Compound Copper Chalcogenide Nanocrystals:
Synthetic Approaches to Fabricate Multi-Component
Semiconductor Nanocrystals for Technological
Applications

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Declaration

I declare that the work described in this thesis is entirely the result of my own work carried out in the University of Limerick, except for the assistance mentioned in the acknowledgements section and the collaborative work for publications.

This thesis has not previously been submitted in whole or in part for the award of a degree at this or any other university.

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Abstract

This thesis describes the development of novel synthetic routes to fabricate a range of multi-component, copper chalcogenide semiconductor nanocrystals using colloidal chemistry. Colloidal routes to ternary and quaternary semiconductor nanocrystals hold significant promise for technological applications, where solution processability combined with size dependent properties offers considerable advantages over bulk fabrication routes to these materials.

The preparation of highly monodisperse, anisotropic CuInGaS$_2$ (CIGS) colloidal nanocrystals is described in Chapter 3. Importantly, the results show that although the synthesis is a one-pot reaction, the formation of CIGS nanocrystals always occurs sequentially, starting with binary copper sulfide, transitioning through ternary copper indium sulfide before the final gallium insertion to yield the quaternary CIGS nanocrystals.

Chapter 4 explores the effect of selenium incorporation to yield quinary CuInGa(Se)$_2$ (CIGSSe) nanocrystals. Interestingly, the formation of thin, hexagonal nanoplates, which display remarkably high diffraction contrast effects known as bending contours, was observed on the surface of each nanocrystal. Through control of the reaction conditions, routes were devised to selectively synthesize CIGSSe nanocrystals with complete phase control, allowing either the wurtzite or cubic crystal structure to be obtained.

Chapter 5 describes the shape controlled synthesis of Cu$_2$ZnSnS$_4$ (CZTS) nanocrystals, with tight control in the size, shape and crystal phase. Subtle changes in the reaction chemistry were observed to have significant effects on the resultant nanocrystal morphology.
An in-situ investigation of the nucleation and growth processes in colloidal wurtzite CZTS nanocrystals is discussed in Chapter 6. Through the use of time-resolved, quick X-ray absorption spectroscopy (QEXAFS), it was possible to successfully monitor the formation of stoichiometric CZTS nanocrystals, in-situ, in a custom built reaction flask. This represents the first report of its kind into studying the nucleation and growth processes of a complex quaternary, nanocrystal system.
**List of Abbreviations**

NC – nanocrystal

0-D – zero dimensional

1-D – one dimensional

2-D – two dimensional

3-D – three dimensional

QD – quantum dot

1-DDT – 1-dodecanethiol

t-DDT – tert-dodecylmercaptan

HDT – hexadecanethiol

TOPO – trioctylphosphine oxide

TOP – trioctyphosphine

TOOP – trioctyphosphite

HPA – hexylphosphonic acid

ODPA – octadecylphosphonic acid

OLA – oleylamine

OA - oleic acid

HDA - hexadecylamine

1-ODE – 1-octadecene

MCC – metal chalcogenide complex

P3HT - poly (3-hexylthiophene)

CdS – cadmium sulfide

CdSe – cadmium selenide
CdTe – cadmium telluride
CdSeS – cadmium sulfur selenide
Cu_{2-x}S – copper (I) sulfide
Cu_{2-x}Se – copper (I) selenide
Cu_{2-x}Te – copper (I) telluride
CuSe – copper (II) selenide
CIS - CuInS_2 - copper indium sulfide
CISe – CuInSe_2 - copper indium selenide
CuSSe - Cu_{2-x}S_ySe_{1-y} – copper sulfur selenide
CGS – CuGaS_2 - copper gallium sulfide
CGSe – CuGaSe_2 - copper gallium selenide
CIGS – CuIn_xGa_{1-x}S_2 - copper indium gallium sulfide
CIGSe – CuInGaSe_2 – copper indium gallium selenide
CIGSSe – CuInGa(SSe)_2 – copper indium gallium sulfur selenide
CTS – Cu_2SnS_3 – copper tin sulfide
CTSe – Cu_2SnSe_3 – copper tin selenide
CZTS – Cu_2ZnSnS_4 – copper zinc tin sulfide
CZTSe – Cu_2ZnSnSe_4 – copper zinc tin selenide
CZTSSe - Cu_2ZnSn(SSe)_4 – copper zinc tin sulfur selenide
CCTSSe - Cu_2CdSn(SSe)_4 - copper cadmium tin sulfur selenide
ZnO – zinc oxide
ZnS – zinc sulfide
ZnSe – zinc selenide
ZnTe – zinc telluride

PbS – lead sulfide

HgS – mercury (II) sulfide

HgSe - mercury (II) selenide

HgTe - mercury (II) telluride

HgCdTe – mercury cadmium telluride

HSAB – hard-soft acid-base

TEM – transmission electron microscopy

SEM – scanning electron microscopy

STEM - scanning transmission electron microscopy

BFTEM – bright field transmission electron microscopy

DF-STEM – dark field scanning transmission electron microscopy

HRTEM – high resolution transmission electron microscopy

HRSEM - high resolution scanning electron microscopy

SAED – selected area electron diffraction

EDX – energy dispersive X-ray spectroscopy

EELS –electron energy loss spectroscopy

EBSD – electron backscatter diffraction

EPD – electrophoretic deposition

FFT – fast Fourier transform

FTIR – Fourier transform infrared spectroscopy

HAADF – high-angle annular dark field

UV-vis – ultraviolet-visible spectroscopy
SERS – surface-enhanced raman spectroscopy

ITO – indium tin oxide

NIR – near-infrared

XRD – X-ray diffraction

XPS – X-ray photoelectron spectroscopy

XAS – X-ray absorption spectroscopy

XANES – X-ray absorption near edge spectroscopy

EXAFS – extended X-ray absorption fine structure

QEXAFS – quick extended X-ray absorption fine structure

CCD – charge coupled device

DOF – depth of focus

LED – light-emitting diode

LUMO – lowest unoccupied molecular orbital

LSPR – localized surface plasmon resonance

HOMO – highest occupied molecular orbital

PL – photoluminescence

PV – photovoltaics

QY – quantum yield

WZ - wurtzite

Z – atomic number

ZB – zinc blende
List of Publications


Chapter 1: Introduction

1.1 Introduction to Semiconductor Nanocrystals

Semiconductor nanocrystals (NCs) are tiny crystalline particles comprised of ~100 to 100,000 clusters of atoms and are 10,000 times smaller than the width of a human hair. They are defined as having one or more external dimensions in the size range of 1-100 nm, with the most exciting structures possessing dimensions in the sub 10 nm size regime. The term ‘nanocrystal’ encompasses a wide range of geometries and in general, they can be classed according to their configuration where their intrinsic properties arise from dimensional restrictions. This allows them to act as zero, one, two or three-dimensional entities. Examples of typical structures include 0-D quantum dots, 1-D nanorods, 1-D nanowires and nanotubes, 2-D nanodiscs and nanosheets and 3-D superstructures or arrays of assembled NCs.

NCs are of immense scientific interest as they effectively bridge the gap between small, individual molecules with discrete energy states and that of bulk, crystalline materials with continuous energy states. In this sense, they constitute a new class of material, taking on an entirely new character by possessing properties which are fundamentally different from those of either discrete molecules or bulk materials. Generally, bulk materials display constant physical properties regardless of size, as the percentage of surface atoms is effectively negligible relative to the total number of atoms in the materials core. However, as the size shifts into the sub 10 nm range, NCs defy these generalities and display major changes in their physical and chemical properties as a direct consequence of the reduction in the NC dimensions.

By solely varying the physical size of the NC, the percentage of atoms at the surface relative to the core significantly increases, causing pronounced internal disruptions.
to the electronic structure and resultant optical properties of the material.\textsuperscript{5} This essentially provides an effective means to tailor the electronic structure and optical properties, giving rise to size-dependent band gaps in semiconductor NCs.\textsuperscript{1,5,22} NCs experience quantum confinement effects and melting point suppression in this regime.\textsuperscript{1,2,23,24}

Binary II-VI NCs such as cadmium based chalcogenides, namely cadmium sulfide (CdS) and cadmium selenide (CdSe), are the most extensively investigated colloidal semiconductor NCs and serve as excellent starting points for understanding how size, shape and composition can be used to govern the materials physical and optical properties.\textsuperscript{1,3,25} For example, in the prototypical material CdS, the band gap can be tuned between 2.5 eV and 4.0 eV,\textsuperscript{1,2} the radiative rate for the lowest allowed optical excitation ranges from several nanoseconds down to just tens of picoseconds\textsuperscript{26} and the melting temperatures varies from 1600°C down to 400°C.\textsuperscript{23} Interestingly, under ultraviolet illumination, 0D NCs (quantum dots) of these materials can emit light of different colours based on a size variation within the particles.\textsuperscript{1,22}

Figure 1 highlights this particular phenomenon and shows how the fluorescence emission of colloidal solution of CdSe NCs results in different wavelengths depending on their size. CdSe NCs typically have a red luminescence but on the sub 10nm scale, the emission derived from the exciton recombination shifts to higher energy. This results in the noticeable colour change in the fluorescence emission from red to green-blue, with decreasing crystal size from 8 nm to 2 nm (as depicted in Figure 1).\textsuperscript{3,4} This increase in the band gap and blue shift of the optical absorption and emission with decreasing crystallite size occurs when the material experiences the effects of quantum confinement.\textsuperscript{2,3,19} The percentage of atoms on the surface of the NC ultimately increases as a result of the overall decreasing NC size, with a 1.2
nm CdSe NC having 88% of its atoms on the surface and emitting a photon having a wavelength at 420 nm, whereas an 8.5 nm sized NC has only 20% surface atoms and emits a photon having a wavelength at 650 nm.\textsuperscript{27}

Figure 1. Fluorescence image of vials containing various sized CdSe quantum dots and the corresponding fluorescence spectrum as a function of size.\textsuperscript{4}

This first systematic study of size-dependent optical properties in CdSe quantum dots was performed more than two decades ago by Henglein\textsuperscript{28} and Brus\textsuperscript{29}. Both studies conclusively proved that quantum confinement of the photogenerated electron-hole pair resulted in the observed size dependent optical properties, with the optical spectrum showing a strong correlation of the colour of the NC solution with their size. It was this discovery that set the cornerstone of more than two decades of intense scientific research into the synthesis, properties and applications of semiconductor NCs, with researchers eager to develop synthetic protocols in a bid to access and assess the materials properties in this size regime.\textsuperscript{25}
1.2 Quantum Confinement

The quantum confinement effect can be observed once the diameter of the material is comparable to or smaller than the length scale characterizing the electronic motion in the bulk material.\textsuperscript{2-5,19} Bulk semiconductors are characterized by a fixed energy difference between the filled and unfilled electronic bands, known as valence band and conduction band, respectively. These energy bands are separated by a region called the band gap which denotes the minimal amount of energy that must be absorbed for the electron energy level to be raised and bridge the band gap.\textsuperscript{20} In the bulk form, the difference between the energy levels is small (due to the large number of atoms), thus the energy levels can be described as continuous. When an electron is excited from the valence band and jumps across the fixed band gap to the conduction band, it leaves behind a positively charged hole in the valence band.\textsuperscript{5,20} This electron-hole pair is collectively called an exciton, and the average physical separation distance between the electron and hole is known as the exciton Bohr radius,\textsuperscript{5,19,20} which is different for each bulk material.

Table 1 shows the exciton Bohr radii of a variety of semiconductors,\textsuperscript{30-40} with a focus on copper based chalcogenides which are the main semiconductor materials studied in this thesis.
Table 1. Bohr Exciton Radii of a variety of semiconductors.

As the band gap is fixed in the bulk form, the energy emitted as the electron falls back to its corresponding position in the valence band is also fixed and this consequently leads to uniform absorption and fixed emission frequencies in the bulk materials. This results in the exciton moving freely throughout the crystal (as the size of the crystal is much larger than the exciton Bohr radius). However, as the size of the semiconductor material approaches the size of its exciton Bohr radius, its properties cease to resemble that of the bulk material and the energy levels are described as being discrete, as there is a finite distance between the energy levels. This results in a widening of the energy gap between the highest occupied electronic states (HOMO) and the lowest unoccupied states (LUMO) as compared to the
bulk\textsuperscript{1,2,19} and it is this concept of discrete energy levels that is referred to as quantum confinement. This is illustrated in Figure 2, where a physical size smaller than the exciton Bohr radius results in a three-dimensional quantum confinement of charge carriers within the quantum dot, with smaller quantum dots possessing larger band gaps. The widening of the energy gap means more energy is required to excite the charge carrier and ultimately, more energetic photons are released when the crystal returns to its normal state.

Figure 2. Relation between the electronic structure of bulk semiconductor solids and 0D quantum dots. Smaller quantum dots have larger band gaps and emit more energetic photons which alter the colour of the light emitted by the particle.\textsuperscript{41}

As a consequence of this, the electronic and optical properties of the NCs become size dependent and therefore can be physically tuned by confining the exciton into one, two or three restricted dimensions.\textsuperscript{5,19,20} The dimensionality of charge carriers in a system in turn determines the distribution of the density of electronic states.\textsuperscript{42}
Figure 3 shows the variation on the density of electronic states (versus energy) for (a) bulk material (3D), (b) 2D where the charge is confined along one direction, (c) 1D confined along two directions and (d) 0D confined in all three directions.

![Figure 3](image.png)

**Figure 3.** Evolution of the density of states function moving from (a) bulk material to (b) one-dimensional confinement in a quantum well (c) two-dimensional confinement in a quantum wire and (d) three-dimensional confinement in a quantum dot.\(^{42}\)

As mentioned above, 0D NCs confine the motion of conduction band electrons and valence band holes in all three directions\(^{19,20}\) and are most notable for their fluorescent properties, particularly when the core 0D NC is encased with a second semiconductor to form a core-shell NC.\(^{19,43,44}\) In fact, 0D NCs have emerged as one of the most promising classes of NCs for biomedical imaging, due to their unique photo-physical properties and the versatility of their surface chemistry.\(^{45}\) They are well suited for advanced fluorescence imaging applications, exhibiting advantages compared to conventional fluorophores, such as size tunable and spectrally narrow light emission, efficient light absorption throughout a wide spectrum and improved brightness with resistance to photobleaching and degradation.\(^{4,45-47}\)

1-D nanorods are an advance in complexity of the basic quantum dot and are essentially quantum dots which are elongated in one particular direction. These 1-D
structures confine the motion of electrons or holes in two spatial directions and possess similar properties to quantum dots along with several notably important and advantageous features. Nanorods possess stronger electric dipoles, have length dependant properties such as absorption and conductivity and show greater size dependant light absorption and emission.

While the short axis of the nanorod, the diameter, preserves the quantized nature of the electronic levels, any variation in the diameter or the nanorod aspect ratio can cause a modification in the band gap energy. A decrease of the nanorod diameter results in a blue shift and an increase in the band gap energy, similar to that of quantum dots, with a decrease in length of the elongated dimension also causing minute changes to the band gap energy. Figure 4 shows how subtle variations in the nanorod length and diameter can dramatically alter the band gap.

![Figure 4. Band gap of CdSe nanorods with different lengths and widths.](image)

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1.3 Cadmium based Semiconductor Nanocrystals

The understanding of colloidal NCs has developed largely around II-VI cadmium chalcogenides, such as CdS and CdSe, due to a well understood reaction chemistry and strong emission characteristics leading to realisable applications ranging from bio-labelling to photovoltaics. In 1993, Murray, Norris and Bawendi developed a relatively simple route to synthesize highly monodisperse, cadmium based semiconductor NCs by thermally decomposing organometallic based precursors. This lead to the establishment of the well known ‘hot-injection’ route that is widely used today. This method afforded exquisite control of the NC size and provided a highly sought after means to both routinely synthesize semiconductor NCs (of CdS, CdSe and CdTe), as well as study their electronic structures, both experimentally and theoretically.

CdS, CdSe and CdTe are important direct band gap semiconductors, which are part of the II-VI family, and have band gaps of 2.4 eV, 1.75 eV and 1.44 eV respectively. As inferred by the name II-VI, these binary semiconductors are created by combining a metal atom with two valence electrons with a non-metal atom with six valence electrons in the outer shell. This gives rise to cadmium chalcogenides (CdS,CdSe, CdTe,), zinc chalcogenides (ZnO, ZnS, ZnSe and ZnTe) and mercury chalcongenides (HgS, HgSe and HgTe). While the cadmium and zinc bases are directly suitable for photovoltaic applications, mercury based HgSe and HgTe are semimetals and have zero band gap energies and inverted band structures. Nevertheless, these compounds, with much smaller band gaps, have attracted considerable interest for optical applications such as photodetectors and lasers due to their tunable infra-red (IR) emission up to wavelengths in the mid IR region. Additionally, HgTe can
easily form a ternary compound with CdTe, known as HgCdTe. This material combination opens up the possibility for band gap tuning by varying the stoichiometry from rich to poor in one metal cation, providing small adjustable bandgaps between 0 and 1.4 eV.\textsuperscript{60,61} This makes it an ideal candidate for use as an imaging agent in infrared photodetectors, particularly in fourier transform infrared (FTIR) spectrometers.\textsuperscript{54,56,60,61}

Of the binary II-VI material systems, CdSe is the most thoroughly studied NC system due to the established synthetic chemistry of achieving high quality NCs, coupled with its high quantum yields and size tunable optical properties.\textsuperscript{3,5,19,27} This, in turn, makes it the material of choice for use in biological investigations where the NCs act as in vivo fluorescent probes or markers for cellular imaging.\textsuperscript{4,45-47} It also acts as an important building block in advanced optoelectronic applications such as quantum dot based light-emitting diodes (LEDs)\textsuperscript{62-64} and quantum dot photovoltaic (PV) devices.\textsuperscript{65,66}

Increased photostability and higher quantum yields can be further achieved by modifying the NC surface through ligand exchange or by growing a shell of a second semiconductor such as CdS, ZnS or ZnSe, which has a larger band gap than the core, to create core-shell NCs.\textsuperscript{43,44,67-71} The original core NCs typically exhibit surface related trap states and act as fast non-radiative, de-excitation channels for the photogenerated charge carriers. Additional overgrowth of a shell efficiently passivates any surface dangling bonds or trap states on the core, giving rise to strongly enhanced fluorescence quantum yields.\textsuperscript{43,44,71}

CdSe NCs are probably most well known for their use in biomedical and optoelectronic applications but their use also stretches into the field of solar energy
conversion. Alivisatos and co-workers demonstrated their viability by fabricating a hybrid nanorod-polymer solar cell, in which elongated CdSe NCs (nanorods) were mixed with the conducting polymer, poly (3-hexylthiophene (P3HT), with CdSe electron-accepting and P3HT hole-accepting. When this inorganic-organic hybrid material was sandwiched between aluminium and indium tin oxide electrodes in a device architecture, it produced a device with a power conversion efficiency of 1.7%. While CdSe and CdS are intrinsic n-type semiconductors, they can be doped p-type with nitrogen or Cu⁺ ions, respectively. CdS was among the first bulk semiconductors to be used for solar cell applications and in fact, it still remains the n-type material of choice for the buffer layer in a PV device, owing to its wide band gap of 2.4 eV and consequent minimal absorption in this layer. When combined with a p-type semiconductor, it forms the core component (or p-n junction) of a PV device.

On the other hand, CdTe is a p-type semiconductor and ideally serves as an absorber layer material. The interest in CdTe arises due to its suitable material properties in that it is a direct band gap semiconductor, having a band gap of 1.44 eV, which makes it ideal for obtaining high efficiency single junction solar cells. CdTe also possesses a correspondingly high absorption coefficient of more than 1 x 10⁴ cm⁻¹ for nearly all wavelengths (shown in Figure 5) so only a small thickness of the material is required.
The first solar cell based on the combination of a bulk CdTe absorber coupled with CdS buffer layer was reported back in 1972 and exhibited an efficiency of 6% but since then, significant improvements have been made, resulting in a considerably elevated efficiency of 16.5%. CdTe is one of the mainstream bulk PV material technologies on the market, along with amorphous silicon and copper indium gallium selenide (CIGSe), and is a successful industrial solar cell technology. Two companies, First Solar in the US and Antec in Germany, produce commercial bulk CdTe based solar PV modules in large quantities and as of February 2014, First Solar announced a further increase in cell efficiency, thus it now stands at 20.4%. However, there are some drawbacks and concerns with the CdTe technology. One of the disadvantages of the CdTe film is that its material band gap cannot be tailored as CdTe is the only stable compound in the Cd-Te phase diagram. Doping is also quite complicated as the Cd vacancy acts as a donor and the Te vacancy acts as an
acceptor, so even a slight non-stoichiometric CdTe composition allows it to retain its p-type character.\textsuperscript{73} There are also concerns about both of the raw materials in this material composition. Cadmium is one of six substances banned by the EU for its adverse effects on the environment and human health and is considered to have a high acute toxicity, thus its use in applications is met with numerous safety concerns.\textsuperscript{54,73,74} Another obstacle in the wide spread application of CdTe based solar cells is the extreme rarity of tellurium as it is counted amongst the rarest materials found in the Earth’s crust.\textsuperscript{73} Thus, less toxic and more abundant alternatives to cadmium based chalcogenides are strongly demanded, with copper chalcogenides in the NC form being attractive alternatives for the fabrication of high quality semiconducting materials, using environmentally-benign, low-cost and earth-abundant compounds.
1.4 **Copper based Semiconductor Nanocrystals**

Copper based chalcogenides hold significant promise for a diverse range of applications from photothermal therapy and thermoelectrics to gas-sensing devices, Li-ion batteries and solar cells.\(^{76-80}\) The simplest copper chalcogenide is copper sulfide (Cu\(_{2-x}\)S) and is by far the most studied binary copper chalcogenide. Cu\(_{2-x}\)S has captured the attention of the broad scientific community, with its rich Cu\(_{2-x}\)S phase diagram, varying stoichiometry and compositionally tunable properties.\(^{76,81-84}\) This material ranges from non-stoichiometric, Cu-rich Cu\(_2\)S (chalcocite) to stoichiometric CuS (covellite). It possesses band gaps of 1.1-1.4 eV for chalcocite (x=0), increasing to 1.5 eV for digenite (x=0.2) and further increasing to 2.0 eV for covellite (x=1.0).\(^{36,76}\) Cu\(_{2-x}\)S and its selenium analogue, copper selenide (Cu\(_{2-x}\)Se), are regarded as being competitive p-type semiconductor candidates owing to the copper vacancies in their lattices.\(^{76}\)

Deeper investigations into the properties of these materials and the demonstrated ability to tailor their semiconducting properties, through careful manipulation of the synthetic conditions, have widely expanded their range of technological applications. These materials serve as important building blocks in optoelectronic, thermoelectric and photocatalytic devices.\(^{76-80}\) Their use also stretches into the fields of medicine, namely in terms of infrared detection and imaging, sensing and photothermal therapy.\(^{85-87}\) Copper chalcogenides were also among the first plasmonic semiconductors reported, showing a distinctive composition-dependent, localized surface plasmon resonance (LSPR) at near-infrared (NIR) wavelengths.\(^{36,76}\)

The earliest thin film solar cells in the 1950s were based on a bulk Cu\(_2\)S absorber coupled to a bulk CdS buffer layer and did show significant promise, capable of
achieving efficiencies up to 10\%\textsuperscript{88,89} However, research into these cells was subsequently abandoned due to copper diffusion into and doping of the CdS layer, combined with the phase instability of chalcocite (Cu\textsubscript{2}S) and its spontaneous transformation to slightly copper deficient djurleite (Cu\textsubscript{1.94}S)\textsuperscript{90-92} Both of these issues ultimately lead to degradation in the final device performance. In fact, this slight copper deficiency was found to reduce photovoltaic efficiencies by 60\% due to shifts in the band gap and a decrease in the minority carrier diffusion length\textsuperscript{90}.

With the dramatic reduction in dimensions in moving from the bulk to NC regime, these doping and diffusion issues can be seen as taking on an entirely new character, leading to the revalidation of Cu\textsubscript{2}S as an active light absorber\textsuperscript{93} Alivisatos and co-workers were among the first to demonstrate the application of chalcocite (Cu\textsubscript{2}S) in NC form, in combination with CdS nanorods and achieved a power conversion efficiency of 1.6\% on conventional glass and flexible plastic substrates\textsuperscript{93}.

Chalcopyrite based thin film solar cells are an extension of the original bulk copper chalcogenide systems and have taken the PV market by storm. They are often cited as being amongst the most promising solar cell technologies for cost effective power generation\textsuperscript{54,73,94-96} The most important chalcopyrite compounds are CuInSe\textsubscript{2} (copper indium selenide), CuInS\textsubscript{2} (copper indium sulfide), CuGaSe\textsubscript{2} (copper gallium selenide) and CuGaS\textsubscript{2} having band gaps of 1.0 eV\textsuperscript{97} 1.5 eV\textsuperscript{37,98} 1.7 eV\textsuperscript{99} and 2.5 eV\textsuperscript{98}, respectively. Since CuInSe\textsubscript{2} has a relatively low band gap, the addition of gallium provides a means to increase this up to 1.5 eV, forming CuInGaSe\textsubscript{2} (copper indium gallium selenide), which has yielded the highest photovoltaic efficiencies to date\textsuperscript{95}.
Research into these chalcopyrite materials in the bulk form goes back to the 1970s when the US Department of Energy initiated a project to investigate several relatively unexplored polycrystalline thin film materials\cite{ref54}, with Boeing demonstrating the first high efficiency of 9.4% based on a CuInSe$_2$ absorber layer\cite{ref100}. Boeing further developed and implemented the basic solar cell configuration that is responsible for the high efficiency device technology, making three principal improvements to the different building blocks of the cell\cite{ref96}. Firstly, the partial substitution of indium with gallium to form CuInGaSe$_2$ resulted in an increase in the band gap of this absorber layer material as well as a substantial increase in efficiency. The second improvement saw a replacement of the initial 1-2μm thick doped (CdZn)S layer with a thin undoped CdS layer accompanied by a conductive ZnO current carrying layer. The third most important change was the replacement of glass ceramic or borosilicate substrates with soda lime glass substrates. This change was initially made for cost reduction purposes but it was later found to contribute to the increased device performance from the indiffusion of sodium from the glass\cite{ref96}.

This observation, that the partial substitution of indium with gallium in the bulk materials provided a facile means to engineer the band gap, opened up new avenues for the exploration and incorporation of a range of p-block/semi metals (In, Ga, Sn, Ge) or transition metals (Zn, Fe). In terms of synthesizing these materials in NC form, Murray et al.’s approach\cite{ref53} proved highly attractive for the low cost fabrication of a range of colloidal nanomaterials\cite{ref101-123}. By adapting the colloidal approach, much higher levels of compositional control can be achieved prior to deposition on a substrate. This can be regarded as a considerable advantage over the conventional multi-stage coevaporation techniques, where significant stoichiometric variations existed in the film composition\cite{ref124-126}. 


Additionally, the reaction chemistry can be modified in such a way as to affect the structural properties (size, morphology, crystal phase) and physical properties (absorption, emission, conductivity) of the resultant NCs.\textsuperscript{3,6,127-129} These NCs can be composed of three-, four- and five-component elements known as ternary, quaternary and quinary semiconductor NCs. Each elemental addition adds a high degree of complexity in controlling the NC composition, requiring a balanced reactivity in the system to prevent the formation of two separate material compositions. Agrawal and co-workers highlighted the true potential of these compound semiconductor NCs in a device by using simple solution processes (colloidal approach for the synthesis and dropcasting/doctor blading to coat the resultant NC ink on substrates), followed by selenization to convert the as synthesized NCs into a thin film.\textsuperscript{103-105,130} The resultant CZT(SSe) thin film showed a conversion efficiency of 7.2\%,\textsuperscript{130} which represented a major step forward towards the use of solution based synthesis and coating processes to achieve high efficiency PV devices through low cost processing steps.
1.5 Classification of Copper based Semiconductor Nanocrystals

In general, copper chalcogenide NCs can be classed into different categories according to the number of elemental components that make up the material composition. The simplest form are binary NCs, composed of copper and one chalcogen: sulfur, selenium or tellurium. This constitutes the I-VI category of semiconductor NCs. The three component or ternary I-III-VI$_2$ compounds, such as copper indium diselenide (CuInSe$_2$) are conceptually derived from the prototypical binary II-VI semiconductors by replacing the two divalent cations with one monovalent cation (group I, Cu) and one trivalent cation (group III, In). Group IV elements such as Sn and Ge can also be incorporated to form I$_2$-IV-VI$_3$ compounds.

![Diagram of Group Combinations, Example, and Type]

**Figure 6.** Relationship between group II-VI, I-III-VI$_2$ and I$_2$-II-IV-VI$_4$

The complexity of these NCs further increases with the formation of quaternary systems and commonly takes the form of I-III-VI$_2$ (i.e. In and Ga incorporation to form CIGS) or I$_2$-II-IV-V$_4$. In particular, I$_2$-II-IV-V$_4$ NCs are formed when two of the trivalent cations are substituted with one divalent cation (such as Zn, Cd or Hg) and one tetravalent cation (Ge, Sn) to form CZTS / CZTSe. The relationship between each category is depicted in Figure 6.
1.5.1 Crystal Phases of Binary Nanocrystal Systems

The simplest copper chalcogenide, copper sulfide, is probably the most complicated in terms of evaluating its crystal phase. This is due to the fact that the Cu-S system exhibits numerous crystal phases, comprising of different stoichiometries and lattice structures over a wide range, as a result of its fast ion conduction at high temperature.\(^\text{36,81-83,131,132}\) The mineralogy of this system is quite interesting and extensive in that copper sulfide can support numerous copper-deficient stoichiometries and as a result is highly self-doped with p-type conductivity.\(^\text{36,76}\) In 1940, Vaughan reported that only the two end stoichiometric members, copper rich Cu\(_2\)S and copper deficient CuS, were known in the copper-sulfur based systems. By 2006, this finding had increased dramatically, with a total of 14 phases being identified.\(^\text{133}\) The most commonly identified Cu\(_{2-x}\)S phases are listed in Table 2.

<table>
<thead>
<tr>
<th>Mineral Name</th>
<th>Chemical Formula</th>
<th>Crystal System</th>
<th>Space Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chalcocite</td>
<td>Cu(_2)S</td>
<td>Hexagonal</td>
<td>P 63/m m c</td>
</tr>
<tr>
<td>Djurleite</td>
<td>Cu(_{1.9375})S</td>
<td>Monoclinic</td>
<td>P 1 21/c 1</td>
</tr>
<tr>
<td>Digenite</td>
<td>Cu(_{1.8})S</td>
<td>Hexagonal</td>
<td>R -3 m</td>
</tr>
<tr>
<td>Roxbyte</td>
<td>Cu(_{1.75})S</td>
<td>Monoclinic</td>
<td>C 2/m</td>
</tr>
<tr>
<td>Anilite</td>
<td>Cu(_{1.75})S</td>
<td>Orthorhombic</td>
<td>P n m a</td>
</tr>
<tr>
<td>Covellite</td>
<td>CuS</td>
<td>Hexagonal</td>
<td>P 63/ m m c</td>
</tr>
<tr>
<td>Villamaninite</td>
<td>CuS(_2)</td>
<td>Cubic</td>
<td>P a -3</td>
</tr>
</tbody>
</table>

**Table 2.** Most commonly encountered phases of copper sulfide, complete with their corresponding crystal systems and space groups.

Chalcocite is known to exist in monoclinic, hexagonal and cubic symmetries and undergoes a phase transition from the monoclinic \(\alpha\)-form (low chalcocite) to the
more disordered, high temperature hexagonal $\beta$-form (high chalcocite) at 103.5 ± 1°C.\textsuperscript{82,134} Low chalcocite is a p-type semiconductor self-doped by copper vacancies and possesses a relatively high carrier mobility. In the low chalcocite form, the sulfur sublattice is nearly hexagonal, whereas the copper ions are organized in a complex fashion, forming a 144-atom unit cell of Cu$_{96}$S$_{48}$, and it is this cation arrangement that leads to an indirect bandgap of 1.21 eV.\textsuperscript{135} As low chalcocite converts topotactically to high chalcocite, the sulfur atoms maintain their approximate positions. However, the copper ions adopt a partially statistical distribution on the lattice sites and so, lose the distinction between interstitial and lattice ions.\textsuperscript{136} This gives rise to the virtually fluid-like ionic mobility in the high chalcocite form and results in the higher symmetry hexagonal crystal structure which is defined by the sulfur framework. This transition only has a subtle effect on the indirect bandgap, increasing it to 1.42 eV, with the disorder in the high chalcocite phase leading to reduced mobility for holes and electrons.\textsuperscript{134,136}

Zheng \textit{et al.} directly visualized the structural transformation (from low chalcocite to high chalcocite) in an individual Cu$_2$S nanorod using aberration corrected transmission electron microscopy, in which heating from the electron beam was sufficient to induce the structural transformation.\textsuperscript{137} This ultimately allowed for the spatial distribution of the two phases within a single nanorod to be tracked in time. Figure 7 shows the trajectory of the structural transformation from low-chalcocite (green regions) to high-chalcocite (red regions). A portion of the Cu$_2$S nanorod was observed to temporarily transform into the high-chalcocite phase at the outer surface of the nanorod.
Figure 7. Trajectory of the structural transformations in a Cu₂S nanorod. (A) Sequential images showing the low-chalcocite structure (green), mixed structure (green and red domains) and the pure high-chalcocite structure (red). (B) Trajectory tracking of the transformation from low-chalcocite (L) to high-chalcocite (H).\textsuperscript{137}

Both phases co-exist in the nanorod for an extended period of time before the high-chalcocite phase propagates concentrically inward until the whole nanorod is transformed into the stable high-chalcocite phase. Once the transformation is complete, the high-chalcocite structure remains and does not convert back to low-chalcocite, even when the electron beam is shut off for a period of time.\textsuperscript{137}

The hexagonal (high chalcocite) phase is stable up to $436 \pm 10^\circ C$, above which it embraces the cubic symmetry.\textsuperscript{138} Since most copper sulfide NCs are synthesized at temperatures above the monoclinic-hexagonal transition temperature, the hexagonal structure is more thermodynamically favourable and even upon cooling below the
phase transition temperature, the nanomaterials retain the hexagonal structure. Thus, reports of NCs crystallizing in hexagonal $\beta$-form are common while the monoclinic $\alpha$-form is only observed when the NCs are grown from copper substrates.\(^8\)

Copper selenide has the similar tendency to crystallize in a large number of phases, comprised of different stoichiometries and crystal systems, as outlined in table 3. Despite these diverse phases, the major materials are Cu$_2$Se or Cu$_{1.8}$Se (berzelianite, face-centered cubic structure) which are highly desired for photovoltaic devices.\(^{139}\)

<table>
<thead>
<tr>
<th>Mineral Name</th>
<th>Chemical Formula</th>
<th>Crystal System</th>
<th>Space Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>Berzelianite</td>
<td>Cu$_2$Se</td>
<td>Cubic</td>
<td>F m -3m</td>
</tr>
<tr>
<td></td>
<td>Cu$_{1.8}$Se</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Klockmannite</td>
<td>CuSe</td>
<td>Hexagonal</td>
<td>P 63/ m m c</td>
</tr>
<tr>
<td></td>
<td>Cu$_{0.87}$Se</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Umanite</td>
<td>Cu$_4$Se$_2$</td>
<td>Tetragonal</td>
<td>P -4 21 m</td>
</tr>
<tr>
<td>Athabascaite</td>
<td>Cu$_2$Se$_4$</td>
<td>Orthorhombic</td>
<td>(unknown)</td>
</tr>
<tr>
<td></td>
<td>CuSe</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Krutaite</td>
<td>CuSe$_2$</td>
<td>Cubic</td>
<td>P a -3</td>
</tr>
</tbody>
</table>

**Table 3.** Most common phases in the copper selenide system.

Copper telluride can also exist in a wide range of compositions and phases, again due to the partially filled d-shell in copper which allows it to adopt multiple oxidation states. In particular, it remains a challenge to synthesize copper telluride nanostructures with well-defined composition, crystal structure and morphology. The main constraints to produce these NCs are the reduced number of tellurium precursors available and the inherent difficulty in balancing their reactivity and compatibility with the other elemental precursors. Nevertheless, copper telluride NCs
have been reported to exist as orthorhombic CuTe or as hexagonal Cu$_2$Te, Cu$_3$Te$_4$ and Cu$_7$Te$_5$.\textsuperscript{140,141}
1.5.2 Crystal Phases of Ternary Nanocrystal Systems

The bulk materials provide the foundation of our crystal system knowledge of the ternary NC systems. In the bulk, CuInS$_2$ and CuInSe$_2$ exhibit the chalcopyrite structure at room temperature in which the copper and indium atoms are ordered within the unit cell. At elevated temperatures, a random distribution of the cations becomes thermodynamically favoured, resulting in the formation of the zinc blende structure above 980°C and wurtzite between 1050 and 1090°C. In contrast to the bulk material, all three crystal structures can be stabilized in NCs at room temperature, with the different unit cell arrangements shown in Figure 8.

Figure 8. (a) Unit cell of the chalcopyrite crystal structure – the copper atoms are in light blue, iron atoms in dark blue and the sulfur atoms are in orange and of larger size. (b) Unit cell of the zinc blende structure – the zinc atoms are in green and sulfur atoms in orange and are of larger size. (c) Unit cell of the wurtzite structure.

The chalcopyrite lattice, named after the mineral copper iron sulfide, is the most well known structure in both bulk and nanocrystalline materials and derives from the group IV class of tetrahedrally bonded semiconductors according to the Grimm-Sommerfeld rule. Their tetrahedral structure can be derived from the cubic zinc...
blende structure - in which the two inter-penetrating face centered cubic lattices are occupied by cations in one sublattice and by anions in the other.\textsuperscript{77} In ternary chalcopyrite, the cations are replaced by one cation of higher valency (In$^{3+}$) and one cation of lower valency (Cu$^{+}$) in an ordered manner,\textsuperscript{79} consequently leading to a reduced symmetry (due to the two kinds of cations). This ultimately results in a primitive cell of eight atoms in the chalcopyrite structure (as opposed to two atoms in the zinc blende structure) and a body centered tetragonal Bravais lattice which is doubled along the crystal c axis.\textsuperscript{77}

In terms of atom arrangement, the sulfur atoms occupy the centre of the tetrahedron, with four cations at each corner but the direct result of bonding to two different cations leads to differing bond lengths and slight lattice distortion along the c-axis. It is this lattice distortion that aids in differentiating the tetragonal and zinc blende crystal system, with minor (101), (103) and (211) reflections evolving with respect to the cubic phase.\textsuperscript{77} It is only when the different cations are randomly distributed in the lattice that we observe the formation of the cubic zinc blende structure. On the other hand, the wurtzite phase can be unambiguously assigned based on its x-ray diffraction pattern which makes its identification easier, as opposed to the chalcopyrite and zinc blende phases.
1.5.3 Crystal Phases of Quaternary Nanocrystal Systems

The most stable structure reported of CZTS and CZTSe is tetragonal kesterite, which is derived from the ternary chalcopyrite structure.\textsuperscript{145,146} Kesterite is characterized by alternating cation layers of CuSn, CuZn, CuSn, CuZn in the direction of the c-axis.\textsuperscript{145} Another phase possible for quaternary CZTS is stannite and its structure differs in terms of the composition of the cation layer, in that it is comprised of ZnSn and pure Cu layers alternating in the c direction. In addition to these structures, there are three different modifications of the kesterite structure, in which exchange of two ions can occur on the cation sublattice.\textsuperscript{147} Figure 9 shows a schematic representation of the different modifications of the kesterite structure.

\textbf{Figure 9.} Schematic representations of (a) kesterite and (b) stannite structures, emphasizing the difference in metal ordering. In addition, schematic representations of three structural modifications of kesterite are shown (c, d, e) which are members of the P\textsuperscript{-42c}, P\textsuperscript{-421m} and P2 space group respectively.\textsuperscript{147}
In Figure 9(c), the Cu and Zn atoms in the $z=1/4$ layer can be exchanged, resulting in a change of the crystal symmetry and space group from I-42d to P-42c. The Cu and Zn atoms can also be exchanged between two layers to give two complete Cu and Zn layers at $z=1/4$ and $z=3/4$ (Figure 9d, P -4 2 1 m space group). Furthermore, the Cu atom at $z=1/2$ can also be exchanged with the Zn atom at $z=3/4$ (Figure 9e, P 2 space group). Thus, these subtle changes pose considerable difficulties in experimentally determining the exact structure, as Cu and Zn possess very similar atomic masses.

Two wurtzite derived structures, wurtzkesterite and wurtzstannite, have also been theoretically reported by Chen et al. These structures differ in terms of the occupation of the Cu, Zn and Sn cations. By controlling the reaction conditions, the thermodynamically metastable, wurtzite structure can be stabilized in NCs at room temperature, in which the Cu, Zn and Sn are randomly distributed in the lattice. The wurtzite phase is particularly exciting as it offers more flexibility for stoichiometry control, entailing band gap engineering by the ability to tune the Fermi energy over a wide range.

The most stable crystal structure of CIGS and CIGSe is the chalcopyrite structure (I-4 2 d space group), in which the Cu, In and Ga ions are ordered in the cation sublattice. Random distribution of these cations leads to the evolution of the zinc blende structure, with the further disordering of these cations yielding the kinetically stable, wurtzite structure with a hexagonal crystal system. Table 4 lists the most well-known crystal phases of I-III-VI$_2$ and I$_2$-II-IV-I$_4$ compounds, complete with information about their respective crystal systems and space groups.
Table 4. Most well-known crystal phases of I-III-VI\textsubscript{2} and I\textsubscript{2}-II-IV-I\textsubscript{4} compounds.

While the wurtzite phase also possesses cations which are randomly distributed in the lattice, similar to zinc blende, it differs in that its structure is non-centrosymmetric and the cations occupy the lattice in a disordered manner. This gives more flexibility in the stoichiometry in the wurtzite structure, as compared to the chalcopyrite phase.
1.6 Solution Approaches to Copper based Semiconductor Nanocrystals

State of the art bulk chalcopyrite devices have been made by energy intensive and ultra high vacuum solid state techniques, in which alternate layers (of copper, indium and gallium) are typically deposited in a multistage coevaporation process. This is then followed by their exposure to a selenium (Se or H\textsubscript{2}Se gas) environment at high temperatures in a specialized reaction chamber.\textsuperscript{150,151} While this technique does produce materials boasting high power conversion efficiencies, their overall fabrication cost is the barrier to large scale integration. By dramatically scaling down the fabrication costs, multi-component, chalcopyrite NCs have the potential to advance the low cost and scalable production of photovoltaics.\textsuperscript{101,102,104,118}

Solution based approaches are the most attractive alternative to the conventional vacuum techniques, not only in terms of cost reduction, but they also offer a much higher level of control over the material stoichiometry prior to deposition. This means that the presence of secondary impurity phases, which are commonly encountered in vacuum deposited films,\textsuperscript{124-126,152} is greatly eliminated, dramatically improving the properties of the device. By yielding NCs in a colloidal solution or “ink” format, low cost coating techniques (i.e. spin coating, printing and spraying) can be employed, further reducing the overall device fabrication costs.\textsuperscript{101,102,105,130,153}

Several synthetic routes have been explored to attain a wide range of compound copper chalcogenide NCs including colloidal methods (heating up or hot injection), involving the thermal decomposition of organometallic or suitable single-source molecular precursors, as well as hydrothermal and solvothermal techniques. The confluence of advances in these solution based routes has dramatically progressed in recent years, with researchers establishing routes to routinely obtain quantum dots,
nanorods, wires and more recently, even more complex shapes such as tetrapods. Of the solution based routes, the colloidal method is the most studied synthetic approach. It is regarded as being the most successful approach for obtaining exquisite size, shape, compositional and phase control in the resulting NCs.
1.6.1 Colloidal / Thermal Decomposition Method

The colloidal/thermal decomposition method is an oxygen-free, organic phase synthetic protocol that involves the dissolution of organic precursors, typically inorganic salts or organometallic compounds,\textsuperscript{156,157} in a high boiling point organic solvent. This ultimately results in the thermal decomposition of those precursors at elevated temperatures.\textsuperscript{3,53,158} The precursors are in turn chemically transformed into active atomic or molecular species (monomers) upon heating, thus providing the essential ingredients for NC formation.\textsuperscript{129}

The colloidal setup, shown in Figure 10, is quite similar to the basic reflux setup employed in organic chemistry, where a single-neck, round bottom flask is directly connected up to a Liebig condenser. However, the colloidal setup differs in that the condenser is connected up to a schlenk line to provide an oxygen-free environment for the synthesis. Additionally, a three-neck flask, as opposed to a single neck flask, is used in this approach, complete with outlets for the temperature finger, condenser and rubber septum /injection port, respectively. The schlenk line is based on a dual manifold design, which allows the facile introduction of an argon gas or vacuum environment for the reaction by means of opening/closing a stopcock on the line.
There are two basic modifications to NC synthesis in the colloidal approach, purely differentiated based on the location of precursors. In the ‘heating up’ approach, all the precursors are present in the flask initially and are heated up to the desired reaction temperature. In the ‘hot injection’ approach, the cationic and anionic precursors are separated from each other. This is achieved through the injection of a ‘cold’ anionic precursor solution into a ‘hot’ cationic precursor solution present in the flask. While both approaches involve an initial burst of nucleation of magic sized nuclei followed by growth on these existing nuclei, the hot injection approach is regarded as being a more defined route to obtain monodisperse NCs due to the separation of the anionic and cationic species until the point of injection. This ultimately results in a single nucleation event leading to equal NC growth and allows for the preparation of highly uniform NCs.
1.6.1.1 Nanocrystal Nucleation and Growth Mechanism

The most famous and widely cited example of the application of nucleation theory is the work done by La Mer and Dinegar in the 1950s. Their extensive studies on the nucleation and growth of sulfur sols, from the decomposition of sodium thiosulfate in hydrochloric acid, resulted in their ground breaking discovery into revealing how the formation of colloids or NCs occurs from a homogeneous, supersaturated medium. Their mechanism suggested that the production of monodisperse NCs requires a temporally discrete nucleation event, followed by slower controlled growth on the existing nuclei. This separation of the nucleation and growth stages is depicted in Figure 11.

Figure 11. Schematic representation showing the different stages of nucleation and growth for the synthesis of monodisperse NCs, as per the La Mer and Dinegar model.
For nucleation to occur, the solution must first be supersaturated, which can be achieved by either directly dissolving the solute at higher temperatures followed by rapid cooling or by adding the reactants in such a way as to produce a supersaturated solution during the reaction. The rapid addition of reagents, by means of an injection into the reaction vessel containing a hot coordinating solvent, raises the precursor concentration above the nucleation threshold for a brief period of time, with the subsequent temperature drop resulting in a supersaturation of particles in the solution.\textsuperscript{53,158,162,164}

The nucleation threshold defines the outcome of the nuclei. In essence, nuclei larger than the critical size will further decrease their free energy for growth and form stable nuclei that grow, while nuclei smaller than the critical size threshold will shrink. In the fast nucleation regime, high concentrations of nuclei are generated, thus resulting in smaller NCs. Conversely, a slow nucleation regime provides a low concentration of seeds, consuming the same amount of precursor and results in larger particles.\textsuperscript{129,158} The existing nuclei can only continue to grow at a rate determined by the slowest step in the growth process and this separates the respective nucleation and growth stages in time. As long as the consumption of reactants by the growing NCs is not exceeded by the rate of precursor addition to solution, no new nuclei can form and additional monomer can only be consumed by the existing nuclei.\textsuperscript{158}

The uniformity of the size distribution is largely determined by the time period over which the nuclei are formed and begin to grow. If the nucleation period is short, the smaller particles grow more rapidly than larger particles as their free energy driving force is larger, resulting in a ‘focusing’ of the size distribution.\textsuperscript{129,159,165} Thus, the requirements for monodispersity can be summarized as follows: (1.) a high nucleation rate leading to the burst of nuclei formation in a short period of time, (2.)
an initial fast rate of growth to rapidly reduce the concentration below the critical nucleation threshold, followed by, (3.) an eventual slow growth rate leading to a long growth period.

Ostwald ripening, the second, distinctive, growth phase occurs when the monomer is depleted due to particle growth.\textsuperscript{158,159} In this process, ‘defocusing’ of the size distribution occurs, in which larger particles continue to grow and the smaller particles dissolve due to their high surface energy.\textsuperscript{129,159} This decrease in saturation ratio increases the critical nuclei size, further promoting the dissolution of particles smaller than the critical threshold. Two size regimes exist at this point, with the critical nuclei size between the extremes of a smaller and larger particle. The defocused size distribution is difficult to revert back to a focused one, unless the growth time is extended to such a point that the smaller nuclei are completely depleted in solution.\textsuperscript{166}
### 1.6.1.2 Reaction Parameters in Colloidal Synthesis

The main parameters in colloidal synthesis are: the choice of inorganic precursors and their respective concentrations, choice of surfactants and solvents which modulate the kinetics of nucleation and the growth rate, injection and growth temperature and growth time. However, it should be pointed out that NCs can only be generated if the constituent atoms can rearrange and anneal during growth.\(^{129}\) This suggests that temperature is one of the decisive factors in determining the optimal growth conditions. With the large reduction in melting temperature as a result of moving from bulk solids down to the nanometre regime, colloidal NCs can be grown at temperatures where common organic molecules are stable (200 – 400°C), as the liquid phase has a lower surface energy than a solid with edges and facets.\(^{129}\) Thus, a wide range of nanomaterials are synthesized at temperatures within this range.

High boiling point solvents such as oleylamine (OLA) and 1-octadecene (1-ODE) are commonly used in colloidal approaches for copper based chalcogenides due to their provision of a wide window of possible reaction temperatures, based on their high boiling points of 350°C and 315°C respectively. 1-ODE is a long chain hydrocarbon and is an alkene with molecular formula of \(\text{C}_{18}\text{H}_{36}\). It is classed as a non-coordinating solvent in that it serves only to dissolve the organic precursors and does not bind to the surface of the growing NCs. While OLA is also a long chain hydrocarbon, having a molecular formula of \(\text{C}_{18}\text{H}_{37}\text{N}\), it is the primary amine of the alkene octa-9-decene and is the most commonly used solvent in NC syntheses to date.\(^{167}\) Both OLA and oleic acid are coordinating solvents, containing polar capping groups and long hydrocarbon chains, and serve a dual purpose as both solvent and stabilizer in the reaction medium as they can effectively bind to the surface of the growing nuclei.\(^{168}\) Coordinating solvents can be used as a means to alter the growth
kinetics and resultant morphology, precluding the need for additional surfactants in the reaction medium. Undoubtedly, careful choice of precursors, solvents and surfactants are the key to the success of this approach.
1.6.1.3 Regulation of Precursor Reactivity – HSAB Theory

The key to forming single phase, multi-component NCs is ensuring that the reactivity of the constituent precursors is balanced – otherwise, the formation of two separate material compositions is encountered. While the use of hard-soft-acid-base (HSAB) theory\textsuperscript{169} remained relatively dormant for precursor selection in binary NC systems, this theory gained huge recognition in the synthesis of multi-component NCs due to the stringent demands to carefully select precursors in which their relative reactivity can be precisely tailored.\textsuperscript{111,170-173}

According to this theory, the tendency of an elemental ion to either donate or accept an electron leads to them being categorized as behaving as a base or an acid, respectively.\textsuperscript{169} They are further classed as possessing hard, borderline or soft character based on their atomic/ionic radius, oxidation state, polarizability and electronegativity. Hard acids tend to react faster and form stronger bonds with hard bases and have an affinity for each other which is ionic in nature. Soft acids and soft bases similarly form tight bounds and have an affinity for each other that is mainly covalent in nature. On the other hand, hard-soft or soft-hard combinations have weaker binding/interactions. Hard acids tend to have small atomic/ionic radii and high oxidation states. Figure 12(a) shows the varying degrees of hard and soft acids, plotted on the softness character versus electronegativity, while a list of hard and soft bases is outlined in Figure 12(b).\textsuperscript{174}
Figure 12. (a) Plot of $X$ (related to electronegativity) versus $Y$ (softness) for various ions. (b) Table outlining the various hard and soft Lewis bases.$^{174}$

Some examples of hard acids include $H^+$, group I alkali ions ($Li^+$, $Na^+$, $K^+$), group II alkali earth ions ($Be^{2+}$, $Mg^{2+}$, $Ca^{2+}$), as well as $Al^{3+}$, $Si^{4+}$ and $Sn^{4+}$. On the other hand, soft acids tend have large atomic/ionic radii and low oxidation states, such as $Cu^+$, $Ag^+$, $Au^+$, $Cd^{2+}$, $Hg^{2+}$.$^{169,174}$
In terms of bases, the most well-known hard bases include OH\(^-\), F\(^-\) (Cl\(^-\) is borderline), carboxylate (CH\(_3\)COO\(^-\)) and carbonate (CO\(_3^{2-}\)), while the category of soft bases includes H\(^+\), I\(^-\), thiolate (RS\(^-\)) and phosphine (R\(_3\)P) to name but a few.\(^{174}\)

A classic example of where the HSAB theory proves extremely useful is in the synthesis of ternary CuInS\(_2\), where copper (I) iodide is selected for its propensity to decrease the reactivity of the Cu\(^+\) ion with the thiol (sulfur precursor).\(^{170}\) Copper (I) iodide (CuI) is the most tightly bonded copper precursor, as opposed to copper chloride (CuCl) or copper acetate (CuAc). Specifically, Cu\(^+\) is a soft acid and I\(^-\) is a soft base and so, tight binding is expected to result in its decreased overall precursor reactivity. Thus, the Cu\(^+\) ion reacts slowly with the thiol sulfur source (soft base, with I\(^-\) > thiol),\(^{170}\) suppressing Cu\(_{2-x}\)S growth which permits the formation of ternary CuInS\(_2\) NCs. This leads to the attainment of new crystal phases that are generally not stable in the bulk form, most notably the wurtzite and zinc blende modifications.\(^{106,108,111,117,170-173,175}\)
1.6.1.4  Shape Control of Colloidal Nanocrystals

Colloidal based approaches have been particularly successful in generating high quality NCs with high monodispersity. Exquisite size control can be achieved in this approach by the facile introduction of organic ligands to the reaction medium, which selectively adhere to specific crystal facets and prevent growth in certain directions.\textsuperscript{7,129,158} This mechanism of selective adhesion to particular crystal facets means that the organic-inorganic interface is crucial in determining the resulting NC morphology.\textsuperscript{129} In essence, organic surface ligands are extremely important in exerting control over nucleation, growth and colloidal stability.

Talapin \textit{et al.} compiled a useful table, detailing the design and structural elements of the different types of surface ligands that can be used in the colloidal NC synthesis, as shown in Table 5.\textsuperscript{3}
Table 5. Different types of surface ligands used in colloidal NC synthesis. (Table modified with respect to published version)

Of these, the most common ligands (shown in the top section of Table 5) are based on organic hydrocarbon molecules with anchoring end groups. The head group
(typically, thio-, amino-, carboxylic-) has a high affinity to the NC surface, whilst the long aliphatic tail extends into the solvent, thereby determining the solubility of the NCs and encasing them with a hydrophobic capped surface for dispersion in non-polar solvents. The head groups are typically metal coordinating groups which are electron donating in character to allow coordination to electron-poor metal atoms at the NC surface.\(^3\)

Trioctylphosphine oxide (TOPO), phosphonic acids, alkyl thiols namely 1-dodecanethiol (1-DDT), oleic acid and alkyl amines, most notably oleylamine (OLA) and hexadecylamine (HDA), are examples of typically employed organic surface ligands.\(^{3,129,176}\) These organic surfactants can also form complexes with the reactive monomer species produced upon heating, with the stability and diffusion rate of these complexes dictated by the reaction temperature. For example, increasing the temperature greatly decreases the stability and binding energies of the surfactants to the NC surface but increases the diffusion rate of the complex, thus favouring nucleation and growth.\(^{129}\) However, there is a high temperature cut off for each reaction system, above which leads to uncontrolled growth or significant changes in the NC phase and morphology. Choosing an appropriate temperature is another important parameter in attaining a narrow size distribution.\(^{3,129}\)

For cadmium chalcogenide NCs, alkylphosphonic acids are recognized as essential ingredients to instigate shape control through their ability to bind strongly to particular facets.\(^{6,7,128,160}\) This, in turn, suppresses growth and prevents the addition of monomer onto these surfaces. An extensive study was carried out by Peng et al. on the shape control of wurtzite CdSe NCs by manipulation of the growth kinetics, through either control of the monomer concentration or judicious selection of surfactants present in the reaction.\(^{128}\)
Monomer concentration in the growth solution was revealed as being one of the determining factors in shape control and shape evolution. When the wurtzite crystal system was overdriven by medium to high monomer concentrations, the unique c-axis of this lattice accommodated this huge surge of monomer by undergoing highly anisotropic and fast growth along the c-axis, thereby resulting in nanorods. Conversely, if the monomer concentration was low, a spherical but faceted morphology was formed (as the elongated nanorods were not compatible with the low chemical potential environment). Thus, in a given synthesis, an increasing monomer concentration leads to the following sequence of NCs: dots, rice grains, rods, followed by branched structures (Figure 13).

![Diagram showing growth paths of CdSe NCs](image)

**Figure 13.** Monomer-concentration-dependent growth paths of CdSe NCs.

Extremely high monomer concentrations can yield complex structures, such as tetrapods, as there is a sufficient supply of monomers for each seed to fully grow arms out in four directions off the seed. The branching point of this structure is a tetrahedral core with zinc blende crystal structure, with each arm of the tetrapod nucleating from four of the (111) facets of the zinc blende seed structure. Consequent arm growth proceeds epitaxially in the [001] direction, with each arm
crystallizing in a hexagonal wurtzite phase and terminated with the (000-1) facet. Manna et al. constructed an atomistic model of this structure, with the exploded view of one arm illustrating the identical nature of the (111) facets of zinc blende core and the (000-1) facets of wurtzite arms, as shown in Figure 14.\textsuperscript{177}

![Proposed model of a CdTe tetrapod showing the zinc blende core with four (111) facets, with each (111) facet projecting a wurtzite rod terminated with a (000-1) facet.\textsuperscript{177}](image)

**Figure 14.** Proposed model of a CdTe tetrapod showing the zinc blende core with four (111) facets, with each (111) facet projecting a wurtzite rod terminated with a (000-1) facet.\textsuperscript{177}

This precise condition of switching from nucleation in the cubic phase to arm growth in the wurtzite phase infers that an underlying energy difference exists in the system to facilitate the formation of this unique structure. Through careful control of the reaction temperature, this energy difference can be exploited to first form the core structure during nucleation at high temperature, with subsequent arm growth occurring at a lower temperature, a condition which favours the wurtzite phase.\textsuperscript{107} Their three dimensional construct is particularly interesting from a photovoltaics point of view, in that the branched shape effectively maximizes the number of sites
for exciton separation while also allowing for directed electron pathways.\textsuperscript{19,178} From an electronics perspective, the tetrapods can be considered as standalone single electron transistors, with the core always addressable by the three supporting arms at the substrate.\textsuperscript{179,180} This ability to systematically control the crystal phase and branching can be used to grow a rich variety of nanomaterials, opening up pathways for extension to other material compositions.

Further manipulation of growth kinetics in this system is also possible through careful selection of the surfactants used. Typically, optimum control is achieved using a binary surfactant mixture such as trioctylphospine oxide (TOPO) and hexylphosphonic acid (HPA) which provides a difference in the growth rates in different crystallographic directions. Pure TOPO is generally not suitable for the growth of CdSe nanorods as growth occurs too quickly.\textsuperscript{6} However, technical grade TOPO contains additional chemical entities/impurities which suppress the growth rate by binding strongly with the cadmium ions, with HPA being identified as the principal impurity in technical grade TOPO.\textsuperscript{181} Rather than rely on the fortuitous presence of these impurities, Peng \textit{et al.} set out to intentionally add varying quantities of this impurity to simulate its effect and discovered that as the quantity of HPA is systematically increased, a controllable transformation from nanoparticles to nanorods occurs.\textsuperscript{6} This lead to the revelation that it is the impurities in technical grade TOPO and more specifically, HPA, that causes elongation of the c-axis to facilitate nanorod formation. In subsequent work, the controlled transformation from spherical to complex elongated shapes (arrow and tree shaped NCs) was highlighted, based on an increased HPA concentration in the reaction medium.\textsuperscript{7}

While the binary II-VI cadmium chalcogenides are heavily reliant on the use of phosphonic acid ligands to instigate shape control, alkyl thiol ligands are highly
renowned for their crystal phase and shape control in copper chalcogenide systems. In particular, the use of 1-dodecanethiol (1-DDT) is cited as a prerequisite for stabilization of the wurtzite phase.\textsuperscript{106,108,111,171,172,182} Furthermore, the use of a thiol combination of 1-DDT and its more sterically hindered counterpart tert-dodecylmercaptan (t-DDT) sets up suitable conditions for nanorod formation.\textsuperscript{106,108,111,175} Interestingly, alkyl phosphonic acids strongly bind to the (002) facets in the hexagonal crystal system, particularly in terms of ternary CuInS\textsubscript{2} and quaternary CuInGaS\textsubscript{2}, and prevent elongation along the c-axis by forming nanoplates as opposed to nanorods.\textsuperscript{111,175}
### 1.6.2 Solvothermal / Hydrothermal Method

The solvothermal synthesis method has aroused considerable attention among research groups for its ability to access increased precursor reactivity and solubility under elevated temperatures and pressures.\textsuperscript{183,184} It is regarded as a modification to the conventional organic solvent based synthetic methods, which have been widely employed for the synthesis of monodisperse NCs since the early 1990s.\textsuperscript{53}

Typically, the process is carried out in a specialized sealed reaction vessel called an autoclave. This consists of an inner Teflon liner, an outer stainless steel shell and a stainless steel cap, all of which capable of withstanding the high temperature and pressure environments created in the vessel over prolonged periods of time.\textsuperscript{176,183,185} This setup is illustrated in Figure 15, in which the autoclave is lined with an inert Teflon liner to protect the outer stainless steel shell from corrosive reagents used in the synthesis, as well as avoiding any contamination from the steel shell.\textsuperscript{183}

![Figure 15. Schematic of a Teflon lined stainless steel autoclave typically used for solvo/hydrothermal synthesis.](image)

When the reactants and solvents are heated under high pressure in the autoclave, the reactants experience considerable increases in their solubility and reactivity,
ultimately speeding up the reaction, which cannot normally occur at standard atmospheric pressure conditions.\textsuperscript{166,176} This results in the subsequent crystallization of the dissolved material from the solvent. While traditional solution based routes are limited by the boiling point of the respective solvent, the solvothermal method possesses the added advantage that it can withstand temperatures up to the critical point of the solvent, provided that they are safe for the vessel.\textsuperscript{185} This merit makes the solvothermal method very flexible and attractive in designing high quality inorganic materials in this reaction system.

When water is used as solvent, the process is more appropriately called hydrothermal synthesis and in turn, possesses desirable merits of using a clean, green, low cost and highly abundant solvent. The synthesis under hydrothermal conditions is usually performed below the supercritical temperature and pressure of water, which lies at 374°C and 218 atm, respectively.\textsuperscript{176} At this critical point, water is said to be supercritical in that it can exhibit characteristics of both a liquid and a gas. It boasts exceptionally high viscosities and can easily dissolve reactants that would otherwise exhibit appreciably low solubilities under ambient conditions.\textsuperscript{166,176} Parameters such as water pressure, temperature and reaction time can be tuned to maintain a high nucleation rate and good resultant size distribution.\textsuperscript{166}

Typically, both the solvothermal and hydrothermal processes for preparing copper chalcogenides consist of a precursor, solvent and an organic additive.\textsuperscript{185} The precursors are usually organometallic compounds, metal complexes or inorganic species, which are subjected to the high pressure environments for extensive periods, some up to 40 hours, in the autoclave. The most commonly used solvents are ethylene glycol, ethylenediamine, ethanol and water.\textsuperscript{183} As the physicochemical properties of
the solvent regulate the precursors reactivity, solubility and diffusion behaviour, solvent choice can also affect size and morphology control.$^{184,185}$

If long alkyl chain fatty acids or amines are chosen as organic surfactants in the system, the resultant NCs will usually possess hydrophobic surface properties.$^{185}$ This inhibits their application in the fields of bioimaging or biomedicine. Ethylene glycol alleviates this problem by producing NCs with hydrophilic surface functionalization.$^{183,185}$
1.6.3 Cation Exchange Method

Cation exchange has become a powerful method for the post-synthetic chemical modification of NCs. For example, cadmium chalcogenide NCs can be transformed into their copper/silver analogues through a single step, room temperature process involving the replacement of cations within the crystal lattice (i.e. \( \text{Cd}^{2+} \)) with a different metal ion (i.e. \( \text{Cu}^{+}/\text{Ag}^{+} \)).\(^{186-193}\) In bulk materials, chemical transformation reactions are slow due to the high activation energies required for the insertion and removal of cations.\(^{187,194}\) However, in NCs, the large surface to volume ratio, coupled with lower activation barriers to diffusing ions, permits rapid cation exchange reactions to occur within seconds at room temperature.\(^{186,187}\) This demonstration of dramatically accelerated kinetics in NCs is an attribute unique to the nanoscale.\(^{186}\)

In a seminal paper in 2004, Alivisatos et al. reported the complete and reversible cation exchange (depicted in the scheme in Figure 16 a) of cadmium based, CdSe nanoparticles (Figure 16 b) into silver based, Ag\(_2\)Se nanoparticles (Figure 16 c) under ambient conditions in a short period.\(^{187}\) The reverse cation exchange reaction from Ag\(_2\)Se to CdSe was also demonstrated, with the TEM image of the recovered CdSe shown in Figure 16 (d).
Figure 16. (a) Scheme of the forward and reverse cation exchange reaction between CdSe and Ag$_2$Se. TEM images of (b) Initial CdSe NCs, (c) Ag$_2$Se NCs transformed from the forward cation exchange reaction, (d) recovered CdSe NCs from the reverse cation exchange reaction.

The cation exchange reaction can be driven at room temperature in NCs by using an excess of the incoming cation (e.g. Cu$^+$) and/or preferential solvation of the parent cation (e.g. Cd$^{2+}$)\textsuperscript{187,195}. In the case of CdS to Cu$_2$S, the transformation occurs within one second at room temperature and is apparent by a colour change from yellow to brown due to the different band gap energies.\textsuperscript{189,191} Based on its classification in the HSAB theory, Cd$^{2+}$ is regarded as a hard acid and so, a hard base such as methanol can preferentially solvate Cd$^{2+}$ to allow for the formation of Cu$_2$S from the parent CdS NC.\textsuperscript{186,190} The reverse cation exchange reaction (from Cu$_2$S to CdS) can also be induced through a high excess of Cd$^{2+}$ ions, coupled with the preferential solvation of Cu$^+$ (a soft acid) with tri-butylphosphine (a soft base).\textsuperscript{190} Partial and complete conversion to Cu$_2$S is also possible by adjusting the concentration of substitutional
cations in the solution and thus, can be used to control the relative volume fraction of the two crystals within the binary heterostructure.\textsuperscript{188,189}

An important feature of the cation exchange process is the preservation of NC shape after the exchange, provided the NC is above the critical size threshold.\textsuperscript{187,192} This threshold (4nm in the case of CdSe) defines the size dimensions that above which, the anion sublattice remains intact and allows the preservation of non-equilibrium shaped NCs such as nanorods and tetrapods.\textsuperscript{187} Conversely, below this threshold, the NC becomes unstable and equilibrates in the form of a lower surface energy morphology (spherical).

Cation exchange gives access to the formation of NCs with compositions, morphologies and crystal phases that are not readily accessible by conventional synthetic methods.\textsuperscript{186,193,196,197} More details on copper chalcogenide NCs that have obtained through the cation exchange process are described in section 1.7, specifically copper sulfide (1.7.1.1) and copper telluride (1.7.1.3).
1.7 Overview of Solution Approaches

The past decade has witnessed phenomenal progress in the development of solution based protocols to fabricate a wide range of copper based semiconductor NCs.\textsuperscript{76-81,198-202} For many applications, it is desirable to fabricate materials with controlled size, shape, crystal phase and stoichiometry that are readily dispersible in solvents. Since these desirable characteristics are known to directly influence the material properties, it is of great interest to explore the synthetic routes to achieve control and tunability of these vital parameters. The successful integration and effective use of these materials in functional devices is greatly dependant on how deep our understanding is of their properties, including surface properties and stability.

While section 1.6 gave a general overview on the solution based routes that have been employed to form a range of copper based semiconductor NCs, namely colloidal methods (section 1.6.1), solvothermal/hydrothermal techniques (section 1.6.2) and cation exchange (section 1.6.3), a more detailed description of the individual NC phases and morphologies will be discussed in the following sections.

Binary NCs formed by these solution routes are discussed in section 1.7.1, specifically copper sulfide (1.7.1.1), copper selenide (1.7.1.2) and copper telluride (1.7.1.3). Ternary NCs are discussed in section 1.7.2, focusing on copper indium sulfide (1.7.2.1), copper indium selenide (1.7.2.2), copper sulfur selenide (1.7.2.3), as well as highlighting other ternary material compositions that have been synthesized (1.7.2.4). In the final section (1.7.3), quaternary NCs are discussed, with emphasis on copper indium gallium sulfide (1.7.3.1), copper indium gallium selenide (1.7.3.2), copper zinc tin sulfide (1.7.3.3) and copper zinc tin selenide (1.7.3.4).
1.7.1 Binary Semiconductor Nanocrystals

1.7.1.1. Copper Sulfide

Of the binary copper based semiconductor NCs, copper sulfide (Cu$_{2-x}$S) NCs are undoubtedly the most studied material category, with the significant number of publications explained by the numerous stoichiometric compositions and phases that can be accommodated. Cu$_{2-x}$S NCs can take on many different morphologies, including nanoparticles, nanoplatelets, nanorods, nanowires, nanowhiskers, nanoflowers, nanoflakes and even hollow nanospheres.

Various methods have been used to synthesize copper sulfide NCs. A hydrothermal method gave Cu$_{1.8}$S nanowires and Cu$_{1.94}$S nanotubes from the reaction of CuCl and thiourea over a 40 hour time period. Amine based linking agents such as triethylenediamine (TEDA), tramethylethylenediamine (TMEA) and di-$n$-butylamine (DBA) proved crucial in this particular synthesis, giving rise to the different morphologies such as nanowire-like, nanotube-like and nanovesicle-like aggregates, respectively. Structurally different nanocrystallites of varying stoichiometries (Cu$_9$S$_8$, Cu$_7$S$_4$ and CuS) could also be formed via the solvothermal reaction of [Cu(NH$_3$)$_4$]$^{2+}$ and thiourea in aqueous ammonia at 60°C. Interestingly, the addition of SnCl$_4$ (an oxidant) in this system resulted in the transformation of sheet-like nanocrystallites of Cu$_9$S$_8$ into needle-like fibers of CuS, whilst the addition of KBH$_4$ (a reducing agent) led to the transformation of Cu$_9$S$_8$ into spherical Cu$_7$S$_4$.

Toluene can also be used as a solvent in the solvothermal system in which hexagonal covellite CuS nanoplatelets were formed from the reaction of copper acetate, carbon disulfide and hexadecylamine (HDA). These in turn, self-assembled into
interesting pillar-like, raft-like and stratiform nanostructures due to Van der Waals
interactions and the mechanism of the packing entropy. While the copper sulfide
NCs prepared by hydrothermal and solvothermal approaches do boast high
crystallinity, size control has proven quite difficult, as indicated by the broad size
distributions and rather unusual morphologies.\textsuperscript{224,225}

Korgel \textit{et al.} demonstrated that a solvent is not always required in the synthesis of
NCs through their development of a ‘solventless’ synthesis approach based on the
thermolysis of a copper alkylthiolate molecular precursor.\textsuperscript{13,207} They revealed that the
rare occurrence of interparticle collisions in this reaction environment meant that
particle growth primarily proceeded by monomer addition to the particle surface.
This lead to the formation of highly monodisperse Cu$_2$S nanorods, nanodiscs,
nanoplatelets.\textsuperscript{13} These nanodiscs were observed to self-assemble into impressive,
three-dimensional colloidal crystals (Figure 17 a). SEM images of more polydisperse
nanodiscs samples are shown in Figure 17 (b,c).
Nanowires can also be formed through simply tailoring the viscosity of the copper precursor. Burda et al. incorporated three different chemical methods (sonoelectrochemical, hydrothermal and solventless thermolysis methods) to synthesize Cu$_{2-x}$S NCs, with adjustment of the reduction potential, pH and different precursor pre-treatments, respectively, resulting in compositional variations from CuS to Cu$_{1.97}$S.

The colloidal chemical synthesis procedure has proven to be a powerful route to synthesize highly monodisperse NCs, with controlled size and shape. The most well-known example of the colloidal synthesis and application of Cu$_2$S NCs was reported by Alivisatos et al. in 2008. Highly monodisperse chalcocite nanoparticles (5.4nm)
were formed by the reaction between copper (II) acetylacetonate, diethylidithiocarbamate, DDT and oleic acid.\textsuperscript{93} The thermal decomposition of different copper based organometallic precursors and elemental sulfur or DDT, provided a means to obtain hexagonal nanodiscs of \( \text{CuS} \),\textsuperscript{206,226} \( \text{Cu}_7\text{S}_4 \)\textsuperscript{209} and \( \text{Cu}_2\text{S} \).\textsuperscript{209,210,227} Variation of the Cu to S precursor ratio in the colloidal approach has also been used to phase selectively synthesize \( \text{Cu}_{2-x}\text{S} \) NCs.\textsuperscript{82,206} Alternatively, single source precursors such alkyl xanthates,\textsuperscript{228} mercaptobenzothiazole,\textsuperscript{229} thiobenzoates,\textsuperscript{211} dithiocarbamates\textsuperscript{214,230,231} and dithiolates\textsuperscript{208} can be used in the colloidal approach and have been shown to yield \( \text{CuS} \),\textsuperscript{228,229} \( \text{Cu}_7\text{S}_4 \)\textsuperscript{211} and \( \text{Cu}_2\text{S} \).\textsuperscript{208,210,230} NCs.

Kruszynska \textit{et al.} created the ideal high chemical potential environment for \( \text{Cu}_{1.94}\text{S} \) nanorod formation by exploiting the high reactivity of the starting materials, copper acetate and tert-dodecylmercaptan (t-DDT).\textsuperscript{110} In this report, nanorod length could be reliably tuned from 10 to 100nm through adjustment of the nucleation temperature. Prior to this, \( \text{Cu}_{2-x}\text{S} \) nanorods could only be attained through cation exchange reactions in which a Cu(I) complex was reacted with CdS nanorods, thus forming \( \text{Cu}_{2-x}\text{S} \) nanorods.\textsuperscript{189,190}

Partial conversion of CdS nanorods into binary CdS-Cu\textsubscript{2}S nanorod heterostructures has also been demonstrated by adjusting the concentration of substitutional Cu\textsuperscript{+} cations in solution. Sadtler \textit{et al.} observed that the Cu\textsubscript{2}S portion of the heterostructured nanorods occurred primarily at one end (Figure 18 a) or both ends (Figure 18 b) of the CdS nanorods.\textsuperscript{189} In the colour composite, energy filtered TEM image (Figure 18 b), the different CdS and Cu\textsubscript{2}S portions are clearly evident, where the orange regions correspond to the Cd mapping and the blue regions correspond to the Cu mapping. This indicated that the cation exchange process started at the ends.
of the nanorod and the Cu$_2$S region grew into the nanorods upon further exchange. The epitaxial interface between the two materials is shown in the HRTEM image in Figure 18 (c), with the lower magnification image in Figure 18 (d) showing the CdS-Cu$_2$S interfaces at different angles.

Figure 18. (a) BF-TEM image of the CdS-Cu$_2$S binary nanorods. (b) Colour composite energy-filtered TEM image. (c) HR-TEM image of an individual CdS-Cu$_2$S nanorod. (d) BF-TEM image where the CdS-Cu$_2$S interfaces can be observed at different angles.

Another morphological variation, in the form of tetradecahedrons (Figure 19 a,b), elongated tetradecahedrons (Figure 19 c,d) and dodecahedrons (Figure 19 e,f) was obtained at relatively high precursor concentrations by means of an oriented attachment and growth mechanism.$^{232}$ Copper sulfide particles have also been employed as seeds or catalysts to form differently structured morphologies such as
matchstick-like \( \text{Cu}_2\text{S-In}_2\text{S}_5 \) heterostructured nanorods and teardrop-like quasi-core/shell \( \text{Cu}_2\text{S-In}_2\text{S}_5 \) NCs.\(^{233}\)

![Figure 19](image)

**Figure 19.** \( \text{Cu}_{2-x} \text{S} \) NCs of varying morphologies, specifically small tetradecahedrons (a-b), elongated tetradecahedrons (c-d) and dodecahedrons (e-f), characterized by TEM (left column) and SEM (right column).\(^{232}\)

The presence of different metal precursors has been observed to have significant effects on the reaction environment and gave rise to rather surprising observations. For example, the addition of varying amounts of an iron organometallic precursor to the reaction provided a means to phase selectively synthesize copper sulfide nanoparticles such as \( \text{Cu}_{1.75} \text{S} \) and the monoclinic and tetragonal modifications of \( \text{Cu}_2\text{S} \).\(^{234}\) This report brought to light the formation of the little studied, tetragonal
chalcocite phase for the first time. This was explained by the fact that the Fe$^{2+}$ ions likely block the pathways by which Cu$^{+}$ ions would diffuse out, allowing the stabilization of the metastable monoclinic and tetragonal forms. In a separate report, the presence of a tin organometallic precursor was shown to induce the formation and self assembly of hexagonal Cu$_2$S nanoplates as opposed to Cu$_2$S nanospheres.$^{235}$

Structural modifications can also be made to Cu$_2$S NCs post-synthesis, in which Cu$_2$S NCs can undergo oxidation in the presence of iodine (I$_2$) to shift the equilibrium towards CuS (covellite phase).$^{138}$ Alternatively, CuS NCs can be reduced from Cu$_{1.1}$S up to Cu$_2$S in the presence of a Cu(I) complex, specifically tetrakis (acetonitrile) copper(I) hexafluorophosphate, with each composition characterized by a different optical response.$^{236}$ In this report, Cu$_{1.1}$S showed strong localized surface plasmon resonance (LSPR) in comparison to Cu$_2$S which displayed no LSPR. Oxidation of a colloidal solution of NCs can also occur if the solution is kept in the same vial for few days, with an in-situ phase transformation from Cu$_{1.8}$S to CuS occurring as a result of an OLA-assisted oxidation process.$^{237}$
1.7.1.2 Copper Selenide

During the past few years, several methods have been applied to prepare copper selenide (Cu$_{2-x}$Se) NCs, including solvothermal$^{238-242}$, sonochemical$^{243,244}$ and microwave-assisted heating.$^{245,246}$ However, the as-prepared NCs generally suffered from the formation of large and uncontrollable aggregates. Optimization of reaction conditions in the colloidal hot injection approach resulted in substantial improvements in the NC quality. Highly crystalline Cu$_2$Se NCs were attained through the injection of Se powder (in 1-ODE) into a mixture of CuCl, OLA and 1-ODE.$^{139}$ These NCs in turn exhibited high conductivity and absorption in the NIR region. 2-D NCs such as nanoplates and thin nanosheets$^{247}$ have also been obtained by simply reducing the quantity of the copper precursor in the reaction flask.

Exquisite size and shape control of Cu$_{2-x}$Se NCs (with hexagonal, bipyramidal and triangular morphologies) has also been demonstrated through the reaction of copper stearate, oleylamine and a selenium-octadecene (Se-ODE) precursor.$^{248,249}$ This resulted in the formation of nanodiscs (Figure 20 a, e), self-assembled nanodisc arrays (Figure 20 b, f), octahedron-shaped NCs (Figure 20 c, g) and triangular, pyramid-like NC arrays (Figure 20 d, h).
Figure 20. TEM and HRTEM images of Cu$_{2-x}$Se NCs with different morphologies, varying from nanodiscs (a,e), columnar self-assembled arrays of nanodiscs oriented perpendicular to the TEM grid (b,f), octahedron-shaped NCs (c,g) and triangular, pyramid-like arrays of Cu$_{2-x}$Se NCs (d,h).

Tunability of the reactivity of the selenium powder precursor can be accomplished through careful selection of the dissolution medium. OLA coordination with selenium powder resulted in low precursor reactivity, whereas a mixed solvent system (of OLA and paraffin) lead to a weakened coordination ability and caused an increase in the selenium reactivity. Choi and co-workers moved away from the traditional selenium powder and investigated imidazoline-2-selenone as a new selenium source. This precursor proved particularly successful in the preparation of high quality Cu$_{2-x}$Se nanodiscs. Selenourea has also been employed as an alternative selenium source and its use, in conjunction with CuCl and OLA, lead to the formation of tightly controlled 16 nm sized Cu$_{2-x}$Se NCs. The NCs in this report were subsequently photoexcited in the presence of human colorectal cancer cells (HCT-116) and displayed remarkable viability for photothermal therapy applications,
with local temperature increases of 22°C and significant cell death being observed after just 5 minutes of laser irradiation.

Surface oxidation, similar to Cu₂S, has also been exploited to controllably tune the electronic properties of the material and has been shown to lead to a solid state conversion of Cu₂Se to the superionic conductor Cu₁.₈Se.\textsuperscript{252} This conversion directly resulted in a change of the current-voltage response from semiconducting to ohmic and yielded a 3,000 fold increase in conductivity, which is particularly appealing for optoelectronic devices. Stepwise addition of a Ce(IV) complex to as-synthesized Cu₂.₈Se NCs has also been shown to induce oxidation forming Cu₁.₆Se NCs.\textsuperscript{253} Interestingly, the NCs could be incrementally restored back to Cu₂Se by addition of a Cu(I) complex. Nanocubes are another interesting geometry that have high potential in optoelectronic and thermoelectric devices due to their maximisation of NC packing. Li \textit{et al.} demonstrated that foreign metal ions could be used to control the morphology of Cu₃Se₂ NCs, changing from spherical NCs (Figure 21 a) to nanocubes (Figure 21 b) in the presence of foreign aluminium ions.\textsuperscript{254}
Figure 21. Morphological control of Cu$_{2-x}$Se NCs via introduction of foreign metal ions. (a) TEM image of quasi-spherical nanoparticles in the absence of aluminium ions (b) TEM image of Cu$_3$Se$_2$ nanocubes formed in the presence of aluminium ions.$^{254}$

While the aluminium (Al$^{3+}$) ions did not incorporate into the Cu$_3$Se$_2$ crystal structure, their presence in the reaction environment promoted crystal growth in a specific direction, instead of stabilizing a particular facet. The authors hypothesized that the Al$^{3+}$ ions blocked the binding of amine ligand to the \{111\} facets, which caused the \{111\} facets to disappear and form nanocubes with \{100\} and \{001\} facets.$^{254}$
1.7.1.3 Copper Telluride

In contrast to their sulfide and selenide counterparts, the synthesis of copper telluride (Cu$_{2-x}$Te) has remained fairly unexplored due to improper control over the NC size and shape attained by various solution based approaches.$^{141,246,255-257}$ Recently, Cabot et al. reported a colloidal hot injection procedure to prepare highly monodisperse copper telluride nanocubes, nanoplates and nanorods.$^{140}$ Their synthesis was based on the reaction of CuCl, trioctylphosphine telluride (TOPTe) and OLA, in the presence of a lithium salt (lithium bis(trimethylsilyl)amide). In this report, the lithium salt was found to be critical to produce monodisperse Cu$_{1.25}$Te NCs, with large irregular sized rectangular plates forming when the lithium salt was not used in the reaction. In two separate reports, spherical Cu$_{2-x}$Te NCs$^{258}$ and uniform Cu$_2$Te nanodiscs$^{259}$ were formed by the hot injection of TOPTe into a mixture of copper(II) acetylacetonate, DDT and oleic acid. The spherical NCs were shown to display an intense localized surface plasmon (LSP) band, in analogy to Cu$_{2-x}$S and Cu$_{2-x}$Se NCs.

Cation exchange has become a particularly powerful technique for generating binary copper chalcogenides from their cadmium analogues by replacing the cations in the NC lattice with Cu$^+$ metal ions. Importantly, the rigidity of the anion sublattice allows for complete preservation of the initial shape during cation exchange. Kriegel et al. took advantage of this shape control in cation exchange reactions to gain access to Cu$_{2-x}$Te NCs via a Cd$^{2+}$/Cu$^+$ exchange reaction, starting from CdTe spheres (Figure 22 a, inset), nanorods (Figure 22 b, inset) and tetrapods (Figure 22 c, inset).$^{260}$ Well-defined Cu$_{2-x}$Te spheres (Figure 22 d, inset), nanorods (Figure 22 e, inset) and tetrapods (Figure 22 f, inset) were obtained, with clear changes in the excitonic features observed as a result of the exchange process. The features characterizing the extinction spectra of CdTe (Figure 22 a,b,c) disappeared
immediately after the exchange was complete and were replaced with a broad spectrum, showing steep extinction in the blue and a pronounced plasmon band in the NIR region (as depicted in Figure 22 d, e, f). The evolution of the plasmon band is particularly characteristic of free carriers in copper-deficient binary chalcogenides.\textsuperscript{36,76}

**Figure 22.** Cation exchange of CdTe to form a variety of Cu$_{2-x}$Te NC morphologies. (a-c) Extinction spectra of CdTe, with inset TEM images of (a) spheres, (b) nanorods and (c) tetrapods. (d-f) Extinction spectra of the cation exchanged Cu$_{2-x}$Te NCs, with inset TEM images of (d) spheres, (e) nanorods and (f) tetrapods.\textsuperscript{260}

Hollow Cu$_{2-x}$Te NCs have also been observed and were formed by the nanoscale Kirkendall effect, in which Cu nanoparticles were formed first followed by the injection of the TOPTe solution.\textsuperscript{261,262}
1.7.2 Ternary Semiconductor Nanocrystals

Of the ternary copper based semiconductor NCs, copper indium disulfide (CuInS$_2$) NCs are the most studied material composition, followed by copper indium diselenide (CuInSe$_2$), with approaches to copper indium telluride (CuInTe$_2$) NCs largely lagging behind. The high cost of indium has further enticed the incorporation of tin to replace indium, thus forming copper tin sulfide (Cu$_2$SnS$_3$) and copper tin selenide (Cu$_2$SnSe$_3$). Complete replacement of indium with gallium is another interesting route that can be undertaken to form copper gallium sulfide (CuGaS$_2$) and copper gallium selenide (CuGaSe$_2$). In particular, the wide band gap of 2.4eV for CuGaS$_2$ has sparked research interest for its use in the production of green light-emitting diodes. Each material combination undoubtedly represents a great synthetic challenge and the key to their formation is related to fine tuning the precursor reactivity to ensure a highly crystalline, single phase material is formed. All of the aforementioned material compositions will be discussed in the following subsections (1.7.2.1 – 1.7.2.4), with emphasis placed on the well studied CuInS$_2$ and CuInSe$_2$ compositions.
1.7.2.1 Copper Indium Sulfide (CIS)

In terms of particle morphology, quasi-spherical CIS nanoparticles are the most common morphology that can be found across the various solution routes from hydrothermal and solvothermal techniques,\textsuperscript{263-266} to the thermal decomposition of molecular single source precursors\textsuperscript{267-270} and organometallic precursors\textsuperscript{67,102,271-274} in colloidal based protocols. CIS nanoparticles generally crystallize in the thermodynamically stable chalcopyrite phase, where the Cu and In atoms are ordered in the cation sublattice sites. Quantum confined CIS nanoparticles (ranging from 3-8 nm) could be formed by reacting copper (I) iodide (or copper (I) acetate) and indium (III) acetate, with 1-DDT and 1-ODE, in the colloidal approach.\textsuperscript{67,170,266,272-279} Solvothermal and hydrothermal reactions report the formation of much bigger NCs, such as nanorods,\textsuperscript{280,281} wires,\textsuperscript{240} cubes\textsuperscript{282} and hollow spheres.\textsuperscript{283,284}

To improve the fluorescence quantum yield (QY) and photostability, the resulting core NCs can be overcoated with a ZnS shell. Huge beneficial effects on the photoluminescence properties of the cores were noted by adapting this procedure, giving rise to substantial increases in the PL QY from 20% up to 60%.\textsuperscript{67,273,274,277-279,285,286} Importantly, these CIS/ZnS NCs represented the first non-toxic (cadmium-free) QDs to be successfully applied for in-vivo imaging.\textsuperscript{67,279,285} Figure 23 shows details of one such example, with TEM images of the core CIS NCs and the corresponding CIS/ZnS core shell NCs shown in Figure 23 (a) and Figure 23 (b,c), respectively. By comparing these CIS/ZnS core/shell NCs under normal light (Figure 23 d) and UV-light (Figure 23 e), their highly luminescent character is apparent under UV illumination. Their application in-vivo imaging is shown in Figure 23 (f), with fluorescence images being captured at desired time intervals to show the temporal evolution of the biodistribution of CIS/ZnS NCs in a mouse.
Figure 23. Cadmium-free core/shell semiconductor NCs applied for in-vivo imaging. TEM images of (a) CIS core NCs and (b,c) corresponding CIS/ZnS at different magnifications. (d) Photograph of different sized CIS/ZnS NCs under normal light and (e) the corresponding image under UV light showing their highly luminescent character. (f) Fluorescence images showing the temporal evolution of the biodistribution of the CIS/ZnS NCs injected intravenously into the tail of a healthy mouse (Figure is modified with respect to the published by merging two separate figures to summarize the findings)\(^{67}\).

To date, core-shell reactions have only been performed on spherical nanoparticles crystallizing in the chalcopyrite phase\(^{67,279,285}\) due to the small lattice mismatch (2-3\%) between the crystal structure of CIS and ZnS\(^{67}\). CIS-ZnS alloyed NCs have also been intensively investigated in recent years due to the fact that the alloyed combination of CIS (Eg = 1.5 eV) with ZnS (Eg = 3.7 eV) creates a family of NCs, with band gaps covering almost the entire visible spectrum\(^{111,287-290}\).
While spherical CIS nanoparticles generally tend to crystallize in the chalcopyrite phase, they can also be formed in the zinc blende phase as reported by Pan et al. in 2008.\textsuperscript{182} In this report, the vital role of capping agents in precisely controlling the crystal structure, from zinc blende to wurtzite, was discovered. Their synthetic strategy deviated from using the common monovalent copper precursors (e.g. copper (I) iodide or copper(I) acetate) to using, for the first time, copper (II) diethyl dithiocarbamate and indium (III) diethyl dithiocarbamate precursors in 1-ODE, with OLA as activation agent. An interesting observation was that the introduction of oleic acid (OA) as a capping agent to the reaction medium enabled nanoparticle formation in the zinc blende phase, while DDT induced the formation of the kinetically stable wurtzite phase. This can be explained through the binding strength between the ligands and metal cations, with weaker binding ligands like OA or trioctyphosphite (TOOP) causing a fast nucleation event, rapidly forming nuclei and consuming large amounts of metallic monomer.\textsuperscript{143,182} This has a knock on effect of suppressing the crystal growth and promoting crystallization in the thermodynamically stable chalcopyrite or zinc blende modification.

While the literature is abound with reports of CIS nanoparticles in the chalcopyrite phase, there have been only a few observations of particles (less than 10nm) in the zinc blende phase.\textsuperscript{143,263,273,285,289} The structural similarity of the chalcopyrite and zinc blende phases, as well as peak broadening due to small crystallite size, makes interpretation of the zinc blende phase difficult in these NCs.\textsuperscript{77}

While weaker binding ligands (such as OA and TOOP) were found to promote the formation of the thermodynamically stable chalcopyrite phase, ligands that bind strongly to metal cations, like DDT and amines such as HDA or OLA, have been used to induce the formation of the kinetically stable wurtzite phase.\textsuperscript{143,149,182,291,292}
These ligands result in the formation of a much smaller amount of nuclei during the nucleation period and leave behind a large amount of monomer during the growth period, thus providing conditions suitable to capture the metastable, wurtzite phase.\textsuperscript{143,182,291}

Reaction temperature has also been shown to have a strong influence on the crystallographic structure of the NCs. Experiments using a single source molecular precursor demonstrated that at both lower temperatures (150-250°C) and higher TOPO concentrations, the wurtzite phase can be stabilized, whereas higher temperatures (350°C) promoted the formation of the zinc blende phase.\textsuperscript{293} This phase transformation was also accompanied with a change in morphology, changing from 2D nanoplates (wurtzite) to tiny 0D quasi-spherical particles (zinc blende). Particles can also be produced in the wurtzite phase by selecting di-tert-butyl disulfide as sulfur source, with the relatively slow release of sulfur being attributed to the stabilization of the wurtzite phase.\textsuperscript{291}

Elongated NCs such as nanorods, which are thermodynamically less stable, are accessible when kinetic control dominates in the reaction environment (i.e. low temperature and high monomer flux). The first report of CIS nanorod formation deserves special mention for it was in this report that it was uncovered that CIS nanorod formation could only proceed through a copper sulfide intermediate.\textsuperscript{123} Similar observations have been reported in subsequent papers.\textsuperscript{111,171} The authors in the first report observed that Cu\textsubscript{2}S (chalcocite) nanodiscs were initially formed in the reaction (Figure 24 a), followed by epitaxial overgrowth of CIS onto one face of the nanodiscs, thus resulting in a biphasic Cu\textsubscript{2}S- CIS heterostructure (Figure 24 b,c).\textsuperscript{123} With increased growth time, the biphasic heterostructure finally gets completely converted in a monophasic CIS nanorod (Figure 24 d). The observed epitaxial
overgrowth and phase transformation is facile for two principal reasons. Firstly, the phase transformation from copper sulfide to CIS involves minimal lattice distortion, as hexagonal Cu$_2$S and wurtzite CIS share the same anion lattice and have a nearly identical packing of the S sublattices. Secondly, the increased growth temperature of 250°C plays a key role by equipping the Cu (I) ions with a high mobility to speed up the exchange with In (III) ions and inducing a superionic conducting state to Cu$_2$S at this temperature.\textsuperscript{294}

![Figure 24](image.png)

**Figure 24.** Schematic of the proposed growth mechanism for CIS nanorods depicted by (a) initial formation of Cu$_2$S nanodiscs, (b) epitaxial overgrowth of CIS onto one face of the Cu$_2$S nanodiscs leading to biphasic nanorods, (c) continued growth of CIS occurs simultaneously with conversion of Cu$_2$S into CIS and (d) monophasic CIS upon reaction completion.\textsuperscript{123}

Higher degrees of anisotropic shape control were later obtained, which lead to the formation of the conventional nanorod morphology, as well as deviations such as P-shaped, bullet-like, droplet-like and spindle-like nanorods.\textsuperscript{111,171} Wurtzite
nanoribbons, with exceptionally long lengths (2-3 um), have also been synthesized by using Cu$_{1.75}$S nanoparticles as catalysts for their growth.\textsuperscript{295} Furthermore, CIS heterostructures, composed of segments of hexagonal Cu$_2$S and tetragonal In$_2$S$_3$, have been observed and form spectacular acorn, bottle and larva shapes with an increase in the reaction temperature and growth time.\textsuperscript{296}
1.7.2.2 Copper Indium Selenide (CISe)

Metal chloride precursors have proven to be highly suitable for the formation of this material composition. The earliest example of CISe nanoparticles was reported in 1999, in which CISe quantum dots were synthesized for the first time through a hot injection technique using CuCl, InCl₃, TOPO and trioctylphosphine- selenide (TOPSe). The TOPO capped CISe quantum dots had a cubic structure and were 4.5 nm in diameter after a lengthy 24-hour reaction at 250°C. Similar sized quantum dots with tetragonal structure were later synthesized (in a significantly shorter growth time of 1 hour) using a mixed solvent system of 1-ODE and DDT.

Stoichiometric control has also been achieved for CISe quantum dots, through a hot injection approach involving the reaction of TOP and bis(trimethylsilyl) selenide to yield indium rich CuIn₅Se₈, CuIn₂.₃Se₄ and CuIn₁.₅Se₃ compositions or TOP and selenium powder to produce the stoichiometric CuInSe₂ composition.

Selenium powder is the most widely used selenium source across the solution based routes, capable of producing a range of morphologies from nanorings and nanowires in colloidal based approaches to atypical nanodandelions, nanowhiskers and ultralong nanorods in solvothermal approaches. Other morphologies, namely pyramidal shaped CISe NCs and quasi-spherical NCs, were formed by switching to selenourea as selenium precursor.

A separate study found that the order of addition of the selenium powder precursor played a crucial role in the resultant crystal phase. Chalcopyrite phase CISe NCs (tetragonal structure) were apparent when selenium was added at 130°C, in contrast to the sphalerite phase (cubic structure) which formed when selenium was added at 285°C. The wurtzite (hexagonal) modification was only attainable if TOP was
employed as a secondary ligand in the synthesis.\textsuperscript{104} Interestingly, the wurtzite modification formed a unique nanoring structure in this synthesis, exhibiting an inner and outer diameter of 5 nm and 25 nm respectively, making it the first of its kind in copper based ternary systems. Following this report, two groups later reported the formation of wurtzite structured nanoplates by selecting diphenyl diselenide, instead of selenium powder, as selenium source.\textsuperscript{120,310} TEM of highly monodisperse CISe nanoplates are shown in Figure 25 (a,b), complete with a HRTEM image of an individual nanoplate (Figure 25 c). The corresponding SAED pattern is depicted in Figure 25 (d), where the (100) and (110) planes appear brighter as a result of the nanoplate morphology.
In terms of the evolution pathway of CISe, it was observed that CISe growth proceeded through the initial formation of CuSe\textsuperscript{118,120}, analogous to Cu\textsubscript{2}S formation in CIS. Hillhouse and co-workers performed a calculation of the Gibbs free energy of the reaction (of metal chlorides with elemental selenium) and revealed that the formation of CISe is highly thermodynamically unfavourable when the individual metal precursors are used as the reactants. This provides further conclusive proof that CISe formation can only proceed through intermediate stages such as the formation of CuSe and InSe.\textsuperscript{311}

**Figure 25.** TEM images of as-synthesized CISe NCs (a,b), complete with HRTEM of an individual NC (c) and SAED pattern (d).\textsuperscript{120}
1.7.2.3 Copper Sulfur Selenide (CuSSe)

NCs with two chalcogens in the anion sublattice have also been synthesized, with control over the anion precursor ratio further permitting band gap engineering.\(^{203,312-317}\) Hexagonal and cubic modifications of \(\text{Cu}_{2-x}S_y\text{Se}_{1-y}\) alloyed NCs have been reported through judicious solvent selection\(^{312}\) and through injection or non-injection of the S/Se mixture.\(^{313}\) Swihart \textit{et al.} followed on from these reports by presenting a general method for broad tuning of the localized surface plasmon resonance (LSPR) by varying S/Se ratio and oleic acid ligand concentration.\(^{316}\) This method demonstrated LSPR absorbance peak tunability from 975nm up to 1650nm. More recently, a DDT and oleic acid solvent combination has been employed to synthesize \(\text{Cu}_{2-x}\text{S}\) (Figure 26 a), alloyed \(\text{Cu}_{2-x}S_y\text{Se}_{1-y}\) (Figure 26 b) and the tellurium derivative \(\text{Cu}_{2-x}S_y\text{Te}_{1-y}\) (Figure 26 c), with the synergetic effect of DDT and oleic acid activating the chalcogen and forming highly monodisperse NCs.\(^{203}\)
Figure 26. TEM images of (a) Cu$_{2-x}$S, (b) alloyed Cu$_{2-x}$S$_y$Se$_{1-y}$ and (c) Cu$_{2-x}$S$_y$Te$_{1-y}$, with inset SAED patterns. The corresponding HRTEM images of each material composition are also shown.\textsuperscript{203}
1.7.2.4 Other Ternary Material Compositions

Several other ternary copper chalcogenide combinations have also been investigated, including CuGaS$_2$, CuGaSe$_2$, Cu$_2$SnS$_3$, and Cu$_2$SnSe$_3$.

CuGaS$_2$ nanostructures are particularly appealing for visible light induced photocatalysis and the production of light-emitting diodes in the green light region due to their wide band gap of 2.4 eV.\(^{318}\) Hydrothermal and solvothermal techniques have been reported for CuGaS$_2$ and gave rise to the formation of aggregated spherical,\(^{265}\) snowflake crystallites\(^{319}\) and exceptionally large spheres.\(^{320}\) Much smaller NCs have been attained through colloidal approaches, with the thermal decomposition of single source precursors forming interesting polytypic nanoplates possessing hexagonal and cubic domains.\(^{321}\) Thermolysis of organometallic precursors has also been shown to form morphologies ranging from nanoparticles and nanowires\(^{322}\) to tadpole-like shaped NCs.\(^{106,318,323}\)

On the other hand, CuGaSe$_2$ is an effective light absorbing material due to its suitable band gap of 1.67 eV.\(^{102,118}\) Sargent and co-workers were the first to report the formation of CuGaSe$_2$ nanoparticles and trigonal nanoplates by adapting the colloidal based approach,\(^{118}\) followed closely by Panthani \emph{et al.}\(^{102}\) However, in the latter case, the CuGaSe$_2$ nanoparticles proved difficult to disperse in non-polar solvents, with more effective capping strategies to Ga-rich NCs being desired. Methods to synthesize quantum dots\(^{324}\) and nanosheets\(^{325}\) of CuGaSe$_2$ have also been reported.

Replacement of gallium with tin has also been investigated, providing a valuable method to engineer the band gap and form I-IV-VI semiconductor nanomaterials. Significant changes in the material band gap are noted with the direct replacement of
gallium with tin, shifting from 2.4 eV for CuGaS$_2^{106,318}$ down to 0.93 eV for Cu$_2$SnS$_3^{326,327}$ and from 1.67 eV for CuGaSe$_2^{102,118}$ down to 0.8-1.1 eV for Cu$_2$SnSe$_3^{109,117}$ Various methods to synthesize Cu$_2$SnS$_3$ have been reported, with solvothermal routes yielding NCs with the tetragonal chalcopyrite structure$^{326,328,329}$ and colloidal routes allowing stabilization of the zinc blende and wurtzite structures.$^{327,330,331}$

Since crystal symmetry is known to influence the electronic material properties, the phase selective synthesis of Cu$_2$SnSe$_3$ NCs (with cubic and hexagonal crystal structures) has been described in a number of recent reports.$^{109,114,117,154,332-334}$ Of these, a particularly interesting morphology was reported by Wang et al. in which tetrapod shaped NCs were obtained in a ternary copper chalcogenide based system for the first time, as shown in Figure 27.$^{109}$ The authors carefully designed the synthetic protocol, with preferential nucleation of the NCs in the cubic phase occurring at the higher temperature. The subsequent temperature ramp down facilitated the low energy transition to allow growth of the metastable wurtzite arms. TEM characterization of the tetrapods was performed in both BF-TEM mode (Figure 27 a) and DF-STEM mode (Figure 27 b). Furthermore, the SAED pattern revealed planes corresponding to both cubic and wurtzite phases in the tetrapods, as shown in the inset of Figure 27 (c). By imaging at an angular offset, the highly crystalline nature of the protruding fourth arm was also observed (Figure 27 d). Linear heterostructures of Cu$_2$SnSe$_3$ have also been reported, in which a wurtzite core was observed to nucleate first, followed by termination at either end in the cubic phase.$^{154}$
Figure 27. TEM characterisation of tetrapod shaped Cu₂SnSe₃ NCs shown in (a) bright field TEM mode, (b) Dark field STEM mode, (c) collection of tetrapods revealing average arm diameters of 28nm and lengths of 17.5nm, with inset SAED pattern indexed to both cubic and wurtzite phase, (d) TEM image of a tetrapod at angular offset showing the highly crystalline nature of one of the protruding arms.¹⁰⁹
1.7.3 Quaternary Semiconductor Nanocrystals

Cu$_2$ZnSnS$_4$ (CZTS), CuInGaS$_2$ (CIGS) and their selenium analogues, Cu$_2$ZnSnSe$_4$ (CZTSe) and CuInGaSe$_2$ (CIGSe), are undoubtedly the most widely studied quaternary semiconductor materials. In quaternary NCs, direct control of the ratio of metal precursors (In/Ga or Zn/Sn) permits band gap engineering through compositional control. Of these, CZTS and CZTSe are particularly attractive and are regarded as viable alternatives for replacing the currently employed silicon, CIGS and CdTe absorber layer materials due to their earth abundant, non-toxic and environmentally friendly character. The following subsections will investigate CIGS, CIGSe, CZTS and CZTSe NCs, focusing on the morphology and crystal phase of the resultant NC, as well as highlighting important literature reports and their revelations for the aforementioned material compositions.
1.7.3.1 Copper Indium Gallium Sulfide (CIGS)

CIGS NCs of varying morphologies have been principally reported through the colloidal based approach. Guo and co-workers were the first to report the formation of CIGS NCs, in which they demonstrated the capability to expand the synthesis of ternary NCs and arrive at the quaternary form (by replacing a fraction of the indium precursor with the corresponding gallium precursor). The approach was based on the thermal decomposition of metal chloride precursors in OLA, followed by injection of the sulfur precursor (S/OLA), which yielded spherical 15nm sized nanoparticles. CIGS NCs with precisely engineered band gaps have also been synthesized in a toluene-thermal approach. In this report, the increasing indium content in the NCs resulted in visibly distinct differences in the colour of NC ink (green to orange, red and black), with UV measurements quantitatively defining shifts in the optical band gap from 2.4 eV to 1.43 eV.

Quantum confined CIGS NCs with chalcopyrite structure have also been synthesized by the microwave decomposition of molecular single source precursors in the presence of ethanedithiol and benzylacetate. In this particular synthesis, microwave assisted growth was favoured over the traditional thermolysis approach as the greater homogeneity in the reaction temperature provided suitable conditions to form size and stoichiometry controlled CIGS NCs.

A scaled-up, CIGS NC hot injection procedure has also been trialled, in which gram scale quantities of CIGS NCs were obtained. Importantly, phase, composition and particle size control were maintained in the up-scaled method, as shown in Figure 28 (a). HRTEM and FFT analysis of an individual nanocrystal (Figure 28b) confirmed
their crystallization in the chalcopyrite phase, with EDX elemental maps (Figure 28c) detecting the presence of Cu, In, Ga and S in the as-synthesized nanocrystals.

**Figure 28.** CIGS NCs prepared via an up-scaled version of the synthesis. (a) TEM image of CIGS NCs, with the histogram providing quantitative information regarding the size distribution. (b) HRTEM image of an individual NC and corresponding FFT indexed to the chalcopyrite phase. (c) STEM-HAADF image of a region of CIGS NCs (i) and the corresponding S (II), Cu (III), Ga (IV) and In (V) EDS elemental maps. 

Wurtzite structured CIGS NCs, exhibiting narrow size distributions and controlled morphologies, were first observed by Wang *et al.* in a carefully designed hot injection protocol. The synthesis involved the thermolysis of metal acetylacetonate precursors (of Cu, In and Ga) in TOPO and 1-ODE, with the injection of a thiol mixture into the reaction flask. This report represented the first observation of the
nanorod geometry for the CIGS composition, with the use of a thiol combination (1-DDT and t-DDT) identified as a prerequisite for nanorod formation. CIS nanorods (Figure 29 a, d), CIGS nanorods (Figure 29 b, e) and CGS tadpole shaped NCs (Figure 29 c, f) were formed in this approach by solely changing the In/Ga ratio in the reaction.  

Figure 29. TEM images of (a) bullet-like CuInS$_2$ NCs, (b) rod-like CuIn$_{0.75}$Ga$_{0.25}$S$_2$ NCs and (c) tadpole-like CuGaS$_2$ NCs, with the corresponding HRTEM images of each composition identified in (d), (e) and (f), respectively.

Following this, a thorough investigation on the colloidal growth of CIGS NCs was reported, as detailed in Chapter 3. Through manipulation of the ligand chemistry, a series of synthetic routes were devised to form a variety of morphologies of the CuIn$_{0.75}$Ga$_{0.25}$S$_2$ composition, ranging from nanorods and nanoplates to atypical L-, hatchet- and tadpole-shaped NCs.
1.7.3.2 Copper Indium Gallium Selenide (CIGSe)

In 2008, two separate groups reported the synthesis of CIGSe NCs in a very close timeframe.\textsuperscript{102,118} In the first literature report, metal acetylacetonate precursors (of Cu, In and Ga) were dissolved initially in OLA before being injected into a hot solution of selenium powder in OLA. This resulted in the formation of triangular shaped CIGSe NCs in the chalcopyrite phase.\textsuperscript{118} The second report yielded a spherical CIGSe morphology by adapting a non-injection protocol in which metal chlorides, selenium powder and OLA were simply heated up to the desired growth temperature.\textsuperscript{102} Single phase CIGSe NCs have also been reported in two separate solution routes but their XRD peaks showed split reflections, which is indicative of the co-existence of a mixture of phases.\textsuperscript{122,338}

Ahmadi and co-workers were particularly interested in understanding how CIGSe NCs evolve in the reaction to control the material stoichiometry and conducted a systematic study on the growth and formation pathway of CIGSe NCs.\textsuperscript{173} In the initial stages after injection of the selenium precursor, crystalline CuSe, Se nanorods, CuGaSe\textsubscript{2} and amorphous nanoparticles of In\textsubscript{2}Se\textsubscript{3} were observed. Complete consumption of the CuSe nanoparticles, along with the dissolution of the Se nanorods and In\textsubscript{2}Se\textsubscript{3} in the second stage, lead to the final evolution of 20nm sized CIGSe NCs with a nearly spherical shape. This progression was monitored by taking aliquots at specified temperatures during the reaction, as illustrated in Figure 30. At 130°C, large CuSe plates were formed (Figure 30 a). Increased heating to 160°C resulted in the evolution of CIGSe NCs and dissolution of the large CuSe plates (Figure 30 b), with further heating to 200° promoting the full dissolution of CuSe (Figure 30 c). At 230°C, spherical nanoparticles of CIGSe were observed (Figure 30 d). The sequential growth process is shown schematically in Figure 30 (e).
Figure 30. TEM images illustrating the overall evolution pathway, in which dissolution of CuSe nanoparticles occurs initially, followed by growth of CIGSe inside these particles at (a) 130°C, (b) 160°C, (c) 200°C, (d) 230°C. (e) Proposed schematic for the growth mechanism of CIGSe.\textsuperscript{173}

As an alternative to the existing CIGSe NC procedures, Jiang \textit{et al.} reported a new ligand exchange process, in which metal chalcogenide complexes (MCCs) served as reagents upon thermal annealing and surface-stabilizing ligands.\textsuperscript{339} By starting from Cu\textsubscript{2}Se NCs and performing a ligand exchange of the initial OLA-capped Cu\textsubscript{2}Se NCs (with In\textsubscript{2}Se\textsuperscript{4-} and gallium selenide MCCs), single phase CIGSe NCs with exceptional colloidal stability were obtained.
1.7.3.3 Copper Zinc Tin Sulfide (CZTS)

Considerable research effort has focused on the synthesis of CZTS NCs. Three groups concurrently reported the colloidal formation of kesterite phase CZTS in 2009, with slight variations existing between each synthetic protocol.\textsuperscript{103,119,340} Guo \textit{et al.} were the first to report the formation of CZTS and obtained polydisperse CZTS nanoparticles (15–25 nm) by reacting copper (II) acetylacetonate, zinc (II) acetylacetonate and tin (IV) bis(acetylacetonate) dibromide in OLA, followed by the injection of the sulfur precursor solution (elemental sulfur in OLA).\textsuperscript{103} A modified method to this saw considerable improvements in nanoparticle monodispersity (12.8 nm ± 1.8 nm), with the simultaneous injection of the metal and sulfur precursor solutions into a flask containing hot trioctylphosphine oxide (TOPO), proving vital in obtaining highly monodisperse NCs.\textsuperscript{340} Steinhagen \textit{et al.} deviated from the aforementioned procedures by adopting a non-injection based approach, in which the precursors were simply mixed together in OLA and heated up to the desired growth temperature.\textsuperscript{119} The synthesis yielded highly monodisperse NCs (10.9 nm ± 2.9 nm) but irregular, faceted CZTS NCs as shown in Figure 31 (a). HRTEM analysis of an individual nanoparticle (Figure 31 b) shows lattice fringes with \(d\) spacing = 0.31 nm, corresponding to the (112) plane of the kesterite phase. An additional SEM image of the as-synthesized NCs dropcast onto a glass substrate is provided in Figure 31 (c).
Figure 31. Colloidal synthesis of CZTS NCs (a) TEM image of a region of NCs demonstrating monodispersity in the as-synthesized NCs. (b) HRTEM image of an individual NCs showing their slightly irregular shape (c) SEM images of NCs dropcast onto gold-coated soda lime glass substrates.\textsuperscript{119}

The interest in fabricating CZTS NCs by solution based approaches saw researchers modifying existing solvothermal methods to allow for their extension to form the highly sought after CZTS NCs. Numerous groups reported solvothermal protocols, employing either ethylenediamine or ethylene glycol as solvent of choice, with nanoparticle aggregation being observed to be a key problem across the developed protocols.\textsuperscript{341-343} Various hierarchical morphologies such as spindle-,\textsuperscript{344} sphere-\textsuperscript{342} and flower-like\textsuperscript{345} nanoparticle arrangements have also been reported by employing thiourea as sulfur source, as opposed to sulfur powder.
Moving away from the solvothermal approach, Shavel and co-workers presented a procedure in which gram scale quantities of high quality CZTS NCs (15 nm in diameter) could be attained, through the reaction of metal-amino complexes and elemental sulfur in a continuous-flow reactor setup. This report demonstrated the first viable route to preparing gram scale quantities of CZTS NCs. Quantum-confined CZTS NCs (2-7 nm in diameter) have also been achieved by reacting metal diethyl dithiocarbamate complexes in OLA. The quantum confinement effect resulted in an increase in the band gap, shifting from 1.5 eV to 1.8 eV, as a direct consequence of reducing the particle size from 7 nm to 2 nm, respectively.

While all the aforementioned synthetic procedures describe the formation of CZTS NCs in the kesterite phase, Lu and co-workers discovered the wurtzite phase in NCs in 2011, two years after the initial observation of the kesterite phase in CZTS NCs. This report demonstrated the key role of DDT in the reaction in stabilizing the metastable phase, with OLA and oleic acid co-operating with DDT and giving rise to the formation of nanoprisms and nanoplates, respectively. Following this crucial observation, highly monodisperse CZTS nanorods (35 nm in length and 11 nm in diameter) were obtained in the absence of amines in a separate hot injection approach by Singh et al. Elongation along the [002] direction was attributed to the injection of a thiol mixture (combination of 1-DDT and t-DDT). Two different nanorod-shaped variations were formed in this synthesis through careful manipulation of the concentration of 1-DDT in the injection. By doubling the concentration of 1-DDT in the thiol mixture, the shape changed from bullet-shaped (Figure 32 a,b) to the more conventional rod-shaped geometry (Figure 32 c,d). Pseudo-spherical nanoparticles were also attained by simply using 1-DDT in the injection, as opposed to the thiol combination.
Figure 32. CZTS nanorods formed by the injection of a thiol mixture into organometallic precursors in the reaction flask. (a) DF-STEM image of CZTS nanorods. (b) HRTEM image, showing the predominant bullet shape on the terminating end facets. (c) DF-STEM image of nanorods formed under a higher 1-DDT concentration. (d) HRTEM image of this sample.\textsuperscript{108}

Another report detailed the formation of a similar, but shorter nanorod morphology in a non-injection protocol through the reaction of metal dithiocarbamate complexes in a mixture of hexadecanethiol (HDT) and trioctylamine.\textsuperscript{348} Important insights into the formation mechanism of the wurtzite phase CZTS were revealed in this report by withdrawing aliquots from the reaction at specified intervals. The crystal structure of the resultant CZTS NCs was found to be dictated by the initial structure of the starting seed, with binary copper sulfide (specifically, monoclinic Cu\textsubscript{1.94}S) particles
forming initially in the presence of HDT. The hexagonal close packing (hcp) array of sulfur ions in monoclinic Cu$_{1.94}$S served as the starting point for the growth of CZTS NCs in the wurtzite phase. On the contrary, Cu$_{1.8}$S particles (with a cubic close packing (ccp) array of sulfur anions) were obtained when HDT was replaced with OLA, ultimately giving rise to CZTS NCs in the kesterite phase. This observation of the importance of the initial formation of Cu$_{2-x}$S seeds has been previously observed in the growth of CIS nanorods.$^{111,123,171}$

While the kesterite and wurtzite structures are dominant in the literature reports of CZTS, an orthorhombic modification has also been observed in a hydrothermal method, based on the assistance of ethylenediamine.$^{349}$ Its crystalline structure was identified through careful analysis of the corresponding XRD pattern and while it does possess a similar pattern on first glance to the wurtzite structure, the difference was only detected by enlarging the view of peaks in the 26-33° range. Nanoplates with a broad size distribution (20-50 nm) were synthesized in this report.
1.7.3.4 Copper Zinc Tin Selenide (CZTSe)

The first wet-chemical based preparation of CZTSe NCs was developed in 2010 by Shavel et al. by the reaction of metal chloride complexes in hexadecylamine (HDA) and 1-ODE, followed by the injection of trioctylphosphine-selenide (TOP-Se). This lead to the formation of highly faceted 20 nm sized NCs. Soon after this report, another hot-injection method surfaced, in which the metal precursors were first decomposed in OLA and were then injected in a hot solvent of selenium powder in OLA. However, the CZTSe NCs prepared by this method lacked a tight degree of shape control, forming a mixture of triangular, hexagonal and plate-like NCs.

An up-scaled colloidal synthesis of cube-like CZTSe NCs, yielding more than ten grams of product per reaction, has also been reported by scaling up the precursor quantities in flasks with 250 mL capacity. Selenium dioxide (SeO\textsubscript{2}) dissolved in 1-ODE was chosen as selenium source in this reaction protocol, based on the virtue of its faster dissolution rate than selenium powder coupled with its ability to be reduced to elemental selenium by OLA or 1-ODE at high reaction temperatures. Figure 33(a) shows a photograph of the scaled up colloidal synthesis in the reaction flask, along with resultant NC ink (Figure 33b) and a gram scale quantity of the NCs (Figure 33c). The cube-like morphology of the as-synthesized NCs is shown in Figure 33 (d), with an SEM image of NC clusters depicted in Figure 33 (e).
Figure 33. Scaled-up method of CZTSe NCs. (a-c) Photograph of the reaction flasks, as-synthesized NC ink and gram scale quantity of the NCs, respectively. (d) TEM and (e) SEM image images displaying the cube-like NC morphology.\textsuperscript{352}

In a subsequent report, Liu et al. took advantage of the strongly coordinating and reducing character of DDT by dissolving selenium powder in a mixture of DDT and OLA, bypassing the conventional requirement of extended heating to dissolve the selenium powder.\textsuperscript{353} This generated a soluble alkylammonium selenide precursor solution, which when injected into a solution of metal chlorides in OLA/DDT, produced quantum-confined CZTSe NCs.

Similar to CZTS, phase selectivity from the kesterite to wurtzite structures of CZTSe can be attained through exquisite control of the reaction chemistry, principally by selection of the metal salt precursors and reaction temperature,\textsuperscript{146} provided that the concentration of diphenyl diselenide (selenium precursor) is kept constant in the
reaction. In terms of CZTSe morphologies, elongated nanostructures such as nanowires have only been attained by using CuSe nanowire bundles as self-sacrificial templates in a solvothermal approach, \(^{354}\) with reports of other elongated CZTSe nanostructures remaining elusive.

Recently, NCs of new material combinations, such as \(\text{Cu}_2\text{ZnGeSe}_4\),\(^ {113,115}\) \(\text{Cu}_2\text{CdSnSe}_4\),\(^ {355}\) \(\text{Cu}_2\text{HgSnSe}_4\)\(^ {116}\) and \(\text{Cu}_2\text{FeSnS}_4\)\(^ {356}\) have emerged, opening up new ways for designing novel functional materials. Control of size, shape and surface properties is crucial in method development for any material combination but a deeper understanding of the underlying reaction mechanisms is still needed for a more rational design of syntheses.
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Chapter 2: Experimental Procedures and Characterization Techniques

2.1 General Synthetic Strategies

Each of the synthetic methods described herein involves the use of the colloidal based solution synthesis approach. As mentioned earlier in Chapter 1, section 1.6.1, this approach involves the thermal decomposition of organometallic precursors in a high boiling point organic solvent, with additional ligands typically employed to instigate size and shape control over the resultant NCs.

Originally introduced by Murray et al. in 1993 for the synthesis of cadmium-based chalcogenides NCs, the approach has been successfully extended to allow for the formation of a wide range of copper-based chalcogenide NCs. In this thesis, CIGS NCs (Chapter 3), CIGSSe NCs (Chapter 4), CZTS NCs (Chapter 5) and CZTS nanorods (Chapter 6) were synthesized using the colloidal approach, with each elemental addition (i.e. In/Ga or Zn/Sn) adding a high degree of complexity in controlling the NC composition.

In terms of the synthesis, the cationic organometallic precursors (Cu, In, Ga or Cu, Zn, Sn) were weighed into the flask initially, along with a coordinating ligand (TOPO) and a solvent (OLA or 1-ODE) to dissolve the metal precursors. While the colloidal method possesses two modifications, purely based on the location of the cationic and anionic precursors (i.e. ‘heating up’ or ‘hot injection’), the ‘hot injection’ approach was used for each material synthesized in this thesis, in that the anionic precursor (S, Se) was injected into the flask at a specific nucleation temperature (e.g. 155°C) to initiate burst nucleation and NC growth. The reaction
mixture was then allowed to heat up to the desired growth temperature (e.g. 250°C) and the NCs were allowed to grow for a specific period of time (typically 30mins).

Figure 1(a) shows a schematic representation of the experimental setup used in this study, where the three-neck reaction flask is connected up to a condenser (from the middle neck of the flask) and to a schlenk line to provide an oxygen-free environment for the NC synthesis. A thermocouple (TC) is consequently connected to one neck for direct temperature monitoring and a rubber septum cap is fitted to the remaining neck of the flask (to allow for injection of the anionic chalcogen) and to keep the flask sealed from the external atmosphere.

Figure 1. (a) Schematic of the experimental setup used in this study. (b) Image of the reaction flask after injection of the anionic precursor. (c) Image of the same reaction flask after increased heating.

Figure 1(b) shows a typical image of the solution colour in the reaction flask after injection of the anionic precursor (S/Se or a mixture of both at 155°C). The solution colour is observed to darken considerably to a dark brown / black colour with increased temperature and time, as depicted in Figure 1(c). The elevated reaction
temperature allows incorporation of the additional metal cations in solution (i.e. In
and Ga or Zn and Sn) into the pre-formed nuclei, forming quaternary (CIGS / CZTS)
NCs or quinary (CIGSSe) NCs. Thus, the formation of the aforementioned material
compositions results in a distinct colour change in the reaction solution after
injection of the anionic chalcogen and increased heating to the final growth
temperature (i.e. 250°C). Specific experimental details are provided in each research
chapter to the synthesis of these materials, with new glassware being used for each
different material composition to avoid contamination.
2.2 Characterization Techniques

2.2.1 Transmission Electron Microscopy (TEM)

Transmission electron microscopy is an incredibly powerful tool in the field of nanotechnology, capable of investigating the morphology, crystal structure (via electron diffraction) and chemical composition (through EDX or EELS) of a wide range of nanomaterials. These instruments have considerably enhanced resolving capabilities than conventional light microscopes owing to the small de Broglie wavelength of electrons.7-9

The first TEM instrument was built back in 1931 by two German scientists, Ernst Ruska and Max Knoll, and was capable of a resolution twice that of the conventional light microscope.7,8 Since then, significant design improvements coupled with technological innovations have opened up a new era of TEM imaging, with exceptional capabilities available at our fingertips. These developments have allowed for spectacular high resolution imaging, where single columns of atoms and their arrangements in nanocrystals can be viewed with unparalleled resolution at the atomic scale7,10 and the different atomic elements can even be identified thanks to EELS attachments. In 2000, another milestone in the history of TEM was reached with the development of aberration corrected TEM,10-12 followed in 2003 by the revelation that aberration corrected HRTEM microscopes could reach sub-Angstrom resolution.13 In-situ TEM measurements can also be conducted to allow for real-time monitoring of chemical reactions at the atomic scale.14 Figure 2 shows a schematic illustration of a typical TEM instrument.
At the top of the column, there is a high voltage electron emitter (typically a tungsten or lanthanum hexaboride, LaB6, filament or field emitter) that generates a beam of electrons that travel down the column. The electrons pass through the thin specimen (thick samples absorb too much of the electron beam) and travel through a series of magnifying magnetic lenses, to where they are ultimately focused onto the fluorescent viewing screen at the bottom of the column and detected by the CCD camera. In essence, the light source of the light microscope is replaced by an electron gun in a TEM, the glass lenses are replaced by electromagnetic lenses (where the power or focal length can be adjusted by changing the current through the lens coil) and the eyepiece is replaced by a fluorescent viewing screen and camera. Another important point is that the column itself is under a very high vacuum to

Figure 2. Transmission Electron Microscopy Diagram.
minimise interactions between the electron beam and air molecules and the instrument is normally operated at accelerating voltages of 200-300kV.

Apertures are holes along the column that can limit the size of the electron beam passing through the column and have different uses depending on their location.\textsuperscript{16} The aperture positioned near the top of the column aperture is known as the condenser aperture and is essentially used to condense and maintain the coherence of the electron beam. On the other hand, the aperture located just below the sample is the objective aperture and is used primarily to control the image contrast.

Lenses also have a very important contribution to imaging in terms of changing the magnification and focusing.\textsuperscript{7,16} The objective lens does the first step of the image magnification and focusing. It also works in conjunction with the objective aperture to generate amplitude contrast. The next lens is the intermediate lens and its positioning and strength controls the magnification of the images or the diffraction pattern. The last lens is the projector lens and is used to focus and, as the name suggests, project the image onto the imaging surface. Features such as beam brightness, current, alignment, focusing and magnification can all be controlled externally.
2.2.1.1 Electron Diffraction

In TEM, the strong interaction between thin crystalline specimens and the electron beam can be used to derive crystallographic information. The interaction and scattering of electrons by atoms in the solid material creates an interference pattern that is unique to the composition of the material.\textsuperscript{7} By measuring the distance from the centre spot to the other various spots, a fully indexed pattern of the crystal structure can be determined. The generated pattern is in reciprocal space so a large lattice will have a corresponding small distance in the electron diffraction pattern. The angles between spots in the diffraction pattern correspond to angles between the various lattice planes for the material thus, allowing for complete structure determination.

The simplest geometry is selected area electron diffraction (SAED) and this pattern is formed by a parallel beam of electrons incident on the specimen, with the field selected using a selected area aperture. Figure 3(a) shows a TEM image of a region of nanocrystals, with the HRTEM image (Figure 3b) allowing the d-spacing to be measured on an individual nanocrystal. The corresponding SAED pattern of the region of nanocrystals, specifically Cu$_2$SnSe$_3$ semiconductor nanocrystals,\textsuperscript{17} is shown in Figure 3(c).
Figure 3. (a) Low-magnification TEM image of Cu$_2$SnSe$_3$ wurtzite NCs. (b) HRTEM image of a single NC. (c) SAED pattern of typical wurtzite NCs.  
(Figure modified with respect to the published version to summarize the findings)

Seven principal reflections or ‘ring’ patterns are observed in the SAED pattern, correlating with the hkl planes in a hexagonal wurtzite crystal system (the specific planes are identified in Figure 3c). Electron diffraction offers an advantage over X-ray diffraction (XRD), in that diffraction experiments can be performed on individual NCs to gather direct information about the precise crystal structure of a single crystal whereas XRD is limited to studying the diffraction over a much bigger sample size area.
2.2.1.2 Scanning Transmission Electron Microscopy (STEM)

STEM is an invaluable tool for nanostructure characterization and provides a range of different imaging modes to facilitate the investigation of elemental composition with atomic level resolution.\textsuperscript{7,18-20} STEM works on the same principle as an SEM (discussed in section 2.2), where a focused beam of electrons is scanned over the sample and the resultant signal is collected to form an image. The main difference between the techniques is that a thin specimen is used for STEM imaging so that the transmission modes of imaging apply. Similar to SEM, secondary or backscattered electrons can also be used for imaging in STEM but transmitted electrons result in much higher signals levels and better spatial resolution.\textsuperscript{7,9,21} One of the key advantages is that multiple detectors can be operated simultaneously, with bright field (BF) and dark field (DF) detectors providing a complementary view of the specimen and allowing the user to collect the maximum possible information from each scan. The BF detector includes the transmitted beam so the holes appear bright, while the DF detector excludes the transmitted beam, thus resulting in the holes appearing dark.

While TEM can be used to distinguish between materials based on differences in Z contrast, it becomes much clearer upon switching to DF-STEM mode. In this mode, the images are formed by very high angle, incoherently scattered electrons which results in the high sensitivity to variations in the atomic number of elements in the sample (Z-contrast).\textsuperscript{20} This is particularly evident in Figure 4, where a gold tipped CdSe nanorod sample is imaged in both BF-TEM mode (a) and DF-STEM mode (b), with the latter image clearly indicating the presence of gold tips dotted along the length of the nanorods.\textsuperscript{22}
Figure 4. TEM and HRTEM (inset) image of gold-tipped CdSe nanorods. (b) DF-STEM image of the same sample, highlight clear contrast differences between the gold tip and the CdSe nanorods.²² (Figure modified with respect to published)

A further advantage of STEM is that it allows the operator to make use of the higher accelerating voltages afforded by TEM and thus, increased specimen penetration is possible, making analysis of atomic level details achievable in thicker samples. The spatial resolution of an electron microscope is limited not only by the wavelength of the illumination source but also by the intrinsic imperfections of electron lenses (aberration caused by spherical lenses). Considerable advances have been made in STEM capabilities in the past few years due to correction of lens aberrations.¹¹-¹³,²⁰ This involves the incorporation of a corrector that causes negative spherical aberration to cancel out positive spherical aberration (an inherent lens defect in all conventional electron microscopes). This gives a total of zero spherical aberration and allows for the highest resolution possible (1 Angstrom or better).¹³

Transmitted electrons that have not been scattered or have just been inelastically scattered give the bright field or phase signal and can be used to exhibit crystallographic information. The BF detector is placed at the same site as the
aperture in BF-TEM and detects the intensity in the direct beam from a point on the specimen. In TEM, the electrons that travel through the sample quickly lose energy depending on the thickness of the sample. The focusing of the different electron energies by the objective lens leads to blurring of the image and loss of resolution and contrast, known as chromatic aberration. In STEM mode, there is no defocusing due to the absence of a lens below the sample, thus it can satisfactorily image samples up to a few microns thick (compared to only half a micron thick in the standard TEM mode).\textsuperscript{7,16,21}

STEM also offers benefits in dark field operation, for example in the HAADF imaging mode.\textsuperscript{23,24} In this case, the inner angle of the dark field detector is made so large that no Bragg diffracted electrons are collected. The images come from elastically scattered electrons that travel close to the atomic nuclei in the crystalline sample. Atomic resolution is possible in this mode without unwanted diffraction contrast that may mask structural information. The dark field signal is directly proportional to the density and thickness of the sample and proportional to the atomic number. Therefore, it is possible to produce images which show contrast due to mass-density or atomic number where heavier elements appear brighter.
2.2.2 Scanning Electron Microscopy (SEM)

SEM is a powerful and indispensible tool for revealing information about the surface topography, chemical composition and crystalline structure of materials that make up the sample.\textsuperscript{25-27} SEM operates by raster-scanning a relatively high energy electron beam (up to 30kV) on a sample, which interacts with atoms on the surface of the material.\textsuperscript{27} These accelerated electrons carry significant amounts of kinetic energy, which is consequently dissipated as a variety of signals through these electron-sample interactions. These signals include secondary electrons, backscattered electrons, diffracted backscattered electrons, photons and heat. Of these, secondary electrons and backscattered electrons are the principal electrons used for imaging samples: secondary electrons are the most valuable for showing morphology and topography while backscattered electrons illustrate contrasts in composition in multiphase samples. Diffracted backscattered electrons are used in EBSD measurements to reveal information about the crystal structure and orientation of the material.\textsuperscript{28} A schematic representation of an SEM is shown in Figure 5.
Figure 5. Schematic diagram of an SEM instrument.\textsuperscript{25}

On first glance, the SEM appears similar to a TEM in that it has an electron optical column housing an electron gun and electromagnetic lenses. However, the column itself is shorter as the only lenses that are needed are those just above the specimen that channel the beam into a fine point (as small as 1nm in diameter) which scans line by line over the sample surface. Another difference is that the accelerating voltages are typically much smaller than those required for TEM (3-30 kV) as SEM is a surface analytical technique.\textsuperscript{19,25,27}
SEM is often used as a complimentary technique to TEM to gain understanding of the 3D morphology of materials. It is a particularly useful as a tool for surveying a larger sample area, with areas ranging from 1cm to 5μm and magnification ranging from 20 – 30,000X. The working distance in SEM can be altered easily during the analysis to bring specific regions of the sample into focus. However, the adjustment of working distance is a trade-off between the depth of focus (DOF) and resolution, with a higher working distance giving a greater DOF but this ultimately decreases the ability to resolve smaller objects. Samples can also be easily rotated and tilted to allow different viewing perspective on the materials which can allow visualization of the orientation of materials from the underlying substrate.

Figure 6 shows SEM cross section images of dense and close packed nanorod assemblies of (a) CdS, (b) CIGS and (c) CdSeS, respectively, which were obtained through electrophoretic deposition of the respective nanorod solutions.
Figure 6. SEM images of (a) CdS nanorods, (b) CIGS and (c) CdSeS nanorods showing multi-layer, vertically aligned nanorod assemblies over large scale areas obtained by electrophoretic deposition.\textsuperscript{29}

In this regard, SEM analysis is more flexible than TEM as it allows for the immediate analysis of nanomaterials on the substrate and provides more in-depth information in terms of the as-prepared nanomaterials orientation, as well as
allowing for a survey over a much larger area. The images indicate that the nanorods are perfectly oriented orthogonal to the substrate, and stack on top to form multilayer nanorod assemblies. Thus, SEM is particularly useful in the characterization of the consequent assembly of as-synthesized semiconductor nanorods.
2.2.3 Elemental Dispersive X-ray Analysis (EDX)

EDX is an X-ray technique that can be used to identify the chemical composition of materials by analysing the characteristic X-rays emitted by the sample after its interaction with the electron beam. It can be coupled with several applications such as SEM, TEM and STEM. This technique provides qualitative information quickly and superimposes the position of K and L shell lines of a given element to aid in correct identification. Quantitative information is also possible, provided that certain parameters are considered. In EDX in SEM, the accelerating voltage is determined by the elements in the samples and so, it should be at least twice that of the highest excitation energy (keV) of any element in the sample to achieve sufficient intensity for the elemental compositions. Beam current is another important parameter, with a higher beam current resulting in a higher X-ray intensity. This, however, can be detrimental to samples which are susceptible to beam damage. EDX can also be used to measure the spatial distribution of elements within samples by raster scanning the beam over a selected area and displaying the intensity of specific elements. This yields element distribution images or ‘maps’. Elemental mapping and elemental line scans are regarded as more precise EDX measurements than the general EDX spectrum, particularly in TEM, as an individual nanocrystal can be marked out for this analysis to directly reveal the elemental composition of single nanocrystals.
2.2.4 X-ray Diffraction (XRD)

XRD is a widely used, analytical tool for obtaining information about the internal structure and phase identification of crystalline materials. The wave like nature of X-rays is exploited in this technique to obtain a series of reflections which are characteristic of the crystalline phases which exist within a material.\(^\text{30}\) Since the wavelength of X-rays is of the order of \(10^{-10}\)m and the interatomic spacing in solids is of the same order, X-rays produce particularly strong diffraction patterns from nanocrystals.

The technique was discovered by German physicist, Max von Laue, back in 1912 where he observed that crystalline substances acted as three-dimensional diffraction gratings by causing a beam of incident X-rays to diffract into many specific directions.\(^\text{31-33}\) After Von Laue’s pioneering research, considerable developments were made in the field of X-ray crystallography, most notably by William Bragg and his son in 1913, where they developed a relationship (Bragg’s Law) that connected the observed X-ray scattering with reflections from evenly spaced parallel planes of atoms within the crystal lattice.\(^\text{32-34}\)

The observed scattering is based on the constructive interference between the incident X-ray waves and parallel planes of atoms in a crystalline sample when conditions satisfy Bragg’s law: \(n\lambda = 2d \sin \theta\), where \(\lambda\) is the wavelength of the incident X-rays in nm, \(d\) is the lattice spacing (distance between the atomic planes) and \(\theta\) is the diffraction angle.\(^\text{32,35}\)

In essence, X-ray diffractometers consist of three basic elements: an X-ray tube, a sample holder and a detector. A typical setup for XRD diffraction is shown in Figure 7.
The X-rays are generated in the cathode ray tube by heating a filament to produce electrons. The electrons are then accelerated towards the anode by applying a voltage and when the electrons have sufficient energy to dislodge inner shell electrons of the anode material, characteristic X-ray spectra are produced. Copper is the most common anode material for diffraction, with CuKα radiation of 1.5418 Angstrom. These X-rays are then filtered to produce monochromatic radiation, collimated to concentrate and directed towards the sample. The detector moves around the sample recording the number of diffracted rays over a series of angles (2θ). The X-ray intensity of these angles is recorded as “counts” or “counts per second”. The experimental data is then compared to a reference spectrum which essentially superimposes the positions and relative intensities of a given crystalline composition. XRD can also be used to quantify the percentage of different phases present by performing Rietveld analysis, in which a least squares approach is used to refine a theoretical line profile with the experimental profile.

One disadvantage of XRD, compared to EDX, is the relatively low intensity of diffracted X-rays. XRD is more sensitive to elements that have high atomic (Z)
numbers. This lower intensity generally means a greater specimen size is needed for analysis, with the information being collected on a much larger area of material. In terms of nanomaterials with dimensions less than 20nm, considerable peak broadening is ordered in the diffraction patterns due to the reduced crystallite size and so, SAED is more accurate for determining the crystal structure of particularly small nanocrystals due to its ability to isolate the diffraction pattern of a single crystal.\textsuperscript{7}
2.2.5 UV-Vis Spectroscopy

UV-vis spectroscopy is the principal technique used to optically characterize nanocrystal solutions by providing the absorbance spectra of a compound in solution. In this technique, the absorption of light energy or electromagnetic radiations causes electrons to be excited from the ground state to the first singlet excited state of the material. A photodetector then measures the difference in energy of the incident light and the transmitted light, which correlates with the energy absorbed by the sample. Double beam instruments have a single light source and monochromator and the beam is then split through a splitter and passes through a series of mirrors to obtain accurate readings of both the reference and the sample of interest. This setup is shown in Figure 8. The UV-vis region relates to a wavelength range of 800-200nm and a band gap energy of 1.5 -6.2eV. Materials with band gaps outside this range require an instrument which has the capability to extend into the NIR region of the spectrum.

![Figure 8. Schematic illustration of a double beam UV-vis instrument.](image)

The Beer-Lambert law is the principle behind absorbance spectroscopy, which relates the absorption to the concentration of the solution for a fixed path length. As the nanocrystal solutions are typically dispersed in non-polar solvents such as
toluene, a blank reference of this solvent is needed at the beginning of the analysis. At high concentrations, nearly 100% of the light is absorbed which results in saturation of the absorption band and a complete flattening in the UV-vis spectrum, thus diluted solutions are generally used to alleviate this issue. The optical band gap of nanocrystal solutions can be directly measured from the UV-spectrum by extrapolation of the linear region of a plot of $(\alpha h\nu)^2$ versus energy, where $\alpha$ represents the absorption coefficient and $h\nu$ stands for the photon energy.
2.2.6 X-ray Photoelectron Spectroscopy (XPS)

XPS, previously known as electron spectroscopy for chemical analysis (ESCA), is a useful technique for determining the surface chemistry of materials and provides both elemental and chemical state information virtually without any restriction on the type of material.\(^{39}\) The technique was developed by Kai Siegbahn in the 1960s on the basis of Einstein’s theory of the photoelectric effect.\(^{40}\) In this technique, the sample is irradiated with soft (low energy) X-ray photons. When the photon excites the electrons of the sample atoms, the entire photon energy is transferred onto the electron and the electrons are ejected from the parent atoms as photoelectrons, equipped with kinetic energy (this only occurs when the X-ray energy is just above the binding energy).\(^{39}\) Only photoelectrons at the extreme outer surface (1nm to 10nm) can escape the sample surface, making this a highly sensitive surface analysis technique.\(^{41}\) The local atomic structure around the target element perturbs the signal and since no two elements share the same electronic binding energies, measurement of this kinetic energy is characteristic of the element from which the photoelectron originated.

A typical survey spectrum of CIGS nanorods,\(^{42}\) as well as schematic diagram of an XPS system\(^{41}\) is illustrated in Figure 9.
Figure 9. (a) XPS survey spectrum of CIGS nanorods indicating that all four elements are present. (b) Schematic diagram of an XPS system.

The position and intensity of the peaks in the resultant energy spectrum provide the desired chemical state and quantitative elemental information. XPS is very sensitive to surface contamination and so, samples must be freshly prepared (i.e. to minimize high surface oxidation) and efficiently washed to remove the organic surface ligands. High resolution spectra can also be measured to determine the oxidation states of the constituent elements in the sample.
### 2.2.7 X-ray Absorption Spectroscopy (XAS)

With the advent of modern bright synchrotron radiation sources, X-ray Absorption Spectroscopy (XAS) has emerged as a powerful technique for local structure determination. This is due to the fact that X-rays are ionizing radiation and so, have sufficient energy to eject a core electron from an atom. XAS can be broken up into two regimes - X-ray absorption near-edge spectroscopy (XANES) and extended X-ray absorption fine structure spectroscopy (EXAFS) – which contain related, but slightly different information about an element's local coordination and chemical state. These regions are depicted in Figure 10 (spectra taken from QEXAFS analysis of Cu K edge as shown in Chapter 6).

![Figure 10. Differentiation between the XANES and EXAFS regions in XAS.](image)

XAS is an incredibly powerful tool, capable of giving information about the distances between central and neighbouring atoms, the number of neighbouring
atoms and changes in the central atom coordination. This ultimately allows for atomic level characterization.

XANES is the region of the absorption spectrum within ~50eV of the absorption edge.\textsuperscript{43} In this region, small shifts in the edge energy are observed due to different valences of the target element, with the local coordination to the element also perturbing the edge shape.\textsuperscript{45,47} In essence, this region is sensitive to oxidation state and geometry.

Above the x-ray absorption edge is the EXAFS region, where oscillations are observed in the energy scan due to the interaction of the ejected electron with the neighbouring atoms.\textsuperscript{43,44,47} This region extends to about 1000eV above an absorption edge of a particular element of the sample. The oscillations in the spectrum are explained as follows; the scattering of the electron wave by neighbouring atoms results in new waves emanating from each scattering site, which are in turn superposed to the initial outgoing wave. This interference of outgoing photoelectrons (with the scattered waves from atoms surrounding the central atom) gives rise to regions of constructive and destructive interference on the high photon energy side of the absorption edge and are observed as local maxima and minima, respectively. The emitted photoelectron can also be thought of as acting as a radar wave, sensing the immediate vicinity of the parent atom and storing the information in the resulting EXAFS oscillations.

Figure 11 shows a schematic representation of the EXAFS process, illustrating the origin of EXAFS oscillations from the interference of the outgoing and backscattered photoelectron wave. In particular, the EXAFS region is sensitive to the radial
distribution of electron density around the absorbing atom and is used for quantitative determination of bond length and coordination number.\textsuperscript{43}

**Figure 11.** Schematic of the EXAFS process illustrating the origin of EXAFS oscillations.\textsuperscript{46}

EXAFS uses the x-ray photoelectric effect (the ionization of inner-shell atomic electrons) and the wave nature of the electron to determine local structures around selected atomic species in the material.\textsuperscript{46} When the incident X-ray energy surpasses the ionization threshold (edge energy), electrons are excited and are ejected from the atom, which registers as a large increase in absorption and a dramatic drop in the transmitted x-ray intensity. This results in an absorption edge, with each element displaying a unique set of absorption edges corresponding to different binding energies of its electrons.

In a typical experimental setup, ionization chambers monitor the intensity of the incident and transmitted monochromatic photon beam through the sample. A schematic representation of the setup used at the Swiss Light Source (SLS) is shown in Figure 12.
In situ EXAFS measurements at the Cu K-edge (8979 eV) and Zn K-edge (9660 eV) were performed at the SuperXAS beamline at PSI (Paul Scherrer Institut, Villigen, Switzerland). The electron beam energy of the PSI storage ring was operated at 2.4 GeV and at a ring beam current of ~400 mA. Further details of the QEXAFS measurements performed at this beamline are discussed in Chapter 6.
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Chapter 3: Systematic Study into the Synthesis and Shape Development in Colloidal CuIn$_x$Ga$_{1-x}$S$_2$ Nanocrystals.

This chapter is presented as published in Chemistry of Materials, with the inclusion of Supporting Information figures in the main text for ease of reading.


3.1 Abstract

This chapter describes a systematic study on the colloidal growth of CuIn$_x$Ga$_{1-x}$S$_2$ nanocrystals and nanorods. The formation of CuIn$_x$Ga$_{1-x}$S$_2$ nanocrystals is shown to occur in several discrete steps, beginning with formation of the binary copper sulfide, transitioning through ternary and subsequently progressing to yield the quaternary form. This allows fine tuning of the aspect ratio through incorporation of amine ligands of differing alkyl chain length giving nanorods ranging from ~7.5 to 14 nm in diameter. The complexity of this system is extensively detailed with a sequential investigation of the effect of amines, thiols, phosphonic acids, in addition to coordinating and non-coordinating solvents on growth protocols. A diverse range of
shape morphologies is attained, ranging from hexagon discs to hatchet shaped crystals, with an optimal synthetic window demonstrated using thiol-amine ligands to generate regular nanorods of controlled dimensions. These nanorods can be assembled over large-scale areas with each nanorod vertically aligned and close packed, allowing for device scale properties defined by the aspect ratio of each building block.
3.2 Introduction

The recent emergence of colloidal synthetic routes to ternary and quaternary I-III-VI$_2$ copper chalcogenide nanocrystals holds significant promise for thermoelectric and photovoltaic applications, where solution processability combined with size dependent properties offers considerable advantages over bulk routes to these materials. A further benefit over top-down methods is that the stoichiometry is defined at the nanoscale ensuring compositional homogeneity in a final layer. For photovoltaic applications, the nanorod form of the nanocrystals is particularly attractive as length dependent properties such as total absorption are independently tunable from diameter dependent properties such as band-gap. We have recently developed strategies to assemble I-III-VI$_2$ nanorods such that ordered arrays extending over device scale areas and over several multi-layers can be obtained. The assemblies show enhancement in the optical absorption as a function of dipolar coupling within the assembly, coupled with high optical absorption coefficients ($10^5$ cm$^{-1}$) which are ideal for thin-film devices.

The colloidal syntheses developed for ternary and quaternary nanocrystals necessarily increase in complexity with the addition of each additional metal cation. In comparison to the well-understood II-VI systems, where size and shape control is routine, the difficulty in balancing the reactivity of 4 different precursors combined with a selection of ligands severely limits comparable control. Notable protocols developed by Zhong and Cabot and co-workers manipulated the hard acid soft base chemistry of each reagent to generate high quality phase pure nanocrystals. Gupta et al reported the first route for nanorod formation where judicious selection of thiol based ligands allowed stabilisation of the wurtzite phase and subsequent growth.
axially along the (002) direction.\textsuperscript{18} The as-formed nanorods showed good size monodispersity, although a feature of the copper chalcogenides that became apparent is the frequent occurrence of defects resulting in L-shaped nanocrystals. These defects in the nanorod structure represented a barrier to assembly protocols which require a tight length and diameter distribution. A modification of this synthesis was reported by Singh et al, where high purity TOPO allowed the formation of regular nanorods (of aspect ratio 2.2) in good yield that were subsequently assembled into highly ordered 2D and 3D arrays.\textsuperscript{9} The experimental observation was that longer growth times resulted in the greater onset of defect formation, resulting in a narrow size window at which regular nanorods could be routinely obtained. As diameter and length independently affect the nanorod properties, strategies to achieve systematic aspect ratio control would be highly advantageous in particular to allow formation of assemblies with tunable properties.

Here, we carry out a thorough investigation on growth in the CuIn\textsubscript{x}Ga\textsubscript{1-x}S\textsubscript{2} nanorod system, with emphasis on the influence of capping ligand on the aspect ratio control of the nanorods. Our investigations show that all quaternary synthesizes occur in discrete steps with initial formation of the binary copper sulfide, progressing through ternary to quaternary dependent on the metal cations. In the present work, a range of long chain amines are incorporated to provide optimal aspect ratio control from 1.8 to 3.3. We also extend the understanding of the investigation of effect of coordinating and non-coordinating solvents on shape and use high resolution transmission electron microscopy (HRTEM) and angular dark-field scanning transmission electron microscopy (DFSTEM) to elucidate the structure of defected nanorods, particularly the L form. The importance of shape control is highlighted where the ability to assemble the nanorods in high density with orthogonal geometry
is shown to be intrinsically linked to nanorod regularity and monodispersity.\textsuperscript{19-29} The resultant assemblies, where the diameter and length of these important semiconductor building blocks is tunable, allows for rational control of the collective properties in a final layer.
3.3 Experimental Section

Materials

All reagents were used as received without any further purification. Copper (II) acetylacetonate (Cu(acac)$_2$, 99.99%), Indium (III) acetylacetonate (In(acac)$_3$, 99.99%), Gallium (III) acetylacetonate (Ga(acac)$_3$, 99.99%), 1-dodecanethiol (1-DDT, >97%), tert-dodecanethiol (t-DDT, 98.5%, mixture of isomers), oleylamine (OLA, 70%, technical grade), propylamine (98%), hexylamine (99%), octylamine (99%), hexadecylamine (HDA, 90%, technical grade) and 1-octadecene (ODE, 90%, technical grade) were purchased from Aldrich. Octylphosphonic acid (OPA, >99%) and Hexadecylphosphonic acid (HDPA, >99%) were purchased from PCI Synthesis. Triocetylphosphine oxide (TOPO, 99%) was purchased from Strem Chemicals.

Synthesis of CuIn$_x$Ga$_{1-x}$S$_2$ Nanorods (R1)

For a typical synthesis of CuIn$_x$Ga$_{1-x}$S$_2$ nanorods, Cu(acac)$_2$ (0.2618g, 1mmol), In(acac)$_3$ (0.3091g, 0.75mmol), Ga(acac)$_3$ (0.0918g, 0.25mmol), TOPO (1.3532g, 3.5mmol) were added to a three-neck round-bottom flask fitted with reflux condenser, rubber septum and temperature finger. 1-octadecene (10mL) was added to the flask to dissolve the precursors. The contents of the flask were evacuated at room temperature for 30mins to eliminate adventitious water and dissolved oxygen. The reaction mixture was then heated to 250-270°C for 30mins under an argon atmosphere and when the temperature reached 155°C, a mixture of 0.25mL 1-DDT and 1.75mL t-DDT was rapidly injected into the system. This resulted in an immediate colour change from dark green to light yellow. After injection, the reaction was allowed to proceed for 15minutes with continuous stirring. Note: Continued growth time to 30mins resulted in the attainment of the undesirable L-
shaped nanorods. During this heating up stage, nanocrystal nucleation can be observed visually at 200-210°C, with the distinctive colour change from light yellow to dark amber to light brown, indicating the formation of the initial copper sulfide particles. Upon further heating, the reaction mixture changes to a dark brown/ black colour and finally, to a dark reddish colour upon full gallium insertion into the lattice. Subsequently, the heating mantle was removed and the reaction vessel was allowed to cool to 80°C.

Washing Procedure: 2-3mL of anhydrous toluene was added initially to quench the reaction. The nanorods were then washed in a 2:1 ratio of toluene to ethanol and centrifuged at 4000rpm for 10mins to yield the dark red centrifuged product. After each centrifugation, the supernatant was removed and the precipitated nanorods were re-dispersed in fresh solvents.

**Synthesis of CuIn$_x$Ga$_{1-x}$S$_2$ Bullet-Shaped Nanorods (R2)**

Bullet-shaped CuIn$_x$Ga$_{1-x}$S$_2$ nanorods were synthesized using the following protocol: Cu(acac)$_2$ (0.2618g, 1mmol), In(acac)$_3$ (0.3091g, 0.75mmol), Ga(acac)$_3$ (0.0918g, 0.25mmol), TOPO (1.3532g, 3.5mmol) and 1-octadecene (10mL) were added to a three-neck round-bottom flask and the reaction mixture was evacuated at room temperature for 30mins. It was then heated to 250-270°C for 30mins under an argon atmosphere and at 155°C, 2.5mL of 1-DDT was rapidly injected into the system. This resulted in an immediate colour change from dark green to light yellow. After injection, the reaction was allowed to proceed for 30minutes with continuous stirring. In this instance, nanocrystal nucleation can be observed visually 11mins after the injection, at a temperature of 200-210°C, with the distinctive colour change from light yellow to dark amber to light brown, indicating the formation of the initial
copper sulfide particles. Further heating resulted in a colour change to a dark brown/black colour and finally, to a dark reddish colour. Subsequently, the heating mantle was removed and the reaction vessel was allowed to cool to 80°C. A similar washing procedure, as outlined in R_1, was conducted.

**Synthesis of CuIn_xGa_{1-x}S_2 Nanorods with aspect ratio control (R_3)**

In this instance, the introduction of amine ligands to the reaction mixture instigated effective aspect ratio control.

**Synthetic Route(R)_{3.1-3.7} – Effect of Amine addition**

Cu(acac)_2 (0.2618g, 1mmol), In(acac)_3 (0.3091g, 0.75mmol), Ga(acac)_3 (0.0918g, 0.25mmol), TOPO (1.3532g, 3.5mmol), the desired amine (Table 1 for details of amine type and quantity) and 1-octadecene (10mL) were added to a three-neck round-bottom flask, followed by evacuated at room temperature for 30mins. The reaction mixture was then heated to 250-270°C for 30mins (insulate flask surroundings with glass wool during this stage to aid heating) under an argon atmosphere and at 155°C, 0.25mL 1-DDT and 1.75mL t-DDT was rapidly injected into the system, resulting in an immediate colour change from dark green to light yellow. After injection, the reaction was allowed to proceed for 15minutes with continuous stirring. Note: Addition of Propylamine or Hexylamine to the RB flask caused the solution to ‘bump’ due to these amines boiling off at their low boiling points. Consequently, the heating mantle was removed and the reaction vessel was allowed to cool to 80°C. A similar washing procedure, as outlined in R_1, was conducted.
Table 1 details the amine ligand and quantity which resulted in the attainment of CuIn$_x$Ga$_{1-x}$S$_2$ nanorods and L, hatchet and tadpole-shaped NCs.

<table>
<thead>
<tr>
<th>Synthetic Route(R)</th>
<th>Name of Amine</th>
<th>Quantity</th>
<th>Resultant NC</th>
</tr>
</thead>
<tbody>
<tr>
<td>#</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.1</td>
<td>Propylamine</td>
<td>0.082mL, 1mmol</td>
<td>Nanorods (25 x 14 nm)</td>
</tr>
<tr>
<td>3.2</td>
<td>Hexylamine</td>
<td>0.132mL, 1mmol</td>
<td>Nanorods (24 x 10.5 nm)</td>
</tr>
<tr>
<td>3.3</td>
<td>Octylamine</td>
<td>0.165mL, 1mmol</td>
<td>Nanorods (24 x 9 nm)</td>
</tr>
<tr>
<td>3.4</td>
<td>Hexadecylamine</td>
<td>0.2415g, 1mmol</td>
<td>Nanorods (25 x 7.5 nm)</td>
</tr>
<tr>
<td>3.5</td>
<td>Hexadecylamine</td>
<td>0.7245g, 3mmol</td>
<td>L-shaped Nanorods</td>
</tr>
<tr>
<td>3.6</td>
<td>Hexadecylamine</td>
<td>1.2075g, 5mmol</td>
<td>Hatchet-shaped NCs</td>
</tr>
<tr>
<td>3.7</td>
<td>Hexadecylamine</td>
<td>2.415g, 10mmol</td>
<td>Tadpole-shaped NCs</td>
</tr>
</tbody>
</table>

Table 1. Details to Synthetic Routes R3.1-3.7 identifying the amine type and quantity added to the flask in the initial step.

**Synthesis of CuIn$_x$Ga$_{1-x}$S$_2$ nanocrystals in a coordinating solvent (R4)**

Cu(acac)$_2$ (0.2618g, 1mmol), In(acac)$_3$ (0.3091g, 0.75mmol), Ga(acac)$_3$ (0.0918g, 0.25mmol), TOPO (1.3532g, 3.5mmol) and Oleylamine (10mL) were added to a three-neck round-bottom flask and the reaction mixture was evacuated at room temperature for 30mins. It was then heated to 250-270°C for 30mins under an argon atmosphere and at 155°C, 0. 25mL 1-DDT and 1.75mL t-DDT was rapidly injected into the system. After injection, the reaction was allowed to proceed for 30minutes with continuous stirring. Nanocrystal nucleation can be observed visually 11mins.
after the injection, at a temperature of 220-225°C, with the distinctive colour change from light yellow to dark amber to light brown, indicating the formation of the initial copper sulfide particles. Further heating resulted in a colour change to a dark brown/black colour and finally, to a dark reddish colour. Subsequently, the heating mantle was removed and the reaction vessel was allowed to cool to 80°C. A similar washing procedure, as outlined in R₁, was conducted.

**Synthesis of CuInₓGa₁₋ₓS₂ Hexagon-shaped disks (R₅)**

Cu(acac)₂ (0.2618g, 1mmol), In(acac)₃ (0.3091g, 0.75mmol), Ga(acac)₃ (0.0918g, 0.25mmol), TOPO (1.3532g, 3.5mmol), Octylphosphonic acid (0.1942g, 1mmol) and 1-octadecene (10mL) were added to a three-neck round-bottom flask and the reaction mixture was evacuated at room temperature for 30mins. It was then heated to 250-270°C for 30mins under an argon atmosphere and at 155°C, 0.25mL 1-DDT and 1.75mL t-DDT was rapidly injected into the system. After injection, the reaction was allowed to proceed for 15minutes with continuous stirring. Subsequently, the heating mantle was removed and the reaction vessel was allowed to cool to 80°C. A similar washing procedure, as outlined in R₁ was conducted. The product yield of the CuInₓGa₁₋ₓS₂ nanocrystals ranged from 90-95% after purification.

**Electrophoretic Assembly of CuInₓGa₁₋ₓS₂ Nanorods**

A 10% w/v toluene solution of the thiol-amine capped nanorods (R₃.₃) was used for electrophoresis. During electrophoresis, the silicon substrates (10mm x 10 mm) were attached onto the negative electrode of two parallel gold-coated copper electrodes, which are separated at 2mm apart. The electrodes are completely immersed in the nanorod solution and a potential of 150-200 V was applied to the substrate for 3 mins.
using a high voltage power supply unit (TECHNIX SR-5-F-300, S/N: BU08/04971). Voltage was monitored using a Black star 3225 MP millimetre.

**Characterization**

For transmission electron microscopy (TEM) analysis, aliquots (0.5-1.0mL) of the reaction mixture were taken by syringe at specified times and quenched via cooling to room temperature. Nanocrystals were precipitated from the reaction mixture and dissolved in toluene. TEM samples were prepared on 200 mesh carbon-coated copper grids (Ted Pella Inc.). TEM and DFSTEM were conducted by using a 200kV JEOL JEM-2100F field emission microscope, equipped with a Gatan Ultrascan CCD camera and EDAX Genesis EDS detector. For EDX analysis, carbon-coated gold TEM grids were used. X-ray diffraction (XRD) analysis of drop-cast films of CuIn$_x$Ga$_{1-x}$S$_2$ nanorods on a glass substrate was conducted using a PANalytical X’Pert PRO MRD instrument with a Cu Kα radiation source (λ = 1.5418 Å) and a 1-D X’celerator strip detector. High resolution scanning electron microscopy (HRSEM) of the nanorod assembly on a Si (111) substrate was performed on a Hitachi SU-70 system operating between 3 and 20kV. UV-vis absorbance spectra were collected on a Cary 5000 UV-vis-NIR spectrophotometer. Samples were diluted in toluene and the spectra were collected in a two-beam transmission mode with pure toluene as a reference. The detector changeover point was set at 1000nm for all measurements. XPS measurements of the drop-cast films of CuIn$_x$Ga$_{1-x}$S$_2$ nanorods on glass substrates were carried out using a Kratos Axis 165 Spectrometer. Samples were flooded with low energy electrons for efficient charge neutralisation. Binding energies (BE) were determined using C 1s at 284.8 eV as charge reference.
3.4 Results and Discussion

Taking aliquots at selected time intervals in the quaternary nanorod synthesis gives important insights into the evolution pathway. Figure 1(a) shows a TEM image of nanocrystals five minutes after injection of the thiol mixture (1-DDT+t-DDT, R₁) at 210°C. The particles are highly monodisperse, with diameters of 7 ± 0.5nm and possessing size variations <5%.

![TEM images showing the different growth stages of CuInₓGa₁₋ₓS₂ nanocrystals.](image)

**Figure 1.** TEM images showing the different growth stages of CuInₓGa₁₋ₓS₂ nanocrystals. (a) Formation of mixed phase copper sulfide particles observed at 5mins (210°C), (b) Formation of CuInS₂ NCs observed at 8mins (235°C), with inset showing a HRTEM image of the anisotropic NCs, (c) Continued growth and heating to 270°C results in the formation of CuInₓGa₁₋ₓS₂ NCs (inset shows a HRTEM image of the characteristic rod shape), (d) TEM image of mixed phase copper sulfide particles formed at 11mins (210°C), (e) Indium incorporation occurs at 15mins (245°C) forming CuInS₂ NCs, with inset HRTEM image of the resultant NCs,
(f) Further gallium incorporation occurs with increased growth time and temperature (270°C) resulting in the formation of CuIn$_x$Ga$_{1-x}$S$_2$ NCs, which adopt a characteristic bullet shape in this system.

The corresponding XRD (Figure 2) shows the presence of mixed phases of copper sulfide, both hexagonal (Chalcocite Cu$_2$S, Covellite CuS) and orthorhombic (Anilite Cu$_7$S$_4$).

![XRD Analysis](image)

**Figure 2.** XRD Analysis of initial mixed phase copper sulfide particles indexed to Hexagonal Chalcocite Cu$_2$S (98-004-5386) as shown by the pink line, Hexagonal Covellite CuS (98-001-7047) as shown by the navy line, and Orthorhombic Anilite Cu$_7$S$_4$ (98-000-5306) as shown by the green line.

The particles observed here are similar in composition to binary copper sulfide particles which also form prior to indium insertion in the ternary CuInS$_2$ system.$^{27,30,31}$ Increasing the temperature to 270°C and allowing growth to proceed for a further 5 minutes results in a transition of the crystal structure to the hexagonal
wurtzite phase, enabling elongation into the rod form (Figure 1b). The hexagonal phase can only be stabilised in nanocrystal form, with the thermodynamically preferred chalcopyrite phase predominant in the bulk material.\textsuperscript{32,33} XRD analysis of these anisotropic nanocrystals (Figure 3a, ii) reveals that copper indium sulfide is formed at this point and possesses a different crystalline structure from that of the previous copper sulfide particles (Figure 3a, i), with no evidence of gallium incorporation at this growth stage despite its presence in solution.

**Figure 3.** X-ray diffraction patterns showing (a) the evolution of the crystal structure of CuIn\textsubscript{x}Ga\textsubscript{1-x}S\textsubscript{2} nanorods from the initial binary mixed phase copper sulfide particles (i), transitioning through ternary CuInS\textsubscript{2} (ii), and finally yielding the resultant CuIn\textsubscript{x}Ga\textsubscript{1-x}S\textsubscript{2} nanorods (iii). (b) Magnification of the (002) peak highlighting the systematic shift to higher 2\(\theta\) with increased Ga content.

The indium insertion into the nanocrystal lattice prior to gallium is expected given that Ga\textsuperscript{3+} is a harder acid compared to In\textsuperscript{3+}. Gallium incorporation only occurs with further growth at this sustained temperature and is observed after a total growth time of 15 mins (Figure 1c).
A noticeable shift to higher $2\theta$ is observed for all peaks in the corresponding XRD with the incorporation of the smaller gallium atom (Figure 3a, iii). Magnification of the (002) XRD peaks in Figure 3(b) reveals a systematic shift of 0.15° to higher $2\theta$, indicating that full gallium incorporation can only occur at the elevated growth time and temperature. The gallium incorporation, in the case of the thiol mixture, results in a broadening of the diameter, rather than an increase in length, in agreement with previous observations here. Importantly, the results show that although the synthesis is a one-pot reaction, the formation of CuIn$_x$Ga$_{1-x}$S$_2$ nanorods always occurs sequentially, starting with binary copper sulfide nanocrystals, transitioning through ternary copper indium sulfide before the final gallium insertion to yield the quaternary CuIn$_x$Ga$_{1-x}$S$_2$ nanorods. XPS data further confirms that all four elements are present in the final stage, as shown in Figure 4.

**Figure 4.** XPS Survey Spectrum of CuIn$_x$Ga$_{1-x}$S$_2$ nanorods indicating that all 4 elements are present.
The progression from binary copper sulfide to quaternary CuIn$_x$Ga$_{1-x}$S$_2$ can also be monitored by UV-vis spectroscopy as shown in Figure 5, with the optical band gap increasing to higher energy with increased growth time. The first aliquot taken at the initial sign of the colour change shows mixed phase copper sulfide particles (Figure 5a), characterized by the steep rise in the absorbance intensity at short wavelengths, with a low intensity onset extending into the NIR region.

**Figure 5.** UV-vis spectra of the initial aliquot of mixed phase copper sulfide particles (a), the second aliquot taken at an intermediate stage of the reaction showing the evolution of CuInS$_2$ (b), and the final aliquot of CuIn$_x$Ga$_{1-x}$S$_2$ nanorods (c).

Furthermore, no plasmon band was apparent in the NIR region for these particles, which is consistent with previous published reports of chalcocite copper sulfide particles.$^{34,35}$ The spectrum of the second aliquot, taken at an intermediate stage in the reaction, shows the emergence of a shoulder at ~1.67eV indicating CuInS$_2$ nanorod formation (Figure 5b).$^{30,31,36,37}$ The final CuIn$_x$Ga$_{1-x}$S$_2$ nanorod spectrum shows a shift to higher energy upon Ga incorporation (Figure 5c) and gives a direct
optical band gap of ~1.8eV, which is in good agreement with previous reports.\textsuperscript{9,18}

The elemental composition of each aliquot was further confirmed by EDX analysis (Figure 6), with the initial particles composed only of Cu and S, the second aliquot containing Cu, In and S with no gallium detected despite its presence in solution, and the final nanorods containing all 4 elements - Cu, In, Ga and S with a final composition of CuIn\textsubscript{0.77}Ga\textsubscript{0.23}S\textsubscript{2}.
Figure 6. EDX Elemental Analysis of aliquots taken at selected time intervals verifying that (a) initial particles are composed only of Cu and S, (b) indium incorporation occurs next with the second aliquot containing nanorods composed of Cu, In and S, (c) the final aliquot containing nanorods composed of Cu, In, Ga and S.

Significant differences in the nucleation kinetics and the overall NC shape can be observed with the use of a single thiol (1-DDT, R$_2$) instead of the thiol mixture (1-DDT+ t-DDT, R$_1$). Firstly, an obvious delay in the nucleation and growth is
apparent, as the solution-colour change (Figure 7) correlating with copper sulfide particle (Figure 1d) formation was slower (i.e. 11mins) as compared to the thiol mixture (i.e. 5mins). The thiols are soft bases with a high affinity for Cu\(^+\) (soft acid) and the slower nucleation and growth suggests a stronger binding in the case of 1-DDT, with the more sterically hindered t-DDT acting to effectively regulate the availability of copper ions.

Here, indium incorporation also occurs prior to gallium after 15 mins (Figure 1e) although only slight anisotropy is evident. The final nanorods formed with 1-DDT are noticeably broadened in size and shape distribution, with a predominant bullet shape on the terminating growth facets (Figure 1f). This difference in shape between the two cases shows that the thiols not only act to regulate the nucleation but also play a part as passivating ligands, affecting the preferential growth along certain facets.
Figure 7. Photographic image of the reaction flask highlighting the solution colour change. (a) Clear yellow colour observed instantaneously after injection of the anionic precursor. (b) Dark amber / light brown colour observed ~3 mins after injection, as temperature approaches 200°C. Light brown colour in flask correlates with copper sulfide formation. (c) Dark brown / black colour observed indicating indium (followed by gallium) incorporation into the lattice.
In binary II-VI nanocrystals, ligands with amine functionality show a strong ability to selectively bind to different growth directions to instigate shape control. We investigated the addition of a series of amine ligands of differing alkyl chain length on the morphology control of quaternary copper chalcogenides (all other parameters remained constant, $R_3$). Figure 8 (a-d) shows both low and high resolution TEM images of CuIn$_x$Ga$_{1-x}$S$_2$ nanorods after incorporation of amine ligands of increasing chain length. There is a noticeable decrease in nanorod diameter and hence, increase in aspect ratio with the use of Propylamine (Figure 8a, $R_{3.1}$), Hexylamine (Figure 8b, $R_{3.2}$), Octylamine (Figure 8c, $R_{3.3}$) and Hexadecylamine (Figure 8d, $R_{3.4}$) while retaining a tight size distribution. We attribute this decrease in nanorod diameter to the boiling points of the respective amines, with Propylamine and Hexylamine quickly driven into the gaseous phase as a result of the reaction temperature increase. This effectively resulted in less amine present in the system and lead to the formation of wider diameter rods. As the chain length of the amine ligand increases from 3 to 16, the aspect ratios of the rods are tuned from 1.8 to 3.3 with excellent reproducibility.

Clear lattice fringes are observed in all four HRTEM images indicating the single crystalline nature of all of the anisotropic nanocrystals, with the measured spacing of $d=0.318\text{nm}$ from the inset FFTs corresponding to the (002) lattice planes of the wurtzite structure. The measured angle of $91.2^\circ$ (measured from FFTs) correlates extremely well with the theoretical angle ($90^\circ$) between the (002) and (010) planes in a hexagonal crystal system.
Figure 8. Low and high resolution TEM images showing the effect of amine ligands with different alkyl chain lengths on the diameter of CuIn$_x$Ga$_{1-x}$S$_2$ nanorods: (a) Propylamine, (b) Hexylamine, (c) Octylamine, (d) Hexadecylamine. The insets show the FFT patterns from the individual HRTEM nanorod images.

Our TEM and FFT analysis is supported by XRD in Figure 9, which shows that CuIn$_x$Ga$_{1-x}$S$_2$ nanorods, obtained by varying the length of the amine alkyl chain, can
be indexed as the wurtzite phase. The XRD peaks in Figure 9 were indexed based on simulated powder diffraction data reported for wurtzite CuInS$_2$ nanorods$^{30-32}$, with a noticeable shift to higher 20 observed for all peaks as a result of incorporation of the smaller gallium atom into the nanocrystal lattice.$^{18}$

**Figure 9.** XRD patterns showing CuIn$_x$Ga$_{1-x}$S$_2$ nanorods synthesized with the incorporation of (a) Propylamine, (b) Hexylamine, (c) Octylamine and (d) Hexadecylamine.
The results of these syntheses are summarized in Table 2, with incorporation of the Hexadecylamine ligand achieving aspect ratios of greater than 3.0.

<table>
<thead>
<tr>
<th>Ligand</th>
<th>N</th>
<th>D (nm)</th>
<th>L (nm)</th>
<th>Average L/D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propylamine</td>
<td>3</td>
<td>14 ±1</td>
<td>25 ± 2</td>
<td>1.79</td>
</tr>
<tr>
<td>Hexylamine</td>
<td>6</td>
<td>10.5 ± 1</td>
<td>24 ± 2</td>
<td>2.29</td>
</tr>
<tr>
<td>Octylamine</td>
<td>8</td>
<td>9 ± 0.5</td>
<td>24 ± 3</td>
<td>2.67</td>
</tr>
<tr>
<td>Hexadecylamine</td>
<td>16</td>
<td>7.5 ± 0.5</td>
<td>25 ± 2</td>
<td>3.33</td>
</tr>
</tbody>
</table>

Table 2. Diameter (D), Length (L) and Aspect Ratio (L/D) of the Nanorods Depicted in Figure 4, synthesized using Amine ligands with Different Alkyl Chain Lengths (N).

A feature of these quaternary copper chalcogenides is the occurrence of apparent growth defects resulting in twinned crystals with a characteristic L shape. These were observed as a significant percentage of nanocrystals in the first reported study\(^{18}\) and in our case were largely eliminated by using a higher purity of TOPO and decreased growth time in the synthesis (R\(_1\)). Although, if growth time is allowed to progress beyond 20 minutes, an increase in L shaped crystals occurs instead of further nanorod elongation. Interestingly, the amine addition offers an insight into this growth protocol. At low concentrations (R\(_{3.1-3.4}\)), the amine collaborates with the thiol mixture offering suitable co-ordination whereas at high amine concentrations (R\(_{3.5-3.7}\)), the desired nanorod formation is disrupted to give a high proportion of these growth defects. Figure 10 (a) and (b) shows typical L-shaped nanorods that are formed using an amine concentration of 3mmol (R\(_{3.5}\)). The diameter of the protruding segment does not correlate with the main rod body and varies from
structure to structure thus, ruling out oriented attachment as a possible mechanism. The top-down TEM view seems to indicate that the L segment grows perpendicular to the c-axis, but closer inspection by DFSTEM reveals that it appears to grow off the main nanorod body at an acute angle rather than perpendicularly, as shown by the red arrows in Figure 10 (c) and (d).

**Figure 10.** (a) HRTEM image of a typical L-shaped nanorod, (b) HRTEM image of an L-shaped nanorod possessing a longer and thinner L segment than that shown in (a), (c) and (d) show further DFSTEM images of L-shaped nanorods at slightly different angles.
At this point, we can make a hypothesis about the possible growth mechanism occurring in this system. As L-shaped nanorods are not attainable in the ternary CuInS$_2$ system, we believe that this shape is directly related to the incorporation of gallium into the lattice. The delayed reactivity of the gallium precursor in the reaction flask may lead to a separate nucleation event upon increasing temperature, resulting in free gallium nuclei in the solution. These could potentially adhere to the nanorod segment and grow off the main CuIn$_x$Ga$_{1-x}$S$_2$ body, yielding a variety of different L length segments which depend on the point at which the NC growth was captured.

Although we have derived the optimal system for the formation of monodisperse nanorods with minimal L shape formation, we observe that deviating outside this range results in the development of diverse morphological changes. Substituting an equal volume of a coordinating solvent (OLA) for the non-coordinating solvent (1-ODE), $R_4$, results in the formation of wider diameter NCs, as shown in Figure 11(a). These distinctive morphology variations can be understood to arise from the differing coordination abilities between these solvents with the metal cations. Thus, we discovered that the use of 1-ODE was critical in this synthesis for the generation of monodisperse nanorods as it solely acts as a medium for dissolving up the acetylacetonate precursors and does not significantly impact the nanorod synthesis and growth kinetics unlike OLA.
Figure 11. HRTEM images highlighting the formation of (a) wide diameter NCs, (b) Low aspect ratio L-shaped NCs, (c) Tadpole-shaped NCs synthesized in the presence of a coordinating solvent. The formation of hexagonally shaped disks (d) is observed in the presence of additional phosphonic acids.

To yield these wider diameter nanorods, we hypothesize that the diameter of the starting copper sulfide particles had to be wider (than the particles as formed as in the 1-ODE system) to facilitate their formation. Analysis of the initial particles confirmed this hypothesis, with particles possessing diameters of $12 \pm 3.5$ nm as shown in Figure 12.
Increasing the growth time resulted in the attainment of low aspect ratio L-shaped and tadpole shaped NCs, as shown in Figure 11 (b) and (c), respectively. Within this kinetic regime, slight variations of shape arise from the differential growth rates of the various faces, as exposure of the low-energy faces does not take place at the same time. Thus, the wide variety of shapes that are observed is a result of capturing the NCs in different stages of their growth. Furthermore, utilization of high injection volumes of coordinating solvents or high amine concentrations ultimately leads to the formation of tadpole shaped NCs in this system.

As TOPO is used as a coordinating solvent in this synthesis, it allowed for the investigation of long chain phosphonic acid ligands instead of the amines. Interestingly, structural changes from the typical elongated nanorods to flattened, hexagonally shaped disks were obtained upon introduction of phosphonic acid ligands (Figure 11d). We observed that varying the length of alkyl chain on these ligands did not appear to have any significant effects on the resultant NC size, with reactions conducted with OPA and consequently with HDPA resulting in the formation of hexagon disks. The phosphonic acid in the case of CuIn$_x$Ga$_{1-x}$S$_2$ clearly
acts as a very strong passivating ligand, for the \{002\} growth facet, with growth only occurring in the \{220\} facet. Formation of hexagonally shaped disks has also been reported in the presence of phosphonic acids in the CuInS\textsubscript{2} system\textsuperscript{30}, where the phosphonic acids instigate sudden changes in the reaction environments by lowering the monomer activity and the chemical potential of the reaction. This ultimately results in the formation of thermodynamically more stable faceted crystals, which crystallize in the hexagonal wurtzite phase as shown in Figure 13.

**Figure 13.** XRD analysis of CuIn\textsubscript{x}Ga\textsubscript{1-x}S\textsubscript{2} hexagon shaped disks synthesized in the presence of OPA (blue line) and consequently in the presence of HDPA (red line).

Figure 14 shows a schematic representation summarizing the influential factors and morphological changes that can occur in this system with ‘0 mins’ indicating the injection of the anionic precursor.
Figure 14. Schematic of the Synthetic Routes and corresponding CuIn$_x$Ga$_{1-x}$S$_2$ morphologies which evolve in each pathway as a function of increased growth time.

The stabilisation of the hexagonal phase with preferential growth along the c-axis is clearly enabled by the presence of the thiol ligands ($R_1$), which have a dual function of chalcogen source and growth modulation. Evidence for the thiol influence on this growth direction is clear from $R_2$ where termination in a bullet shape, as opposed to the regular rod, suggests a different binding energy in a kinetically controlled regime.

In all reaction pathways, the observation that the starting point is the binary copper sulfide is important for growth control. This is particularly the case for aspect ratio control in $R_3$ where the amine at low concentrations dictates the size of copper sulfide nanocrystals, ultimately allowing diameter control in the final rod. The decreasing copper sulfide nanoparticle size ($R_{3.1-3.4}$) suggests a more effective capping ability of the amine functionality as the chain length increases. This is likely due to the longer aliphatic chains allowing for more effective colloidal stabilisation.\textsuperscript{7,39} Interestingly, these amines at low concentrations do not interfere
with the thiol function, allowing for aspect ratio control with rod lengths typically saturating at 25 nm. However, there is a tight time and concentration window in which the regular rod shape can be retained. Outside of this, there is a strong propensity in this system for non-regular shape formation, L, hatchet and tadpole shapes, once the system is perturbed either by excess amine (R_{3.5-3.7}) or by changing to a coordinating solvent (R_4), as shown in Figure 15.
Figure 15. TEM images of the various CuIn$_x$Ga$_{1-x}$S$_2$ morphologies obtained outside the optimal synthetic window. (a-b) show diverse L shaped nanocrystals formed in 3mmol of HDA (R$_3$.5). (c-d) show hatchet-shaped nanocrystals formed in 5mmol of HDA (R$_3$.6). (e-f) show tadpole-shaped nanocrystals formed in 10mmol of HDA (R$_3$.7). (g) shows wide diameter nanocrystals synthesized in oleylamine solvent (R$_4$). (h) shows a later aliquot of nanocrystals synthesized in oleylamine solvent (R$_4$) where tadpole formation is apparent.
EDX analysis of these alternate shapes (Figure 16) confirmed the presence of all 4 elements - Cu, In, Ga and S - and more importantly, that stiochiometric variations did not exist despite differences in nanocrystal shape.

**Figure 16.** EDX Elemental Analysis of (a) L-shaped Nanorods formed by R3.5, (b) Hatchet-shaped NCs formed by R3.6, (c) Tadpole-shaped NCs formed by R3.7.
The attainment of these alternate shapes by solely increasing amine ligand concentrations did not affect the final nanocrystal stoichiometry, but simply influenced the overall nanocrystal shape. Furthermore, optical absorbance measurements of the alternate shapes (Figure 17) did not yield a shift in the optical band gap to higher energy, indicating no stoichiometric variations existed between the alternate shapes.

**Figure 17.** UV-vis spectra of (a) L-shaped Nanorods formed by R3.5, (b) Hatchet-shaped NCs formed by R3.6, (c) Tadpole-shaped NCs formed by R3.7.

The high amine concentrations most likely raise the energy of the (002) face resulting in uncontrollably fast growth conditions, leading to exposure of the lower-energy crystal faces. Consequently, growth progresses on these lower-energy faces to minimize the surface area of the high-energy (002) face, producing the hatchet and tadpole-shaped NCs. Similar phenomena were observed in II-VI nanocrystals in high phosphonic acid conditions.\(^{39,40}\) However, addition of phosphonic acid ligands (R\(_5\)) to our system results in completely different crystal habits, with discs of the hexagonal wurtzite phase more stable, indicating that growth along the [002]
direction is completely inhibited in this case. As the hexagonal wurtzite phase is only stable in the nanocrystal form, with no evidence in the bulk, this is therefore a thermodynamically less favoured system that would explain the high propensity for defects particularly for long reaction times.

Additionally, we investigated the effect of different copper precursors (Figure 18) by solely changing the copper precursor in the reaction and keeping all other parameters constant.

Figure 18. TEM images of CuIn$_{x}$Ga$_{1-x}$S$_{2}$ nanocrystals synthesized using the following copper precursors: (a) Copper(I) Acetate, (b) Copper(I) Chloride, (c) Copper(I) Iodide, (d) Copper(II) Nitrate Trihydrate, (e) Copper(II) Acetylacetonate.

This study revealed that copper (I) acetate, copper (I) chloride and copper (II) acetylacetonate lead to the attainment of CIGS nanorods, while copper (I) iodide and copper (II) nitrate proved highly unsuitable for forming nanorods. This is related to
the intricate and differing reactivity of the copper precursors based on their classification in the hard-soft acid-base (HSAB) theory.$^{12,41}$

Despite this complexity, the optimised amine/thiol protocol ($R_{3.1-3.4}$) allows formation of nanorods possessing high uniformity across length and diameter critically with aspect ratio control. Tailoring the nanocrystals in this fashion and subsequently stacking the nanorods into vertical arrays allows complete control of the layer architecture at the nanoscale. Here, the amine-thiol capped nanorods ($R_{3.3}$) are aligned from a solution in toluene using the electrophoretic protocol we recently demonstrated for $R_1$ nanorods.$^9$ The nanorods have an inherent dipole due to the non-centrosymmetric wurtzite lattice and a net charge due to ligand coverage. The dipole and charge are affected by the aspect ratio and optimal conditions for assembly of $R_3$ nanorods was attained by adjusting key parameters in the deposition (namely applied voltage, deposition time and solution concentration). Figure 19 (a) shows a top down image of a monolayer sheet of vertically assembled $\text{CuIn}_{x}\text{Ga}_{1-x}\text{S}_2$ nanorods, exhibiting a high degree of hexagonal ordering.
Figure 19. (a) Top down TEM image of a monolayer 2D sheet of vertically assembled and close packed CuIn$_x$Ga$_{1-x}$S$_2$ nanorods. (b) Top down HRTEM image of a single nanorod with clear lattice fringe spacing of $d=0.318\text{nm}$ corresponding to the (002) plane of the wurtzite structure. (c) Representative SEM image showing the sequential deposition of 2D sheets into 3D multilayer vertically aligned nanorod assemblies.

The top down HRTEM image of a single nanorod, as shown in Figure 19 (b) in this close-packed assembly, shows lattice fringes with a distance of 0.318nm, which matches perfectly with the (002) plane of the wurtzite structure. The multilayer and close packed nature of the assembly is shown in Figure 19 (c), with a density of nanorod packing attained at $2.47 \times 10^{13}$ nanorods per 20 layer assembly, with each rod axially aligned.
3.5 Conclusion

A systematic study of the evolution pathway for CuIn$_x$Ga$_{1-x}$S$_2$ nanorods shows that the quaternary form proceeds through discrete binary and ternary steps as each metal cation sequentially incorporates. Although the growth system is highly complex, we show that aspect ratio control of regular nanorod shapes can be obtained by judicious addition of amine ligands in the presence of thiols, with the aspect ratio showing a good correlation with the ligand chain length. A synthetic window is apparent as a function of precursor selection, ligand concentration and growth time, with a dramatic increase in morphological variations occurring outside the optimum conditions. The aspect ratio control in CuIn$_x$Ga$_{1-x}$S$_2$ nanorods allows for rational design of device scale assemblies, with collective properties tunable at the discrete nanorod level.
3.6 References


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Chapter 4: Remarkable Bending Contours Revealed in CIGSSe Semiconductor Nanocrystals

Status: Publication in Progress

4.1 Abstract

Herein, we report a comprehensive study on the synthesis of CuInGa(S_{1-x}Se_{x})_2 (CIGSSe) nanocrystals, ranging from 0D particles in the cubic phase to 2D nanoplates in the metastable wurtzite phase. A detailed electron microscopy analysis reveals that the 2D nanoplate structures can adopt planar or concave shapes, with the latter being composed of dark fringes on the nanoplate surface that are unequivocally assigned to bending contours on the (0002) plane. This observation is further supported through TEM tilting experiments and displaced aperture dark field images to identify the principal dark bend contours, as well as HRTEM, DFSTEM and SEM images of the lateral sides of the nanoplate. By tilting an individual nanoplate around the goniometer alpha axis, diffraction patterns were collected at 1° increments, thus allowing us to reconstruct the patterns into a three dimensional volume. Furthermore, our investigations reveal precisely the contribution of certain surfactants in the
reaction medium, allowing synthetic control to form nanoparticles, planar nanoplates and novel concave nanoplates of CIGSSe.

**Keywords** nanocrystal, CIGSSe, bending contours, bent nanoplate

### 4.2 Introduction

Colloidal nanocrystals of compound copper chalcogenides in the form of I-III-VI$_2^{1-10}$ and I$_2$-II-IV-VI$_4^{11-18}$ materials are potential building blocks for low-cost, thin film absorber layer materials in photovoltaic devices. Their solution processability combined with low toxicity, high radiation stability and high optical absorption coefficients are optimal for efficient PV but also have allowed application in thermoelectric and photocatalytic devices.$^{19-25}$ Of these quaternary semiconductors, CuInGaSe$_2$ (CIGSe) have shown the highest efficiencies,$^{26-28}$ with Cu$_2$ZnSnS$_4$ (CZTS) also attractive due to the high abundance of the constituent elements.$^{11-15,29}$ The most efficient devices have included a selenization process during sintering to allow for enhanced grain growth, converting the nanocrystals into a bulk thin-film.$^{1,11,12,30,31}$ Typically, this is carried out by saturating the layer in a selenium atmosphere during heating. As there is a known volatility of the metal ions under these conditions, this process can lead to a change in stoichiometry and therefore band gap that it is difficult to control.$^{30,32}$ Additionally, if the starting chalcogen is sulfur, it is also difficult to control the extent of selenium/sulphur interchange which also affects the band gap.$^{11,30,32,33}$ We have recently shown with CZTSSe crystals that we can accurately tune the band gap over a fixed range by directly controlling the sulfur/selenium ratio during the nanocrystal growth.$^{34}$ In this system, we observed that the selenium precursor not only affected the composition but also impacted the
obtainable nanocrystal shapes by passivating growth directions that were preferential in the sulfur rich system.

In this report, we explore the effect of selenium incorporation in colloidal semiconductor copper indium gallium sulfur selenide (CIGSSe) nanocrystals that gives rise to 0D nanoparticles, 2D nanoplates, as well as a novel shape morphology where 2D nanoplates can also form with a concave shape (similar to a contact lens.)

This atypical concave nanoplate manifests as regular diffraction fringes in both TEM and STEM mode (bending contours), originating from curvature on the (0002) plane. These diffraction contrast effects occur from slight angular variations between atomic planes with respect to the direction of the incident electron beam.\(^{35-38}\) This results in atomic planes rocking into and through the Bragg condition. In perfectly crystalline structures, bending contours do not exist as the atomic planes lie parallel to each other with no angular variations existing.\(^{39}\) However, when a crystalline structure is buckled, the planes deviate from their archetypal parallel arrangement to each other, giving rise to small angles between the electron beam and the local atomic planes within the bend area of the crystal.\(^{35,36,39}\) The situation becomes further complicated for a specimen with three-dimensional bending, with both concave and convex surfaces greatly contributing to the diffraction effects and leading to the observation of star-like fringes with a defined crossing points.\(^{39-41}\)

Such bending contours in nanocrystal systems have previously observed in single metal (Ag, Au, Pt) nanocrystals\(^{40-42}\) as well as silver halide microcrystals that most commonly form in the cubic crystal structure.\(^{43}\) They have also been observed in binary nanocrystals systems, specifically in ZnS\(^{44-46}\) and SnO\(_2\) nanoribbons,\(^{47,48}\) SnS\(_2\) nanoplates\(^{49}\) and CdSe nanosaws\(^{50}\) with hexagonal crystal structures. To the best of
our knowledge, this is the first report of colloidal CIGSSe semiconductor nanocrystals crystallizing in the hexagonal wurtzite form, as well as the first observation of bending contours in a complex copper chalcogenide system. A thorough synthetic chemistry study is presented where we can control the ligand chemistry to phase selectively synthesize nanocrystals, with cubic or hexagonal crystal systems, and also the shape topography to give rise to nanocrystals both with and without curvature.
4.3 Experimental Section

Materials

All reagents were used as received without any further purification. Copper (I) iodide (CuI, 99.999%), Indium (III) acetylacetonate (In(acac)₃, 99.99%), Gallium (III) acetylacetonate (Ga(acac)₃, 99.99%), 1-dodecanethiol (1-DDT, >97%), diphenyl diselenide (DPSe, 98%), oleylamine (OLA, 70%, technical grade), trioctylphosphine oxide (TOPO, 99%) and 1-octadecene (ODE, 90%, technical grade) were purchased from Aldrich.

Synthesis of CIGSSe Nanoparticles (R1)

CIGSSe nanoparticles can be synthesized using the following procedure: CuI (0.095g, 0.5mmol), In(acac)₃ (0.1030g, 0.25mmol), Ga(acac)₃ (0.0918g, 0.25mmol) were added to a three-neck round-bottom flask fitted with reflux condenser, rubber septum and temperature finger. 1-Octadecene (5mL) was added to the flask to dissolve the precursors and the flask was evacuated at 50°C for 30mins. The reaction mixture was then heated to 250°C (10°C /min) under an argon atmosphere and at 175°C, a mixture of 1-DDT (1mL), DPSe (0.078g, 0.25mmol) and OLA (1mL) was rapidly injected into the system. After injection, the reaction was allowed to proceed for 25 minutes with continuous stirring. Subsequently, the heating mantle was removed and the reaction vessel was allowed to cool to 80°C. The nanoparticles were washed three times with a 1:2 ratio of toluene to iso-propanol and centrifuged at 4000rpm for 7mins. They were re-dispersed in toluene for further analysis.
Synthesis of CIGSSe Conventional Shaped Nanoplates (R2)

CIGSSe nanocrystals with the conventional nanoplate like morphology can be synthesized using the following protocol. CuI (0.095g, 0.5mmol), In(acac)\textsubscript{3} (0.1030g, 0.25mmol), Ga(acac)\textsubscript{3} (0.0918g, 0.25mmol) were added to a three-neck round-bottom flask. Oleylamine (5mL) was added to the flask to dissolve the precursors and the flask was evacuated at 50°C for 30mins. The reaction mixture was then heated to 250°C under an argon atmosphere. At 175°C, a mixture of 1-DDT (1mL), DPSe (0.078g, 0.25mmol) and OLA (1mL) was rapidly injected into the system. After injection, the reaction was allowed to proceed for 15 minutes with continuous stirring. Subsequently, the heating mantle was removed and the reaction vessel was allowed to cool to 80°C. The nanoplates were then washed three times with a 1:2 ratio of toluene to iso-propanol and centrifuged at 4000rpm for 7mins to yield the dark red centrifuged product.

Synthesis of CIGSSe Nanoplates with Concave-like Morphology (R3)

For a synthesis of CIGSSe nanoplates with concave like morphology, CuI (0.095g, 0.5mmol), In(acac)\textsubscript{3} (0.1030g, 0.25mmol), Ga(acac)\textsubscript{3} (0.0918g, 0.25mmol), TOPO (0.6766g, 1.75mmol) were added to a three-neck round-bottom flask. 1-Octadecene (5mL) was added to the flask to dissolve the precursors. The contents of the flask were evacuated at 50°C for 30mins to eliminate adventitious water and dissolved oxygen. The reaction mixture was then heated to 250°C (10°C /min) under an argon atmosphere and at 175°C, a mixture of 1-DDT (1mL), DPSe (0.078g, 0.25mmol) and OLA (1mL) was rapidly injected into the system. After injection, the reaction was allowed to proceed for 25 minutes with continuous stirring. Subsequently, the heating mantle was removed and the reaction vessel was allowed to cool to 80°C.
**Washing Procedure and Size-Selective Centrifugation:** 2-3mL of anhydrous toluene was added initially to quench the reaction. The nanocrystals were then washed in a 1:2 ratio of toluene to iso-propanol (IPA) and centrifuged at 4000rpm for 7min. After this centrifugation, the supernatant was removed and the precipitated nanocrystals were re-dispersed in toluene and further washed in a 1:2 ratio of toluene to IPA and centrifuged at 4000rpm for 7mins. After this centrifugation, the supernatant was discarded. The precipitate was re-dispersed in toluene and centrifuged at 2000rpm for 1 minute. At this point, size selective centrifugation results in the concave nanoplates precipitating out in the bottom of the vial and the nanoparticles remain behind in solution. The concave nanoplates are redispersed in fresh toluene for subsequent analysis.

**Characterization**

For transmission electron microscopy (TEM) analysis, nanocrystals were precipitated from the reaction mixture and dissolved in toluene. TEM samples were prepared on 200 mesh carbon-coated copper grids (Ted Pella Inc.). TEM and Dark-field scanning transmission electron microscopy (DFSTEM) was conducted by using a 200kV JEOL JEM-2100F filed emission microscope, equipped with a Gatan Ultrascan CCD camera and EDAX Genesis EDS detector. Samples for EDX were prepared on carbon-coated nickel TEM grids. X-ray diffraction (XRD) analysis of drop-cast films of CIGSSe nanocrystals on a glass substrate was conducted using a PANalytical X’Pert PRO MRD instrument with a Cu Kα radiation source (\(\lambda = 1.5418 \ \text{Å}\)) and a 1-D X’celerator strip detector. High resolution scanning electron microscopy (HRSEM) was performed on nanocrystals dropcast onto a Si (111) substrate and the analysis was conducted on a Hitachi SU-70 system operating between 3 and 20kV.
4.4 Results and Discussion

In colloidal nanocrystal syntheses, the nature of solvents plays a key role in influencing the morphology as well as the crystallographic phase of the nanocrystals.\textsuperscript{3,51-53} Figure 1 shows the synthesis result of CIGSSe nanoparticles, specifically $\text{Cu}_{0.5}\text{In}_{0.25}\text{Ga}_{0.25}(\text{S}_{0.25}\text{Se}_{0.25})_2$, that were formed in synthetic route R1 by employing 1-octadecene (1-ODE) as sole solvent. The dark-field scanning transmission electron microscopy (DF-STEM) image in Figure 1(a) shows that the nanoparticles formed with good monodispersity, having an average diameter of $6.5 \pm 2$ nm. The as-synthesized nanoparticles have a slightly irregular faceted shape and deviated from the conventional spherical morphology, as depicted in Figure 1(b). The selected area electron diffraction (SAED) pattern, shown in Figure 1(c), shows three principal diffraction rings in agreement with the (111), (220) and (311) planes constituting the zinc blende phase. X-ray diffraction (XRD) was employed as a bulk analysis technique to ensure compositional homogeneity across the CIGSSe nanoparticle samples. The resultant XRD diffractogram (Figure 1d) shows major reflections at 2$\theta$ values corresponding to the (111), (200), (220) and (311) planes of the cubic structure. The appearance of a minor reflection at 32°2$\theta$, assigned to the (200) plane, further confirms their crystallization in the zinc blende phase as opposed to chalcopyrite.\textsuperscript{3,51} Energy-dispersive X-ray spectroscopy (EDX) was performed on the as-synthesized nanocrystals dropcast onto a carbon coated nickel grid and confirmed that all five elements were present in the sample, with an atomic ratio of Cu : In : Ga : S : Se equal to 0.28 : 0.14 : 0.15 : 0.23 : 0.20, as shown in Figure 1(e).
Figure 1. Characterization of CIGSSe nanoparticles formed in synthetic route R1 by employing 1-ODE as sole solvent. (a) DF-STEM image of as-synthesized CIGSSe nanoparticles. (b) Bright-field (BF) TEM image. (c) Corresponding SAED pattern. (d) XRD pattern of as-synthesized nanoparticles indexed to zinc blende phase of CIGSSe. (e) EDX spectra with measured relative atomic% ratio.

The preference for nanoparticle crystallization in the zinc blende phase, in the presence of 1-ODE solvent, is attributed to the coordinating nature of the solvent. 1-
ODE is classed as a neutral non-coordinating solvent and so, it does not bind to the nanocrystal surface. This results in an increased cationic precursor reactivity and induces the formation of a large number of nuclei in solution because of the weak ligand strength to the metallic monomers.\textsuperscript{51,53} While the coordinating solvent, 1-dodecanethiol (1-DDT), is present in the reaction, serving a dual purpose as sulfur source and stabilizer, its coordinating ability is undermined by the high relative concentration of 1-ODE in the reaction environment. The realization of fast nucleation in this reaction consequently suppresses nanocrystal growth, with the low concentration of monomers available for growth entailing slow growth condition. This condition favours the formation of the thermodynamically stable zinc blende modification.\textsuperscript{51}

Conversely, ligands with high bond strength can induce the formation of the kinetically stable wurtzite phase.\textsuperscript{51,53-56} By replacing 1-ODE with the coordinating solvent, OLA, 2D nanoplates of CIGSSe crystallizing in the wurtzite phase were obtained (synthetic route R2). Figure 2(a) shows a typical overview DF-STEM image of the as-synthesized nanocrystals, with the nanoplates lying side by side to minimize their surface energy on the grid. BF-TEM images (Figure 2(b,c)) clearly depict the formation of relatively narrow size distributions of planar nanoplates, having dimensions of $16 \pm 4.5 \text{ nm}$ in diameter. A HRTEM image of an individual nanoplate was acquired, as shown in Figure 2(d), with the inset FFT showing spots indexed to the (100), (010) and (110) planes of a hexagonal structured crystal lattice.
Figure 2. CIGSSe nanoplates formed in synthetic route R2 by using OLA as sole solvent. (a) Overview DF-STEM image of the as-synthesized nanocrystals. (b) BF-TEM image showing high monodispersity. (c) Higher magnification TEM image of a region in (b), detailing the exact nanocrystal morphology. (d) HRTEM image of an individual planar nanoplate, with inset FFT pattern. (e) Higher magnification image showing clear lattice fringes with a measured d_{100} spacing of 0.33 nm. (f) XRD pattern of the nanoplate sample.
Angular measurements were performed on the inset FFT pattern depicted in Figure 2(d), with the measured angle of 60.5° between the (100) and (010) planes correlating with the theoretical angle measurement (60°) between these planes in a hexagonal crystal system. Clear lattice fringes with measured d-spacing of 0.33nm were further identified in Figure 2(e) and were matched to the (100) plane of the wurtzite structure. Their crystalline structure was also characterized by XRD and shows reflections corresponding to the (100), (002), (101), (102), (110), (103), (112) planes in the wurtzite phase.

The wurtzite phase selectivity in this synthesis is enabled through the use of the coordinating solvent OLA. Similar reports with amines playing a key role in the stabilization of the wurtzite phase have been observed in other copper based chalcogenide nanocrystal systems.6,7,51,54 The high bond strength between the cationic precursors and OLA resulted in a smaller amount of nuclei during the nucleation period as they originated from a reaction between stable precursor-OLA complexes (i.e. CuI-OLA, In(acac)₃-OLA and Ga(acac)₃-OLA complexes ). The low monomer consumption during the nucleation period meant that a high concentration of monomers was available for the growth period,51 providing conditions suitable to stabilize the metastable wurtzite phase and the attainment of flat nanoplates.

Based on this demonstration of phase selectivity, we explored the synthesis further by using a combination of a non-coordinating (1-ODE) and a different coordinating solvent (trioctylphosphine oxide, TOPO), giving rise to mixed or binary solvent system in the flask initially. As hypothetically expected, the synthesis affords the formation of nanoparticles and nanoplates which is rational based on the previous observations that the preference for a non-coordinating solvent (1-ODE) or coordinating solvent (OLA) yielded nanoparticles or nanoplates, respectively.
However, the nanoplates in this particular synthesis (formed with 1-ODE and TOPO combination, synthetic route R3) are significantly different to those formed under the sole use of OLA (synthetic route R2). As two morphologies, nanoplates and nanoparticles, develop simultaneously in the reaction, a size selective centrifugation (SSC) procedure was applied to selectively analyze the concave shaped nanoplates from the nanoparticles.

**Figure 3.** (a) Low resolution TEM image of as-synthesized nanocrystals. (b) Schematic representation of the SSC process. (i) TEM image highlighting the mixture of concave nanoplates and nanoparticles obtained after the reaction. (ii) DF-STEM image of concave nanoplates obtained by centrifugation of the initial vial (marked 1). (iii) DF-STEM image of isolated nanoparticles remaining in the supernatant after vial (marked 1A) has undergone centrifugation. The isolated nanoparticles are transferred to empty vial (marked 1B). Schematic illustrations for each step of the SSC process are depicted in (b, iv-vi).

Figure 3(a) shows an overview, low resolution TEM image of a concentrated solution of as-synthesized nanocrystals, highlighting the attainment of both concave nanoplates and nanoparticles in this reaction (1-ODE and TOPO binary solvent...
mixture, synthetic route R3). The SSC process to selectively separate these morphologies is depicted in Figure 3(b). After the washing steps have been completed after the nanocrystal synthesis, the vial containing the as-synthesized nanocrystals (marked vial 1) contains a mixture of both morphologies, shown in the TEM image in both Figure 3 (a) and Figure 3(b, i), as a result of the high centrifugation speed and long centrifugation time. By implementing a slower centrifugation speed and shorter time to vial 1, the concave nanoplates precipitate out at the bottom of the vial (labelled as 1A), with the supernatant being transferred to an empty vial (marked as 1B). DF-STEM images of the obtained concave nanoplates and isolated nanoparticles are shown in Figure (3b, ii) and Figure (3b, iii) respectively. A schematic illustration of the morphology separated from each step of the SSC process is depicted in Figure 3 (b, iv-vi).

From the low resolution TEM image in Figure 4 (a), extensive regions of concave nanoplates are observed, with each nanoplate displaying distinctive star like fringes on their surface. Furthermore, each nanoplate possesses a well defined crossing point, as shown in Figure 4(b), in which the dark bands merge toward the central region of the nanoplate which corresponds to the [002] zone axis of the crystal. These dark bands are diffraction contrast effects and arise from angular variations between atomic planes with respect to the incident electron beam.\textsuperscript{35,39,57} At these locations, the electrons are strongly diffracted and most of these scattered electrons are absorbed at the TEM objective aperture,\textsuperscript{57} thus giving rise to dark bands in the resultant TEM image (Figure 4b).
Figure 4. (a) Low resolution TEM image of a collection of concave nanoplates. (b) Higher magnification TEM image of three individual concave nanoplates. (c) Dark field (DF) STEM image showing the reverse contrast in DF mode. (d) Higher resolution DF-STEM with clearly defined crossing points on each of the nanoplates. (e) SAED pattern identifying the seven distinctive planes in a hexagonal crystal lattice. (f) XRD analysis of concave nanoplates.
The dark bands observed in BF-TEM occur as bright bands in DF-STEM mode, as depicted in Figure 4(c,d). In Figure 4(d), the higher resolution DF-STEM image shows three principal bright bands from separate edges of the nanoplate, with three weaker intensity bands also evident in between these main bright bands. The SAED pattern, shown in Figure 4(e), displays seven distinctive rings and indexed to the (100), (002), (101), (102), (110), (103), (112) planes in the hexagonal crystal lattice. Furthermore, the hexagon structure of the nanoplates resulted in an increased intensity being observed in the SAED pattern for the (100) and (110) planes.

XRD analysis was also employed to confirm the crystallographic structure of the concave nanoplates. Reflections corresponding to the wurtzite phase are evident in the pattern, as shown in Figure 4(f). However, upon closer inspection, an increased intensity of the (002), (100) and (112) wurtzite derived planes is noted. This is due to peak overlap with the (111), (220) and (311) cubic planes and this observation, coupled with the appearance of a peak at 32°2θ (characteristic of the (200) plane in a cubic lattice), reveals that there is also a contribution from a zinc blende phase in the XRD pattern. This contribution from the zinc blende phase is attributed to the nanoparticles, which form in parallel in the reaction and are difficult to fully and cleanly separate from the concave nanoplates despite repeated washing procedures. The presence of these additional peak contributions in the XRD also entails the possibility of polytypism in these nanocrystals (i.e. the co-existence of two crystal phases in separate domains of the same crystal). This possibility is not overlooked, with subsequent analysis verifying the observation that the concave nanoplates are indeed, single crystalline, wurtzite derived structures.
A series of elemental line scans specifically measuring across the high contrast bands and across the central crossing point (or what appears like the apex of the nanoplate) were performed as shown in Figure 5. Consistent signals were maintained throughout line scans, thus confirming that no compositionally inhomogeneities existed in the concave nanoplates.

![Figure 5](image)

**Figure 5.** EDX Elemental line scan analysis (a-c) DFSTEM images of a single bent nanoplate, with EDX elemental line scans conducted through regions of the nanoplate to ensure no compositional inhomogenieties arise across the nanoplate.

The following sections are dedicated to the detailed electron microscopy investigation on the crystalline structure of the concave nanoplates, as well understanding the origin of the high contrast bands on each nanoplate. Figure 6 shows the resultant HRTEM imaging of an individual nanoplate. In Figure 6(a), three principal dark contrast bands are evident across the nanoplates that merge toward the central region of the nanoplate. The discontinuity of dark bands (at the regions
identified by the arrows in Figure 6(a)) reveals that the surface of the nanoplates is not entirely flat and appears buckled, consisting of a surface step parallel to the surface. Similar discontinuity in the bend contours has been previously observed for single metal nanoplates.\textsuperscript{40} This is particularly evident in Figure 6(a) at the opposing regions of the nanoplates (marked by arrows) and gives rise to the concave-like morphology of each nanoplate. Figure 6(b) shows HRTEM imaging of the central section, marked in (a), and is divided into quadrants for higher magnification imaging. Figure 6(c-f) shows the corresponding high resolution images of each quadrant, revealing the highly crystalline nature across each of the dark contrast bands.
Figure 6. HRTEM analysis of an individual concave nanplate. (a) TEM image of a single nanoplate, with central region marked for HRTEM analysis. (b) Magnified image of the highlighted region in (a). (c-f) Higher resolution images of each quadrant marked in (b) showing the highly crystalline nature of the dark contrast bands on the concave nanoplates.

This atypical concave structure manifests as regular diffraction fringes in both TEM (Figure 6) and STEM mode (as previously observed in Figure 5). Such a contrast
variation is referred to as “bending contours”\textsuperscript{35} and in this particular system, the contours originate from curvature on the (0002) plane of the wurtzite structure. Using dark field imaging, it was possible to isolate images particular to each of the diffracted beams, with the bending contours apparent as bright fringes in DF-STEM mode. An individual concave nanoplate (shown in Figure 7a) was selected for this analysis. The splitting of the contours as they diverge from the central crossing point in Figure 7 (a) is easily identifiable and consistent for each nanocrystal due to the fulfilment of Bragg’s law in a thin area of the crystal. By displacing the objective aperture and selectively allowing transmission of the corresponding diffraction spots (marked in Figure 7 (b)), the bending contours could be individually imaged as shown in Figure 7 (c) – (h) and correspond directly to those areas where Bragg’s law is exactly fulfilled.

\textbf{Figure 7.} Dark field analysis of the bending contours. (a) Bright field TEM image of a single nanoplate. (b) Corresponding single crystal diffraction pattern.(c-h) Dark field analysis of each contour by displacing the objective aperture.
The higher contrast bending contours (spots marked 1-3) originate from the \{11-20\} family of planes that constitute the outer hexagon of the diffraction pattern in Figure 7(b). The weaker/lower contrast contours on the underside of the plate result from the \{10-10\} family of planes, constituting the inner hexagon (spots marked 4-6) of the diffraction pattern. The acquired image of each bending contour can be additionally confirmed by drawing a line perpendicular from the marked spot (as identified in Figure 7(b)) to the central spot constituting the electron beam.

Additionally, bending contours can be unequivocally identified in TEM tilting experiments\(^{35,37}\) as the particular positions of the bending contours are observed to move upon tilting the sample. Figure 8 shows a schematic representation outlining the origin of bending contours for a nanoplate symmetrically bent either side of the Bragg condition before and after the tilting experiment. Figure 8(a) shows that at 0° tilt angle (i.e. before tilting), three distinctive bend contours are evident in the nanoplate as a result of the hkl planes exactly fulfilling the Bragg condition, as depicted in Figure 8(c). Tilting the sample (Figure 8b) in either the positive or negative direction causes the bending contours to move as they are not fixed to any particular position in the specimen.\(^{35,37}\) Thus, the Bragg condition is satisfied at some different location within the crystal and causes the bend contour to shift to a new position in the image,\(^{35}\) as depicted in Figure 8d.
Figure 8. Scheme showing the origin of bend contours in bright field mode for a specimen symmetrically bent either side of the Bragg condition (a) before tilting (b) after tilting. (c) Schematic illustration of the corresponding TEM image at 0° (no tilt), with (d) showing the projected image after tilting.

To estimate the angles of crystal curvature, we conducted a TEM tilt series in bright field mode by tilting an individual concave nanoplate in the range of $-10^\circ < \theta < 10^\circ$. From the top down view at 0° tilt (Figure 9a), the contours are cleanly split to form a star like pattern and this indicates that a net concave curvature exists around this central crossing point. By tilting the nanoplate in small increments (as depicted in Figure 9b), the crossing point of the bending contours is observed to move off the central region of the nanoplate.
Figure 9. Tilt Series of a 110nm sized bent nanoplate. (a-d) shows the corresponding TEM images of tilts at 0, 3, 5, 10°, respectively. (e-h) shows the results of tilting in the negative direction at angles of 0, -3, -5, -10°, respectively.

Further increases in the tilt angle to +5.0° (Figure 9c) and +10.0° (Figure 9d) result in gradual rotations of the bending contours from the centre of the nanoplate and towards the nanoplate edge. In Figure 9(d), the crossing point of the bending contours reaches the edge at a tilt angle of +10.0°, inferring that an angle of net curvature of ~10.0° exists in the nanoplate. Figure 9 (e-h) shows the corresponding TEM images obtained by tilting the nanoplate at the same angular increments to directly correlate the effect of tilting in the positive and negative directions, with bending contours not being fixed to any point in the specimen.

Further evidence highlighting the concave structure is provided in Figure 10 by SEM, DFSTEM and HRTEM characterization of the lateral sides of the nanoplates. From the top down SEM image in Figure 10(a), the nanoplates are observed to adopt two orientations, either lying parallel or perpendicular to the underlying substrate. By zooming in on the marked region in Figure 10(a), it becomes apparent that the
nanoplates are not entirely flat and appear to be buckled with a slight degree of curvature (Figure 10b).

**Figure 10.** Side by side stacks of nanoplates. (a) SEM image of a region of nanoplates. (b) Magnified image of the highlighted region in (a) in which a concave nanoplate can be observed. (c) DF-STEM image showing collections of nanoplates stacked side by side to one another (d) BF-TEM where bending to various extents can be clearly observed. (e) Higher magnification TEM image, with a calculated bend of 7° on the surface of the nanoplate. (f) HRTEM image of the side view, with inset FFT.
For TEM imaging, side by side stacks of the nanoplates were imaged by dropcasting a solution of the sample onto holey carbon TEM grids, where the nanoplates were found to deposit preferentially in a perpendicular orientation to the support film of the grid. Figure 10 (c) shows a DF-STEM image revealing collections of nanoplates stacked side by side to one another. The thickness of the nanoplate can be directly measured from this side view and a thickness of ~8 nm is apparent. Bending to various extents can be clearly observed in the BF-TEM image in Figure 10 (d), as indicated by the marked arrows in the image. Based on the calculation from image Figure 10 (e), the angle of net curvature on this particular nanoplate is calculated to be ~7°. This shows a good agreement with the degree of bending observed in the TEM tilting series. A HRTEM image of the lateral side of the nanoplates is shown in Figure 10 (f), with inset FFT showing strong reflections associated with the (002) planes as a result of the perpendicular placement of nanoplates on the grid.

In terms of understanding the synthetic chemistry in the reaction, the nature of solvents has been demonstrated to play a key role in the resultant morphology and crystal phase in this synthesis. By choosing 1-ODE as solvent, 0D nanoparticles in the zinc blende phase were observed. Replacement of 1-ODE with the coordinating solvent, OLA, gave rise to planar 2D nanoplates and provided conditions suitable for the formation of the metastable wurtzite phase. However, the implementation of a mixed or binary solvent mixture, comprised of 1-ODE and the coordinating ligand TOPO, resulted in the formation of 0D nanoparticles and novel 2D concave nanoplates. To fully elucidate the mechanism of formation of the concave morphology, TOPO was selected as sole solvent in the reaction while all other reaction parameters were kept constant. Interestingly, the reactions performed with
TOPO as sole solvent resulted in the formation of a variety of different sized 2D nanoplates, each possessing a net concave curvature as shown in Figure 11.

Figure 11. CIGSSe nanoplates formed by selecting TOPO as the sole solvent. (a) Low resolution TEM image of agglomerated nanoplates. (b) Higher magnification TEM image of a collection of nanoplates, with two nanoplates identified for further analysis. (c,d) Higher magnification images of the identified nanoplates where bending contours are evident on the nanoplate surface.

Figure 11 (a) shows a low resolution TEM image of the as-synthesized nanoplates, in which the nanoplates tend to cluster together in regions on the TEM grid. A higher magnification image of a collection of nanoplates reveals that each nanoplate possesses bending contours, similar to those observed earlier in this report. However, the nanoplates in this reaction possess greater size fluctuations, some up to 250 nm in diameter, as shown in Figure 11 (b) and this is attributed to the different binding energies between the solvents in the reaction. Higher magnification images of the
identified nanoplates (marked in Figure 11 (b)) are depicted in Figure 11(c,d). The observation of bending contours in this particular reaction infers that TOPO is inherently responsible for creating the curvature on the nanoplates and causes strain in the internal crystal structure.

Further analysis of an individual concave nanoplate was conducted to detect the presence of defects and strain centres in the crystal structure. One example of such a defect is the stacking fault where atomic planes within the crystal structure are abruptly displaced by a fraction of the interatomic spacing. Figure 12 (a) shows a BF-TEM image of an individual nanoplate, with the central merging crossing point lying on the underside of the nanoplate. The corresponding SAED pattern is shown in Figure 12(b) in which weak streaked reflections can be observed. By displacing the objective aperture and selectively allowing transmission of the marked reflections (marked in Figure 12 (b)), dark field (DF) images were acquired as shown in Figure 12(c) and (d). These marked spots correspond to reflections from the \( \frac{1}{2}\{10-10\} \) and \( \frac{1}{2}\{11-20\} \) family of planes. From the DF image in Figure 12(c), non-regular stacking faults buried in the internal crystal structure are apparent in the nanoplate that cannot be observed in the standard BF-TEM images. Stacking faults in a different region of the nanoplate are observed in Figure 12(d).
**Figure 12.** (a) TEM image of an individual concave nanoplate. (b) Corresponding SAED pattern from the nanoplate, with streaking of spots observed in the pattern. (c) Dark field image of spot (marked DF1). (d) Dark field image of spot (marked DF2).

Based on the streaks observed in the diffraction pattern, we conducted a tilt series by tilting an individual concave nanoplate through 60° around the goniometer alpha axis and collecting diffraction patterns in 1° increments. A total of 61 diffraction patterns were obtained from this tilt series. These patterns were then background subtracted, shifted onto a common axis and reconstructed into a three dimensional volume using a series of matlab scripts. From the reconstructed volume, diffraction spots corresponding to a hexagonal crystal are visualized when the pattern is viewed along two dimensions as shown in Figure 13(a). However, upon viewing the pattern in the third dimension, the reflections are observed to stack parallel to one another, as is evident in Figure 13(b). This can be explained by stacking faults in the crystal and
these faults cause small changes in the unit cell length in the third unit cell axis and thus, shift the reflection position in reciprocal space.

Figure 13. Reconstruction of diffraction patterns into a three dimensional volume. (a) Diffraction pattern viewed along two dimensions, with the reflections inferring perfect hexagonal ordering in this view. (b) Diffraction pattern viewed along the third dimension. (c) Higher magnification view of the image in (b) showing discrete reflections.

At lower angles close to the central spot, the reflections tend to be larger and appear like continuous rods of density. However, at higher angles, where sharper reflections are typically observed, the reflections are observed to be discrete and non-overlapping (Figure 13c). This infers that clear changes exist in the unit cell length. Further work is required in order to fully verify the structure and stacking fault relationship, most probably through superspace and Aperiodic modelling of the structure and is currently beyond the scope of this work.
4.5 Conclusion

We have developed a facile, low-cost method to synthesize quinary CIGSSe nanocrystals in the form of 0D nanoparticles and 2D nanoplates, crystallizing in the zinc blende and wurtzite phase, respectively, through manipulation of solvents used in the reaction. Furthermore, we observed the formation of 2D nanoplates with a net concave curvature on the surface of each nanoplate. This atypical concave nanoplate manifests as regular diffraction fringes in both TEM and DF-STEM mode, which originate from curvature on the (0002) plane. Based on TEM tilting experiments and displaced aperture dark field images, the dark fringes on the nanoplates were unequivocally assigned to bending contours and revealed that the nanoplates were symmetrically bent either side of the central crossing point. HRTEM, DFSTEM and SEM images of the lateral sides of the nanoplate also confirmed the existence of a net concave curvature on the nanoplate surface. Our experiments revealed that TOPO induces the formation of buckled nanoplates and its presence causes dramatic changes in the internal crystal structure which lead to the creation of non-regular stacking faults buried in the nanoplates. By reconstructing diffraction patterns of the crystal in a three dimensional volume, these stacking faults were observed to cause small changes in the unit cell length, with the reflections appearing as discrete, non-overlapping entities that were shifted in reciprocal space.
4.6 References


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Chapter 5: Shape Controlled Colloidal Synthesis of 

Cu$_2$ZnSnS$_4$ (CZTS) Semiconductor Nanocrystals

Status: Publication in Progress

5.1 Abstract

This chapter describes a facile and highly efficient colloidal route to systemically tailor the morphologies of semiconductor nanocrystals, composed of the Cu$_2$ZnSnS$_4$ (CZTS) material combination. Through exquisite control of reaction chemistry, a variety of anisotropic CZTS morphologies were formed, ranging from nanorods and ellipsoids to atypical capsule-, tadpole- and P-shaped nanocrystals, with each shape dictated by the concentration of amine solvent in the reaction. Furthermore, judicious selection of the metal precursors allowed for the attainment of distinctive polytypic nanocrystals, composed of zinc blende and wurtzite derived crystal structures. These polytypic nanocrystals, having engineered structural defects in separate domains of the same crystal, have the potential to induce changes in the optical and electronic
properties thus, providing new possibilities for photovoltaic and optoelectronic devices.

**Keywords:** CZTS, shape control, polytypic, semiconductor nanocrystals

### 5.2 Introduction

Developments in colloidal nanocrystal synthesis have allowed for a paradigm shift in materials design, where the physical properties (i.e. absorption, emission, conductivity) and structural properties (i.e. size, morphology, crystal phase) can be optimized by precisely controlling the synthetic conditions and chemical environment.\(^1\)-\(^5\) Solution based synthetic routes to fabricate a range of copper-based semiconductors, namely CuInS\(_2\) (CIS), CuInSe\(_2\) (CISe), CuInGaS\(_2\) (CIGS) and Cu\(_2\)ZnSnS\(_4\) (CZTS), have recently attracted a great deal of attention.\(^6\)-\(^18\) Of these, CZTS has become a research hotspot and has captured the attention of the broad scientific community due to its use of highly earth abundant and inexpensive elements.\(^19\)-\(^26\) While considerable advances in the synthesis and shape control of wurtzite structured CIS,\(^8,27\)-\(^33\) CISe\(^11\),\(^34\) and CIGS\(^12,14\) nanocrystals have been demonstrated, a similar degree of progress in forming precise shape morphologies in the CZTS system has remained elusive. Our group previously developed the first optimized colloidal protocol to form highly monodisperse CZTS nanocrystals in the nanorod geometry by adopting a hot injection approach.\(^23\) Subsequently, CZTS nanorods have also been attained by adopting non-injection (heating up) approaches.\(^35\)-\(^37\) Recently, Zhang et al demonstrated the ability to tailor the morphology of CZTS nanocrystals (in the form of sphere, rod and rice-like shapes) and control the crystal phase (in the form of kesterite and wurtzite structures) by tuning the nature of solvents and sulfur source, respectively.\(^38\)
The co-existence of two crystal phases in a single nanocrystal (referred to as polytypism) is also possible in nanocrystals and is a phenomenon that has already been widely observed in tetrahedrally coordinated semiconductors, most notably Si,\textsuperscript{39,40} III-V\textsuperscript{41-43} and II-VI\textsuperscript{44,45} nanostructures, as a result of their large atom stacking freedom. In colloidal based routes, tetrapod\textsuperscript{44-46} and octapod\textsuperscript{47} nanocrystals with branched configurations have been realized and are the most prominent examples of controlled polytypism engineering in single nanostructures to date. Zinc blende (ZB) and wurtzite (WZ) modifications are the two most commonly observed polymorphs and possess relatively low energy differentials, thus switching between these polymorphs is possible kinetically through temperature modulation or by selective ligand attachment.\textsuperscript{44} Previous reports of Cu-based polytypic nanocrystals have been observed, particularly in relation to Cu\textsubscript{2}ZnSn(SSe)\textsubscript{4} (CZTSSe)\textsuperscript{48} and Cu\textsubscript{2}CdSn(SSe)\textsubscript{4} (CCTSSe)\textsuperscript{49} nanocrystals where linearly arranged polytypic nanocrystals with rugby ball-like and bullet-like morphologies were formed, respectively. More recently, Wang and co-workers synthesized Cu\textsubscript{2}SnSe\textsubscript{3} (CTSe) tetrapods\textsuperscript{46} and linear polytypic heterostructures\textsuperscript{50} while the work of Zamani et al and Cabot et al reported the formation of Cu\textsubscript{2}Cd\textsubscript{x}SnSe\textsubscript{y} (CCTe) polypods\textsuperscript{51} and Cu\textsubscript{2}GeSe\textsubscript{3} (CGSe) nanoparticles,\textsuperscript{52} respectively.

In this work, we report a facile and highly efficient route for producing a diverse range of wurtzite structured CZTS morphologies. By solely varying the concentration of amine solvent in the reaction, we observe the formation of nanorods and ellipsoids, as well as atypical capsule-shaped, tadpole-shaped and P-shaped nanocrystals. The inherent reactivity of metal precursors, specifically the copper and zinc precursor, was also revealed to significantly influence the reaction environment, entailing the evolution of multi-phase polytypic CZTS nanocrystals with wurtzite
and zinc blende domains. Two distinctive CZTS morphologies, namely acorn-shaped and pencil-shaped nanocrystals, were obtained in this system and to the best of our knowledge, this represents the first observation of polytypic nanocrystals constituting the CZTS material combination. Through HRTEM imaging, XRD and FFT analysis, the polytypic nanocrystals were observed to be comprised of well-defined zinc blende and wurtzite crystal frameworks in separate domains of the same crystal, with high resolution measurements allowing clear visualization of their differing atom stacking arrangements.
5.3 Experimental Section

Materials

All reagents were used as received without any further purification. Copper(II) acetylacetonate (Cu(acac)$_2$; >99.99%), Copper(I)chloride (CuCl $>$99.99%), Zinc acetate (Zn(Ac)$_2$, >99.99%), Zinc (II) chloride (ZnCl$_2$$>$99.99%), Tin(IV) acetate (Sn(Ac)$_4$, >99.99%), Trioctylphosphine oxide (TOPO, 99%), 1-dodecanethiol (1-DDT, 98%), tert-dodecylmercaptan (t-DDT, 98.5%, mixture of isomers), 1-Octadecene (ODE, 90%, technical grade) and Oleylamine (OLA, technical grade, 70%) were purchased from Aldrich.

Synthesis of CZTS Nanorods with Bullet-like morphology (R$_1$)

In a typical synthesis of CZTS nanorods, Cu(acac)$_2$ (0.6545g, 2.5mmol), Zn(Ac)$_2$ (0.2292g, 1.25 mmol), Sn(Ac)$_4$ (0.4435g, 1.25mmol), TOPO (3.383g, 8.75 mmol) and 1-octadecene (25mL) were added to a three-neck, round-bottom flask, fitted with reflux condenser, rubber septum and temperature finger. The contents of the flask were evacuated at 50°C for 30mins to eliminate adventitious water and dissolved oxygen. The reaction mixture was then heated to 250°C (30°C /min) under an argon atmosphere and at 155°C, a 5mL thiol mixture (comprised of 4.375mL t-DDT and 0.625mL 1-DDT) was rapidly injected into the system. After injection, the reaction was allowed to proceed for 30minutes with continuous stirring. Subsequently, the heating mantle was removed and the reaction vessel was allowed to cool to 80°C.

Washing Procedure: 2-3mL of toluene was added initially to quench the reaction. The nanocrystals were then washed twice with a 1:2 ratio of toluene to iso-propanol
(IPA) and centrifuged at 4000rpm for 7mins to yield the dark red centrifuged product. After each centrifugation, the supernatant was removed and the precipitated nanorods were re-dispersed in toluene for further characterization.

Synthesis of CZTS Nanocrystals with different morphologies (R₁- R₅)

A diverse range of CZTS morphologies were formed through variation of the 1-octadecene : oleylamine (ODE:OLA) solvent ratio, as outlined in table 1 below. All other synthetic parameters were kept constant, as per CZTS nanorod route (R₁).

<table>
<thead>
<tr>
<th>Synthesis Route #</th>
<th>ODE: OLA Solvent ratio (mL)</th>
<th>Resultant Morphology</th>
<th>Shape Illustration</th>
</tr>
</thead>
<tbody>
<tr>
<td>R₁</td>
<td>25.0 : 0</td>
<td>Nanorod</td>
<td><img src="image" alt="Nanorod Shape" /></td>
</tr>
<tr>
<td>R₂</td>
<td>22.5 : 2.5</td>
<td>Ellipsoid-shape</td>
<td><img src="image" alt="Ellipsoid Shape" /></td>
</tr>
<tr>
<td>R₃</td>
<td>17.5 : 7.5</td>
<td>Tadpole-shape</td>
<td><img src="image" alt="Tadpole Shape" /></td>
</tr>
<tr>
<td>R₄</td>
<td>7.5 : 17.5</td>
<td>Capsule-shape</td>
<td><img src="image" alt="Capsule Shape" /></td>
</tr>
<tr>
<td>R₅</td>
<td>0 : 25.0</td>
<td>P-shape</td>
<td><img src="image" alt="P Shape" /></td>
</tr>
</tbody>
</table>

Table 1. Details of Synthetic Routes (R₁-R₅) identifying the ODE: OLA solvent ratio added to the flask in the initial step.
Synthesis of Polytypic CZTS Nanocrystals with Acorn-like morphology (R₆)

Polytypic CZTS nanocrystals with an acorn-like morphology were synthesized using the following protocol. CuCl (0.099g, 1mmol), Zn(Ac)₂ (0.0917g, 0.5 mmol), Sn(Ac)₄ (0.1774g, 0.5mmol), TOPO (1.3532g ,8.75 mmol) and oleylamine (25mL) were added to a three-neck round-bottom flask. The flask was evacuated at 50°C for 30mins and was then subsequently heated to 250°C (30°C /min) under an argon atmosphere. When the temperature reached 155°C, a 2mL thiol mixture (comprised of 1.75mL t-DDT and 0.25mL 1-DDT) was rapidly injected into the system. After injection, the reaction was allowed to proceed for 30minutes with continuous stirring. Subsequently, the heating mantle was removed and the reaction vessel was allowed to cool to 80°C. A similar washing procedure, as outlined in R₁, was conducted.

Synthesis of Polytypic CZTS Nanocrystals with Pencil-like morphology (R₇)

Polytypic CZTS nanocrystals with a pencil-like morphology were synthesized using an identical protocol to that as outlined in route R₆ except with the following exception: Zn(Ac)₂ precursor is replaced with Zn(Cl)₂ (0.068g, 0.5mmol).

Characterization

The morphology of the CZTS nanocrystals was characterized by transmission electron microscopy (TEM) and angular dark-field scanning transmission electron microscopy (DFSTEM) using a 200 kV JEOL JEM-2011F, equipped with a Gatan Ultrascan CCD camera and EDAX Genesis EDS detector. TEM samples were prepared by drop-casting the precipitated nanocrystals in toluene onto 200 mesh carbon-coated copper grids (Ted Pella Inc.). For EDX analysis, carbon-coated nickel
TEM grids were used. X-ray diffraction (XRD) analysis of drop-cast films of CZTS nanocrystals on a glass substrate was conducted using a PANalytical X’Pert PRO MRD instrument with a Cu Kα radiation source (λ = 1.5418 Å) and a 1-D X’celerator strip detector.
5.4 Results and Discussion

Stabilization of the metastable wurtzite phase in semiconductor nanocrystals is highly attractive from both a stoichiometric and shape control perspective. Firstly, the random cation distribution (of Zn/Sn ions) in the wurtzite phase offers flexibility for stoichiometry control which is advantageous for fabrication of photovoltaics since it provides the ability to tune the Fermi energy over a wide range.\textsuperscript{8,30,53} Secondly, it allows for the formation of anisotropic nanocrystals in which elongation occurs along the unique c-axis of the hexagonal crystal lattice,\textsuperscript{3-5,8,14} with the elongated dimension serving to enhance total absorption and directional charge transfer, in contrast to the nanorod diameter which dictates the material’s band gap.

Figure 1 shows the formation of highly monodisperse, thiol-capped CZTS nanocrystals, synthesized as per Singh et al’s report\textsuperscript{23} (synthetic route R1), in which 1-octadecene (ODE) was employed as sole solvent.

The as-synthesized nanorods possess high degrees of shape and size control, as shown in Figure 1(a), with the nanorods having an average length of 38 ± 2 nm and diameter of 11 ± 0.6 nm. HRTEM analysis of an individual nanorod (Figure 1b) reveals that the nanorods are highly crystalline in nature, with a predominant bullet shape on the terminating end facets. The measured angle of 90.5° (measured from inset FFT pattern, Figure 1b) correlates with the theoretical angle (90°) between the (002) and (010) planes in a hexagonal crystal system. From the magnified view in Figure 1(c), a d-spacing of 0.32 nm was measured in the nanorod and shows good agreement with the (002) plane of the wurtzite structure.
Figure 1. CZTS bullet-shaped nanorods formed in synthetic route R1. (a) Bright field (BF) TEM image of as-synthesized nanorods lying parallel to the TEM grid. (b) HRTEM image of an individual nanorod, with inset FFT pattern. (c) HRTEM image highlighting nanorod elongation in the [002] growth direction. (d) Top down TEM image of CZTS nanorod assembly in which the nanorods are aligned orthogonal to the TEM grid. (e) HRTEM image of a magnified area showing a close packed CZTS nanorod monolayer. (f) HRTEM of a single CZTS nanorod.

Interestingly, the as-synthesized nanorods adopt two distinctive orientations following sample preparation on the TEM grid, either lying parallel or perpendicular orientations to the underlying grid. Figure 1(d) shows a top down TEM view of the spontaneous organisation of the nanorods into vertically aligned clusters, after drying of the droplet on the TEM grid. Their spontaneous self-assembly is primarily enabled by the high uniformity of the as-synthesized nanocrystals coupled with the strong coordinating ability of thiols (1-DDT and t-DDT) to the metal rich cations on the
nanocrystal surface.\textsuperscript{54} HRTEM imaging of a magnified area (Figure 1e) reveals the perfect, close-packed hexagonal nanorod ordering, with the top down view of an individual nanorod (Figure 1f) showing a measured $d_{002}$ spacing of 0.32\text{nm}. Furthermore, the top down image allows for additional characterization of the nanorod structure and indicates that the sidewalls of the nanorod are formed by the \{100\} family of lattice planes of the hexagonal crystal structure, specifically the (100), (010), (1-10) planes.\textsuperscript{23,26}

The observation of the wurtzite structure in this system was additionally supported by XRD analysis, as shown in Figure 2. Seven principal reflections are apparent in the pattern and are indexed to the (100), (002), (101), (102), (110), (103), (112) planes constituting the hexagonal system of CZTS.

![XRD pattern of the obtained CZTS bullet-shaped nanorods.](image)

**Figure 2.** XRD pattern of the obtained CZTS bullet-shaped nanorods.

While CZTS nanorods are formed by employing ODE as sole solvent, ellipsoid shaped nanocrystals can be obtained using a mixed solvent system composed of 22.5mL ODE and 2.5mL OLA. The presence of a small quantity of OLA in the flask induces significant changes in the chemical environment and the resultant
nanocrystals, entailing the evolution of ellipsoid shaped nanocrystals as shown in Figure 3. From the low resolution BF-TEM images in Figure 3(a,b), relatively narrow size distributions of ellipsoid shaped nanocrystals were formed, having dimensions of 18nm ± 1.5 nm in length and 12 ± 2.5 nm in diameter. HRTEM imaging of an individual nanocrystal, as shown in Figure 3(c,d), provides further clarification of the exact nanocrystal morphology.

Figure 3. CZTS ellipsoid-shaped nanocrystals formed in synthetic route R2. (a,b) Typical BF-TEM images of the as-synthesized nanocrystals. (c) HRTEM image of an individual ellipsoid nanocrystal. (d) Higher resolution TEM image of the tip of this particular ellipsoid, with a measured $d_{200}$ interplanar spacing of 0.32 nm.
The increased diameter in the ellipsoid morphology, as opposed to nanorods, infers that OLA preferentially binds to the (002) nanocrystal facet in this system. While OLA causes clear changes in the nanocrystal shape, its effects are solely limited to morphological control and its presence does not exert phase control in this reaction, evidenced by the attainment of wurtzite structure in theses nanocrystals. The highly crystalline nature of this structure is depicted in Figure 3(d), where the perfect atom stacking arrangement (AB/AB for the wurtzite system) is visualized along the tip of the ellipsoid. The measured d-spacing of 0.32 nm in this nanocrystal also matches well with the (002) plane of the wurtzite phase.

Further increases in the concentration of OLA in the solvent mix (17.5mL ODE : 7.5mLOLA, route R3) significantly perturbed the reaction environment and lead to the formation of tadpole-shaped nanocrystals, as shown in Figure 4(a). These unusual, tadpole-shaped nanocrystals were approximately 32.5 ± 4 nm in length and 25 ±2.1 nm in diameter across the top section of the tadpole. While the overview TEM image (Figure 4a) gives the impression that these nanocrystals are highly monodisperse, closer inspection reveals the formation of two slight morphological variations of the tadpole-shape (Figure 4b) as a result of capturing the nanocrystals at different stages in their growth.
Figure 4. CZTS tadpole-shaped nanocrystals formed in synthetic route R3. (a) Overview TEM image of the as-synthesized nanocrystals. (b) HRTEM image illustrating the slight deviations in the nanocrystal shape. (c) HRTEM image of an individual tadpole-shaped nanocrystal, with inset FFT pattern. (d) Higher resolution TEM image of the highlighted region marked in (c) showing clear lattice fringes with a measured $d_{100}$ spacing of 0.354 nm. (e) HRTEM image of a slightly modified, tadpole-shaped nanocrystal, with inset FFT pattern. (f) Higher resolution TEM image of the identified section in (e).
HRTEM analysis was conducted on both shape variations to evaluate the precise atomic stacking arrangements constituting these respective shapes. Figure 4(c) shows the HRTEM image of one such shape, with inset FFT pattern indexed to the (100), (010) and (110) planes of the wurtzite structure. Specific angular measurements were performed on the FFT pattern depicted in Figure 4(c), with the measured angle of 60.9° between the (100) and (010) planes correlating extremely well with the theoretical angle measurement (60°) between these planes in a hexagonal crystal system. Clear lattice fringes with measured d-spacing of 0.354 nm were further identified in Figure 4(d) and were matched to the (100) plane of the wurtzite structure, providing further evidence that OLA binds to the (002) facets and restricts growth along the (002) face.

A second, slightly modified, tadpole-shaped nanocrystal, shown in Figure 4(e), was also formed in this synthesis due to the different growth rates of the various faces within this kinetically controlled regime. Strong reflections indexed to the (100), (010) and (110) planes of the wurtzite structure are apparent in the FFT pattern, as depicted in the inset in Figure 4(e). Furthermore, high resolution analysis of the indicated region in Figure 4(e) shows the intricate atom stacking arrangements along the (100) plane.

Tadpole shaped nanostructures have also been previously reported in different copper chalcogenide systems, specifically in CuGaS$_2$ (CGS)\textsuperscript{14,55} and CuInGaS$_2$ (CIGS) nanocrystals.\textsuperscript{12,14} Based on our observations, the increased proportion of amine in the ODE : OLA solvent combination raises the energy of the (002) face and leads to the exposure of the lower-energy crystal faces. This results in growth progressing along the (100) faces (as evidenced by the HRTEM images in both Figure 5(d) and (f)) to minimize the surface area of the high energy (002) face.
Similar phenomena have been observed previously in the II-VI nanocrystals\textsuperscript{4,45} and more recently in the I-III-VI\textsubscript{2} nanocrystal system when the system was perturbed by excess OLA or hexadecylamine (HDA).\textsuperscript{12}

Further modulation in the OLA concentration in the solvent mixture (7.5mL ODE : 17.5mLOLA, route R4) lead to the formation of highly faceted and capsule-shaped nanocrystals, as shown in Figure 5. DF-STEM measurements (Figure 5a,b) revealed that the nanocrystals possess tight degrees of shape control and are relatively monodisperse.
**Figure 5.** CZTS capsule-shaped nanocrystals formed in synthetic route R₄. (a,b) DF-STEM images and (c,d) BF-TEM images of as-synthesized CZTS nanocrystals. (e) HRTEM image of an individual capsule-shaped nanocrystal. (f) Higher magnification TEM image of the highlighted region marked in (e) showing clear lattice fringes with a measured $d_{100}$ spacing of 0.356 nm.
From the BF-TEM images in Figure 5 (c,d), the capsule shaped nanocrystals were measured to have diameters of $29 \pm 2$ nm across the top section and $20.5 \pm 1.5$ nm across the narrowest section of the capsule. Greater fluctuations were noted in terms of their length, having dimensions of $37 \pm 5.5$ nm, and this was attributed to the differing exposure of their lower-energy crystal faces. The progression of growth perpendicular to the c-axis is particularly evident from the FFT pattern in the inset in Figure 5 (e) and the $60^\circ$ angle between the (100) and (010) planes. The intricate atom stacking arrangement (AB/AB stacking) of these wurtzite structured nanocrystals is depicted in the HRTEM image in Figure 5(e), with a measured $d_{100}$ spacing of 0.356 nm.

Distinctive contrast differences within the nanocrystals are evident in the HRTEM images in Figure 5(d,e), with darker regions being noted in the central region of the nanocrystals. The general explanation for contrast variations in BF-TEM mode can be understood to directly arise from mass-thickness and diffraction.\textsuperscript{56} In particular, mass-thickness contrast is commonly observed in nano-heterostructures in which heavier elements represent more powerful scattering centres than lighter elements and so essentially, heavier atoms appear darker than lighter atoms.\textsuperscript{57-59} To determine whether the contrast difference observed in these nanocrystals is attributed to compositional variations, high resolution DF-STEM measurements were first conducted (Figure 6 a) to bring the desired nanocrystals into the field of view. Elemental line scans were subsequently conducted on these nanocrystals by mapping from the tip to the end segment via the central, darker contrast region of the nanocrystal. Despite the observed high contrast difference in the central region, all Cu, Zn, Sn and S atoms appear to be distributed homogeneously and no noticeable heterostructures or compositional fluctuations are observed in the elemental line...
scans, as shown in Figure 6(b). Furthermore, XRD analysis (see Figure 8 for an overview of XRD patterns for each shape) ruled out the presence of binary Cu$_{2-x}$S or ternary phases in the nanocrystals, with reflections characteristic to the wurtzite phase only being observed. Thus, we believe that the contrast difference is aroused from a variation in diffraction under TEM, coupled with the high amine concentrations perturbing the chemical environment during the synthesis, thus leading to non-regular, shape formation in this system.

![Figure 6](image)

**Figure 6.** (a) DF-STEM image showing two concave-shaped nanocrystals, complete with marked line for EDX elemental line scan. (b) Corresponding results of EDX line scan.

Complete replacement of the ODE solvent with OLA (i.e. 0mL ODE : 25mL OLA, route R5) lead to the formation of P-shaped nanocrystals, as shown in Figure 7(a). From the HRTEM image in Figure 7(b), two morphologies are apparent in the resultant nanocrystals, evolving as P-shaped nanocrystals and capsule-like nanocrystals, similar to those obtained in route R4.
Figure 7. CZTS P-shaped nanocrystals synthesized as per synthetic route R5. (a) Low resolution TEM image of as-synthesized nanocrystals. (b) Higher magnification TEM image of a region shown in (a). (c) HRTEM image of an individual P-shaped nanocrystal. (d) Higher magnification TEM image of the highlighted region marked in (c). (e) HRTEM image of a P-shaped nanocrystal lying in a different orientation on the TEM grid. (f) Higher magnification TEM image of the identified segment marked in (e).
In terms of dimensions, the P-shaped nanocrystals are approximately 25 ± 1.5 nm in length and are 19.5 ± 2 nm in diameter (measured from the nanorod edge to the tip of the P shape). A closer look at the nanocrystals reveals that they consist of a hemisphere-like segment located on top of an elongated nanocrystal. Higher magnification TEM images (Figure 7 c,e) show individual P-shaped nanocrystals, lying in slightly different orientations on the TEM grid. The inset FFT pattern of each shape can be indexed to the (002) and (010) planes, oriented at 90° angles to each other as shown in the measured FFT in Figure 7(c) and (e). Figure 7(d) shows a magnified view of the region highlighted in (c) showing remarkable degrees of clarity of the atom stacking arrangement (AB/AB stacking), complete with a measured d_{002} spacing of 0.316 nm. Figure 7(f) shows the highlighted area in Figure 7(e), with the different orientation of the nanocrystal on the grid resulting in a different directional view of the stacking arrangement.

P-shaped nanocrystals of CIS have been previously observed by Kruszynska et al, with the addition of TOPO (a hard Lewis base and coordinating solvent) decreasing and regulating the activity of the indium precursor (a hard Lewis acid) in their system.\textsuperscript{8} Herein, we hypothesize that the substantial increased concentration of OLA (another well known coordinating solvent) in the reaction environment causes rapid decomposition of the cationic precursors, leaving only a small amount of precursors behind for the second growth stage. The unreacted precursors left behind in this reaction consequently result in continued growth of the nuclei, forming large and irregular shaped nanocrystals, principally distinctive P-shaped nanocrystals in this specific synthetic route (R\textsubscript{5}). Similar observations in relation to OLA expediting the precursor decomposition process have also been previously reported in copper based chalcogenide nanocrystals.\textsuperscript{8,30,60-62}
XRD measurements were conducted on each of the diverse morphologies, ranging from the conventional nanorod geometry (R₁) to ellipsoids (R₂), tadpole-shaped (R₃), capsule-shaped (R₄) and P-shaped nanocrystals (R₅). The resultant XRD pattern for the nanocrystals obtained in each route is shown in a stacked format for clear visual comparison in Figure 8. Each pattern displays strong reflections attributed to the (100), (002), (101), (102), (110), (103), (112) planes constituting the hexagonal system of CZTS and show good agreement with the simulated CZTS wurtzite pattern.
Figure 8. XRD patterns of the different CZTS morphologies synthesized in routes R1-R5, specifically nanorods (R1), ellipsoid-shaped nanocrystals (R2), tadpole-shaped nanocrystals (R3), capsule-shaped nanocrystals (R4) and P-shaped nanocrystals (R5). Simulated XRD pattern of CZTS nanocrystals is included for comparison and correct plane indexing.

While synthetic routes R1-R5 involved modulation of the OLA concentration in the ODE:OLA solvent mixture, each route afforded the formation of a differently shaped nanocrystal crystallizing with a single phase, hexagonal wurtzite structure. Interestingly, a change in the metal precursors (specifically utilizing cationic precursors containing chloride counter ions) resulted in the formation of multi-phase
or polytypic nanocrystals in this system, adopting acorn-like and pencil-like morphologies.

By selecting OLA as the reaction solvent and replacing the copper (II) acetylacetonate precursor, Cu(acac)$_2$, with copper (I) chloride (CuCl), acorn-like polytypic nanorods were achieved in route R6, as shown in Figure 9(a). The HRTEM image in Figure 9(b) reveals much finer details on their exact morphology. The nanocrystals have dimensions of 30.8 ± 1.8 nm in length and 20.5 ± 1 nm in diameter and consist of wide bullet-like shape, with a smaller abrupt hemisphere-like section at one side of the bullet. This gives rise to their so-called acorn-like morphology as designated in this report. Their crystalline structure was further characterized by XRD, as depicted in Figure 9(c), with the main peaks indexed to the (100), (002), (101), (102), (110), (103), (112) planes of the wurtzite structure. The increased intensity of the (002), (110) and (112) peaks, coupled with the appearance of peaks at 33.0° and 63.4°2θ (characteristic of the (200) and (400) planes in a cubic lattice), further confirms the presence of an additional cubic phase in these nanocrystals. The aforementioned stronger intensity of the (002), (110) and (112) planes, indexed to the wurtzite structure, occurs as a result of peak overlap of the (111), (220) and (311) planes in the zinc blende phase.
Figure 9. Polytypic CZTS Nanocrystals with Acorn-like morphology synthesized in R₆. (a) Low resolution TEM image of the as-synthesized nanocrystals. (b) Higher magnification TEM image aiding in identifying their morphology. (c) XRD pattern of the as-synthesized nanocrystals. (d) HRTEM image of an individual polytypic nanocrystal. (e) FFT pattern of the narrow segment constituting the zinc-blende crystal domain. (f) Magnified HRTEM image of the zinc blende domain. (g) HRTEM image of the interface between the separate domains. (h) FFT pattern of the wider segment of the acorn-shaped nanocrystal comprising the wurtzite domain. (i) Magnified HRTEM image of the wurtzite domain.
A HRTEM image of an individual polytypic nanocrystal is shown in Figure 9(d), with two regions identified in the nanocrystal for detailed analysis. Each nanocrystal possesses well defined zinc blende and wurtzite crystal frameworks in separate regions of the same crystal. In particular, the smaller segment of the acorn shape was observed to crystallize in the cubic zinc blende phase and the wider bullet-like segment of the acorn was comprised of hexagonal wurtzite phase. The corresponding FFT pattern (Figure 9e) of the smaller segment of the acorn shape, as identified in Figure 9(d), is fully indexed to the cubic crystal structure. A magnified HRTEM image of the zinc blende domain is shown in Figure 9 (f) and allows for precise measurements of the d-spacing and the angles formed between the different planes in the crystal structure. Interplanar spacings of 0.33 nm, 0.27 nm and 0.34 nm were indexed to the (111), (200) and (11-1) planes of the zinc blende structure, respectively. The angles between these observed planes were also determined, as shown in Figure 9(f), and were calculated to be 55.2° (between the (111) and (200) planes) and 70.8° (between the (111) and (11-1) planes), which shows good agreement with the theoretical values of 55° and 71° for these planes in a cubic structured crystal.

Figure 9(g) shows a magnified HRTEM image of the interface of the zinc blende (ZB) and wurtzite (WZ) derived structures where the lattice mismatch induced stress is particularly evident. The ZB derived structure possesses a well defined anion stacking sequence of ABC/ABC (viewed along the [111] direction), in contrast to the AB/AB stacking sequence in the WZ structure (viewed along the [0001] direction). Thus, the upper region in this image is labelled ZB while the lower region is identified as WZ. The corresponding FFT pattern (depicted in Figure 9(h)) and the
magnified HRTEM image (Figure 9(i)) of the WZ section revealed d-spacings of 0.34nm and 0.33nm, indexed to the (0002) and (10-10) planes of the WZ structure.

Of the copper based organometallic precursors, copper chloride (CuCl) displays the fastest reactivity due to its soft acid (Cu\(^{+}\)) and hard base (Cl\(^{-}\)) assignments in the hard-soft acid-base (HSAB) theory and this infers that a weak binding interaction (increased precursor reactivity) exists in CuCl. We hypothesize that this increased precursor reactivity, coupled with the use of OLA as solvent, results in an expedited precursor decomposition process that significantly affects nanocrystal nucleation and growth. This ultimately tunes the chemical environment and allows for the co-existence of ZB and WZ derived structures in separate domains of the same crystal.

In a separate report, Wang et al. also discovered that the use of metal chlorides as cation precursors provided optimal control in the formation of tetrapod and linear heterostructures comprised of Cu\(_2\)SnSe\(_3\) (CTSe).\(^{46,50}\)

Another linearly arranged, polytypic morphology was also attained in this system as shown in Figure 10. While synthetic route R\(_6\) involved the selection of CuCl and zinc acetate (Zn(Ac)\(_2\)), as copper and zinc precursors respectively, we observed that the further replacement of Zn(Ac)\(_2\) with the Zn(Cl)\(_2\) precursor resulted in the formation of pencil-like CZTS polytypic nanocrystals. From the low resolution TEM images in Figure 10(a), the pencil shaped nanocrystals are observed to be relatively monodisperse and have dimensions of 34 ± 2 nm in length and 17.5 ± 1.5 nm in diameter.
Figure 10. Polytypic CZTS Nanocrystals with Pencil-like morphology synthesized in R7. (a) Low resolution TEM image. (b) Higher magnification TEM image revealing finer morphological details. (c) XRD pattern of the as-synthesized nanocrystals. (d) HRTEM image of an individual polytypic nanocrystal. (e) FFT pattern of the central segment comprised of the WZ structure. (f) Magnified HRTEM image of the WZ domain. (g) HRTEM image of the interface between the separate domains. (h) FFT pattern of the tip segment of the pencil-shaped nanocrystal composed of the ZB structure. (i) Magnified HRTEM image of the ZB domain, complete with angular measurements between the identified planes.
XRD analysis (Figure 10c) indicates that the nanocrystals are assuredly composed of both wurtzite and cubic phases. This is inferred by the enhanced intensity of the (002), (110) and (112) wurtzite derived planes as a result of peak overlap with the (111), (220) and (311) cubic planes. Furthermore, the evolution of peaks at 32.9° and 63.4° can be assigned to the (200) and (400) planes, providing additional confirmation of the presence of a cubic phase in these nanocrystals.

An individual pencil-shaped nanocrystal is shown in the HRTEM image in Figure 10(d). Two segments are identified in the nanocrystal for detailed analysis, positioned at regions on and below the interface of the separate crystalline domains. An FFT pattern (Figure 10e) shows that the highlighted region below the interface crystallizes in the wurtzite phase, with (0002) and (10-10) being identified in the pattern and lie at 90° angles to each other. These exact planes are marked in the magnified HRTEM image (Figure 10f) based on the measured d-spacings of 0.33 nm and 0.35 nm, respectively. The growth direction of this nanocrystal occurs along the c-axis, which is the characteristic growth direction for elongated nanocrystals of the WZ phase.

The equivalent (111) atomic planes in ZB and (0002) planes in WZ gives rise to stacking faults at the interface region of the separate crystal domains, as depicted in Figure 10(g). An FFT pattern of the marked ZB region directly above the interface (as highlighted in Figure 10d) can be fully indexed to a ZB derived structure, shown in Figure 10(h). From the magnified HRTEM image (Figure 10i), d-spacings of 0.33 nm, 0.275 nm and 0.35 nm were measured and can be indexed to the (111), (200) and (11-1) planes of the cubic structure, respectively. Furthermore, the observation of angles equal to 71° (between the (111) and (11-1) planes) and 55° (between the
(111) and (200) planes) shows good agreement with the theoretical angles for these planes in a cubic structured crystal.

The realization that the nature of a solvent plays a key role in controlling the nanocrystal morphology is reflected in this work through the direct observation of a vast range of shape variations by solely manipulating the ODE: OLA solvent ratio. Design and the inherent reactivity of the metal organometallic precursors, specifically copper and zinc, has also been demonstrated to be crucial in influencing both the nanocrystal shape and crystallinity, as inferred by the co-existence of two crystal phases in individual nanocrystals.
5.5 Conclusion

In summary, we have developed a series of synthetic routes to obtain a range of diverse CZTS morphologies through modulation of the amine concentration in a mixed solvent system comprised of ODE and OLA (R\textsubscript{1}-R\textsubscript{5}). While ODE solvent is prerequisite for nanorod formation, incremental quantities of OLA in the reaction caused perturbations in the chemical environment, entailing the evolution of atypical morphologies, namely ellipsoid, tadpole, capsule and P-shaped nanocrystals. The inherent reactivity of the metal precursors, specifically the copper and zinc precursor, was also revealed to have an effect in this system by providing optimal conditions to achieve multi-phase or polytypic nanocrystals. Replacement of the copper precursor, Cu(acac)\textsubscript{2}, with CuCl, lead to the formation of polytypic acorn-shaped nanocrystals (R\textsubscript{6}). Further replacement of the zinc precursor, ZnAc\textsubscript{2} with ZnCl\textsubscript{2}, resulted in pencil-shaped nanocrystals (R\textsubscript{7}). Both morphologies were revealed to be comprised of separate ZB and WZ domains, with the abruptness of the interface being clearly visualized in HRTEM measurements. This demonstrated ability to controllably engineer different polymorphs within single nanostructures provides additional opportunities to engineer the physical, optical and electronic properties and opens up new avenues for band gap tuning and electronic band alignment of semiconductor nanomaterials.
5.6 References


(11) Wang, J.-J.; Wang, Y.-Q.; Cao, F.-F.; Guo, Y.-G.; Wan, L.-J. Synthesis of Monodispersed Wurtzite Structure CuInSe2 Nanocrystals and Their Application in


Chapter 6: In-Situ Investigation of the Nucleation and Growth Processes of Colloidal CZTS Nanorods by Time-Resolved X-ray Absorption Spectroscopy

Status: Publication in Progress

6.1 Abstract

This chapter describes an in-situ investigation on the nucleation and growth processes of colloidal Cu$_2$ZnSnS$_4$ (CZTS) nanorods by time resolved X-ray absorption spectroscopy (synchrotron radiation) using a custom built reaction flask and a remotely controlled, fast injection system. With a time resolution of more than 40 Hz, it was possible to in-situ follow the reaction in real time while recording X-ray absorption near edge spectra (XANES) at the K-edge of Cu and Zn. Detailed analysis of the Cu K-edge XANES region revealed that a burst of Cu$_2$S nucleation was observed at 153.9°C and 175 ms after the anionic precursor injection, as inferred by the observation of a sharp peak at 8982 eV. As the reaction proceeded, distinct
changes in the Cu K-edge XANES region were observed in the spectra at specific temperatures. This allowed identification of the precise temperature dependence of the remaining Sn$^{4+}$ and Zn$^{2+}$ ions to diffuse into the nanocrystals and form quaternary CZTS. Additional monitoring of the Zn K-edge XANES region allowed visual deduction of the onset of zinc incorporation into the nanocrystals. To aid in interpreting the in-situ QEXAFS measurements, a separate aliquot study was performed by withdrawing aliquots from the reaction mixture at selected intervals and analyzing the resultant nanocrystals ex-situ under TEM and EDX. This gave insights into the complete growth pathway, allowing an understanding of the shape evolution as a result of increasing temperature and time.

**Keywords:** CZTS, in-situ, nanocrystal nucleation, QEXAFS, XANES
6.2 Introduction

Multi-component copper-based semiconductor nanocrystals, namely CuIn$_x$Ga$_{1-x}$S$_2$ (CIGS) and Cu$_2$ZnSnS$_4$ (CZTS), have demonstrated significant promise as next generation photon absorbing layers and have gained high recognition owing to their high energy conversion efficiencies, high optical absorption coefficients, good photostability and relatively low toxicity.$^{1-10}$ Of these, CZTS has been actively studied due to its use of naturally abundant and non-toxic elements.$^6$-11 Recently, solution based approaches have attracted much attention due to their ease of scalability, cost-effectiveness and the versatility of the nanocrystals to be used as inks in a wide range of printing techniques.$^1,2,6,12,13$

Whilst much work has been devoted to developing adaptable solution approaches to prepare high quality, multi-component nanocrystals, the underlying mechanistic processes leading to nanocrystal nucleation and subsequent growth processes are still poorly understood.$^{14-19}$ Insights into the kinetics of nanocrystal nucleation and growth are highly desirable to understand how the starting materials transform in solution to generate nanometer-sized inorganic particles.$^{16,20}$ Recent investigations on CZTS nanocrystals have focused on examining their evolution pathway through the use of in-situ X-ray diffraction (XRD),$^{21}$ grazing- incidence small-angle and wide-angle X-ray scattering (GISAXS/GIWAXS),$^{22}$ surface-enhanced Raman scattering (SERS),$^{23}$ as well as transmission electron microscopy (TEM) and energy-dispersive X-ray (EDX) analysis of aliquots extracted from the reaction flask at desired intervals.$^{24-27}$ Despite these studies, it has still remained challenging to probe the rapid nucleation process and the state of nascent nuclei that dominate in the reaction, typically within tens of seconds of the anionic chalcogen precursor injection.$^{14,19,28}$
In-situ experimentation with time resolution represents the most viable means to unravel the key stages in nanocrystal nucleation and emphasizes the requirement of a technique, sensitive to the temporal evolution around an atomic species, to overcome the limitation of conventional characterization techniques.\textsuperscript{20} In-situ x-ray absorption spectroscopy (XAS) is a valuable technique and has been used to investigate the surface induced changes in nanocrystals and probe the local structure in the interior and at the surface of a variety of solid-state materials due to the high X-ray penetration depth.\textsuperscript{29-33} XAS is broken up into two regimes - X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS), which contain related, but slight different information about an element's local coordination and chemical state.\textsuperscript{30} Within ~50 eV of the absorption edge is the XANES region, which is highly sensitive to changes in the local chemical environment such as oxidation states and unoccupied electronic states, with the local coordination to an element and its symmetry also perturbing the edge shape.\textsuperscript{34,35} Above the x-ray absorption edge is the EXAFS region, where oscillations are observed in the energy scan due to the interaction of the ejected electron with the neighbouring atoms.\textsuperscript{29,30,35} The EXAFS region is sensitive to the radial distribution of electron density around the absorbing atom and is used for quantitative determination of bond length and coordination number.\textsuperscript{30,34}

Of the colloidal based nanocrystals, in-situ EXAFS measurements on CdSe nanocrystals at the Se K absorption edge have been reported and reveal that CdSe nucleation completes within several seconds upon injection of the anionic precursor.\textsuperscript{36-38} EXAFS measurements have also been acquired on as-synthesized CdTe,\textsuperscript{39-42} CZTS\textsuperscript{43} and CZTSSe\textsuperscript{44} nanocrystals. Herein, we show the promising capability of quick-EXAFS (QEXAFS) in-situ measurements to unravel the key
nucleation and growth stages in CZTS nanocrystals. With a time resolution of more than 40 Hz, we were able to follow the reaction in-situ and in real time while recording XANES spectra at the K-edge of Cu and Zn. Furthermore, this work represents the first report of its kind by directly transmitting the X-ray beam through the conventional three-neck flask used in colloidal approaches. By designing a custom built flask, in which the X-ray beam can penetrate, and a remotely controlled, fast injection system, we monitored the nucleation and growth stages of CZTS nanocrystals as the reaction proceeded, with increasing growth time and temperature.
6.3 Experimental Section

Materials

All reagents were used as received without any further purification. Copper(II) acetylacetonate (Cu(acac)$_2$; >99.99%), Copper(I)chloride (CuCl >99.99%), Copper(I) acetate (CuAc >97%), Zinc acetate (Zn(Ac)$_2$, >99.99%), Zinc (II) chloride (ZnCl$_2$>99.99%), Tin(IV) acetate (Sn(Ac)$_4$, >99.99%), Trioctylphosphine oxide (TOPO, 99%), 1-dodecanethiol (1-DDT, 98%), tert-dodecylmercaptan (t-DDT, 98.5%, mixture of isomers), 1-Octadecene (1-ODE, 90%, technical grade) and Oleylamine (OLA, technical grade, 70%) were purchased from Aldrich.

Synthesis of CZTS Nanorods

In a typical synthesis of CZTS nanorods, Cu(acac)$_2$ (0.6545g, 2.5mmol), Zn(Ac)$_2$ (0.2292g, 1.25 mmol), Sn(Ac)$_4$ (0.4435g, 1.25mmol), TOPO (3.383g ,8.75 mmol) and 1-octadecene (25mL) were added to a three-neck 50mL round-bottom flask, fitted with reflux condenser, rubber septum and temperature finger. (High precursor concentrations were used to ensure a high signal at the Cu K absorption edge was obtained.) The contents of the flask were evacuated at 100°C for 30mins to eliminate adventitious water and dissolved oxygen. The reaction mixture was then heated to 230°C (30°C /min) under an argon atmosphere and at 155°C, a 5mL thiol mixture (comprised of 4.375mL t-DDT and 0.625mL 1-DDT) was rapidly injected into the system. After injection, the reaction was allowed to proceed for 30minutes with continuous stirring. Subsequently, the heating mantle was removed and the reaction vessel was allowed to cool to 80°C.
Washing Procedure: 2-3mL of toluene was added initially to quench the reaction. The nanocrystals were then washed twice with a 1:2 ratio of toluene to iso-propanol (IPA) and centrifuged at 4000rpm for 7mins. After each centrifugation, the supernatant was removed and the precipitated nanorods were re-dispersed in toluene for further characterization.

**Design Modifications to the Reaction Flask and Heating Mantle**

Specific modifications were made to the reaction flask to allow the X-ray beam to transmit through the flask for direct monitoring of nanocrystal nucleation and growth. A custom built three-neck, round bottom flask (50mL capacity) was used for the reaction (Figure 1a), which contained two inlet holes at opposing sides of the flask. Two stainless steel fittings were fixed into place at these inlets and each fitting was designed to contain a ‘window’ at the inner most part of the fitting, allowing the incoming and exiting X-ray beam to pass through the flask. Kapton was chosen for the window on the basis that it showed repeated ability to withstand the organic solvent direct (1-ODE), despite its direct contact with the solvent even at the elevated reaction temperatures. The kapton foil also allowed transmission of the X-ray beam through the flask. During the reaction, the window and the area above these fittings was completely covered by the metal precursors and the solvent.
Figure 1. Photographs of the modified reaction flask and heating mantle. (a) Custom built three-neck reaction flask used in the reaction, complete with stainless steel fittings. The kapton window (orange) can be visibly observed in this photograph. (b) Side view of the reaction flask showing both stainless steel fittings inserted into the flask. (c) Modified heating mantle, in which hollow stainless steel rods were inserted into the aforementioned fittings in the flask.

The heating mantle housing was also modified to accommodate the reaction flask and fittings by drilling similar diameter holes / openings into opposing sides of the plastic insulating component of the mantle. Hollow stainless steel rods were consequently inserted into these openings to provide a direct path from the stainless steel fittings through the heating mantle and were the point of entry for the X-ray beam into the flask. A photograph of the custom built reaction flask positioned in the heating mantle is shown in Figure 1c for clarity.
Modification to Anionic Precursor Injection System

A remotely controlled anionic precursor injection system was designed to capture the initial nanocrystal nucleation stage and was controlled from outside the beamline experimental hatch. The injection system was comprised of numerous components and valves, all of which worked in sequence to instigate a rapid and efficient injection at the selected injection temperature. The anionic precursor (i.e. thiol mixture) was housed in an injection tube as shown in Figure 2a. A piston was secured in the region above the thiol mixture in the tube. The injection tube was fitted onto the middle outlet of the reaction flask and was clamped in place (Figure 2b). A long stainless steel tube was attached above the injection tube and was bent into a spiral shape (depicted in Figure 2c,d) to prevent the reaction flask from breaking as a result of the injection process.

Figure 2. Photographs of the anionic precursor injection system. (a) Injection tube containing the thiol mixture. (b) Injection tube fitted onto the reaction flask and clamped in place. (c) Numerous components constituting the injection system. (d) Complete reaction setup in experimental beamline hatch.
This spiral-shaped tube was consequently connected up to the explosion chamber which was the key component of the injection system. Spontaneous combustion in the explosion chamber provided significant force to rapidly push down a piston in the explosion chamber. This consequently pushed down the second piston in the injection tube and rapidly injected the thiol mixture into the flask.

In terms of the reaction setup, a three-neck 50mL round bottom flask was used into which the cationic precursor quantities were added. The following components were attached from each outlet of the flask respectively: a temperature finger complete with thermocouple for direct temperature monitoring, a reflux condenser with a valve attachment for Argon or vacuum environment in the flask and the anionic precursor injection tube (Figure 2d). This ultimately allowed us to directly monitor the reaction and remotely control the reaction temperature and injection of the anionic precursor.

**In-Situ Measurements**

Quick-EXAFS (QEXAFS) measurements were collected at the SuperXAS-X10DA beamline at PSI (Paul Scherrer Institut, Villigen, Switzerland). The electron beam energy of the PSI storage ring was operated at 2.4 GeV and at a ring beam current of ~400mA. In-situ QEXAFS measurements at the Cu K-edge and Zn K-edge were performed in transmission mode, using ionization chambers to monitor the radiation intensity (incident intensity $I_0$ and transmitted intensity $I_t$). Internal energy calibration was accomplished by the simultaneous measurement of the absorption of a Cu foil placed between two ionization chambers. EXAFS data was collected up to 1000 eV past the absorption edge. QEXAFS analysis of the resultant spectra was performed on a specialized computer program developed by the authors.
**Ex-situ Characterization**

For transmission electron microscopy (TEM) analysis, 2mL aliquots of the reaction mixture were taken by syringe at specified times and quenched via cooling to room temperature. Nanocrystals were precipitated from the reaction mixture and dissolved in toluene. TEM samples were prepared on 200 mesh carbon-coated copper grids (Ted Pella Inc.). TEM and Dark-field scanning transmission electron microscopy (DFSTEM) was conducted by using a 200 kV JEOL JEM-2100F filed emission microscope, equipped with a Gatan Ultrascan CCD camera and EDAX Genesis EDS detector. Samples for EDX were prepared on carbon-coated nickel TEM grids.
6.4 Results and Discussion

Figure 3a shows a schematic representation of the experimental setup used at the SuperXAS-X10DA beamline for the XAS measurements. By implementing a QEXAFS monochromator, a time resolution of more than 40 Hz was acquired per spectra, thus allowing data to be collected every 25 ms at high resolution as the reaction proceeded. Data was collected in transmission mode using ionization chambers, positioned at each side of the reaction flask (depicted in Figure 3a), to monitor the intensity of the incident and transmitted radiation through the reaction flask. This complete setup allowed us to in-situ follow the CZTS nanocrystal reaction in real time while recording XANES spectra at the K-edge of Cu and Zn. Spectra were recorded from 100°C up to the final growth temperature of 230°C, following the temperature ramp profile as shown in Figure 3b. Specific temperature points were marked in the profile to highlight the major spectral changes that were observed throughout the experiment at these points. An indentation point is also apparent in the temperature profile (Figure 3b) at 155°C and is observed to decrease slightly to 153.9°C, correlating with the fast injection of the ‘cold’ thiol mixture at this temperature.
Figure 3. (a) Schematic of setup at SLS SuperXAS beamline. Reaction setup shown without heating mantle and the modified injection system for clarity. A photograph of the reaction flask (containing the cationic precursor and solvent) before the measurements were performed is shown in the inset. (b) Temperature ramp profile performed during the reaction for the QEXAFS measurements with specific points in the profile marked.

To aid in interpreting the in-situ QEXAFS measurements, aliquots were withdrawn from the reaction mixture at desired intervals and the resultant nanocrystals were consequently analyzed ex-situ under TEM and EDX. This allowed us to gain insights into the complete growth pathway, with an understanding of the shape evolution at specific points as a result of increasing temperature and time. After the injection of the thiol mixture, the reaction solution immediately changed colour from green to
yellow in the reaction flask, thus initiating the start of the nucleation process. Figure 4 summarizes the TEM analysis of aliquots taken at 10° temperature increments from the reaction mixture, ranging from 180°C to 230°C. Although aliquots were also withdrawn from the flask at 160°C and 170°C, it was difficult to obtain nanocrystals (after the centrifugation process) in these aliquots due to the extremely small size of the crystallites formed in the initial stages. In the first feasible aliquot, taken at 180°C and 4.5 minutes after the thiol injection, a yellow coloured solution was still evident in the vial as shown in Figure 4a. TEM analysis of this aliquot (Figure 4a, i-ii) revealed tiny clusters of nuclei had already formed at this point, with imaging of individual nanocrystals proving complicated due to their minute dimensions. Due to the high reactivity between the copper precursor and the thiol, \( \text{Cu}_{2-x}S \) nuclei are expected to form in the initial stage of this reaction, owing to the preferential reaction between the soft acid (\( \text{Cu}^+ \)) and soft base (thiol, R-SH).\(^{45}\) Similar observations for the formation of \( \text{Cu}_{2-x}S \) nuclei in the early stages of ternary and quaternary copper chalcogenides have been previously reported.\(^{5,23,24,26,27,46-48}\)

At 190°C and 6.5mins after injection, the second aliquot was removed from the reaction flask (Figure 4b) and the colour of the solution was observed to be slightly darker in colour as compared to the previous aliquot, implying a change has occurred in nanocrystal growth. The resultant nanocrystals at this point (Figure 4b, i-ii) are irregular in shape and are approximately 3.6 nm ± 0.6 nm in diameter, with the dimensions of the nanocrystals increasing as a result of the temperature rise. At 200°C, highly monodisperse spherical nanoparticles are evident across the TEM grid (Figure 4c i-ii) and possess dimensions of 6 nm ± 1 nm. The colour of the solution is noted to be orange-brown at this point (Figure 4c) and this in itself provides a basis
to visually decipher the formation of highly monodisperse Cu$_{2-x}$S nanocrystals in the reaction.

Figure 4. TEM Analysis of the evolution pathway to CZTS nanorods, with aliquots removed from the reaction flask at 10°C increments after injection of the thiol mixture, specifically at (a) 180°C, (b) 190°C, (c) 200°C, (d) 210°C, (e) 220°C and (f) 230°C. The corresponding TEM images (at different magnifications) for each aliquot at the specified temperatures are shown in (i,ii).

At 210°C, a morphological change is observed in the nanocrystals (Figure 4d, i-ii), changing from spherical to rhombus-like nanocrystals, with measured dimensions of 15 nm ± 1.5 nm in length and 11 nm ± 1nm in diameter at the widest point. The colour of the solution correspondingly changed to a dark brown / black solution (Figure 4d), thus identifying the temperature rise as important at this stage. At 220°C, another change in the morphology is observed in the nanocrystals, with the resultant nanorods possessing a bullet shape on the terminating growth facets (Figure
4e, i-ii). It was difficult to visually detect changes in the solution colour at this point as a dark brown/black solution continually existed beyond 210°C, as depicted in the photographs of the vials in Figure 4d and Figure 4e. In the final aliquot at 230°C and approximately 14 minutes after the thiol mixture injection, highly uniform nanorods were obtained, with low polydispersity (< 5%) in both length and diameter. This is further evidenced by the spontaneous organisation of the rods into vertically aligned nanorod clusters after drying of the droplet on the TEM grid (Figure 4f, i-ii). Nanocrystal growth was allowed to proceed at 230°C for a further 15 minutes before the reaction was cooled down to 80°C.

Figure 5 details dark field scanning transmission electron microscopy (DF-STEM) images of the resultant nanocrystals obtained at 200°C, 210°C and 220°C and their corresponding EDX elemental line scans.
Figure 5. DF-STEM of aliquots taken at (a) 200°C, (b) 210°C and (c) 220°C. The corresponding higher magnification image and and elemental line scan analysis of aliquots taken at the aforementioned temperatures are shown in (d), (e) and (f) respectively.

Highly monodisperse spherical nanocrystals obtained at 200°C are shown in Figure 5a. EDX line scan analysis of this sample across the measured line (depicted in Figure 5d) revealed that the nanocrystals were composed of two elements at this stage, specifically Cu and S. At 10°C above this aliquot, a morphological change from spherical to rhombus shaped nanocrystals was observed (Figure 5b), with EDX analysis of this sample detecting minor quantities of tin in the nanocrystals as shown in the line scan in Figure 5e. This signals the onset of tin incorporation into the nanocrystals at 210°C. At 220°C, bullet-shaped nanorods were formed in the reaction (Figure 5c) and EDX line scans across this sample detected equal quantities of both zinc and tin in the nanorods (Figure 5f). These observations clearly identify the region between 200°C and 220°C as crucial in the formation of CZTS nanorods, with
both tin and zinc incorporating into the pre-formed Cu$_{2-x}$S nuclei, respectively, and within a short timeframe in this narrow temperature range.

In-situ QEXAFS measurements were collected for both the K absorption edges of Cu (8979 eV) and Zn (9660 eV) under standard ring conditions of 2.4 GeV and 400 mA beam current. In the data evaluation process, spectra were collected in real time every 25 ms, with the most significant changes in the spectra being highlighted and are correlated back to the temperature log that was recorded in sequence during the measurements. These significant changes in the spectra are designated as fingerprints of the species present in the reaction flask at the specific intervals. This allowed us to match the QEXAFS data reliably with the corresponding temperature of the reaction, as well as relate the data to the observations obtained from TEM and EDX analysis of the aliquots. Figure 6 shows an overview of the QEXAFS data obtained at both Cu and Zn K-edges, with each spectra offset by +1 for clarity.

![Figure 6](image)

**Figure 6.** Overview of QEXAFS data obtained at Cu K-edge and Zn-K-edge, with temperature correlation for each spectra shown in the legend.

The first spectra obtained at 150°C was acquired before the thiol injection at a Cu K absorption edge energy of 8998 eV. The shape of the first peak at this edge energy
describes the Cu\textsuperscript{2+} species present in the flask in the form of the copper organometallic precursor, Cu(acac\textsubscript{2}).

Immediately after injection, changes in the resultant spectra were observed. The spectra acquired from the first 175 ms after injection suffered pronounced disruptions as a result of the fast injection and so, a blind time of 175 ms after injection was observed in the measurements. Thus, the spectra shown at 153.9°C represented the first real-time spectral fingerprint of the species present in the reaction flask. Figure 7 shows detailed analysis of the Cu K-edge XANES region, with spectra acquired before injection (150°C), immediately after injection (153.9°C) and at an elevated temperature (185°C).

**Figure 7.** (a) Analysis of the Cu-K edge at the XANES region for spectra acquired at 150°C, 153.9°C and 185°C. (b) Magnified view of (a) showing precise measurements from the spectra.

From the comparison of these spectra, a down-shift is observed in the Cu K-edge energy and the shape of the spectra before and after the injection, as shown in Figure 7a. The onset of the peak at 8982 eV and its observation immediately after the injection signifies that a burst of nucleation has already occurred at this point, entailing the formation of Cu-S bonds as inferred by the sharp peak at 8982 eV. With
increasing temperature, the intensity of this peak rises sharply and reaches a maximum absorption intensity at 185°C. From the magnified view in Figure 7b, the Cu-S peak remains steady at 8982 eV and does not undergo a shift to higher energies, thus indicating that no change in the oxidation state of Cu has occurred after injection. By comparison of the peak shape with reference XANES data obtained for the different oxidation states of Cu, this peak was assigned as having a Cu\(^{+}\) oxidation state\(^{49}\) and it exists in this state from the onset of injection. This observation indicates that phase pure Cu\(_2\)S nuclei form in the initial stages in the reaction, a phase which proves extremely difficult to observe from aliquot studies due to the fast oxidation of Cu\(_2\)S into copper deficient phases such as Cu\(_{1.94}\)S.\(^{24,26}\)

The sharp rise in absorption edge intensity (by 0.45 counts) was attributed to the increasing particle size in the reaction as a result of the temperature rise and is in good agreement with the experimental TEM observation. Spectral interpretation became particularly interesting as the temperature increased beyond 200°C. Figure 8a shows the comparison of spectra obtained at 185°C and 207°C.

**Figure 8.** (a) Analysis of the Cu-K edge at the XANES region for spectra acquired at 185°C and 207°C. (b) Magnified view of (a) showing the disappearance of the peak at 8982eV at 207°C.
Pronounced decreases in the absorption edge feature were observed as a result of the increasing temperature, with the peak decreasing fully in intensity at 207 °C, as shown in the magnified view in Figure 8b. This correlates with the change in morphology in the resultant nanocrystals (from spherical to rhombus-like) obtained from the aliquot withdrawn at 210°C and is thus, related to the diffusion of Sn⁴⁺ ions into the pre-formed Cu₂S nuclei and the onset of Cu-Sn-S bond formation. The detection of minor quantities of tin in the EDX line scans of nanocrystals obtained at 210°C (Figure 5e), as well as the significant decrease in the intensity of the Cu-S peak from the Cu K-edge in the XANES region provides a rational explanation behind the low quantities of tin at this stage as tin is just beginning to diffuse into Cu₂S. Thus, this observation implies that a temperature of greater than 207°C is required to instigate tin incorporation into the pre-formed nanocrystals. Furthermore, the decrease in peak intensity at 207°C infers that Cu-S bond formation has ceased and Cu-Sn-S formation commences beyond this point.

Based on the shape of the Cu K-edge in the XANES region, Cu can be described as having a Cu⁺ oxidation state and exists as the Cu₃SnS₄ phase. While Cu₄SnS₄ is also a possibility, the absence of a maximum pronounced peak at 8990 eV infers that Cu does not exist in a tri coordinated arrangement,⁵⁰ which is observed for the Cu₄SnS₄ structure. Instead, it exists in a four coordinated tetrahedral arrangement of Cu in sulfides, in the form of Cu₃SnS₄.⁵⁰ Tan et al recently detected the similar presence of a ternary Cu₃SnS₄ phase by surface-enhanced Raman scattering (SERS) measurements conducted on aliquots withdraw from the CZTS reaction.²³ The observation of tin incorporation, prior to zinc, in the colloidal CZTS nanocrystal system has been reported previously and is consistent with the findings in this report.¹¹,²³,²⁴
Shortly after Cu-Sn-S bond formation (207°C), another significant change in the spectra is observed at 215°C, as depicted in Figure 9a, b. The appearance and continued evolution of a peak at 8984 eV signifies the subsequent diffusion of Zn$^{2+}$ ions into the pre-formed nanocrystals, thus forming Cu-Zn-Sn-S bonds. Based on TEM and EDX analysis of the aliquot taken at 220°C, zinc and tin are present in stoichiometric quantities in the nanocrystals at this temperature (Figure 5f), with the nanocrystals incurring a morphological change from a rhombus-like shape to nanorods (Figure 5c).

**Figure 9.** (a) Analysis of the Cu-K edge at the XANES region for spectra acquired at 207°C, 215°C and 230°C. (b) Magnified view of (a) showing the onset of the peak at 8984 eV at 207°C and its increase in absorption intensity at 230°C. (c) Investigation of changes in the Zn K-edge at the different specified temperatures. (d) Enhanced magnification view of (c) focusing on spectra acquired at 207°C, 215°C and 230°C.
The latter observation of Zn\(^{2+}\) incorporation is confirmed through direct monitoring of the XANES region for the Zn K absorption edge (Figure 9c). No distinct changes are observed in the spectra obtained in the XANES region for the Zn K-edge until a temperature of 215°C is reached. From the magnified view in Figure 9d, a shift to lower energy occurs at Zn K absorption edge, specifically shifting from 9665 eV to 9660 eV upon comparison of the spectra acquired at 207°C and 215°C. This 5 eV shift implies the onset of Zn\(^{2+}\) diffusion into the nanocrystal. Further heating to 230°C results in a slightly higher absorption edge intensity by 0.1 counts, signalling zinc incorporation at this point. This gives rise to stoichiometric CZTS nanorods, complementing the TEM observations where full zinc and tin incorporation was noted at a temperature of 220°C. At the XANES region for the Cu K-edge spectra (230°C), the post edge structure is observed to consist of three distinct maxima at 8984 eV, 8998 eV and 9007 eV (Figure 9a) and is a fingerprint of a four-coordinated tetrahedral Cu arrangement with sulfur atoms.\(^{50}\)

Based on the compilation of ex-situ TEM and EDX observations of aliquots withdrawn from the reaction and in-situ QEXAFS measurements at the Cu-K edge and Zn-K edges, the proposed growth mechanism for CZTS nanorods can be devised. Figure 10 shows a schematic illustration summarizing the observation from both measurements.
Figure 10. Schematic illustration of the proposed growth mechanism for CZTS nanocrystals. Differences in the reactivity of the metal precursors result in several steps in the mechanism, starting with the formation of Cu$_{2-x}$S nuclei, followed by the diffusion of Sn$^{4+}$ into the pre-formed nuclei to form Cu-Sn-S bonds (CTS), before the final Zn$^{2+}$ incorporation yielding Cu-Zn-Sn-S (CZTS).

In the initial nucleation stages, a burst of Cu$_2$S nucleation occurs, leading to the instigation of Cu-S bond formation. This is particularly evident through direct monitoring of the XANES region at the Cu-K absorption edge, with the immediate onset of a sharp peak at 8982 eV. As a result of the temperature increase, a sharp rise in peak intensity at this edge is noted and is related to the increased absorption area in solution due to the increasing size of the spherical Cu$_2$S particles. The XANES measurements indicate a maximum intensity is reached at 185°C and remains up to a temperature of 200°C. TEM measurements of aliquots withdrawn from the reaction mixture at 180°C, 190°C and 200°C further confirmed a diameter increase from 3.6 nm to 6 nm in the resultant particles. As no initial shifts to higher Cu K-edge energies were noted, the oxidation state of Cu$^+$ remains steady throughout the
nucleation stage. The presence of Cu$_2$S and the structure of its anion sublattice, comprised of a hexagonal close packing (hcp) array of sulfur ions, is regarded as crucial in dictating the final nanocrystal structure, with Cu$_2$S acting as a template for further growth.$^5$24,26,46,47

Beyond 200°C, distinctive changes in the QEXAFS spectra are apparent, particularly the rapid decrease of the peak at 8982 eV at the Cu K-edge XANES region in the spectra at 207°C. This indicates a cessation of Cu-S bond formation and commencement of tin incorporation (in the form of Sn$^{4+}$ ions) into the pre-formed Cu$_2$S nuclei. No changes in the XANES region of the Zn K-edge are observed at this stage, thus eliminating Zn incorporation into the nanocrystals. The onset of tin diffusion infers a morphological change in the nanocrystals, resulting in the attainment of rhombus-like nanocrystals as visualized in TEM. EDX line scans across these nanocrystals detected high counts of Cu and S but minimal counts of Sn. Based on the QEXAFS data, this EDX observation is explained by the fact that diffusion of Sn$^{4+}$ only begins at temperatures beyond 207°C.

The next spectral fingerprint was obtained at 215°C, with changes noted in both the Cu K and Zn K absorption edges. The evolution of a peak at 8984 eV at the Cu K-edge, as well as the peak shift at the Zn K-edge from 9665 eV to 9660 eV, provides conclusive evidence that zinc becomes active at this temperature and starts diffusing into the nanocrystals to form quaternary CZTS nanocrystals. Zinc incorporation (in the form of Zn$^{2+}$ ions) resulted in a change in the morphology and caused an elongation in the resultant nanocrystals to form the highly attractive rod geometry. The CZTS nanorods crystallize in a hexagonal wurtzite phase,$^{10}$ with the phase transformation from binary Cu$_2$S to quaternary CZTS via ternary CTS involving
minimal lattice distortion.\textsuperscript{24,27} This is due to the nearly identical packing of the S sublattices of hexagonal Cu\textsubscript{2}S and wurtzite structured CZTS.\textsuperscript{24}

By recording QEXAFS data in real time, we have shown the promising capability of in-situ QEXAFS measurements to unravel the key stages in the nucleation and growth of quaternary CZTS colloidal nanocrystals by detecting clear changes at both the Cu K and Zn K absorption edges.
6.5 Conclusion

We have presented an in-situ QEXAFS study into the nucleation and growth of colloidal CZTS nanorods synthesized in a custom built, three-neck reaction flask, complete with a modified injection system for the anionic precursor injection. Spectra were acquired at both the Cu K-edge and Zn K-edges in situ and in real time, with a time resolution of 25 ms per spectra. Detailed analysis of the Cu K-edge XANES region revealed that a burst of Cu$_2$S nucleation was observed at 153.9°C and 175 ms after the anionic precursor injection, as inferred by the observation of a sharp peak at 8982 eV. The nascent nuclei in the flask were assigned as having a Cu$^+$ oxidation state, with this oxidation state remaining constant during the temperature rise to 200°C. As the reaction proceeded, distinct changes in the Cu K-edge XANES region were observed in the spectra at specific temperatures, identifying the precise temperature dependence of the remaining Sn$^{4+}$ and Zn$^{2+}$ ions to diffuse into the nanocrystals and form quaternary CZTS. Tin was observed to first incorporate into the pre-formed spherical Cu$_2$S nuclei at 207°C, with its incorporation causing a morphological change in the resultant nanocrystals from spherical to rhombus-like nanocrystals as confirmed by TEM observations. Zinc incorporation followed closely behind and was revealed to begin diffusing into the nanocrystals at a temperature of 215°C, based on detailed analysis of the Zn K-edge XANES region. Its incorporation resulted in the attainment of nanorods, with TEM and EDX analysis providing additional confirmation of zinc and tin incorporation in the aliquot extracted at 220°C. These findings enrich our understanding of the nucleation and growth process of CZTS nanorods and demonstrate the highly sensitivity of QEXAFS to detect subtle changes in the local chemical environment.
6.6 References


(30) Frenkel, A. I. Applications of extended X-ray absorption fine-structure spectroscopy to studies of bimetallic nanoparticle catalysts, *Chemical Society Reviews* 2012, 41, 8163.


6.7 Addendum

C.C, J.J. and A.S. discussed the experiments. A.S. and K.M.R developed the colloidal synthesis of CZTS nanorods. C.C, J.J. and O.M. planned and conducted the experiments at the SuperXAS beamline. C.C. calculated and weighed the precursor quantities required for the experiments. J.J designed the remotely controlled injection system. C.C. conducted the aliquot study and performed the ex-situ TEM and EDX measurements. O.M. designed the monochromator and programmed the software used to analyse the QEXAFS data. C.C. evaluated the real-time measurements and temperature correlation and wrote this manuscript. R.F, T.U and K.M.R. supervised the project.
Chapter 7: Conclusions and Recommendations for Further Study

7.1 Overall Conclusions

The colloidal solution synthesis approach employed in this thesis allowed for the formation of multi-component copper chalcogenide semiconductor NCs. This work demonstrates that the colloidal approach, initially introduced by Murray et al. in 1993 for the synthesis of binary cadmium chalcogenides NCs,\(^1\) can be successfully extended to allow for the formation of a wide range of multi-component, copper chalcogenide NCs. The ample chemical and structural freedom in quaternary chalcogenides has been explored, through the incorporation of p-block metals/semi metals (In, Ga, Sn) or transition metals (Zn), to form CIGS, CIGSSe and CZTS NCs.

General conclusions and recommendations for further study on each of the materials synthesized in this thesis are discussed in the following sections. Conclusions and future directions are divided per chapter: CIGS NCs (Chapter 3), CIGSSe NCs (Chapter 4), CZTS NCs (Chapter 5) and the in-situ study into nucleation and growth of CZTS nanorods (Chapter 6).
7.1.1 Conclusions and Future Directions from Chapter 3

In Chapter 3, a systematic study on the colloidal growth of CIGS nanocrystals and nanorods was described. In particular, taking aliquots at selected time intervals during the reaction gave important insights into the evolution pathway in this system. Although the synthesis was a one-pot reaction, the formation of CIGS nanocrystals was observed to occur in several discrete steps, beginning with formation of the binary copper sulfide nanoparticles, transitioning through ternary CIS and subsequently progressing to yield the quaternary CIGS form. The progression from binary copper sulfide to quaternary CIGS was monitored by TEM, XRD, UV-vis and EDX (of aliquots withdrawn from the reaction) to provide a complete picture of the change in morphology, crystal structure and composition as the reaction progressed. Fine tuning of the nanorod aspect ratio was also demonstrated through the incorporation of ligands of differing alkyl chain length, with the change in aspect ratio showing a good correlation with ligand chain length.

While the optimal synthetic window for nanorod formation was demonstrated, using a combination of thiol- and amine-based ligands, deviating outside this range resulted in the development of a diverse range of shape morphologies. A strong propensity of non-regular shaped formation was observed, with L-, hatchet- and tadpole-shaped NCs evolving when the system was perturbed by increased concentrations of amine (HDA) or a coordinating solvent (OLA). Despite the complexity of the reaction, the optimized amine/thiol protocol allowed for the attainment of nanorods possessing high uniformity across length and diameter. Their vertical and close packed assembly was demonstrated by using an electrophoretic deposition protocol, with each nanorod aligning orthogonal to the underlying
substrate after the deposition process. This allowed for complete control of the absorber layer architecture at the nanoscale.

Future investigations should examine the incorporation of the CIGS nanorods into a NC based PV device, in which the CIGS nanorods (comprising the absorber layer) would ideally be assembled on molybdenum-coated ITO glass substrates (back contact), followed by consequent assembly of CdS nanorods (constituting the buffer layer), a ZnO/ZnO:Al transparent conducting oxide layer and Al/Ni top contacts. Complete testing of the power conversion efficiency of this device architecture should be investigated.

Post-synthetic ligand exchange strategies should also be explored, in an attempt to decrease the residual carbon left behind after thermal decomposition of the ligands used in the synthesis. This residual carbon is known strongly deteriorate the overall electronic properties of the film.²

HRSEM and high resolution real-time XRD measurements of the annealing process would be an extremely interesting study, with a recent report highlighting the capability of these techniques to directly monitor grain size propagation as annealing occurs.³ Effect of temperature, atmosphere and annealing time would allow for accurate definition of the grain size from rod fusion in the CIGS composition.
7.1.2 Conclusions and Future Directions from Chapter 4

Chapter 4 extended the colloidal synthesis to a five-component NC system, copper indium gallium sulfur selenide (CIGSSe), to explore the effect of selenium incorporation in the resultant NCs. A thorough synthetic chemistry study was presented, in which NCs were phase selectively synthesized with cubic or hexagonal crystal systems. This gave rise to the formation of 0D nanoparticles or 2D nanoplates, respectively. The phase selectivity in this system was based on tuning the reaction environment, through the coordinating nature of the solvent. In particular, the use of ODE solvent provided fast nucleation and slow growth conditions, entailing the formation of the thermodynamically stable zinc blende phase. On the contrary, the strong binding ability of OLA with the metal cations lead to slow nucleation and fast nanocrystal growth, thus providing conditions favourable for stabilization of the wurtzite phase.

Furthermore, the shape topography was also tailored to and gave rise to NCs both with and without curvature. Through detailed electron microscopy examinations, the 2D nanoplate structures were observed to adopt planar or concave shapes, with the latter being composed of dark fringes on the nanoplate surface. The dark fringes were revealed to be diffraction contrast effects and were unequivocally assigned to bending contours on the (0002) plane, based on a TEM tilt series of individual concave nanoplates and displaced aperture dark field images. HRTEM, DF-STEM and SEM images of the lateral sides of the nanoplate further confirmed the existence of a net concave curvature.

In terms of the synthetic chemistry, TOPO was found to be inherently responsible for inducing the formation of the concave nanoplates by causing dramatic changes in the
internal crystal structure. This lead to the creation of non-regular stacking faults buried in the nanoplates, which were viewed in displaced aperture DF-STEM images. A 3D reconstruction of diffraction patterns also revealed the presence of stacking faults in the crystal, with small changes in the unit cell length leading to the appearance of discrete reflections that were shifted in reciprocal space.

While controlling the shape of a NC may initially seem like a scientific curiosity, its impact goes far beyond aesthetic appeal.\textsuperscript{4} To date, the shape of single metal NCs have been shown to govern its localised surface plasmon resonance (LSPR) properties and its merit in applications such as SERS.\textsuperscript{5,6} Future work should investigate how the NC shape (0-D NCs and 2-D nanoplates) in multi-component copper chalcogenides, specifically CIGSSe NCs, affects the optical and electronic properties. Shape topography (i.e. planar or concave nanoplates) should also be examined. As the aforementioned shapes are based on the same material composition, this would allow for a direct correlation of NC shape with any alteration in their properties.

NCs with a concave curvature are expected to show unexplored or a considerable enhancement of properties relative to their planar or convex counterparts.\textsuperscript{4,6} Such a study would emphasize how the optical and electronic properties can be predictably tuned in CIGSSe NCs by shape-controlled syntheses and bring about new opportunities for their implementation in a range of applications, including catalysis, surface plasmon resonance, surface-enhanced spectroscopy and optical sensing.
7.1.3 Conclusions and Future Directions from Chapter 5

In chapter 5, a series of routes to systemically tailor the morphologies of CZTS NCs were developed. By solely increasing the concentration of OLA in the mixed solvent system (OLA and ODE), a variety of anisotropic morphologies, ranging from nanorods and ellipsoids to atypical capsule-, tadpole- and P-shaped nanocrystals, were obtained. The attainment of these shapes lead to the realisation that an increased proportion of OLA in the reaction environment significantly raised the energy of the (002) face and lead to the exposure of lower-energy crystal faces. This resulted in growth progressing along the (100) faces to minimize the surface area of the high energy (002) face, with HRTEM and FFT measurements confirming this hypothesis.

Furthermore, judicious selection of the metal precursors in the reaction provided optimal conditions to achieve multi-phase or polytypic nanocrystals. In particular, the replacement of the copper precursor, Cu(acac)$_2$, with CuCl, lead to the formation of acorn-shaped polytypic nanocrystals. Additional replacement of the zinc precursor, ZnAc$_2$ with ZnCl$_2$, resulted in pencil-shaped polytypic nanocrystals. Through HRTEM imaging, XRD and FFT analysis, the polytypic nanocrystals were observed to be comprised of well-defined zinc blende and wurtzite crystal frameworks in separate domains of the same crystal, with the abruptness of the interface being visualized in HRTEM measurements.

Future investigations should examine the effect of CZTS NC shape on the optical and electronic properties, an area which has remained relatively dormant in relation to multi-component copper chalcogenides. In particular, the polytypic nanocrystals (having engineered structural defects in separate domains of the same crystal) have
the potential to induce significant changes in the optical and electronic properties, thus opening up new avenues for band gap tuning and electronic band alignment of CZTS semiconductor nanomaterials.\textsuperscript{7,8}
7.1.4 Conclusions and Future Directions from Chapter 6

An in-situ QEXAFS investigation of the nucleation and growth processes of colloidal CZTS nanorods was presented in Chapter 6. By using time resolved XAS (synchrotron radiation), coupled with a custom built flask and fast injection system, it was possible to in-situ follow the CZTS reaction in real time while recording XANES at the K-edges of Cu and Zn. Detailed analysis of the Cu K-edge XANES region revealed that a burst of Cu$_2$S nucleation was observed 175 ms after the anionic precursor injection, as inferred by the evolution of a sharp peak at 8982 eV. The nascent nuclei in the flask were assigned as having a Cu$^+$ oxidation state, with this oxidation state remaining constant during the temperature rise to 200°C.

Distinct changes at the Cu-K absorption edge were observed in the spectra as the reaction proceeded. This allowed for precise identification of the temperature at which the remaining Sn$^{4+}$ and Zn$^{2+}$ ions diffused into the pre-formed Cu$_2$S nuclei, with tin diffusing at 207°C and zinc diffusing at 215°C. Full incorporation of tin and zinc resulted in the attainment of CZTS nanorods, based on ex-situ TEM and EDX analysis of an aliquot from the reaction extracted at 220°C. Additional monitoring of the Zn K-edge XANES region confirmed the onset of zinc incorporation, with changes observed in the XANES region at 215°C. These findings enrich our understanding of the nucleation and growth process of CZTS nanorods and demonstrate the highly sensitivity of QEXAFS to detect subtle changes in the local chemical environment.

In-situ XRD, UV-vis-NIR and SAXS measurements would be extremely interesting to detect changes in the crystal structure, optical properties and crystallite size,
respectively. In particular, the high susceptibility of Cu$_{2-x}$S nanocrystals to oxidation prevents accurate determination of the exact crystal structure of the nuclei in aliquot studies. Thus, in-situ experimentation with time resolution represents the most viable means to unravel the underlying mechanistic processes leading to NC nucleation and should be employed in further studies.
7.2 References


