{5} are mainly ZnS caps (homogeneous NC\textsubscripts{5} are ZnS caps oriented with their flat face on the support film). Treatment with or without Sn\textsuperscript{4+} was for 10 min. CE reaction with Sn\textsuperscript{4+} was carried out at 120 °C and 160 °C without TOP. Compared to the results obtained using Sn\textsuperscript{4+}, ZnS caps in Panel a have not ripen into spherical ones, indicating lower reaction rates. Panel b shows that one of the ZnS caps of NH\textsubscript{5} was removed after being heated in oleylamine. This contrasts with the dissolution of both caps during treatment with Sn\textsuperscript{4+} in oleylamine. Therefore, both in the presence and absence of TOP, Sn\textsuperscript{4+} shows the ability to affect the reaction rate, rather than being incorporated into NH\textsubscript{5}.

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3.6.5 Experimental Section

**Chemicals.** All chemicals were used as received. Indium chloride (InCl₃, 98%), tin (IV) chloride (SnCl₄, reagent grade, 98%), tin (II) chloride (SnCl₂, reagent grade, 98%), di-tert-butyl disulfide (97%), oleylamine (70%, OAm), and trioctylphosphine (TOP, technical grade, 90%) were purchased from Sigma-Aldrich. CuCl₂·2H₂O and toluene were purchased from Fisher Scientific.

**Synthesis of Roxbyite Cu₂₋ₓS Template NCs.** The method for preparing roxbyite Cu₂₋ₓS NCs was adapted from Li and co-workers’ report with some modifications.⁴⁰ In a typical synthesis, 1 mmol of CuCl₂·2H₂O was dissolved in 10 mL of OAm, and the solution was held under flowing argon at ambient temperature for 30 min before heating to 180 °C. Then, 4 mL of di-tert-butyl disulfide was injected into the mixture and the solution was held at this temperature for 15 min. To collect the NCs, 10 mL of ethanol was added, followed by centrifuging at 4000 rpm for 1 min. To remove excess di-tert-butyl disulfide and OAm, the NCs were washed by precipitation with ethanol and centrifugation followed by redispersion in chloroform. This purification process was applied to all of the NCs described in the following sections. The NCs could be redispersed in organic solvents including chloroform, hexane, and toluene.

**Synthesis of Cu₁.₈₁S-ZnS NHs.** The synthesis of Cu₁.₈₁S-ZnS NHs was adapted from Ha and co-workers’ report with some modifications. The roxbyite Cu₂₋ₓS NC dispersion was prepared by dispersing 35 mg dry roxbyite Cu₂₋ₓS NCs in 8 mL of TOP. A mixture of 250 mg ZnCl₂ and 10 mL of OAm was held under flowing argon at ambient temperature for 30 min before heating to 180 °C. The mixture was held at this
temperature for 30 min before cooling to 55 °C. During the cooling process, 20 mL of toluene was added. 8 mL of the roxbyite Cu$_{2-x}$S NC dispersion was injected into the mixture and the mixture was held at 55 °C for 60 min. To collect the NHs, 10 mL of ethanol was added, followed by centrifuging at 4000 rpm for 1 min.

**Cation Incorporation into Cu$_{1.81}$S-ZnS NHs without TOP.** The NH dispersion was prepared by dispersing dry NHs (one batch, typically ~22.5 mg) in 5 mL of OAm. A mixture of 0.15 mmol SnCl$_4$ (or InCl$_3$ or SnCl$_2$) and 10 mL of OAm was held under flowing argon at ambient temperature for 30 min before heating to 160 °C. Then, 5 mL of NH dispersion was injected into the mixture, and it was held at this temperature for 30 min. To collect the NHs, 10 mL of ethanol was added, followed by centrifuging at 4000 rpm for 1 min.

**Cation Incorporation into Cu$_{1.81}$S-ZnS NHs Using TOP.** The NH dispersion was prepared by dispersing dry NHs (one batch, typically ~22.5 mg) in 5 mL of TOP. A mixture of 0.15 mmol SnCl$_4$ (or InCl$_3$ or SnCl$_2$) and 10 mL of OAm was held under flowing argon at ambient temperature for 30 min before heating to 160 °C (for InCl$_3$ or SnCl$_2$) or 120 °C (for SnCl$_4$). Then, 5 mL of the NH dispersion was injected into the mixture, and it was held at this temperature for 5 min (30 min for the InCl$_3$ case). To collect the NHs, 10 mL of ethanol was added, followed by centrifuging at 4000 rpm for 1 min.

**Cation Incorporation into Roxbyite Cu$_{2-x}$S NCs Using TOP.** The roxbyite Cu$_{2-x}$S NC dispersion was prepared by dispersing 35 mg dry roxbyite Cu$_{2-x}$S NCs in 5 mL of TOP. A mixture of 0.3 mmol InCl$_3$ (or SnCl$_2$) and 10 mL of OAm was held under
flowing argon at ambient temperature for 30 min before heating to 160 °C. Then, 5 mL of the Cu_{2-x}S NC dispersion was injected into the mixture, and it was held at this temperature for 30 min. To collect the NHs, 10 mL of ethanol was added, followed by centrifuging at 4000 rpm for 1 min.

**Characterization.** Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-2010 at an accelerating voltage of 200 kV. High-resolution TEM (HRTEM) images were obtained on a FEI Tecnai G2 F30 at an accelerating voltage of 300 kV. High angle annular dark field scanning TEM (HAADF-STEM) images, HR-STEM images and STEM energy dispersive X-ray spectroscopy (STEM-EDS) maps were collected using a JEOL JEM-ARM200F STEM equipped with spherical aberration correctors on the image, at an accelerating voltage of 200 kV. TEM grids were prepared by dropping a dilute NC dispersion onto a carbon-coated copper or nickel TEM grid and allowing the sample to dry under air. Size distributions were obtained from TEM images by measuring at least 100 NCs from multiple TEM images from different areas of the grid, using Nanomeasurer v. 1.2. Powder X-ray diffraction (XRD) measurements were carried out using a Rigaku Ultima IV diffractometer with a Cu Kα X-ray source. Samples for XRD were prepared by drop-casting concentrated NC dispersions onto glass slides.
Chapter 4. The Applications of Copper Chalcogenide Nanocrystals for Electrocatalysis and Photothermal Effect

4.1 Controlled Synthesis of Covellite Nanoplatelets for Anisotropic Electrocatalysis

4.1.1 Introduction

Transitional metal sulfide (TMS) nanomaterials have drawn considerable attention as possible electrocatalysts for the oxygen reduction reaction (ORR), oxygen evolution reaction (OER) and hydrogen evolution reaction (HER).\textsuperscript{205-207} ORR is one of the most fundamentally and technologically important reactions in electrochemistry. It occurs at the cathode of polymer electrolyte membrane fuel cells and metal-air batteries and its rate strongly influences the performance of these devices.\textsuperscript{208, 209} Pt-free ORR electrocatalysts using TMS nanocrystals (NCs) have potential advantages including low cost, comparable electrochemical activity to precious metals, and tunable physical and chemical properties that make them worthy of study as replacements for Pt-based catalysts. In addition to the widely explored Fe-S, Ni-S, and Co-S systems,\textsuperscript{210-213} copper sulfide [Cu$_{2-x}$S (0 $\leq$ x $\leq$ 1)] NCs have also drawn attention recently.\textsuperscript{45, 64, 214-216} Among many possible crystal phases and compositions of Cu$_{2-x}$S, covellite CuS shows promising electron mobility and free hole density that favor its use in electronic and catalytic applications. Moreover, covellite CuS also shows anisotropic electrical conductivity, with much higher conductivity along the directions perpendicular to the c-axis of the crystalline unit cell than parallel to the c-axis.\textsuperscript{217} This reflects the layered structure of covellite, with higher conductivity within layers than across layers.
MSs, especially CuS NCs, are also known for their size-dependent physical and chemical properties. Thus, the ability to vary the size of CuS NCs can be valuable. Several studies have reported synthesis of CuS NCs with tunable sizes and fixed composition.\textsuperscript{39, 218} However, the range of size variation of CuS NCs has been limited. Covellite CuS NCs preferentially adopt a plate-like morphology due to their lamellar structure, in which layers are linked by S-S bonds, and basal planes are well passivated by ligands.\textsuperscript{36} The lateral dimensions of the plates are potentially tunable over a wide range while maintaining a constant thickness of a few layers of atoms. Nonetheless, a robust synthesis of covellite CuS NPls with a wide range of diameters is still needed. NPls with a broad range of sizes are not only useful for understanding size- and morphology-dependent performance in applications such as electrocatalysis, but can also provide inspiration for design of other layered nanostructures by colloidal synthesis. Moreover, prior studies have shown that covellite NPls can be used as templates for synthesis of many different binary, ternary, quaternary TMSs and TMS-based heterostructures \textit{via} cation incorporation and exchange processes.\textsuperscript{4, 55, 126, 143, 219-221} Thus, a study using CuS has potential to be generalized to a broad range of materials that are experimentally accessible in the same NPl form.

There have been numerous reports on size-dependent ORR activities of nanoparticles and 1D nanorods/nanowires of precious metals such as Au, Pd, Pt, and their alloys. The ORR activity improvements of these noble metal NCs are mainly attributed to increased surface area and to surface contraction in very small NCs.\textsuperscript{222-226} 2D nanosheets of layered TMSs are fundamentally and technologically intriguing. A variety of 2D TMS
nanosheets have strong in-plane but weak out-of-plane electronic interactions, producing strong anisotropy of electronic properties. Most of these 2D nanosheets have fixed thickness of one to a few atomic layers, but uncontrolled lateral dimensions and shape. As a result, understanding of the effects of lateral dimensions and morphology the anisotropic electronic properties and catalytic activity of these 2D nanomaterials remains elusive. Moreover, the effect of specific crystal facets on electrochemical performance can be maximized using controllable anisotropic structures that expose the most active facets. Therefore, here, we study covellite CuS NPs of controllable lateral dimensions to provide insight into these effects in 2D nanomaterials. To this end, we investigate anisotropic electrocatalysis of the ORR on NCs of well-defined plate-like morphology with large aspect ratio and anisotropic conductivity.
4.1.2 Synthesis and Characterizations of Covellite CuS Nanoplatelets

The covellite CuS NPs are synthesized by reacting AS with Cu-OAm precursor in toluene. Our group previously reported that the diameter of CuS NPs can be varied from 8 to 35 nm by a room-temperature approach.\textsuperscript{18} Diameters of hexagons are reported as mean ± one standard deviation, according their excircles. Size-distribution histograms for this and subsequent samples are presented in Figure 4-1. The size of CuS NPs was controlled by varying the initial ratio of Cu:S in and the manner of sulfur precursor injection (ranging from one large addition to many small additions). Here, we extend our previously-reported method to produce NPs up to 105 nm diameter, so that we can systematically investigate the effect of lateral dimensions on ORR catalysis over a broad range. Top-view HR-STEM imaging shows that the copper atoms of the CuS NPs are hexagonally packed, with an interatomic spacing of 0.23 nm. This spacing matches the distance (2.3 Å) between two neighboring copper atoms in a covellite unit cell viewed along the c-axis. As shown in Figure 4-2b, there are ∼8 layers of copper atoms along thickness of the NPs (c-axis of covellite unit cell). Based on the symmetry of the NPs, the thickness contains one complete unit cell in the middle, with one additional copper atom layer above and below the central unit cell. A STEM-HAADF image and corresponding EDS element maps for the CuS NPs (Figure 4-2c) confirm the expected co-localization of Cu and S. The HRTEM images of 25 nm CuS NPs are displayed in Figure 4-3b. As revealed by HRTEM analysis, the obtained NPs have a hexagonal crystal structure, exhibiting main (110) and (100) lattice fringes with \(d\)-spacings of 1.9 and 3.3 Å, respectively. The (006) planes were observed on the edge of
the NPls, indicated by lattice fringe of 2.7 Å along the edge of NPls. TEM and HRTEM images show that the NPl grow in the (100) and (010) directions, but not in the (001) direction, indicating that the thickness of NPls remains fixed as their diameter increases.

![Size distribution histograms of covellite CuS NPls.](image)

**Figure 4-1.** Size distribution histograms of covellite CuS NPls.

![HR-STEM images of covellite CuS NPls and corresponding elemental mapping.](image)

**Figure 4-2.** (a) Top view and (b) side view HR-STEM images of covellite CuS NPls. (c) HAADF image and corresponding elemental mapping for CuS NPls, with a scale bar of 20 nm.

We synthesized larger CuS NPls by mild heating (70 °C) during the reaction. CuS NPls with average diameter of 48.3 ± 2.8 nm (denoted as CuS-45) are synthesized by reacting 1.5 mmol Cu$^{2+}$ with 1.5 mL AS solution for 20 min. Monodisperse CuS NPls
are produced, but are accompanied by some smaller NPs. Careful size-selective centrifugation was employed to separate the larger NPs from the small CuS NPs, leaving monodispersed CuS-45 NPs (Figure 4-3c). Ostwald ripening allows larger particles to grow larger by consuming the dissolution products of smaller ones. Consistent with this mechanism, extending the reaction to 120 min yields 68.0 ± 2.9 nm CuS (denoted as CuS-65) NPs. As shown in Figure 4-3d, formation of monodisperse CuS-65 NPs was accompanied by elimination of smaller NPs, suggesting that the smaller NPs dissolved and were consumed by CuS-45 NPs. No size-selective centrifugation was required in this case. To further increase the size of the NPs, we changed the amount and injection manner of the AS solution. Based on our previous discussion, excess AS can partially remove OAm ligands from the NPs, enabling additional growth of NPs. The synthesis of ~85 nm CuS NPs is similar to those described for CuS-45 NPs, however, addition 1 mL AS solution was injected after 5 min of the first injection. The resulting NPs had a diameter of 84.7 ± 3.4 nm (denoted as CuS-85) and were accompanied by some small NPs. Selective centrifugation was applied to separate the small NPs from the CuS-85 NPs. The preparation of 105 nm CuS NPs was similar to the CuS-65 case, in which extended reaction time produces larger and monodisperse NPs with diameter of 103.3 ± 4.9 nm (denoted as CuS-105). The TEM images of CuS-85 and Cu-105 NPs are presented in Figure 4-3e,f, respectively. The platelet-wide Moiré fringes observed for some overlapping NPs suggested them to be single crystalline.
Figure 4-3. TEM images of covellite CuS NPs with different diameters. The top-view and side-view are shown for each size of NPs. In panel b, I and II are HRTEM images of 25 nm CuS NPs, III and IV show the FFT of the regions of the corresponding HRTEM images in the outlined squares. The scale bar in panel b-f are 2, 20, 50, 50, 50 nm, respectively.

To further investigate the growth mechanism of covellite CuS NPs, we analyzed the NPs growth at different reaction times for the reaction that ultimately produced CuS-105. As shown in Figure 4-4a, some ~60 nm NPs formed when the AS solution was injected into Cu-OAm complex immediately. However, the product mainly consists of ~25 nm NPs, which then re-dissolved into the solution due to higher surface area and surface energy compared to larger NPs. Material dissolved from the small NPs can deposit on the large NPs, producing even larger NPs. This process is supported by the trend of growth of larger NPs and elimination of smaller NPs (Figure 4-4a-g), which is consistent with the discussion above. During growth, the top and bottom surfaces are well passivated by ligands. Therefore, only the edge planes are relatively active, which allows more effective ion absorption and Cu-S bond formation. As a result,
all small NPIs were eliminated and CuS-105 NPIs were produced at the end of the experiment (120 min). The overall growth mechanism of NPIs is shown schematically in Figure 4-4g.

Figure 4-4. (a-g) TEM image of NPI growth at different reaction times. (h) Schematic illustration of mechanism of NPI growth. All panels share a same magnification with a scale bar of 100 nm.

A XRD study on these NPIs was carried out to identify the crystal phase as well as investigate size-dependent diffraction patterns. As shown in Figure 4-5, XRD patterns of all NPIs matched the covellite CuS phase. However, different relative intensities in the XRD patterns were observed, due to variation of NPI sizes. Although the diameter of the NPIs grew to over 100 nm, the (006) planes, which are perpendicular to the c-axis and lie in the plane of the NPIs, produced relative weak and broad diffraction intensity because of the limited thickness of the NPIs. All patterns were normalized to same intensity of the peak from (103) planes because it is clear and strong for all sizes.
of NPIs. Because the (110) planes are parallel to the c-axis of the covellite unit cell and to the NPI thickness, the intensity of the corresponding peak increases, and its width decreases, with increasing NPI size. The same tendency was observed in peaks associated with the (101) and (102) planes, but these did not become nearly as sharp as the (110) planes, because they are not parallel to the c-axis. Moreover, as NPIs grew, they had higher crystallinity, as indicated by more distinctive peaks at around 30°.

Figure 4-5. XRD patterns of covellite CuS NPIs with different sizes.
4.1.3 Electrochemical Characterization of Covellite CuS Nanoplatelets

We next studied the activity of the covellite CuS NPs for the electroreduction of oxygen in alkaline solution. To prepare NP-based catalysts for ORR, we deposited NPs on a carbon support (Vulcan XC-72) via sonication of a mixed dispersion of NPs and carbon, first in hexane and then in ethanol, in each case followed by centrifugation to remove the ligands on the NPs.230, 231 The obtained CuS/C catalysts were then uniformly deposited onto a glassy carbon rotating ring disk electrode (GC-RRDE) at a constant loading of 60 µg/cm². As shown in ORR steady-state polarization plots for CuS/C at a rotation rate of 900 rpm (Figure 4-6a), the onset potential of the ORR for all CuS/C catalysts was near 0.90 V, suggesting the nature of active sites is similar for all of these NPs. We note that the ORR activity of these CuS/C electrocatalysts increased with increasing NP size. CuS-105 was found to have the best ORR activity, with a half-wave potential (E_{1/2}) of 0.80 V. In contrast, the smallest CuS NPs (shortest diameter, ~8 nm) had the lowest E_{1/2} (0.70 V), indicating the lowest ORR activity. The ORR activities (in E_{1/2}) for intermediate sizes of NPs were nearly uniformly distributed between 0.70 - 0.80 V, producing a consistent trend of increasing ORR activity with increasing size. Because the loading of CuS/C remains identical for the ORR measurements, decreasing the size only exposes more edge facets of NPs, while the total area of top and bottom surfaces remains fixed. Thus, the similar nature of active sites implies that the edges of the NPs are relatively inactive for ORR, compared to top and bottom surfaces. Therefore, we propose that the ORR activity of the CuS NPs is anisotropic. Interestingly, the limiting current density of CuS NP catalysts increased
with NPl diameter. This could relate to the mass transfer in the CuS NPl catalyst films. When the CuS NPl diameter is small, they may be deeply embedded in the carbon supports, which produces a more tortuous pathway for mass transport of oxygen to the NPls.

To gain further insight into the role of covellite CuS NPls in the ORR process, the reaction kinetics were studied at various electrode rotation rates from 400 to 2500 rpm. The current density increased with increasing rotation rate. The corresponding Koutecky–Levich plots show nearly linear behavior, and the parallel fitting of current densities from different voltages indicates first-order reaction kinetics for O₂ dissolution. The electron transfer number (n) is calculated to be 3.76-3.97, suggesting the CuS-carbon nanocatalyst favors a 4e oxygen reduction process. The proposed 4e process is also supported by minimal formation of H₂O₂ during the ORR process. Figure 4-7 shows that the measured H₂O₂ yields of CuS-25, CuS-65 and CuS-105 are all below 5%, over the potential range of 0.1 - 0.8V. These results are in good agreement with the Koutecky-Levich plots, yielding a 4e oxygen reduction process.
Figure 4-6. (a) ORR steady-state polarization curves of covellite CuS NPs with different size. (b) ORR steady-state polarization curves for CuS-105 NPs with varying electrode rotation rates. (c) Koutecky-Levich plots of the ORR for CuS-105 NPs. (d) Tafel plots for ORR on CuS-105 NPs.

Figure 4-7. H₂O₂ yield measured with the carbon supported CuS-25, CuS-65, and CuS-105 catalysts in O₂-saturated 0.1 M NaOH at room temperature with rotation rate of 900 rpm.

The kinetics of ORR on carbon supported CuS NPs was further investigate by their Tafel plots, shown in Figure 5d. Here we focused on the kinetic range (0.6 V - 0.85 V) and the corresponding Tafel slopes listed in Table 4-1. These Tafel plots show distinct low and high overpotential regions, separated at ~0.78 V. This transition in Tafel slope suggests a change in the rate-determining step when the overpotential increased from low to high. All of the CuS-based nanocatalysts exhibited similar Tafel slopes in the low overpotential range, again suggesting similar ORR reaction mechanisms. This is also consistent with our observation and deduction that these CuS NPs all have similar active sites. The corresponding Tafel slope in the high overpotential range increased with increasing CuS NPI size, due to the dominance of mass transport-limited catalytic reaction which was influenced by the size of the anisotropic CuS NPs. Compared with the results using carbon black only (E½ ≈ 0.68 V), the large CuS NPs
provide much better charge transfer and migration efficiency.

Table 4-1. Tafel slopes based on ORR data for CuS NPIs with various size as indicated.

<table>
<thead>
<tr>
<th>Size</th>
<th>Tafel slope (mV/decade)</th>
<th>Low Overpotential</th>
<th>High Overpotential</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>carbon black</td>
<td></td>
<td>-45.84</td>
<td>-334.3</td>
</tr>
<tr>
<td>CuS-8</td>
<td></td>
<td>-39.11</td>
<td>-365.76</td>
</tr>
<tr>
<td>CuS-25</td>
<td></td>
<td>-41.28</td>
<td>-537.4</td>
</tr>
<tr>
<td>CuS-45</td>
<td></td>
<td>-48.29</td>
<td>-1070.53</td>
</tr>
<tr>
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<td></td>
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</tr>
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<tr>
<td>CuS-105</td>
<td></td>
<td>-37.57</td>
<td>-1122.17</td>
</tr>
</tbody>
</table>

Figure 4-8 shows typical TEM images of the CuS-25 and CuS-105 NPIs anchored on the carbon support. CuS NPIs have higher contrast in the image compared to carbon. Moreover, instead of NPI aggregation after surface ligands were removed, we observed a uniform space between NPIs, leaving accessible surface area for ORR process. Interestingly, both sizes of CuS NPIs self-assembled onto the carbon support during preparation of the nanocatalyst. Lower magnification TEM images with higher concentrations of nanocatalysts indicate that most of NPIs are self-assembled into columnar stacks on the carbon support instead of laying down (Figure 4-9).

Figure 4-8. The TEM images of (a) CuS-25 NPIs and (b) CuS-105 NPIs deposited on carbon substrate.
Combining all the results and observations, we can propose a mechanism of size-dependent ORR activity enhancement. Given that the total mass of the NPs remains the same for test with each NP size, and the active sites of all covellite CuS NPs are nearly the same, we conclude that the key factor that affects the overall electrochemical activity is electron transfer rate and efficiency. The efficiency originated from the significant charge transfer from carbon to CuS NPs, promoting electron transport through the whole electrocatalyst film. Compared to large NPs, electrons on the small NPs not only have to hop through neighboring vacancies on the NP but hop to another NP. However, electron transfer on large NPs is more efficient because of their continuous and high-crystallinity planes. Large CuS NPs have less interfacial barriers for charge transfer, producing higher electron transfer rate and thereby higher electrocatalytic activity. This reflects the fact that CuS NPs possess anisotropy of both conductivity and electrochemical activity. A schematic illustration of different electron transfer mechanisms on large and small NPs is depicted in Figure 4-10.
Figure 4-10. Schematic illustration of different electron transfer mechanisms on different CuS NPs.
4.1.4 DFT-Calculated Oxygen Adsorption Energy and Facets-dependent ORR behavior.

Catalytic and electrocatalytic properties of crystalline materials depend not only on material composition but also on the exposed surface facets. In this work, reducing the diameter of CuS NPls, with fixed thickness, only increases the specific surface area of side surfaces, while that of top and bottom surfaces remains the same. This is also consistent with the similar nature of active sites observed in electrochemical experiments. Therefore, based on the experimental results, the side surfaces of CuS NPls are expected to be relatively electrochemically inert. To further investigate the size- and facet-dependent ORR behavior of the CuS NPls, we employed density functional theory (DFT) to analyze the oxygen adsorption energy, a commonly used descriptor for ORR activity, on different NPl surfaces.

Figure 4-11. (a) Structural model of covellite CuS. Potential ORR surfaces: (b) (110) planes with mixed Cu1 and Cu2 atoms, (c) Cu2 terminated and (d) Cu1 terminated (001) planes. The arrows indicate the cleavage planes.
Covellite can be described as being composed of layers of triangular CuS₃ units (denoted as Cu₁), each sandwiched between two layers of CuS₄ tetrahedra (denoted as Cu₂). Each triple layer is linked to the triple layers above and below it via disulfide bonds. We note that the notations Cu₁ and Cu₂ indicate the chemical environment of copper atoms in bulk covellite, and their chemical properties will be different on an exposed (001) or (110) surface, due to the change of ligands and surface relaxation. Given that the (110) and (006) planes were observed in top view and side view HRTEM images respectively, the exposed top and bottom surfaces of CuS NPs could be Cu₁ or Cu₂ atom terminated (001) planes, while (110) planes on the side surfaces have mixed Cu₁ and Cu₂ terminations. For each covellite CuS unit cell, cleavage on (110) planes can lead to exposure of two Cu₁ atoms and four Cu₂ atoms. The kinetically most favorable reaction pathway for the ORR process catalyzed by nonprecious-metal catalysts in alkaline solution is considered to be a molecular oxygen associative or dissociative adsorption mechanism (see Experimental Section for computational details). In the dissociative mechanism, the O₂ molecules dissociate before they are hydrogenated, while in the associative mechanism they are hydrogenated before they dissociate. We referenced the step energies for each electrode half reaction to a standard hydrogen electrode (SHE) by replacing the energy of a proton-electron pair E(H⁺ + e⁻) with the energy of a hydrogen molecule E(H₂). This will eliminate the effect of proton concentration and allow the result to be compared directly with the experimental results (E vs. RHE).
Figure 4-12(a-d) illustrates the geometry and energy of adsorbed O2 for the ORR intermediates on different surfaces of CuS NPs. Oxygen adsorption, the rate-determining step of ORR, was more promoted on Cu2 terminated (001) planes than on those with Cu1 atom termination or on (110) planes with mixed Cu1 and Cu2 termination. The relative energy profile of the ORR process on each CuS surface was calculated, as shown in Figure 4-12e. For the (110) surfaces, the indicated adsorption energies correspond to the average value for Cu1 and Cu2 as active sites. The results show that adsorption of the oxygen molecule is preferred on the Cu2 site of the CuS (001) surface, with the lowest adsorption energy of -0.26 eV. Thus, the O2 adsorption on Cu2 terminated (001) planes is exothermic. For the (110) surface, the computed adsorption energy of O2 on Cu1 atoms is -0.012 eV. In all other cases of associative or dissociative mechanisms, the first adsorption step is energetically unfavorable, with positive $\Delta E_{\text{abs}}$. Compared with the (001)-Cu1 termination and side surfaces with mixed Cu1 and Cu2 sites, the overpotential for the associative mechanism at the (001)-Cu2 termination is found to be $\sim$0.55 eV, in good agreement with the experiments. And the overall electrochemical process at Cu2 sites is more easily initiated. Therefore, DFT results support the conclusion that CuS NPs, particularly Cu2 terminated (001) planes, have an excellent potential for ORR.

Based on the HR-STEM image, the thickness of each CuS NPl contains one unit cell, sandwiched by a layer of copper atoms above and below it. The symmetry of the nanostructure then requires the layers of Cu2 sites to be exposed on the top and bottom surfaces. Although the very few layers of copper atoms and complex synthesis
conditions produce some ambiguity and uncertainty in the determination of Cu termination of exposed facets, the basal planes possess lower overall O2 adsorption energy and thereby are more favorable to initiate ORR.

**Figure 4-12:** Optimized surface structures for intermediates in ORR reaction and DFT study on different CuS surfaces. (a) O₂ adsorbed on the Cu1 terminated (001) surface, forming a peroxo bridge between two Cu atoms. (b) Dangling O₂ bound to Cu2 terminated (001) surface. (c) Dangling O₂ bound to the Cu1 atom on the (110) surface with the Cu atom bounds to two sulfur atoms. (d) Dangling O₂ bound to the Cu2 atom on the (110) surface with the Cu atom bound to three sulfur atoms. (e) Reaction free energy diagrams for Cu1 terminated (001) surfaces (red), Cu2 terminated (001) surfaces (blue), and (110) surfaces (green). Both bridge-like and dangling O₂ adsorption mechanisms were applied to each CuS surface, and the stable surfaces are presented after surface relaxation. The oxygen adsorption energy on (110) surfaces is calculated separately.
4.1.5 Experimental Section

Chemicals. All chemicals were used as received. Oleylamine (70%, OAm), was purchased from Sigma-Aldrich. Cu(NO$_3$)$_2$·2.5H$_2$O, toluene, and ammonium sulfide (21.2% wt% in water) were purchased from Fisher Scientific.

Preparing CuS NPls. For the synthesis of ~65 nm hexagonal CuS NPls (detailed synthesis parameters are listed in Table 4-2), 1.5 mmol of Cu(NO$_3$)$_2$·2.5H$_2$O was dissolved in a mixture of 10 mL of OAm and 10 mL of toluene, then heated to 70 °C under an argon flow. 1.5 mL of ammonium sulfide (AS) solution (21.2% in water) was injected into the Cu-OAm to form CuS NPls. After 2 h, 10 mL of ethanol was added to destabilize the NPl dispersion, followed by centrifugation at 4000 rpm for 1 min. To remove excess AS and OAm, the NCs were washed by precipitation upon addition of ethanol followed by redispersion in chloroform. The NPls could be redispersed in organic solvents including chloroform, hexane, and toluene.

<table>
<thead>
<tr>
<th>Size (nm)</th>
<th>Cu$^{2+}$ (mmol)</th>
<th>AS solution (mL)</th>
<th>Reaction Time (min)</th>
<th>AS Injection Manner</th>
<th>Selective Centrifugation</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>0.5</td>
<td>0.8</td>
<td>0.5</td>
<td>50 µL×16 with an interval of 30 sec</td>
<td>No</td>
</tr>
<tr>
<td>25</td>
<td>1.5</td>
<td>1.35</td>
<td>20</td>
<td>450 µL×3 with an interval of 1 min</td>
<td>No</td>
</tr>
<tr>
<td>45</td>
<td>1.5</td>
<td>1.5</td>
<td>20</td>
<td>single injection</td>
<td>Yes</td>
</tr>
<tr>
<td>65</td>
<td>1.5</td>
<td>1.5</td>
<td>120</td>
<td>single injection</td>
<td>No</td>
</tr>
<tr>
<td>85</td>
<td>1.5</td>
<td>2.5</td>
<td>20</td>
<td>1.5 mL+1 mL (after 5 min)</td>
<td>Yes</td>
</tr>
<tr>
<td>105</td>
<td>1.5</td>
<td>2.5</td>
<td>120</td>
<td>1.5 mL+1 mL (after 5 min)</td>
<td>No</td>
</tr>
</tbody>
</table>
**Characterization.** Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-2010 at an accelerating voltage of 200 kV. High-resolution TEM (HRTEM) images were obtained using a FEI Tecnai G2 F30 at an accelerating voltage of 300 kV. High angle annular dark field scanning TEM (HAADF-STEM) images, HR-STEM images, and STEM energy dispersive X-ray spectroscopy (STEM-EDS) maps were collected using a JEM-ARM200F STEM equipped with spherical aberration correctors on the image at an accelerating voltage of 200 kV. TEM grids were prepared by dropping a dilute NC dispersion onto a carbon-coated copper or nickel TEM grid and allowing the sample to dry under air. Powder X-ray diffraction (XRD) measurements were carried out using a Rigaku Ultima IV diffractometer with a Cu Kα X-ray source. Samples were prepared by drop-casting concentrated NC dispersions onto glass slides.

**Preparing CuS-carbon catalyst.** Firstly, 40 mg Vulcan XC-72 carbon black was mixed with 10 mg of dried CuS NDs in 5 mL hexane, following by sonication for 30 min. Then, the mixture of CuS-carbon was separated via centrifugation at 5000 rpm for 1 min. The precipitate was redispersed in 5 mL ethanol, following by sonication for 60 min. The CuS-carbon mixture was obtained by centrifugation at 5000 rpm for 1 min. 1 mL isopropanol and 20 µL Nafion solution was added into 10 mg CuS-carbon, following by sonication for 30 min. The CuS-carbon catalyst was deposited onto the GC-RRDE with constant loading of 60 µg/cm² (~12 µg/cm² of CuS NPs) and air-dried for 5 min at 60 °C.
Electrochemical Measurements. All electrochemical measurements were performed using a CHI Electrochemical Station (Model 760b) equipped with high-speed rotators from Pine Research Instruments. A glassy carbon rotating ring disk electrode (GC-RRDE) was used as the working electrode. Each catalyst powder (10 mg) was mixed with isopropanol (1.0 mL) and a 5 wt% Nafion® dispersion (20 µL) to produce the catalyst ink. The obtained catalyst ink was deposited onto the GC-RRDE and air-dried at 60 °C. Each measurement was performed in a three-electrode electrochemical cell using a graphite electrode as the counter electrode and Hg/HgO electrode as the reference electrode. H₂ at 1.0 atm was bubbled into a calibration tube fitted with a Pt wire with a Pt black layer to calibrate the reference electrodes and to be able to convert to reversible hydrogen electrode (RHE). The ORR polarization curve was recorded via staircase voltammetry with a step of 50 mV in 0.1 M NaOH saturated with O₂ at 900 rpm.

Computational methods. Calculations were done using spin-polarized density functional theory (DFT) with the Perdew-Burke-Ernzerhof (PBE) functional augmented with dispersion correction DFT-D3 of Grimme (with zero damping), using Vienna ab initio Simulation Package (VASP). Projected augmented wave (PAW) pseudopotentials were used for Cu (valence 3d¹⁰4s¹), S (valence 3s²3p⁴), and O (valence 2s²2p⁴) as treatments of ion cores. We used an energy cutoff of 400 eV for the plane wave basis set, along with a Gaussian-smearing width of k_BT = 0.05 eV for partial occupancy of states near the Fermi level. We used a Monkhorst-Pack k-points grid generated using the methodology of Wisesa, et al., to accelerate the calculations.
applied zero-point energy (ZPE), enthalpy (S), and entropy corrections to reaction energies as proposed by Valdes and co-workers gathered in Table 4-3.\textsuperscript{241}

We performed calculations of the oxygen reduction reaction on covellite CuS (001) and (110) surfaces as periodic slabs. Two CuS (001) slabs with two different terminations were defined (with surfaces marked Cu1 and Cu2 in Figure 4-11).\textsuperscript{242} Each had a hexagonal surface cell with dimensions of 7.60 Å × 37.00 Å (γ = 120.0°) and four copper atoms exposed on the surface. The CuS (110) slab had an orthorhombic surface cell with dimensions of 16.47 Å × 6.60 Å × 27.43 Å, and 6 copper atoms exposed at the surface. All slab models contained seven layers of ions, and a vacuum space of at least 14 Å to avoid interactions between surfaces and their periodic images. All systems were optimized with a force convergence criterion of 0.01 eV/Å while the bottom two layers were fixed.

\textbf{Table 4-3.} Zero Point Energy Corrections and Entropic Contributions to the Free Energies

<table>
<thead>
<tr>
<th></th>
<th>ZPE</th>
<th>TS</th>
</tr>
</thead>
<tbody>
<tr>
<td>*</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>O*</td>
<td>0.05</td>
<td>0.00</td>
</tr>
<tr>
<td>OH*</td>
<td>0.35</td>
<td>0.00</td>
</tr>
<tr>
<td>OOH*</td>
<td>0.41</td>
<td>0.00</td>
</tr>
<tr>
<td>OO*</td>
<td>0.10</td>
<td>0.00</td>
</tr>
<tr>
<td>H2O</td>
<td>0.56</td>
<td>0.67</td>
</tr>
<tr>
<td>H2</td>
<td>0.27</td>
<td>0.41</td>
</tr>
<tr>
<td>1/2 O2</td>
<td>0.32</td>
<td>0.05</td>
</tr>
<tr>
<td>H2O2</td>
<td>0.69</td>
<td>0.72</td>
</tr>
</tbody>
</table>

We investigated the two possible reaction mechanisms previously suggested.

The associative mechanism proceeds via the absorption of molecular O\textsubscript{2} followed by reduction:

1. O\textsubscript{2} + * (site) + H\textsuperscript{+} + e\textsuperscript{−} = HOO*
2. HOO$^*$ + H$^+$ + e$^-$ = H$_2$O + O$^*$

3. O$^*$ + H$^+$ + e$^-$ = HO$^*$

4. HO$^*$ + H$^+$ + e$^-$ = H$_2$O + *

The dissociative mechanism proceeds via O-O bond breaking followed by reduction:

5. $\frac{1}{2}$ O$_2$ + * (site) + H$^+$ + e$^-$ = HO$^*$

6. HO$^*$ + H$^+$ + e$^-$ = H$_2$O + *

Structures of the O$_2$ absorption intermediate for the several slabs are shown in Figure 4-12. The energies are given in Table 4-4.

The key energies are the “absorption energies” defined as:

$$E(\text{abs}) = E(*-O_2) - E(*) - E(O_2)$$

for the associative mechanism;

$$E(\text{abs}) = E(*-O) - E(*) - \frac{1}{2} E(O_2)$$

for the dissociative mechanism.

Gibbs free energy were calculated as: $\Delta G = \Delta E + \Delta ZPE - T\Delta S$. We used a standard hydrogen electrode (SHE) at pH=0, p = 1 bar, and T = 298.15 K as a reference. The free energy of electron ($\Delta G[\text{e}^-]$) and proton ($\Delta G[\text{H}^+]$) are replaced with $\Delta G[\text{H}_2] + e U$, where U is the external potential versus SHE. To bypass the poor DFT description of the O$_2$ ground state molecule, the free energy of di-oxygen molecule was calculated as $\Delta G[O_2] = 4.92 \text{ eV} + 2\Delta G[\text{H}_2\text{O}] - 2\Delta G[\text{H}_2]$.

The overpotential for the associative mechanism was determined as

$$\text{OP} = \max(\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4) + 1.23 \text{ eV},$$

Where G1, G2, G3, and G4 are the reaction free energies for steps (1), (2), (3), and (4) respectively. The overpotential for the dissociative mechanism was determined similarly as

$$\text{OP} = \max(\Delta G_5, \Delta G_6) + 1.23 \text{ eV}$$
### Table 4-5. Oxygen Molecule Absorption Energy

<table>
<thead>
<tr>
<th>Surface / active site</th>
<th>Mechanism</th>
<th>E(ads)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(001) Cu2</td>
<td>Dissociative</td>
<td>0.75</td>
</tr>
<tr>
<td>(001) Cu1</td>
<td>Dissociative</td>
<td>1.52</td>
</tr>
<tr>
<td>(110) Cu1 site</td>
<td>Dissociative</td>
<td>1.03</td>
</tr>
<tr>
<td>(110) Cu2 site</td>
<td>Dissociative</td>
<td>0.62</td>
</tr>
<tr>
<td>(001) Cu2</td>
<td>Associative</td>
<td>-0.26</td>
</tr>
<tr>
<td>(001) Cu1</td>
<td>Associative</td>
<td>0.42</td>
</tr>
<tr>
<td>(110) Cu1 site</td>
<td>Associative</td>
<td>-0.01</td>
</tr>
<tr>
<td>(110) Cu2 site</td>
<td>Associative</td>
<td>0.52</td>
</tr>
</tbody>
</table>

### Table 4-6. Step energy and overpotential for ORR associative and dissociative mechanisms.

<table>
<thead>
<tr>
<th>Surface / active site</th>
<th>Mechanism</th>
<th>E(ads)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(001) Cu2</td>
<td>Dissociative</td>
<td>0.75</td>
</tr>
<tr>
<td>(001) Cu1</td>
<td>Dissociative</td>
<td>1.52</td>
</tr>
<tr>
<td>(110) Cu1 site</td>
<td>Dissociative</td>
<td>1.03</td>
</tr>
<tr>
<td>(110) Cu2 site</td>
<td>Dissociative</td>
<td>0.62</td>
</tr>
<tr>
<td>(001) Cu2</td>
<td>Associative</td>
<td>-0.26</td>
</tr>
<tr>
<td>(001) Cu1</td>
<td>Associative</td>
<td>0.42</td>
</tr>
<tr>
<td>(110) Cu1 site</td>
<td>Associative</td>
<td>-0.01</td>
</tr>
<tr>
<td>(110) Cu2 site</td>
<td>Associative</td>
<td>0.52</td>
</tr>
</tbody>
</table>

1. \( \text{O}_2 + \text{O}^* + \text{H}^+ + e^- = \text{HO}_2^* \)
2. \( \text{HO}_2^* + \text{H}^+ + e^- = \text{H}_2\text{O} + \text{O}^* \)
3. \( \text{O}^* + \text{H}^+ + e^- = \text{HO}^* \)
4. \( \text{HO}^* + \text{H}^+ + e^- = \text{H}_2\text{O} + \text{O}^* \)
5. \( \frac{1}{2} \text{O}_2 + \text{O}^* + \text{H}^+ + e^- = \text{HO}^* \)
6. \( \text{HO}^* + \text{H}^+ + e^- = \text{H}_2\text{O} + \text{O}^* \)

<table>
<thead>
<tr>
<th>Step Reaction</th>
<th>Energy (eV)</th>
</tr>
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<tbody>
<tr>
<td>(001) Cu2</td>
<td>-0.68</td>
</tr>
<tr>
<td>(001) Cu1</td>
<td>-0.10</td>
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<tr>
<td>(110) 1/3 Cu1 + 2/3 Cu2</td>
<td>-0.41</td>
</tr>
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<table>
<thead>
<tr>
<th>Step Reaction</th>
<th>Energy (eV)</th>
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<tbody>
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<td>(001) Cu1</td>
<td>-0.84</td>
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<td>(110) 1/3 Cu1 + 2/3 Cu2</td>
<td>-1.29</td>
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<table>
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<th>Energy (eV)</th>
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<tbody>
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</tr>
<tr>
<td>(001) Cu1</td>
<td>-1.70</td>
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<td>-1.98</td>
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<tbody>
<tr>
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<tr>
<td>(001) Cu1</td>
<td>-2.29</td>
</tr>
<tr>
<td>(110) 1/3 Cu1 + 2/3 Cu2</td>
<td>-1.24</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Step Reaction</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(001) Cu2</td>
<td>-1.31</td>
</tr>
<tr>
<td>(001) Cu1</td>
<td>-0.17</td>
</tr>
<tr>
<td>(110) 1/3 Cu1 + 2/3 Cu2</td>
<td>-1.22</td>
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<tr>
<th>Step Reaction</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(001) Cu2</td>
<td>-1.15</td>
</tr>
<tr>
<td>(001) Cu1</td>
<td>-2.29</td>
</tr>
<tr>
<td>(110) 1/3 Cu1 + 2/3 Cu2</td>
<td>-1.24</td>
</tr>
</tbody>
</table>

| Overpotential of associative mechanism | 0.55 | 1.14 | 0.82 |
| Overpotential of dissociative mechanism | 0.08 | 1.06 | 0.02 |

220
4.2 Controlled Synthesis of Cu$_{2-x}$Se Nanoparticles as Near-Infrared Photothermal Agents and the Irradiation Wavelength Matter for Photothermal Therapy

4.2.1 Introduction

Copper chalcogenide nanomaterials are well known for their strong and tunable near-infrared (NIR) absorbance due to localized surface plasmon resonance (LSPR). The LSPR arises from collective oscillation of free holes associated with copper deficiency. This useful optical phenomenon has spawned new applications in theranostics, nanophotonics, and nanoelectronics. Among these potential applications, photothermal therapy (PTT), a treatment in which an agent absorbs light and dissipates the energy as heat to ablate cancer cells, has attracted considerable attention. Conventional photothermal agents such as gold nanostructures suffer from relatively large dimensions and limited absorbance in the NIR region. These limitations have driven recent interest in copper chalcogenide nanostructures with much smaller size and LSPR absorbance that is tunable over a wide range. The size- and composition-dependent LSPR of Cu$_{2-x}$S and Cu$_{2-x}$S$_3$Se$_{1-y}$ NCs has been extensively studied. However, reports on Cu$_{2-x}$Se are relatively rare, particularly with respect to tuning their LSPR absorbance over a wide range. One reason lies in the difficulty of preparing high-quality, water-dispersible and biocompatible Cu$_{2-x}$Se NPs. Another might be the relatively low mutual affinity of copper and selenium, resulting in limited size or composition control and tunability for a single synthetic approach, compared to Cu$_{2-x}$S.

In the present study, we synthesized high-quality Cu$_{2-x}$Se NPs with controllable and ultra-small size, such that they are promising candidates for biological applications.
More importantly, we show how to manipulate their NIR absorption band by precisely controlling their particle size and copper deficiency. We also introduce a facile method to transfer oleylamine (OAm)-capped hydrophobic Cu$_{2-x}$Se NPs into water via TWEEN coating. The aqueous dispersions of TWEEN-coated Cu$_{2-x}$Se NPs are extremely stable in water, a feature that is desirable for NIR PTT. Theoretically, longer irradiation wavelength permits deeper tissue penetration for biological applications. Both the NIR-I (800-1000 nm) and NIR-II (1000-1700 nm) spectral ranges are considered “biological windows” of relatively low absorbance and scattering by tissues and biological fluids. Our subsequent research explored the relationship between the irradiation wavelength and photothermal conversion efficiency, which is lacking in prior literature on these materials. Our work not only offers a robust approach to prepare size-tunable aqueous Cu$_{2-x}$Se NP dispersions but also provides insights into the importance of irradiation wavelength for PTT.
4.2.2 Controlled Synthesis of Cu$_{2-x}$Se Nanocrystals with Tunable LSPR

The Cu$_{2-x}$Se NPs were produced by injecting Se-OAm precursor into Cu-OAm complex at elevated temperature. As shown in Figure 4-13a, monodisperse Cu$_{2-x}$Se NPs with a mean diameter of 6.0 ± 0.5 nm can be prepared by reacting 0.5 mmol Cu$^+$ with 2 mL Se-OAm precursor at 130 °C for 10 min. Size-distribution histograms for this and subsequent samples are presented in Figure 4-14. Knowing that the LSPR energy of Cu$_{2-x}$Se is governed by their size, shape and composition, we then gradually increased the reaction time and temperature to produce larger Cu$_{2-x}$Se NPs. Transmission electron microscopy (TEM) images in Figures 4-13b-d shows that the size of Cu$_{2-x}$Se NPs can be increased to 13.1 ± 0.8 nm while maintaining a narrow size distribution. The high-resolution TEM image in Figure 1e reveals that the Cu$_{2-x}$Se NPs are single crystalline, with an observed lattice spacing of 0.20 nm, corresponding to the (220) planes of the berzelianite Cu$_{1.4}$Se phase. STEM-EDS elemental maps of the Cu$_{2-x}$Se NPs (Figures 4-13f) confirm the expected co-localization of Cu and Se.
Figure 4-13. (a-d) TEM images of Cu_{1.8}Se NPs with different diameters, (e) typical HRTEM image of Cu_{1.8}Se NPs, (f) HAADF-STEM image and corresponding elemental maps for Cu and Se.

Figure 4-14. Size distribution histograms for all samples.

The XRD patterns of Cu_{2-x}Se NPs of different diameters are presented in Figures 4-14a. Cu_{2-x}Se NPs with diameter of 6 nm contain both berzelianite Cu_{1.8}Se and umangite Cu_{1.5}Se phases (black pattern). The Cu_{1.5}Se phase was gradually eliminated, leaving pure Cu_{1.8}Se NPs, upon increasing the reaction time and temperature (magenta pattern). This phase evolution accompanies the increasing size of Cu_{2-x}Se NPs (shape evolution). Because Se^{2-} has relatively weak bonding to Cu^{+}, synthesis of Cu_{2-x}Se with mild heating produces more copper-deficient phases (compared to stoichiometric Cu_{2}Se). Increasing the time and temperature can increase the reactivity of Se-OAm precursors, producing larger and single phase Cu_{1.8}Se NPs. This observation is also consistent with our previous discussions and other recent reports.\textsuperscript{76,248}
Figure 4-15. (a) XRD patterns of Cu$_{2-x}$Se NPs with different sizes. (b) UV-vis-NIR absorbance of Cu$_{2-x}$Se NPs with different sizes.

Cu$_{2-x}$Se has an inherently high concentration of free holes in its valence band. It has strong NIR absorbance due to LSPR oscillation. According to the Drude model, the LSPR energy of Cu$_{2-x}$Se NPs is dependent upon the complex dielectric function of the plasmonic material, the size, shape, and damping parameter, and the dielectric constant of the environment of the NCs. As shown in Figures 4-15b, the UV-vis-NIR spectra of Cu$_{2-x}$Se NPs reveal that the LSPR absorbance red-shifts and slightly broadens with increasing NP size and the shift to pure berzelianite phase. The 6 nm Cu$_{2-x}$Se NPs exhibit the highest energy LSPR peak at a wavelength of ~1000 nm, while the largest (13 nm) NPs have an LSPR peak near 1300 nm. The decrease in LSPR energy with increasing size of the Cu$_{2-x}$Se NPs is mainly due to decreased free carrier concentration in the larger particles, although the increase in particle size may also affect the damping parameter for the particles. The shift to lower copper deficiency with increasing size, reflected in the XRD patterns of Figures 4-15a is consistent with the red-shift of LSPR wavelength with increasing size observed in Figures 4-15b. To further understand the optical response of the NCs, their absorption spectra were simulated using a simple Drude model for the complex dielectric function. We extracted
density of free carriers (holes, \(N_h\)), damping constant (\(\gamma\)), and diameter (\(d\)) by fitting the measured NC absorbance spectra (simulation details are provided in the experimental section). The results indicated that the shift in wavelength of the absorbance peak of the Cu\(_{2-x}\)Se NPs is dominated by the changing density of free carriers and therefore the plasmon frequency, while the size of the NCs makes a minor contribution to the absorbance shift. Therefore, during the growth of the Cu\(_{2-x}\)Se NPs, the redshift of the LSPR absorbance is mainly attributed to the elimination of the umangite Cu\(_{1.5}\)Se phase and the resulting reduction in free hole concentration.
4.2.3 Photothermal Effect of Cu$_{2-x}$Se Nanocrystals with Tunable LSPR

One of the prerequisites for using Cu$_{2-x}$Se NPs as a PTT agent is that they can be stably dispersed in aqueous media. Thus, we must transfer the hydrophobic Cu$_{2-x}$Se NPs into water. TWEE 20 is a commercially available surfactant with excellent biocompatibility, which can facilitate the transfer of hydrophobic Cu$_{2-x}$Se NPs into the aqueous phase. Here we selected Cu$_{2-x}$Se NPs with an average diameter of 10 nm as the photothermal agent. As shown in Figure 4-16a, the coating of TWEE 20 on the Cu$_{2-x}$Se NPs was formed by hydrophobic interactions between the aliphatic tails of TWEE 20 and the oleylamine layer on the NP surface. The photographs of Figure 4-16a show the Cu$_{2-x}$Se NPs dispersed in different solvents (hexane and water) before and after the surface modification. Figure S2 suggests that the absorbance spectrum, as well as the size and morphology are almost unchanged after TWEE 20 coating. Figure 4-16b shows the absorbance of HPLC water and different concentrations of hydrophilic Cu$_{2-x}$Se NPs in aqueous solution (with water absorbance subtracted).

![Figure 4-16](image)

**Figure 4-16.** (a) Schematic illustration of the preparation of the hydrophilic Cu$_{2-x}$Se NCs with Tween 20 surface functionalization. (b) UV-Vis-NIR absorbance spectra of pure water and the aqueous solution containing different concentrations of hydrophilic Cu$_{2-x}$Se NCs. (c-e) Temperature elevation of pure
water and the aqueous solution containing different concentrations of hydrophilic \( \text{Cu}_{2-x} \text{Se} \) NPs under 808 nm, 980 nm, and 1210 nm laser irradiation, respectively. Note: the power density used for 808, 980, and 1210 nm laser irradiation are all measured at 1.5 W/cm\(^2\).

![Absorbance spectra of Cu\(_{2-x}\)Se NPs before and after Tween 20 surface functionalization. TEM images indicate that the NPs are well dispersed before and after Tween 20 surface functionalization.](image)

**Figure 4-17.** Absorbance spectra of \( \text{Cu}_{2-x} \text{Se} \) NPs before and after Tween 20 surface functionalization. TEM images indicate that the NPs are well dispersed before and after Tween 20 surface functionalization.

In a further set of experiments, we examined the temperature elevation of HPLC water (a control experiment) and aqueous solutions containing different concentrations of \( \text{Cu}_{2-x} \text{Se} \) NPs under the irradiation of 808, 980 and 1210 nm lasers (Q-Photonics) with a power density of 1.5 W/cm\(^2\), respectively, as shown in the **Figures 4-18c-e**. In terms of the control experiment of HPLC water, as it has different absorbance at 808, 980, and 1210 nm, the temperature of HPLC water are increased by 1.3, 4.8, and 8.3 °C from the room temperature in 10 min. With the rise of the concentration of \( \text{Cu}_{2-x} \text{Se} \) NPs, the temperature of their aqueous solution increases accordingly under the irradiation of certain wavelength, but the heating rate differs significantly based on different wavelengths (i.e., 808, 980, and 1210 nm). As illustrated in **Figure 4-18a**, the temperature changes \( (T_{\text{max}}-T_{\text{surf}}) \) based on the room temperature are increased by 9.2,
10.4 and 11.1 °C for Cu$_{2-x}$Se NPs (200 µg/mL) in 10 min under the irradiation of 808, 980 and 1210 nm lasers, respectively. The temperature changes ($T_{\text{max}} - T_{\text{water}}$) based on the temperature of HPLC water (a control experiment) in 10 min are calculated to be 8.0, 5.7, and 2.7 °C.

Photothermal conversion efficiency is one of important indexes to evaluate photothermal agents. Next we measured the photothermal conversion efficiencies ($\eta$) of Cu$_{2-x}$Se NPs (200 µg/mL) under the irradiation of different wavelengths (i.e., 808, 980, and 1210 nm) at a given power density, according to a widely used method.$^{247,253}$ The $\eta$ value was calculated (see Experimental Section for details) as follows:

$$\eta = \frac{hS(T_{\text{max}} - T_{\text{surv}}) - Q_{\text{dis}}}{I(1-10^{-A_{\text{wav}}})}$$

where $h$ is the heat transfer coefficient, $S$ is the surface area of the container, and the value of $hS$ is obtained from Figure 4-18c. $T_{\text{max}} - T_{\text{surv}}$ is the temperature change of Cu$_{2-x}$Se NPs solution at the maximum steady-environmental temperature, $I$ is the power of the laser, $A_{\text{wav}}$ is the absorbance of Cu$_{2-x}$Se NPs at certain irradiated wavelength, and $Q_{\text{dis}}$ expresses heat dissipated from light absorbed by the solvent and the container.

As calculated from Figures 4-18a-c, by measuring the temperature profile of Cu$_{2-x}$Se NPs (200 µg/mL) aqueous solution during heating and cooling processes, the thermal equilibrium time constants ($\tau_s$) of the system were determined to be 198, 137, and 119 s, and the corresponding photothermal conversion efficiency $\eta$ were further calculated to be 42.4%, 36.1%, and 18.9% under 808, 980 and
1210 nm lasers irradiation, respectively. From the results, it can be found that the higher the absorbance of water at certain wavelength, the lower the photothermal conversion efficiency of Cu$_{2-x}$Se NPs aqueous solution. This is reasonable because at a given power density, as the absorbance of water goes higher, more photon energy is absorbed by water, and less photon energy is absorbed by Cu$_{2-x}$Se NPs, leading to a decreased contribution from Cu$_{2-x}$Se NPs to water heating. This phenomenon definitely gives us a hint that we have to carefully choose suitable NIR wavelength to realize good PTT treatment performance. Considering the relationship between photothermal conversion efficiency and irradiation wavelength, despite NIR-II (1000-1700 nm) might allow for a deeper tissue penetration compared to NIR-I (800-1000 nm), which might not be that desirable for PTT application. Therefore, we suggest that the irradiation wavelength used for PTT application should not go beyond 1100 nm.

**Figure 4-18.** (a) Plot of temperature elevation of pure water and aqueous solution containing different concentrations of hydrophilic Cu$_{2-x}$Se NPs over a period of 600 s versus the wavelength of laser irradiation. (b) The photothermal profile of hydrophilic Cu$_{2-x}$Se NPs aqueous solution (1 mL, 200 µg/mL) irradiated with 808, 980, and 1210 nm lasers for 10 min at a power density of 1.5W/cm$^2$, followed by natural cooling to room temperature. (c) Linear time data versus $-\text{Ln}(t)$ obtained from the cooling period of (b). The time constant ($\tau_s$) for heat transfer from the system is determined to be 198 s, 137 s and 119 s for 808, 980, and 1210 nm lasers, respectively.
4.2.4 Experimental Section

Chemicals. All chemicals were used as received. Copper (I) chloride (CuCl, ≥99.995%), selenium powder (Se, trace metals 99.5%), oleylamine (70%, OAm), 1-octadecene (ODE, technical grade, 90%), and TWEEN 20 were all purchased from Sigma-Aldrich.

Preparing Se-OAm Precursors. A mixture of 10 mmol of selenium powder and 10 mL of OAm was held under flowing argon at ambient temperature for 30 min before heating to 320 °C. The solution was held at this temperature for 20-30 min until a homogeneous solution was formed.

Synthesis of Cu$_{2-x}$Se NPs. A mixture of 0.5 mmol CuCl, 8 mL of ODE, and 2 mL of OAm was held under flowing argon at ambient temperature for 30 min before heating to 200 °C. The mixture was then cooled to 180 °C (or as indicated), followed by injection of 2 mL of the Se-OAm precursor. The solution was held at this temperature for 10 min (or as indicated). To collect the NPs, 10 mL of ethanol was added, followed by centrifuging at 5000 rpm for 1 min. To remove excess OAm, the NPs were washed by precipitation upon addition of ethanol, followed by redispersion in chloroform. The NPs could be redispersed in organic solvents including chloroform, hexane, and toluene.
<table>
<thead>
<tr>
<th>Precursor (Cu/S)</th>
<th>Temperature (°C)</th>
<th>Reaction time (min)</th>
<th>Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 mmol/2 mL</td>
<td>130</td>
<td>10</td>
<td>6.0 ± 0.5 nm</td>
</tr>
<tr>
<td>0.5 mmol/2 mL</td>
<td>180</td>
<td>10</td>
<td>8.0 ± 0.7 nm</td>
</tr>
<tr>
<td>0.5 mmol/2 mL</td>
<td>180</td>
<td>60</td>
<td>10.3 ± 0.5 nm</td>
</tr>
<tr>
<td>0.5 mmol/2 mL</td>
<td>220</td>
<td>60</td>
<td>13.1 ± 0.8 nm</td>
</tr>
</tbody>
</table>

**Preparation of Tween 20 functionalized Cu\(_{2-x}\)Se NPs.** Tween 20 were employed to achieve the water-solubility of oleylamine coated Cu\(_{2-x}\)Se NPs. Briefly, 10 mg Cu\(_{2-x}\)Se NPs were dispersed in 5 mL hexane. Then, 20 µL Tween 20 was added into the 5 mL hexane solution containing 10 mg Cu\(_{2-x}\)Se NPs mentioned above. After 20 min of sonication, the mixture was added slowly to 10 mL HPLC water in a 80 °C water bath until hexane was completely evaporated. The Tween 20 functionalized Cu\(_{2-x}\)Se NPs were collected by centrifugation, and then washed with water twice.

**Characterization.** Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-2010 at an accelerating voltage of 200 kV. High-resolution TEM (HRTEM) images were obtained on a FEI Tecnai G2 F30 at 300 kV. High-angle annular darkfield scanning TEM (HAADF-STEM) images and STEM energy-dispersive X-ray spectroscopy (STEM-EDS) maps were collected using a JEOL JEM-ARM200F STEM equipped with spherical aberration correctors on the image, at an accelerating voltage of 200 kV. TEM grids were prepared by dropping a dilute NC dispersion onto a carbon-coated copper or nickel TEM grid and allowing the sample to dry under air. Size distributions were obtained from TEM images by measuring at least 100 NCs from multiple TEM images from different areas of the grid, using Nanomeasurer v.1.2. Powder X-ray diffraction (XRD) measurements were carried out.
using a Rigaku Ultima IV diffractometer with a Cu Kα X-ray source. Samples were prepared by drop-casting concentrated NC dispersions onto glass slides. UV–vis–near-IR spectra of NC dispersions in hexane were taken on a Shimadzu UV-3600. The photothermal heating characterization of all the samples were measured with an infrared camera (FLIR Systems Inc., Boston, MA), using 808, 980 and 1210 nm diode lasers (Q-Photonics). All the samples were dispersed in HPLC water and sonicated for 1 min. For each experiment, a 1 mL liquid was transferred into a 10 × 10 mm quartz cuvette. HPLC water was used as the control. The laser power was calibrated to a fluence of 1.5 W/cm² using a powermeter (Coherent Inc., Santa Clara, CA). Measurements were performed by irradiating the cuvette horizontally for 10 min and simultaneously collecting thermal images to determine the temperature of the solution using the infrared camera and ThermoVision software (FLIR Sys., Boston, MA).

**Calculation of the photothermal conversion efficiency**

The photothermal conversion efficiency of the hydrophilic Cu2-xSe NPs was determined according to the previous method. Detailed calculation is given as following:

$$\eta = \frac{hS(T_{max} - T_{surr}) - Q_{dis}}{I(1-10^{-A_{av}})}$$  \hspace{1cm} (1)

Where \(h\) is the heat transfer coefficient, \(S\) is the surface area of the container, and the value of \(hS\) is obtained from the Eq.4 and **Figure 4-18c**. The temperature changes \(T_{max} - T_{surr}\) of the Cu2-xSe aqueous solution were 9.2, 10.4 and 11.1 °C for Cu2-xSe NPs (200 µg/mL) in 10 min under the irradiation of 808, 980 and 1210 nm lasers. The laser power \(I\) used here is 0.537 W. The absorbance of the Cu2-xSe NPs at 808, 980, and 1210 nm \(A_{808}, A_{980}, A_{1210}\) are 0.57, 1.04, and 1.24. \(Q_{dis}\) expresses heat dissipated from the light.
absorbed by the solvent and container. In order to obtain $hS$, a dimensionless parameter is introduced as followed:

$$\theta = \frac{T - T_{sur}}{T_{max} - T_{sur}}$$  \hspace{1cm} (2)$$

A sample system time constant $\tau_s$ can be calculated as Eq. 3.

$$t = -\tau_s \ln(\theta)$$  \hspace{1cm} (3)$$

According to **Figure 4-18c**, $\tau_s$ were determined to be 198, 137, and 119 s for 808, 980, and 1210 nm irradiation.

$$hS = \frac{m \rho C}{\tau_s}$$  \hspace{1cm} (4)$$

In addition, $m$ is 1 g and $C$ is 4.2 J/g·°C. Thus, according to Eq. 4, $hS$ are deduced to be 2.1, 3.1 and 3.5 mW/°C, respectively.

$Q_{dis}$ expresses heat dissipated from the light absorbed by the quartz sample cell itself, and it was measured independently using a quartz cuvette cell containing pure water.

Thus, substituting according values of each parameters to Eq. 1, the 808, 980, and 1210 nm light-to-heat conversion efficiencies ($\eta$) of the Cu$_{2-x}$Se NPs can be calculated to be 42.4%, 36.1%, and 18.9% under 808, 980 and 1210 nm irradiation.
Chapter 5. Summary and Future Work

5.1 Summary

In this dissertation, we mainly focussed on: (1) developing a rapid room-temperature method for synthesis of metal sulfide NCs with tunable optical properties; (2) investigating reversible interconversion between different Cu_{2-x}S phases and morphologies, (3) incorporating various cations into distinct Cu_{2-x}S templates to produce controllable homogeneous or heterogeneous nanostructures; (4) preliminary studies of the application of these materials for electrocatalysis and photothermal heating.

In Chapter 1, we provided some basic background on plasmonic copper sulfide-based nanomaterials. The self-doped copper chalcogenide NCs exhibit strong NIR LSPR due to the presence of a high concentration of free holes, which arises from their copper deficiency. In Section 1.2, we presented a novel room-temperature synthesis of covellite CuS NPls. The lateral dimensions of CuS NPls were controlled over a wide range while maintaining a constant thickness of 4 nm. The ability to control the aspect ratio (lateral dimensions, at fixed thickness) was achieved using different initial Cu:S ratios and different sulfur precursor injection methods. The NCs exhibit LSPR absorbance that depends upon their aspect ratio and can be tuned over a range of more than 600 nm. In section 1.3, we generalized this rapid, low-temperature synthetic method to produce various different metal sulfide NCs, including binary Ag_{2}S, PbS, CdS, and SnS; ternary AgInS_{2} (AIS), CuInS_{2} (CIS), Cu_{2}SnS_{3} (CTS); and quaternary Cu_{2}ZnSnS_{4} (CZTS). The size, morphology and thereby optical properties can be
modified by changing the initial cation to sulfur ratios and the reaction time. These discoveries provide a simple, rapid, and room-temperature methodology to synthesize metal sulfide (especially CuS) NCs with well controlled size and morphology.

In Chapter 2, we focused on morphology and crystal phase interconversion between different copper sulfide NCs. These transformations opened new possibilities for the well-controlled colloidal synthesis of these nanomaterials with combinations of phase, size, shape, and LSPR energy not previously obtainable. In section 2.1, we demonstrated a reversible morphology, crystal phase, and composition interconversion between two stoichiometric extremes in the copper sulfide family of materials: covellite CuS and high chalcocite Cu$_2$S. The forward transformation (from CuS to Cu$_2$S) was realized by reacting dodecanethiol (DDT) with plasmonic CuS NPls. On the other hand, the reverse transformation (from Cu$_2$S to CuS) was initiated by adding oleic acid-sulfur (OA-S) to Cu$_2$S NPls that exhibited no localized surface plasmon resonance (LSPR). In section 2.2, we converted biconcave djurleite Cu$_{1.94}$S NPls to covellite CuS NPls with flat surfaces by adding OA-S. The shape evolution is attributed to the preferential plate-like morphology of covellite CuS, resulting from its intrinsic layered structure and stable (001) planes. 2–x

In Chapter 3, we presented our recent advances on cation incorporation into Cu$_{2-x}$S NCs. We have incorporated monovalent Ag$^+$, divalent Cd$^{2+}$, Zn$^{2+}$, Mn$^{2+}$, Pb$^{2+}$, and Sn$^{2+}$, trivalent In$^{3+}$, Fe$^{3+}$ and Ga$^{3+}$ and tetravalent Sn$^{4+}$ and Ge$^{4+}$ into different Cu$_{2-x}$S NCs, producing controllable heterogeneous and homogeneous nanostructures. In section 3.1, tin precursors with two different air-stable oxidation states were
incorporated into covellite CuS NPs with or without DDT, producing two distinct phases of CTS NCs: incorporation of Sn$^{2+}$ alone produced kuramite Cu$_3$SnS$_4$; incorporation of Sn$^{4+}$ with DDT produced mohite Cu$_2$SnS$_3$. We demonstrated that Sn$^{2+}$ (or DDT) can serve as a mild reducing agent to break disulfide bonds to facilitate subsequent cation diffusion. In section 3.2, we incorporated In$^{3+}$ into covellite CuS to produce CIS NPs. Next, we synthesized biconcave djurleite Cu$_{1.94}$S NPs by treating the CIS template NPs with additional Cu$^+$ ions. Upon initiation of the CE reaction, the In$^{3+}$ ions diffuse out of the CIS crystal lattice, and the remaining copper sulfide adopts the djurleite phase almost instantly. This rapid phase transition produces numerous vacancies and defects before Cu$^+$ ions can diffuse into the nanostructures. We attribute the formation of a biconcave shape to the assembly and migration of these defects. In section 3.3, we synthesized different types of biconcave metal sulfide (CdS, ZnS, MnS and CIS) NPs using biconcave djurleite Cu$_{1.94}$S NPs as templates. We showed that the ability to preserve the biconcave morphology is associated with the similar hcp packing of anionic sublattice for these metal sulfides. Cation exchange (CE) reactions using other cations led to shape evolution and loss of the biconcave structure. In section 3.4, we treated covellite CuS NPs with Ag$^+$ to investigate mechanisms of Ag$^+$-based CE reactions in CuS NPs. The Ag$^+$ incorporation process is strongly concentration dependent, producing plate-satellite CuS-Ag$_2$S and biconcave-particle Ag$_2$S-Ag heterostructures using relatively small and large quantities of Ag$^+$, respectively. We attribute the formation of these heterostructures to the presence of reactive edge surfaces (compared to relatively inert top and bottom surfaces) of the template NPs.
and the nanoscale Kirkendall effect. In Section 3.5, we summarized all the observations of the previous sections, conclusively demonstrating a general rule of valence selectivity of cation incorporation into copper sulfide nanocrystals. This valence selectivity, which arises from conflicts between charge balance and cation coordination, can strongly influence the results of cation incorporation into copper sulfide nanocrystals (i.e. determine whether homogeneous or heterogeneous nanostructures are generated). In the previous sections, the cation incorporation (or exchange) reactions were based on a homogeneous Cu$_{2-x}$S template. However, in Section 3.6, we explored the process of tin and indium incorporation into Cu$_{1.81}$S-ZnS nanoheterostructure (NH). We demonstrated that the outcomes of cation incorporation were strongly influenced by heterocation identity and valence and by the presence of a Cu-extracting agent. The selectivity of cation incorporation depends upon both the cation itself and the heterodomains in which CE reactions take place. The final NCs emerge in many forms including homogeneous NCs, heterodimers, core@shell NHs and NHs with three different domains. We believe these studies not only provide new insight into the structure, morphology, composition and crystal phase evolution of copper sulfide-based nanomaterials, but also provide inspiration for design of previously unavailable nanostructures.

In Chapter 4, we presented two examples of using copper chalcogenide NCs for practical applications: electrocatalysis and photothermal heating. In section 4.1, on the basis of our previously-demonstrated room-temperature synthesis (section 1.2), we developed a well-controlled method to synthesize monodispersed hexagonal covellite
CuS NPs, whose lateral diameters were tunable over a wide range (from 8 to over 100 nm) while the thickness of the NPs remained constant at ~2 nm. We showed that the ORR activity increased with increasing size (diameter at constant thickness) of the NPs. After combining our experimental results with density functional theory calculations, we attribute the size-dependent enhancement to anisotropy of electrical conductivity and electrochemical activity. The DFT calculations predicted that the lowest oxygen adsorption energy was on preferentially exposed, Cu2-terminated (001) surfaces. In section 4.2, we manipulated the NIR absorption band of copper selenide (Cu2-xSe) nanoparticles (NPs) by precisely controlling their size and copper deficiency. By transferring the Cu2-xSe NPs from organic phase to aqueous phase, we investigated the relationship between the illumination wavelength and photothermal conversion efficiency. The results suggested that use of wavelengths above 1100 nm, where water has a relatively strong absorbance, negatively impacts the photothermal conversion efficiency of Cu2-xSe NPs.
5.2 Recommendation for Future Work

Although the integrated results of the studies presented in this dissertation allow us to draw many new conclusions about structures and properties of copper sulfide-based nanomaterials and their mechanisms of formation and evolution, each conclusion appears to be accompanied by more open questions. Fortunately, the methods developed in this dissertation provide a framework for tackling many of these open problems. The following briefly introduces several promising future directions for this work.

The broad class of metal sulfide semiconductor nanomaterials has been of great interest over the past few years. In this dissertation as well as in the broader inorganic nanochemistry, the preparation of copper sulfide-based nanomaterials has been well developed with respect to both synthesis and emerging applications. Two-dimensional nanomaterials, in particular layered transition metal-sulfide (TMS, i.e. MoS₂ and WS₂) nanosheets, have also attracted intense attention because of their potential applications as chemically active electrocatalysts for hydrogen evolution and optically active materials in optoelectronics. However, reports on solution-phase synthesis of these TMS nanosheets with precisely controlled composition and morphology are still very rare. Traditional synthesis approaches such as chemical exfoliation and chemical vapor deposition always produce TMS nanosheets with large lateral dimensions and ill-defined shapes. Therefore, developing chemical methods for preparing layered TMS nanosheets, and van der Waals interaction-based devices using them, especially under ambient conditions with rapid fabrication processes, are both challenging and
Cesium lead halide perovskite (CsPbX₃, X = Cl, Br, and I) NCs have emerged as a class of semiconductor nanomaterials with intriguing properties, including tunable bandgap, large absorption coefficient, broad absorption spectrum, high charge carrier mobility, which enable it with a broad range of photovoltaic and optoelectronic applications. Unlike the layered TMS nanosheets, colloidal CsPbX₃ NCs with different sizes and morphologies (nanocubes, nanowires, nanoplates) have been produced using methods similar to those employed for preparation of traditional metal sulfides (e.g. Cu₂₋ₓS, CdS and CuInS₂). Nevertheless, reports on CsPbX₃-based NC heterostructures are still very limited. We propose to integrate CsPbX₃ NCs with other NCs with tunable optical properties (Ag, Au, Cu₂₋ₓS, CdS, Ag₂S NCs with visible and NIR LSPR absorbance or emission). On one hand, core/shell or other well-designed nanostructures could potentially stabilize the inorganic perovskite domain. On the other hand, for example, the plasmonic Cu₂₋ₓS domain in Cu₂₋ₓS-CsPbX₃ heterostructures may harvest more light at NIR wavelengths and transfer the energy to the CsPbX₃ domain for PL enhancement. We note that heterostructures including Cu₂₋ₓS-MoS₂ and CdS-MoS₂ have been recently reported.¹⁹¹ These structures exhibit enhanced photocatalytic activity toward HER under visible light irradiation. Colloidal synthesis of these proposed heterostructures can enable high quality, property tunable, and scalable hybrid systems.

In the previous sections, we have reported various novel nanostructures (e.g. biconcave metal sulfide NPls, Cu₂₋ₓS-CdS hybrid NPls and Cu₂₋ₓS-In₂S₃-ZnS triple
domain nanobrightostructures) with unique combinations of materials, tunable compositions and novel morphologies. Our future work should focus on developing their applications in photonics, electrocatalysis, photovoltaics and optoelectronics. These copper sulfide-based heterostructures possess great potential in nano/micro photoelectric devices because of their “built-in” p-n heterojunctions. Moreover, our observations of facet- and size-dependent anisotropic electrochemical properties of covellite CuS NPs provides an example of electrochemical study on precisely controlled nanostructures.

Although this dissertation has mainly focused on interconversion among various copper sulfide-based materials, including incorporation of extrinsic elements and emerging applications, we should mention that other exciting work is being done on morphology control and other aspects of these nanomaterials. With continued advances in the synthesis of this diverse family of nanomaterials, improved understanding and control of their physicochemical properties, and exploration of many new applications, this field of research should remain fertile for many years to come.
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