Colloidal Synthesis of Multinary Metal Chalcogenide Nanocrystals with Composition, Shape and Crystal Phase Control

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*Kuch to Bahut Nek Maine Kiya Hoga Zindagi Mein,
Ittefaqan hi Nahi Wo Tumhe Mere Liye Banata.....*
For my dad, who gave me the name ‘Doctor Sahab’ long before I decided my career path. Miss you so much.
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 novel colloidal approaches towards the synthesis of multicomponent semiconductor nanocrystals with tight control over morphology, composition and crystal phase. The thorough study of the complexity of the reaction mechanism and judicious selection of ligands and metal precursors along with temperature windows provide exquisite control over the sequential nucleation and growth events leading to the evolution of desired shapes and phase in synthesized nanocrystals.

Preparation of highly monodisperse and homogenous CdSe$_x$S$_{1-x}$ nanorods with tunable aspect ratios is reported in Chapter 3. The optical properties are compositionally tunable with the relative molar ratios of the chalcogens (Se/S). Importantly, the combined influence of Se/S composition and ligand concentration on shape control is explored to hold the desired aspect ratios for each composition. The synthetic protocol is sufficiently robust to allow good control of nanorod aspect ratios, suited for their rational assembly either into vertical superstructures or into 1D rail-tracks depending on the net charge.

Chapter 4 describes controlled engineering of shape and crystal phases in colloidal synthesis of complex quinary Cu$_2$ZnSn(SSe)$_4$ semiconductor nanocrystals. Combination of coordinating solvent and phosphonic acid entails the evolution of atypical polytypic heterostructure whose shape could be controlled by the nature of metal precursors. Furthermore, polytypism could be ruled out while retaining anisotropy allowing for single-phase wurtzite nanorods by using non-coordinating solvent with phosphonic acids.

Chapter 5 explores the synthesis of copper based metal tellurides ranging from binary to quaternary compositions via ligand assisted colloidal approach. The gradual
changes in the nanocrystal composition were observed to have dramatic effect on the shape, dispersity and crystal phase of nanocrystals. A solution based phase transformation of multicomponent semiconductor nanocrystal system is detailed in Chapter 6. Metastable wurtzite nanocrystals were transformed into highly stable zinc-blende and kesterite phases by solution based post treatment approach and thermal annealing method respectively. This phase transformation approach gives clear insight about the phase-to-phase and phase to ligand relationships in multinary nanocrystal systems.
List of Abbreviations

0-D – zero dimensional

1-D – one dimensional

1-DDT – 1-dodecanethiol

2-D – two dimensional

3-D – three dimensional

BF-STEM – bright field scanning transmission electron microscopy

CdS – cadmium sulphide

CdSe – cadmium selenide

CdTe – cadmium telluride

CV – Cyclic voltammetry

CZTS – Cu$_2$ZnSnS$_4$ – copper zinc tin sulphide

CZTSe – Cu$_2$ZnSnSe$_4$ – copper zinc tin selenide

CZTTe – copper zinc tin telluride

CZTSSe – Cu$_2$ZnSn(SSe)$_4$ – copper zinc tin sulphide selenide

DF-STEM – dark field scanning transmission electron microscopy

EDX – energy dispersive X- ray spectroscopy

FFT – Fast Fourier transform

HAADF – high angle annular dark field
HDA – hexadecylamine

HPA – hexylphosphonic acid

HRTEM – high resolution transmission electron microscopy

HSAB – hard-soft acid-base

OA – oleic acid

ODPA – octadecylphosphonic acid

OLA – oleylamine

PL – Photoluminescence

SAED – selected area electron diffraction

SEM – scanning electron microscopy

STEM – scanning transmission electron microscopy

t-DDT – tert-dodecylmercaptan

TDPA – tetradecylphosphonic acid

TEM – transmission electron microscopy

TOP – trioctylphosphine

TOPO – trioctylphosphine oxide

UV-Vis – Ultraviolet-Visible

XRD – X-ray diffraction

XPS – X-ray photoelectron spectroscopy
List of Publications


Chapter 1: Introduction

A part of this chapter appeared in-

1.1 Semiconductor Nanocrystals

Semiconductor nanocrystals are a unique class of mesoscopic materials that are intermediate between bulk solids and molecular clusters. The size of these materials generally lies between 1 to 100 nm, containing anywhere between 100 to 100,000 atoms. The extent of fine ordering of atoms in the nanocrystals distinguishes them from the molecular clusters.

![Fluorescence image of CdSe nanocrystals](image)

Figure 1. Fluorescence image of CdSe nanocrystals.

Elements or compounds in nanocrystal form are fully crystalline with comparable lattice parameters to the bulk. Control over the nanocrystal size, shape, and composition allows the tailoring of the physical properties leading to their potential applications in various fields, such as solar energy harvesting, optical and electro-optical applications, biological tagging, and medical diagnostics.

The semiconductor nanocrystals have been investigated in photonic applications due to their size and shape tunable intense bright emission with wide excitation spectra and narrow emission bandwidths. CdSe is one prototypical semiconductor nanocrystal system where narrow emission spectra could be tuned as a function of
the nanocrystal size. This is evident from Figure 1 which shows range of visible colours that can be observed for CdSe nanocrystal suspension throughout the entire visible spectra from blue to red with increasing diameter.

1.2 Quantum Confinement Effect and Band-Gap Tuning in Semiconductor Nanocrystals

Bulk materials have continuous conduction and valence energy bands separated by a fixed energy gap. With the decreasing size, energy bands collapse into more discrete, atomic-like states with energies dependent on the particle radius (as shown in Figure 2).  

![Figure 2](image_url)

Figure 2. Comparison between the electronic structure of molecule, semiconductor nanocrystals and bulk semiconductor materials. In bulk semiconductors materials, electrons can be excited from the lower energy valence band to a higher-energy conduction band. The difference between the energies of these two bands is known as the band gap energy. The absorbed photons excites electron–hole pairs which are bound by Coulomb interaction in the initial stage and form an exciton. Later, the electron–hole pairs, either dissociate to
facilitate conductance, or recombine to irradiate photons. In semiconductor nanocrystals, when the dimensions are restricted to nanoscale, excitons undergo confinement effects in the nanosized regime, and their wave functions are trapped in a confined small space. Due to this quantum confinement effect, the electronic structure of the nanocrystals is transformed to atom-like discrete or quantized energy states from the continuous electronic bands of bulk materials as presented in Figure 2. The first basic model of the behaviour of a system having quantum confinement was developed by L. E. Brus et al. The quantum confinement effect is considered to be equivalent to the quantum mechanical “particle in a box,” in which the energy of the particle is inversely proportional to the size of the box. Based on the physical size of the material, confinement can be either in one dimension (quantum films or quantum wells, known as the first examples of quantization in nanoscale materials), in two dimensions (quantum rods or wires), or in three dimensions (quantum dots). The quantum confinement effect has led to unique and significant size dependent physical properties in semiconductor nanocrystals or quantum dots. This relationship between the nanocrystal size and band gap energy allows for the tuning of band gap related absorption and luminescence by changing the crystal size. The band-gap increases, when the size of the nanocrystal is smaller than their Bohr radius. Equally important, the energy of the band gap absorption (and thus the nanocrystal colour) and that of the emission increases and become sensitive to the size of the particles which is clearly evident in Figure 3. The fluorescence spectra shows that when the CdSe nanocrystals are reduced in size, the emission wavelength of the band-edge PL shifts from red to blue ultimately increasing the band-gap of the nanocrystals.
Figure 3. (a) Size-tunable fluorescence spectra of CdSe nanocrystals and (b) illustration of the relative particle sizes, from left to right, the particle diameters are 2.1 nm, 2.5 nm, 2.9 nm, 4.7 nm, and 7.5 nm.\textsuperscript{19}

1.3 Colloidal Synthesis of Semiconductor Nanocrystals

Synthesis of colloidal nanocrystals is a combination of solution chemistry and crystal growth. One of the very first developed methods for the synthesis of semiconductor nanocrystals was a bi-phase technique, based on the precipitation of nanocrystals within inverse micelles.\textsuperscript{29} Nanoscaled water droplets (dispersed phase) were stabilized in an organic phase (continuous phase) by an amphiphilic surfactant forming micelles. These micelles function as nano-reactors for nanocrystal growth and prevent at the same time the nanocrystal aggregation. Alternatively, a monophase procedure was also developed. It employed homogenous aqueous solutions of suitable reagents and surfactant-type stabilizers. The surfactants bind to
the nanocrystal and stabilize them in solution preventing their agglomeration. Both of these methods involve simple room temperature experimental approaches and the usage of standard solvents and chemicals. A disadvantage is that the control over the size dispersion is poor due to which crucial protocols for the separation of polydisperse nanocrystals have to be applied in order to achieve small fractions of monodisperse samples.\textsuperscript{30}

**Figure 4.** An illustration of nanocrystal synthesis via colloidal approach.

In early 90’s, a high temperature colloidal method employing organic solvents was introduced for the fabrication of monodisperse cadmium based nanocrystals i.e., CdS, CdSe and CdTe.\textsuperscript{30} This procedure involves a single, temporally short nucleation event followed by slower growth on the existing nuclei. The reaction flask containing hot coordinating solvent/ligand is injected with molecular precursors. The temperature is maintained sufficiently high for the rapid decomposition of the molecular precursors, forming a super saturation of species (monomers) in solution
that is relieved by nucleation of nanocrystals. Upon nucleation, the monomers further sustain their subsequent enlargement by diffusion controlled growth. This colloidal approach has been evolved considerably over the years to produce finer quality of monodisperse nanocrystals of desired shapes, sizes and physical properties.

In a typical colloidal synthesis method as shown in Figure 4, cationic precursors are loaded in a three neck round bottom flask with the organic solvent and surfactants. This flask is then connected to a schlenk line and is flushed with an inert gas. The temperature of the reaction flask is increased up to 80–120 °C to melt the surfactant. The flask is evacuated and kept under vacuum at the same temperature for next 30-60 min to remove any volatile impurities and water. This step is essential for most of the syntheses, as some of the reactants may be pyrophoric or sensitive to air. After this step, the reaction flask is again flushed with inert gas and the temperature is increased in order to form a complex between the cationic precursors and the surfactants. If the organic solvent being used in the synthesis is coordinating in nature, it also participates in the formation of cationic complex. Depending on the type of the precursor and the surfactants, the formation of a complex takes place between the temperature ranges of 130-250 °C. For example, the complex between Cd precursor and phosphonate ligands is formed around 230-240 °C during the growth of CdE (E = S, Se or Te). Typically, in copper based multi-component semiconductor nanocrystals synthesis, the complex between precursors and phosphonates/amines (surfactants) is formed at lower temperatures 140-180 °C. This complex is then injected with the anionic precursors dissolved in organic surfactants, to initiate the nucleation and growth of nanocrystals. After injection the colour of the solution changes, indicating the reaction between the anionic precursors and the cationic complexes. The reaction is then ramped to and maintained at a
higher temperature held for growth and shape evolution. After the reaction, the as-
synthesized nanocrystals are isolated from the solution and suspended in toluene or
hexane. A non-solvent such as IPA or ethanol that is miscible with the first solvent
but has an unfavourable interaction with the capping groups is added to the solution.
It minimizes the barrier to aggregation and destabilizes the nanocrystal dispersion,
causing their flocculation. When this solution is centrifuged, the nanocrystals
precipitate at the bottom of the vials, which are redispersed in a variety of solvents
for further use.

1.4 Mechanism of Nucleation and Growth for Colloidal Nanocrystals

In a colloidal synthesis approach, three major components are involved, precursors,
organic ligands and solvent. In some cases, the ligand also serves as the solvent. For
example, OLA could act as solvent due to its liquid nature and also could act as
ligand due to its amine functionality. When the components are heated in a reaction
flask at relatively high temperature, the precursors are transformed into active
molecular species known as monomers. These monomers grow in due course of time
whose growth is affected by the ligands present in the solution. The whole process of
nanocrystal formation involves two steps: nucleation and growth. The reaction or
decomposition of precursors at high temperature in the initial flask leads to the super
saturation of monomers followed by burst of nucleation of nanocrystals. Nucleation
is generally a single, short and temporary event which is then followed by a
comparatively slower growth of nanocrystals. This is achieved by incorporation of
additional monomers present in the reaction flask on the existing nuclei. The first
classical approach to describe the process of nucleation and growth of nanocrystals
was based on LaMer burst nucleation and Ostwald ripening. It was initially
modelled by Reiss in 1951,\textsuperscript{35} with a proper model being developed ten years later by Lifshitz, Slyozov and Wagner.\textsuperscript{36} More recently in 1997, Watzky and Finke formulated an approach of constant slow nucleation followed by autocatalytic growth.\textsuperscript{37} All these mechanisms of growth and nucleation (Figure 5) have been well elucidated over the years by different in- and ex-situ spectroscopic and microscopic measurements.

![Figure 5. Schematic illustration of mechanisms of nucleation and growth followed by nanocrystals in solution.\textsuperscript{38}](image)

### 1.4.1 La Mer Mechanism

According to the La Mer mechanism, the crystal formation mechanism can be conceptually separated into the nucleation and growth stages. The initial case of study was the synthesis of sulphur sols from the decomposition of sodium thiosulfate. La Mer and Dinegar explained that the sulphur sol evolved in the solution by a two-step process: the first to form free sulphur from the thiosulfate and the second form sulphur sols in solution.\textsuperscript{34}
The process of nucleation and growth in the solution through the La Mer mechanism can be divided into three portions (Figure 6) - (1) A quick increase in the free monomer concentration; (2) The “burst nucleation” of the monomers; (3) Subsequent growth occurring under the control of the diffusion of the monomers through the solution.

**Figure 6.** The stages of nucleation and growth for the preparation of nanocrystals in the framework of the La Mer model.  

1.4.2 Ostwald Ripening

Ostwald ripening was the first mechanism to describe the secondary growth stage in nanoparticle formation. According to this theory, growth is caused by the change in
solubility of nanocrystals dependent on their size. The smaller particles redissolve in the solution owing to their high solubility and the surface energy and in turn the larger particles grow even more. On the other hand, Digestive ripening is effectively the inverse of Ostwald ripening. In this case, smaller particles grow at expense of the larger ones. This process of formation is also controlled by the surface energy of the particle where the larger particles redissolve and smaller particles grow.

1.4.3 Finke-Watzky Two Step Mechanism

It is a two-step mechanism in which nucleation and growth happen simultaneously. The first step is a slow continuous nucleation, and the second is the autocatalytic surface growth which is not diffusion controlled. While, this mechanism is different from classical theories of nucleation and growth, it still follows the critical size condition as described in any classical nucleation mechanism.

1.4.4 Coalescence, Attachment and Intraparticle Growth

Coalescence and orientated attachment are two very similar concepts of growth. The only difference they acquire is the orientation of the crystal lattice at the grain boundary in the final nanocrystal. In the case of coalescence, there is no particular preference of crystal facets for the attachment whereas the orientated attachment is an aligned attachment along a continuous crystal plane. Intraparticle growth/diffusion was first described by Peng et al. in early 2000s. It is the modification in the shape of the nanoparticles due to the diffusion of monomers along the surface of the crystal. It only occurs at very high monomer concentrations, when due to the internal potential gradient, the high energy facets dissolve and the low energy facets grow.
1.5 Control Parameters for the Evolution of Colloidal Nanocrystals

A systematic adjustment of the reaction conditions — time, temperature, and concentration and chemistry of precursors and ligands is needed to control the monodispersity, shape, size and phase of the as-synthesised nanocrystals. In general, the size of the nanocrystals increases with increasing reaction time, as more material adds to the surfaces of nanocrystals. The rate of addition of the material over the surface of existing nuclei is increased at high temperature. Therefore, it is crucial to choose an optimised temperature of growth that is high enough for proper rearrangement of atoms and low enough to confine the over-growth of the nanocrystals. Another important parameter in the synthesis of colloidal nanocrystals is the choice of precursor molecules. The precursors should rapidly decompose to yield monomers, which are eventually followed by nucleation and growth of nanocrystals. Final key parameter is the type and concentration of adhering organic ligands molecules employed in the generation of nanocrystals. Since half of the atoms making up a nanocrystal are usually on its surface, the surface and ligand interface kinetics becomes one of the controlling factors in growth along the different facets of the nanocrystals. This ultimately manages the shape and size of the resulting nanocrystals.

1.5.1 HSAB Theory

For synthesizing monodisperse binary, ternary or quaternary semiconductor nanocrystals, the reactivity of the ionic precursors and the ligands should be well balanced. In 1963, Pearson proposed the hard-soft acid-base (HSAB) theory that explained many trends in stability of the complexes between Lewis acids and bases by classifying them into “hard” and “soft” categories.\(^\text{42}\) Hard (lewis) acids prefer to
bind to hard (lewis) bases and soft (lewis) acids prefer to bind to soft (lewis) bases. The key aspects of Pearson’s hard and soft acids and bases (HSAB) principle were originally developed for metal coordination compounds. However, it can be efficiently applied to the bonding of ligands to the nanocrystal surface and to identify the ideal precursors for controlling the reaction rate.\textsuperscript{43} The rate of reaction for a particular precursor will be lowered when they consist of hard to hard or soft to soft bonds which require more energy to break up. For example, among common copper precursors, copper acetate (CuAc) is more reactive than copper iodide (CuI). Cu\textsuperscript{+} is a soft or borderline acid and Ac\textsuperscript{-} is a hard base which breaks down faster than CuI where I\textsuperscript{-} is a soft base. Similarly, Zn\textsuperscript{2+} being a borderline Lewis acid forms stronger bonds with Cl\textsuperscript{-} (borderline Lewis base) but is weakly bonded with Ac\textsuperscript{-}, which is a hard base. Thus, Zn(ac)\textsubscript{2} can give Zn\textsuperscript{2+} more readily than ZnCl\textsubscript{2}, and leads to faster incorporation of Zn\textsuperscript{2+} into the copper sulfide nuclei during the formation of multinary nanocrystals.\textsuperscript{44} Figure 7 illustrates the acidity of metal ions and basicity of common ligands used in the preparation of semiconductor nanocrystals. HSAB-based generalization of ligand exchange reactions are very useful for predicting the binding affinity between a specific ligand and a given nanocrystal components. However, the HSAB principle has an inadequate predictive power and does not essentially state all possible ligand exchange routes.
Figure 7. (a) Acidity of common metal ions as soft- acids. (b) Basicity of common ligands as soft bases. \(^{45}\)

### 1.5.2 Ligands

The ligands/surfactants play a very important role in deciding the shape and size of the nanocrystals. They also influence the solubility, surface charge, and the effective volume of the nanocrystals. During the growth of nanocrystals, surfactants are adsorbed on the surface of the crystal to form an active capping shell which stabilizes the growing nanocrystals in the solution. The relative binding energies of the surfactants to different facets controls their growth rates. The most commonly used
organic surfactants (listed in Table 1) are the long carbon chain molecules having functional groups such as amines, phosphonic acids, carboxylic acid groups etc. The importance of ligands has been widely studied by different researchers. Peng et al found that the binding strength as well as the steric factors associated with the ligands influences the activity of monomers during the synthesis of CdSe nanocrystals. The concentration of the monomers could be controlled by ligands which in turn controls the morphology of the resulting nanocrystals. Herman and his co-workers have reported that variation in concentration ratio of short chain phosphonic acids to long chain phosphonic acids could lead to the tuning of diameter and aspect ratios of CdSe nanorods. Moreover, Manna and co-workers showed that by varying the concentration of methylphosphonic acid (MPA) the shape of CdTe nanocrystals could be tuned from 0-D dots to 1-D rods to 3-D tetrapods. However, various studies on the effect of ligands on the shape evolution of nanocrystals during colloidal synthesis has indicated that for a controlled growth and desired shape evolution, an effective strategy should be applied which involves using a mixture of surface agents. This mixture should contain one longer chain surfactant which binds to the crystal facets firmly hindering the growth of the facets and one short chain ligand which is weakly bound permitting rapid growth.
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**Table 1** Organic Ligands used for the synthesis of multinary semiconductor nanocrystals described in this thesis.
1.6 Shape Evolution in Colloidal Semiconductor Nanocrystals

The colloidal approach for nanocrystal synthesis allows the formation of various shapes of nanocrystals such as dots, rods, wires, cubes and tetrapods. Since, the physiochemical properties of the nanocrystals are greatly influenced by their morphology; it is very important to explore the growth mechanisms which lead to the formation of particular shapes during the synthesis. In a seminal work, Peng gave insights about the shape evolution in II-VI semiconductor nanocrystals synthesised by using the hot injection colloidal approach.\textsuperscript{49} He stated that the concentration of the monomers in the growth solution is the determining factor for the evolution of shapes. If the monomer concentration in the solution is well controlled, the monodispersity among the shape and size of the nanocrystals can be achieved. Once the magic sized nuclei are formed after the nucleation stage, low monomer concentration decreases the chemical potential of the solution leading to the evolution of nanodots. The medium monomer concentration supports the isotropic 3-D growth of the existing nuclei to form rice-shaped nanocrystals. In the case of high monomer concentrations, 1-D growth is favoured and nanorods are formed. In the situation of very high monomer concentration, the sequence of growth events can lead to the formation of branched structures such as tetrapods, dendrimers etc. These

\textbf{Figure 8.} Monomer concentration dependent growth of CdSe nanocrystals.\textsuperscript{49}
branched structures are the most complex structures produced so far in colloidal nanocrystal synthesis.

A possible alternative mechanism of shape evolution involves the interplay between organic ligands and the crystal surface at high temperature.\textsuperscript{50, 51} It was confirmed by different research groups that the onset of kinetic shape control can be extensively tuned by selective adhesion of a ligand on a particular crystal facet and before the reaction reaches the stage of equilibrium. This allows any metastable nanocrystal shape to be obtained by tuning the reaction parameters. This could be explained by the concept of dynamic solvation according to which during the growth stage of nanocrystal formation, ligands are rapidly exchanged on the nanocrystals surface. When the evolving crystal is faceted, the exchange rate of the ligands will be different on the different facets. The introduction of a ligand that selectively adheres to a particular crystal facet can be used to effectively lower the energy and slow the growth rate of that facet relative to others which can ultimately result into different anisotropic shape formation.\textsuperscript{51}

1.7 Crystalline Phases in Semiconductor Nanocrystal Systems

The final shape determination of the nanocrystals is dependent on the crystallographic phase of the initial seed during the nucleation event (as shown in Figure 9).\textsuperscript{52}
Among various crystalline phases, the most stable phase is highly dependent on the reaction environment such as temperature during the nucleation, choice of ligands and precursors etc. Once the crystalline phase is determined in the flask, the characteristic unit cell structures of the growing seeds influence the further growth of nanocrystals. For example, if the nucleating seeds prefer to have an isotropic unit cell structure (cubic), then 0-D nanostructures are expected due to isotropic growth. On the contrary, anisotropic unit cell structures such as hexagonal induce anisotropic growth in the nanocrystals. II-VI compound semiconductors include the cations of zinc and/or cadmium combined with anionic sulphur; selenium and/or tellurium generally crystallize in two types of phases, namely, zinc blende and wurtzite. Zinc blende and wurtzite phases belong to cubic and hexagonal lattice structures respectively. Both are characterized by tetrahedrally coordinated atomic sites, with a staggered or eclipsed dihedral angle. The stacking sequence of the (111) plane of zinc blende is represented by ABCABCABC repeating pattern, whereas for wurtzite structures, it is represented by the ABABAB pattern (as shown in the Figure 10). In
the CdS system, zinc blende seeds form tetrahedral nanocrystals where four (111) faces are formed at low temperatures. On the other hand, under high temperature conditions (280-320 °C), wurtzite-phased seeds give rise to 1-D nanorods of CdS.\textsuperscript{54}

\textbf{Figure 10.} (a) Hexagonal (wurtzite) and (b) cubic (zinc blende). Red and green balls represent Cd and S atoms, respectively.\textsuperscript{55}

In I–III–VI\textsubscript{2} bulk materials such as CuInS\textsubscript{2} and CuInSe\textsubscript{2}, zinc blende and wurtzite phases are the thermodynamically favoured and are only stable at above 900 °C. However, as nanocrystals they could be stabilized at room temperatures along with chalcopyrite crystal structure. Chalcopyrite is a tetrahedral structure derived from the cubic zinc blende structure in which zinc is replaced by cations of lower valency (Cu\textsuperscript{+}) and higher valency (In\textsuperscript{3+}) in the cation sublattice (Figure 11(a)) resulting into a reduced symmetry. It leads to a primitive cell constituting eight atoms and to a body centered tetragonal Bravais lattice. When the cations of different valency are distributed randomly, the cubic zinc blende structure is observed (Figure 11(b)). In some cases, the formation of nanocrystals in the hexagonal wurtzite type structure has also been observed (Figure 11(c)).
Figure 11. (a) Unit cell of the chalcopyrite crystal structure (copper atoms in light blue, iron atoms in dark blue, and sulphur atoms in orange and larger size). (b) Unit cell of the zinc blende structure. (c) Unit cell of the wurtzite structure (zinc atoms in green and sulphur atoms in orange and larger size).56

In I2-II–IV–VI4 nanocrystals, Cu$_2$ZnSnS$_4$ (CZTS) and Cu$_2$ZnSnSe$_4$ (CZTSe), the stoichiometry is even more complicated because of the odds of formation of more than one phase during nucleation. This is due to the difference in the reactivity coefficient of the cationic precursors. The tetragonal kesterite structure derived from ternary chalcopyrite structure is the most stable structure reported in these nanomaterials. It is formed by alternation of cation layers (CuSn and CuZn) along the c-axis. Another crystal structure observed in quaternary nanocrystals is the stannite structure. The difference between stannite and kesterite lies in the composition of cation layers. Here, Sn, Zn and Cu layer are arranged alternatively along the c-axis. Along with these phases, wurtzite and zinc-blende phases could also be synthesized in nanocrystal forms.
1.8 Colloidal Multinary Metal Chalcogenide Nanocrystals

The colloidal semiconductor nanocrystals are generally categorized according to their constituting element groups (Figure 13). The first category is II-VI semiconductor nanocrystals comprised of elements such as Zn, Cd, Hg (II element group) and S, Se, Te (VI element group). The second category is the ternary compounds i.e. I-III-VI$_2$ semiconductor nanocrystals which are conceptually derived from II-VI compounds by replacing the two divalent cations from II group element by one monovalent and one trivalent cation. Further substitution of trivalent cations with one divalent and one tetravalent cation leads to the formation of I$_2$-II-IV-VI$_4$ semiconductor compounds.
1.8.1 II-VI Semiconductor Nanocrystals

The family of II-VI semiconductor nanocrystals comprises Zn/Cd/Hg (as the II element group member) and S/Se/Te (as the VI element group member) together forming binary, ternary or quaternary compounds. These nanocrystals are of great interest for both fundamental studies and technical applications from the past 25 years due to their convenient chemical processibility and strong size dependent properties.\textsuperscript{6, 30, 50, 57} Synthesis of high quality CdSe, CdS, CdTe, ZnS, ZnSe etc, has been playing a very critical role in the advancement of nanocrystal-based solar cells,\textsuperscript{8, 58, 59} light-emitting diodes,\textsuperscript{60, 61} and fluorescent lables.\textsuperscript{62-64} For the development of promising and reproducible colloidal methods of synthesizing II-VI semiconductor nanocrystals, two major strategies have been employed widely over the past 25 years. The first approach involves heating of the colloidal solution of the ion precursors over an extended period of time at high temperature (also known as non-injection approach).\textsuperscript{65} In the second case, nucleation and growth processes are separated by injecting the anion precursor rapidly at high temperatures (>300 °C) to induce nucleation and then reducing the temperature for growth of nanocrystals with
narrow size distribution. Murray et al. reported the use of dimethyl cadmium (Cd(CH₃)₂) as the cadmium precursor for the synthesis of Cd chalcogenide nanocrystals. Later, synthetically convenient, less toxic and cheaper cadmium oxide (CdO) was introduced to replace Cd(CH₃)₂ as it provided new opportunities to produce large scale of high quality semiconductor nanocrystals.

Cadmium chalcogenides i.e. CdS, CdSe and CdTe are direct band-gap semiconductors with theoretical band-gaps of 2.5 eV, 1.70 eV and 1.44 eV respectively. These band-gaps are dependent on the size and shape of the nanocrystals and can be tuned over a range to suit a specific application. For example, Bawendi et al showed that the band gap of CdSe can be varied from 1.9 eV to 2.7 eV by changing the size of the CdSe nanoparticle from 5.5 nm to 2.3 nm. Along with the band gap, the photoluminescence of these CdSe nanoparticles can also be varied from the red to the blue region of the visible spectrum.

Among the wide range of II-VI semiconductor nanocrystals, CdSe has been the most extensively studied system. It has been chosen as nanocrystal model by different research groups over years for explaining kinetics of nucleation, growth and shape evolution. Apart from fundamental studies, synthesis of CdSe nanocrystals as 0-D (quantum dots), 1-D (nanorods), 2-D (nanosheets) and 3-D (tetrapods and octapods) structures has also been widely exploited for development of fluorescent labels, light- emitting diodes, solar cells and other electronic devices as shown in Figure 14. Recently, Peng et al has shown the optical property studies and photovoltaic applications of rod-coil copolymer and CdSe nanocrystal hybrids.

Even more recently, Manna et al has reported the synthesis of pyramid shaped wurtzite CdSe nanocrystals exhibiting reverse crystal polarity by using a hot-injection approach and chloride ions as shape-directing additives.
Figure 14. TEM images of colloidal CdSe nanocrystals with different shapes (a) nanoparticles;\textsuperscript{73} (b) hexagonal nanodisc;\textsuperscript{74} (c) nanocubes;\textsuperscript{74} (d) arrow shaped;\textsuperscript{75} (e) nanorods;\textsuperscript{6} (f) tetrapods.\textsuperscript{75}

Colloidal CdS nanocrystals are exploited for electronic and energy conversion applications.\textsuperscript{67} However, among the bulk intrinsic n-type semiconductor materials, CdS thin films were one of the first to be used in solar cell applications due to its wide band-gap and minimal light absorption property.\textsuperscript{76} It is still used as the n-type
material for buffer layers in photovoltaic device such as CIGS-based solar cells and CZTS based solar cells.\textsuperscript{77} Opposite to this, CdTe is a p-type semiconductor and has been acknowledged as a very promising material for nanocrystal based and thin-film solar cells.\textsuperscript{78-81} It has a direct band-gap of 1.44 eV that corresponds optimally to the solar spectrum for photovoltaic energy conversion. It also has a high absorption coefficient, $>5 \times 10^5$ cm$^{-1}$, due to which a layer of 2$\mu$m is enough to absorb 99% of photons of the energy greater than the band-gap of the material. According to the recent reports, CdTe solar cell has achieved the efficiency of 21.0 ± 0.4%.\textsuperscript{82} Most of the technological applications of II-VI semiconductor nanocrystals rely on their optical properties. Colloidal nanocrystals are generally passivated by the capping ligands in solution which exhibit surface related trap states. These trap states act as fast non-radiative de-excitation channels for photogenerated charge carriers and reduce the fluorescence quantum yield. Growth of a shell layer of a second semiconductor over the core material to form a core-shell nanostructure not only improves the surface passivation and photo-stability of the core nanocrystals but also enhanced the quantum yield of the material.\textsuperscript{83} It was shown by several research groups that the emission wavelength could be tuned in a broader spectral window for the II-VI nanocrystals, by judicious selection of core and shell materials having appropriate band alignment.\textsuperscript{84} The most common approach to coat the core nanocrystals by various layers of the shell materials is called SILAR (successive ion layer adsorption and reaction) method.\textsuperscript{85} It is based on coating one layer at a time by alternate injections of cationic and anionic precursors. The shell material slowly diffuses into the core, causing a substantial shift of the emission wavelength towards shorter wavelength. The most studied core-shell structures to date are CdSe/ZnS, CdSe/CdS nanocrystals in dots, rods, plate and tetrapod shapes due to the small
lattice mismatch between the core and shell materials.\textsuperscript{69, 86, 87, 88} Due to their enhanced quantum yield, core-shell II-VI nanostructures are regarded as ideal materials to be used in light emitting diodes (LEDs), photocatalysis, photovoltaics and biolabelling.\textsuperscript{89-96}

![Diagram](image)

**Figure 15.** Schematic diagram illustrating the structural difference between homogenous alloy, gradient alloy and core-shell structure.\textsuperscript{97}

The band-gap engineering is possible by tuning the size of nanocrystals or formation of shell around the core crystal. Another means of tailoring the band-gap of a semiconductor nanocrystal system is by tuning the crystal composition via controlling the stoichiometry of the constituents. This could be achieved by formation of alloy of two semiconductors with different energy gaps. Alloyed materials exhibit properties which are not only distinct from the properties of their bulk counterparts but also from those of their parent semiconductors. They possess additional composition-dependent properties as well as properties arising due to quantum confinement effects.\textsuperscript{97} For example, the size-dependent emission wavelength of the CdSe nanocrystals can be tuned over the whole visible spectrum but the near-infrared (NIR) region is outside its spectral range. Interestingly, when CdSe and CdTe semiconductors are alloyed together to form \( \text{CdSe}_x\text{Te}_{1-x} \)
nanocrystals, light emission is observed in the NIR spectral window too.\(^9\) These NIR-emitting nanocrystals are important materials for various biomedical applications. Additionally, alloys of CdSe with ZnSe (i.e., Zn\(_{x}\)Cd\(_{1-x}\)Se nanocrystals) are employed successfully in short-wavelength optoelectronic devices due to their property of emitting blue light with excellent efficiency.\(^9\) Alloyed semiconductor nanocrystals are conventionally categorised into two types (1) Homogeneous alloys with a uniform internal structure; and (2) Heterogeneous alloys having a gradient internal structure. Figure 15 shows the difference between nanocrystals having homogenous alloyed, heterogeneous alloyed and core-shell structures. Interesting applications of alloyed nanocrystals has been demonstrated such as CdSe\(_{x}\)Te\(_{1-x}\) nanocrystals for near-infrared-emitting nanocrystals,\(^10\) Zn\(_{x}\)Cd\(_{1-x}\)Se nanocrystals for short-wavelength visible emission,\(^9,10,11\) CdSe\(_x\)S\(_{1-x}\) nanorods for lasing applications and use of glutathione-capped Zn\(_{x}\)Hg\(_{1-x}\)Se nanocrystals for selective detection of Cu\(^{2+}\) ions.\(^11\)

### 1.8.2 I-III-VI\(_2\) Semiconductor Nanocrystals

Synthesis of colloidal nanocrystals (such as CdTe, PbS) and their deposition as an ‘ink’ to fabricate the absorber layers in thin film solar cell motivated the search for economical and less toxic ternary and quaternary semiconductor materials offering high flexibility for band-gap tuning. Synthesis of I-III-VI\(_2\) nanocrystals such as CuInS\(_2\) (CIS), CuInSe\(_2\) (CIS), CuInGaS\(_2\) (CIGS) and CuInGaSe\(_2\) (CIGSe) nanocrystals have drawn considerable attention over the past few years due to the high efficiency (\(> 20\%\)) achieved in their bulk thin film solar cells.\(^11\) On the other hand, CIGS nanocrystal based solar cells has shown the efficiency of 12\%.\(^11\) These materials are direct band-gap semiconductors with a theoretical band-gap of 1.53 eV and 1.05 eV for CIS and CIGSe respectively. They also possess high absorption
coefficients~ $10^5$ cm$^{-1}$ which makes them strong candidates for use as absorber layer materials in solar cells. Additionally, their size and composition tunable photoluminescence characteristic can be exploited in optoelectronics and biotechnology applications. Due to these promising applications, I-III-VI$_2$ nanocrystals have drawn large research attention on their synthetic methodologies for controlled phases and band-gaps and on their long-term stability in solutions and devices.
Figure 16. (a-d) TEM images of different morphologies obtained in I–III–VI$_2$ semiconductor nanocrystals, (a) CuInSe$_2$ hexagonal nanocrystals;$^{108}$ (b) CuInSe$_2$ trigonally shaped nanocrystals;$^{109}$ (c) CuGaS$_2$ tadpoles;$^{110}$ (d) CuInGaSe$_2$ nanorods;$^{111}$ (e) Variation in optical band gap of chalcopyrite-type I-III-VI$_2$ semiconductor nanocrystals.$^{112}$
The colloidal syntheses of these materials are more complex than the II-VI materials due to the involvement of multiple precursors and ligands. The most common ligands used in the synthesis are ODE, OA, OLA, HDA, DDT, TOP and TOPO. A suitable balance between these ligands, metal and chalcogenide precursors and temperature give rise to interesting shapes of nanocrystals occurring in chalcopyrite, zinc-blende or wurtzite crystal phases.

Phase selection in these nanocrystals is generally influenced by the metal and chalcogenide precursors used for their colloidal synthesis. For example, use of thiourea, SeO$_2$, elemental S and elemental Se as anion sources tend to crystallize the nucleating seed into thermodynamically more stable crystal phases such as chalcopyrite and zinc-blende.$^{113-115}$ On the other hand, precursors such as DDT, diphenyldiselenide and tert-dodecylmercaptan (3-DDT) induce the growth in metastable wurtzite phase.$^{116,117}$ The first phase tunable synthesis of I-III-VI$_2$ nanocrystals i.e. CIS was demonstrated by Pan et al, where exchange of surfactants from OA to DDT causes the transformation of the nanocrystals from zinc-blende to wurtzite phase.$^{118}$ Formation of wurtzite CISe nanocrystals were first reported by Brutchey et al. by using diphenyldiselenide as selenium source.$^{117}$ Due to the advances in colloidal synthesis methodologies and understanding of the surface-ligand interplay, nanocrystals can be formed in desired shapes with well controlled monodispersity to suit the application requirements (as shown in Figure 16(a-d)). Spherical, trigonal and pyramidal shapes are dominant morphologies when CuInS$_2$, CuInSe$_2$, CuInGaS$_2$ and CuInGaSe$_2$ nanocrystals are stabilized in chalcopyrite or zinc blende phases.$^{109,119,120}$ Interestingly, when the synthesized nanocrystals are wurtzite in nature, nanorods, nanowires and nanoplates with axial directional growth along the c-axis can be obtained easily.$^{110,111}$ Ryan and co-workers have reported the detailed shape
study of wurtzite CIGS nanocrystals with anisotropic shape evolution. They showed
the formation of diverse range of shape morphologies such as hexagon discs,
nanorods, tadpoles, p-shaped and hatchet shaped nanocrystals by controlling the
thiol-amine ligands ratios.\textsuperscript{111}

The band-gaps of these I–III–VI\textsubscript{2} nanocrystals range between 1.3-3.4 eV (as shown
in Figure 16(e)). The tunability in band-gaps of these materials can be achieved by
three possible methods- (1) by adjusting the anion ratios; (2) by adjusting the cation
ratios; (3) by scaling down the size of the nanocrystals.\textsuperscript{115, 121} Tuan et al. reported the
synthesis of chalcopyrite CuIn(S\textsubscript{1-x}Se\textsubscript{x})\textsubscript{2} nanocrystals with compositionally tunable
band-gap from 0.98 to 1.46 eV by varying the S/Se ratio.\textsuperscript{121} On the other hand,
Sargent et al. showed that band-gap tunability can be achieved by varying relative
concentrations of In and Ga precursors in the synthesis of Cu(InGa)Se\textsubscript{2}.\textsuperscript{115} The
synthesized Cu(InGa)Se\textsubscript{2} nanocrystals were reported to have a bandgap value of 1.2
eV, which is larger than CuGaSe\textsubscript{2} nanocrystals (1.03 eV) and smaller than CuInSe\textsubscript{2}
(1.7 eV) nanocrystals. Size dependent optical band-gap tuning in I–III–VI\textsubscript{2} quantum
dots as observed by Omata et al. gives the advantage of covering a wide wavelength
range from ultraviolet to near-infrared.\textsuperscript{112}

The photoluminescence properties of I–III–VI\textsubscript{2} materials such as CuInS\textsubscript{2} or AgInS\textsubscript{2}
could be improved by formation of core-shell structures using ZnS as shell material.
ZnS provides many interesting features: it shows very good chemical stability, it is
cost-effective, has a large band gap (3.6 eV) and a very less lattice mismatch (2-3%) with CuInS\textsubscript{2} and AgInS\textsubscript{2}. The synthesis of CuInS\textsubscript{2}/ZnS core-shell nanocrystals occurs
generally in two-steps, where a ZnS shell is grown on the surface of CuInS\textsubscript{2}
nanocrystals by adding zinc stearate or zinc acetate as zinc precursor to the colloidal
solution of core CuInS\textsubscript{2} crystals.\textsuperscript{12} The quantum yield of the resulting core-shell
nanocrystals is generally higher than the CuInS$_2$ nanocrystals illustrating the role of Zn ions in passivating the volume/surface related trap states.$^{122}$ Applications of these materials as “nanocrystal inks” for photovoltaic devices or solid discs for thermoelectric devices require at least one gram of nanocrystal powder. This calls for the need of scalability of the nanocrystal syntheses. For large production, non-injection colloidal approaches are highly suited. Different groups have shown the synthesis of CIS and CISSe nanocrystals with a yield > 1 gram by using non-injection heating up approach.$^{119, 121}$

![Figure 17. TEM images of (a) Cu$_2$ZnSnS$_4$ nanocrystals; (b) Cu$_2$ZnSnSe$_4$ nanocrystals; (c,d) Cu$_2$ZnSnS$_4$ nanorods; (e) Cu$_2$CdSnS$_4$ nanocrystals; (f) Cu$_2$ZnGeS$_4$ nanocrystals. $^{123-127}$](image-url)
1.8.3 I\textsubscript{2}-II-IV-VI\textsubscript{4} Semiconductor Nanocrystals

The quaternary semiconductor nanocrystals such as Cu\textsubscript{2}ZnSnS\textsubscript{4} (CZTS), Cu\textsubscript{2}ZnSnSe\textsubscript{4} (CZTSSe) and their analogues drew world-wide attention due to their outstanding performance in thin-film solar cells and earth-abundant composition. The highest efficiency for CZTS based thin film solar cell is recorded to be 8.5%.\textsuperscript{128} Moreover, alloying the CZTS and CZTSe counterparts to form CZTSSe based thin film solar cells via solution growth shows the efficiency of 12.6% as reported by IBM Research Centre.\textsuperscript{82}

CZTS and CZTSe adopt a tetragonal kesterite structure in bulk form which is considered to be theoretically derived from the chalcopyrite crystal structure by cation substitution. As nanocrystals, they could exist in various crystal phases such as cubic zinc-blende, tetragonal stannite and hexagonal wurtzite crystal structure. The first colloidal syntheses of CZTS nanocrystals were reported in 2009 by three different groups simultaneously. Steinhagen et al used a heating up approach where a mixture of the ion precursors and OLA was heated to 280 °C (Figure 17 (a)).\textsuperscript{123} Guo \textit{et al.} followed a hot injection protocol by injecting the sulphur precursor solution (elemental sulphur in OLA) into the solution of the metal precursors in OLA at high temperature.\textsuperscript{129} Riha \textit{et al.} injected both cation and anion precursors in trioctylphosphine oxide (TOPO) at high temperature and showed a better control over the monodispersity than other two methods.\textsuperscript{130} The crystalline phase of the nanocrystals was identified to be the kesterite phase. Cabot and co-workers reported the first synthesis of highly monodisperse Cu\textsubscript{2}Zn\textsubscript{x}Sn\textsubscript{y}Se\textsubscript{1+x+y+2} nanocrystals by reaction between metal amino complexes and TOP-Se solution at high temperature (Figure 17 (b)).\textsuperscript{124} These nanocrystals were stabilized in tetragonal stannite form. After these reports, several groups have performed different variations in synthesis protocols to
achieve high monodispersity, high stability and phase purity in CZTS and CZTSe based nanocrystals. By replacing the elemental S and Se with precursors such as thiol and diphenyl diselenide, growth of copper based multinary nanocrystals could be achieved in the meta-stable wurtzite phase. The wurtzite phase is the kinetically favoured phase which could be stabilized generally when nucleation is very fast and the growth is carried out below 230 °C. The wurtzite phase also gives access to the anisotropic growth in the nanocrystals. Formation of prism and plate-like shapes were formed when thiols were used along with OLA during the synthesis of wurtzite CZTS nanocrystals. Singh et al. showed that in the absence of alkylamine as solvent, use of thiol mixture (1-DDT and tert-DDT) lead to the formation of wurtzite CZTS nanorods with high monodispersity (Figure 17(c,d)). Furthermore, Yu et al. demonstrated that DDT and diphenyl diselenide can be used together to synthesise CZTSSe nanocrystals.

![Figure 18](image_url)

**Figure 18.** (a) Band gap energies determined from the optical absorption of Cu$_2$ZnSn(S$_{1-x}$Se$_x$)$_4$ colloidal nanocrystals; (b) Low-temperature photoluminescence (PL) emission of Cu$_2$ZnSn(S$_{1-x}$Se$_x$)$_4$ nanocrystals with varying values of $x$. Band-gap tunable CZTSSe nanocrystals could also be synthesised by adjusting Se/S concentration in the reaction. Prieto and co-workers reported the synthesis of tetragonal CZTSSe nanocrystals where the S/Se ratio was adjusted by tuning the
relative concentration of sulphur and selenium powder in the anion stock solution (Figure 18 (a)).

The bandgap of the nanocrystals can be controlled in the range of 1.52 eV to 1.47 eV. Chen et al. synthesised kesterite CZTSSe alloyed nanocrystals giving access to the band-gap tuning between 1.0 eV and 1.5 eV.

Compared with kesterite derived alloys, wurtzite derived alloys are much more difficult to synthesize as they need control over two-fold energetic metastability. Yu et al. reported composition and band-gap tunable wurtzite CZTSSe nanocrystals with a tunable bandgap range from 1.00 eV to 1.5 eV that shows good agreement with the ab initio calculations.

Singh et al. showed the first low temperature photoluminescence emission study of wurtzite CZTSSe nanocrystals with a compositionally tunable bandgap ranging between 0.9-1.4 eV (Figure 18 (b)).

The bandgap tunability in I₂-III-IV-VI₂ semiconductor nanocrystals can also be achieved by adjusting the cation ratio as shown by Hillhouse and co-workers. They reported the synthesis of Cu₂Zn(Ge₁₋ₓSnₓ)S₄ (CZTGeS) nanocrystals modified from CZTS nanocrystals by replacing tin precursor (Sn(acac)₂Cl₂) with an equivalent molar amount of germanium precursor (GeCl₄).

The bandgap of the CZTS nanocrystals can be increased from 1.5 to 1.93 eV by increasing the Ge content.

Recently, a variety of potential elemental combinations involving the elements such as Cu, Zn, Sn, Fe, Ge, Cd to synthesis multinary semiconductor nanocrystals has opened new ways to design novel functional materials. Development of quaternary materials modified from CZTS and CZTSe nanocrystals such as Cu₂ZnGeSe₄, Cu₂CdSnSe₄ and Cu₂FeSnS₄ has set new standards in controlling shape, phase, composition and monodispersity of nanocrystals simultaneously (Figure 17 (e, f)).

126, 127
Recent progress in understanding the underlying reaction mechanisms by the combination of state-of-the-art microscopic, spectroscopic and diffraction techniques has allowed creation of more rational design of syntheses. Regulacio et al. performed a detailed shape evolution study for quaternary metal chalcogenide nanocrystals.\textsuperscript{138} They proposed a formation mechanism for WZ-derived CZTS nanocrystals based on the precise characterization of intermediate products via an aliquot study. They concluded that during the synthesis of anisotropic wurtzite derived CZTS nanocrystals by the heating up approach, hexagonal Cu\textsubscript{1.95}S nanocrystals are formed at the nucleation stage. The anisotropic growth starts at one side of the Cu\textsubscript{1.95}S nanocrystals with fast cation exchange between the Cu\textsubscript{1.95}S and Zn and Sn cations in the solution subsequently leading to phase-pure WZ derived CZTS nanocrystals. Later, Shavel et al. observed that tetragonal CZTS nanocrystals as synthesised in a flow-reactor also follow the same formation pathway.\textsuperscript{139} The reactivity of Cu, Zn and Sn sources are in the order of Cu > Sn > Zn and Sn and Zn atoms eventually enter the nucleated Cu\textsubscript{2}S nanocrystals through cation exchange. Tan et al. used surface-enhanced Raman scattering (SERS) spectroscopy to confirm the phase purity of wurtzite CZTS nanocrystals synthesized by the hot injection protocol.\textsuperscript{140} Due to the superior selectivity and sensitivity of SERS, they were able to elucidate the growth mechanism of CZTS nanoparticle formation. It was revealed that the shape evolution in hot-injection protocols also occur in three major stages: First, Cu\textsubscript{2−x}S nanoparticles are nucleated which is followed by diffusion of Sn\textsuperscript{4+} into Cu\textsubscript{2−x}S nanoparticles to form the Cu\textsubscript{3}SnS\textsubscript{4} (CTS) phase and diffusion of Zn\textsuperscript{2+} into CTS nanoparticles to form the CZTS phase. The studies on shape evolution and formation mechanism confirmed that the ternary (I–III–VI\textsubscript{2}) and quaternary (I\textsubscript{2}–II–IV–VI\textsubscript{4}) materials share the same evolution pathway.
1.9 Polytypism

Polytypism can be defined as the occurrence of two crystal polymorphic forms within the same particle.\textsuperscript{141} It is generally prevalent in tetrahedrally coordinated IV, III–V and II–VI semiconductors crystals due to large atom stacking freedom, among which hexagonal wurtzite (WZ) and cubic zinc blende (ZB) are two very commonly observed polymorphs.\textsuperscript{142} The (111) plane of the cubic ZB lattice structure can interface well with the (002) plane of the hexagonal WZ structure allowing for ease of transition between growth in either phase to create polytypes.\textsuperscript{143} This allows for the nucleation of a particle in one crystal phase with the subsequent transition to growth in another crystal phase leading to shape morphologies that are not possible in single crystal systems.

\textbf{Figure 19}. Schematic illustration of the polytypic nanocrystal growth with different morphology.\textsuperscript{144}
For example, branched 3-D morphologies are obtained when the nucleation takes place in ZB with subsequent growth in WZ (Figure 1). The faceting of the ZB seed is such that it has eight (111) crystalline facets that each can serve as nucleation points for subsequent transition to growth of WZ. The formation of tetrapod nanocrystals are obtained when the four (111) ZB facets (more reactive facets compared to four (111) ZB facets) allow the epitaxial growth of wurtzite pods. Octapod nanocrystals are obtained when all the eight (111) ZB facets serve as nucleation facets for epitaxial growth of WZ pods under suitable conditions (Figure 19(a)). Branched polytypes of this form with nucleation in ZB and then subsequent growth in WZ have been observed with, tetrapods of CdSe,\textsuperscript{50, 145, 146} CdTe,\textsuperscript{51, 57, 146} CdS,\textsuperscript{75, 147} ZnSe,\textsuperscript{148, 149} ZnTe\textsuperscript{150} and multipods of CdSe/CdS\textsuperscript{143, 145, 151} and CdSe/CdTe.\textsuperscript{143} Polytypes arising from nucleation in the WZ phase with subsequent growth in ZB are always linear 1-D structures.\textsuperscript{152} In WZ, there are only two opposite (002) facets that can allow transition to epitaxial growth of ZB tips. Additionally, the reactivity of +(002) facet differs from that of −(002) facet which gives access to localize the ZB tip selectively on one or both ends of the WZ core (Figure 19(b)).\textsuperscript{144} The most common route to polytypic nanocrystals is the colloidal hot-injection method as it allows separation of cationic and anionic species until nucleation (injection) and facilitates different temperatures for nucleation and growth. This allows nucleation in the kinetically stable phase and growth in the thermodynamically stable phase with increasing temperature. Consequently, the tetrapod polytypes are more commonly found in II-VI nanocrystals where ZB is the metastable nucleating seed whereas linear morphologies are common in I-III-VI nanocrystals and their derivatives where the wurtzite seed is metastable.\textsuperscript{144, 152}
1.9.1 Binary II-VI Semiconductor Polytypic Nanocrystals

In the II-VI semiconductor nanocrystal system, Alivisatos and coworkers demonstrated complete control over the shape of CdSe nanocrystals using a colloidal approach in the early 2000s. They varied three fundamental reaction parameters: ratio of the surfactant in the growth solution (Hexylphosphonic acid (HPA)/Trioctylphosphine oxide (TOPO)), volume of initial injection and time dependence of monomer concentration. While a major observation of this work was the discovery that different combinations of surfactants can speed up or slow down growth rates along certain crystal directions to affect shape control in a single crystal system, they also observed more complex tetrapod shapes that could only arise from polytypism. Initially, this was observed as a random event sometimes aided by unintentional impurities in different batches of phosphonic acid surfactants. The frequency of occurrence of random polytypism was also observed to be greater with CdTe in comparison to their sulfur or selenium analogues. In the very first studies of polytypic morphologies in II-VI inorganic materials, the serendipitous occurrence of branched nanocrystals was considered to be a result of difference in the growth rate of different crystal facets as a function of time.
Figure 20. II-VI polytypic nanocrystals (a) Crystal model of CdTe Tetrapod; (b) Transmission electron microscope (TEM) image of a CdTe Tetrapod; (c) High resolution- TEM (HRTEM) image of CdSe multi-pod nanocrystals synthesized by using monofunctional phosphonic acids (Propylphosphonic acid and tetradecylphosphonic acid); (d) HRTEM image of CdSe hyperbranched nanocrystals synthesized by using bifunctional phosphonic acid (2-carboxyethylphosphonic acid) with tetradecylphosphonic acid.\textsuperscript{57,146}

In a seminal work on high yield synthesis of CdTe polytypic tetrapods by Manna \textit{et al.}, independent tuning of the pod length and diameter was achieved by manipulation of growth kinetics.\textsuperscript{57} CdTe has an energy difference between ZB and WZ phases large enough that at elevated temperatures, (10 mEV) high quality of WZ growth is preferred with selective nucleation in the ZB structure. Using long alkyl
chain phosphonic acid (Octadecyl phosphonic acid (ODPA)) as the ligand selectively stabilizes the non-polar lateral facets of the CdTe WZ phase which are not equivalent to the CdTe ZB phase (Figure 20 (a, b)). Presence of excess ODPA per Cd\(^{2+}\) (lower Cd/ODPA ratio) decreases the reactivity of the Cd precursor and slows down the growth rate resulting into larger diameters of the pods. On the other hand, a high Cd/Te ratio increases the growth rate and results into longer pod growth in WZ phase. The formation and stability of CdE (E=Te, Se, S) tetrapod structures were studied intensively by different research groups to determine the effect of various ligands, monomer reactivity and temperature on the polytypic nanocrystal growth in binary systems.\(^{50, 51, 75, 146, 154-159}\) Each of these factors is inter-dependent, yet interesting observations on the growth mechanism becomes apparent if one is used as a control factor. Take for example temperature, Cheon et al showed that the number of WZ pods growing from the (111) ZB planes in CdS could be increased from one to four by reducing the temperature of growth from 300 °C to 120 °C with all other reagents in their synthetic protocol remaining constant.\(^{147}\) The thermodynamic influence on the occurrence of polytypism was best observed by Huis et al. who showed that post synthetic transformation of uncapped (ligand free) spherical zinc-blend CdSe seeds into polytypic tetrapods or octapods having WZ pods by annealing the samples at high temperature.\(^{157}\) The ZB to WZ local structural transition starts from the outer most layers proceeding into the inner layers as predicted by molecular dynamic simulations and confirmed by in-situ TEM. In a colloidal system, additives such as quaternary ammonium salts in addition to the phosphonic ligands\(^{158}\) have also shown to induce branching during growth in good agreement with similar observations with respect to short chain phosphonic acid impurities with CdE.\(^{160}\) Control of such factors that allow for branching can be exploited to give
hyperbranched (more than 4 pod) nanocrystals under optimum conditions. Kanaras et al showed that, low concentration of the chalcogenide precursor, presence of short alkyl chain and/or bifunctional phosphonic ligands as surfactants allows the formation of snow-flake like polytypic structures by growth of multi WZ pods from a ZB derived core (Figure 20 (c, d)).

To date, polytypic zinc chalcogenides have shown higher yield when synthesized by thermochemical methods based on evaporation and condensation vapour processes or solvothermal processes. In colloidal approaches, precursor reactivity have been investigated and tuning of supersaturation conditions to provide thermodynamic control of the growth mode and enable switching between the ZB and WZ structures.

### 1.9.2 I₂-III-VI Semiconductor Polytypic Nanocrystals

Similar to the II-VI binary and ternary semiconductor nanocrystals, I-III-VI semiconductors such as CuInS₂ (CIS), CuInSe₂ (CISe) and CuInGaSe₂ (CIGSe) are considered theoretically to be derived from the binary ZnSe through replacing part of Zn atoms by Cu, In and Ga atoms. Since, the binary ZnSe have the ZB and WZ structures, therefore ternary and quaternary nanocrystals have the corresponding ZB-derived and WZ-derived structures. The most stable states are the ZB-derived phases, however by manipulating the reaction kinetics, metastable WZ phases can also be formed. Furthermore, unexpected polytypism can also be observed in these systems during the solution based colloidal synthesis. The first example of polytypism in these multinary systems was randomly discovered by Korgel et al. during CuInS₂ nanodisks synthesis where the WZ phase interfaces with significant chalcopyrite (CH) domains across (002)\textsubscript{WZ}/(112)\textsubscript{CH} stacking faults. Later, different
researchers found that during the colloidal synthesis, at lower temperatures the meta-stable wurtzite form of CuInS$_2$ occurs as nanoplates but as the number of metal cations decrease with further progression of the reaction, WZ-ZB polytypism occurs in the system.$^{165,166}$ Furthermore, partial or complete substitution of Ga or Fe in the crystal lattice of CuInS$_2$ to form CuInGaS$_2$ (CIGS), CuGaS$_2$ or CuInFeS$_2$ also results into the occurrence of WZ-ZB or WZ-CH polytypism.$^{167-170}$ However, formation of branched morphologies or 1-D linear structures were not reported in Cu-In-Ga-S/Se systems.

**Figure 21.** (a) The cover art showing a 3D model of different nanoparticles type formed, hexagonal, cubic, linear heterostructure, and tetrapod, highlighting the ability to synthetically control the formation of each in a single system; (b) TEM image of Cu$_2$SnSe$_3$ tetrapods (c) TEM image of Cu$_2$SnSe$_3$ linear heterostructures; (d) TEM image of pencil shaped Cu$_2$ZnSnS$_4$ (CZTS) polytypic nanocrystals.$^{171-173}$
1.9.3 $I_2$-II-IV-VI$_4$ Semiconductor Polytypic Nanocrystals

Separation of nucleation and growth events into two different phases to form branched polytypic nanocrystals is much more difficult in the ternary and quaternary compounds than the binary compounds as it involves many more reaction parameters to balance. We reported the first time, formation of tetrapods in ternary Cu$_2$SnSe$_3$ (CTS) nanocrystals showing the possibility of complex 3-D structures in the case of multinary semiconductors (Figure 21 (a-b)). The high temperature injection (310 °C) favoured the nucleation in ZB and subsequent growth at a slightly lower temperature (295 °C) lead to the formation of WZ arms. The interface between the ZB and the WZ phases shared the same planes as they do in the case of CdTe or CdSe. The polytypism can be tuned in both 3-D branched shape and 1-D rod shapes by judicious selection of different precursors, ligands and reaction temperature. The formation of linear heterostructures (1-D nanocrystals) requires the nucleation at low temperatures to facilitate formation of the metastable WZ seed (Figure 21 (c, d)). Temperature ramp with further progression of the reaction leads to the epitaxial growth of ZB derived structure on the two (002) facets of the wurtzite seed (Figure 21(c)). The reactivity coefficients of the metal precursors and their compatibility with the ligands have a huge impact on the formation of single or separate domains in nanocrystals.

Formation of linearly arranged ZB-/WZ-/ZB polytypic CZTSSe nanocrystals in rugby-ball shape was also shown by Yu and co-workers. These nanocrystals were found to have two possible typical sequences at the WZ-ZB interface i.e. $\cdots$ABC/AB$\cdots$AB/CBA$\cdots$ and $\cdots$ABC/AB$\cdots$AB/ABC$\cdots$. The first case reflects that the central WZ-derived domain acts as a twinning plane of ZB-derived structure whereas in the latter case it looks like that one ZB-derived nanoparticle is separated
by a WZ-derived domain. When the wurtzite plate acts as seed both (0002)WZ facets can serve as nucleation facets for the epitaxial growth of ZB pods. Additionally, due to the difference between the reactivity of +\((002)\)WZ and -(002)WZ facet, it is possible to selectively grow one or two ZB structure from the wurtzite facet (Figure 22(a)). In a different piece of work, the same authors showed that the epitaxial growth of ZB derived tips in rugby ball shaped polytypic Cu\(_2\)CdSn(SSe)\(_4\) nanocrystals can be localized to just one (002) facet of wurtzite disc by increasing the Cd molar concentration in the reaction flask to form bullet-shaped geometry.\(^{144}\) Beside the formation of this linear geometry, branched morphology is also possible in the quaternary systems. Cabot and co-workers were successful in synthesizing polarity driven branched Cu\(_2\)CdSnSe\(_4\) nanocrystals.\(^{174}\) The initial seeds are zinc-blende in nature with pentahedral morphology giving rise to wurtzite derived branches by a twining mechanism (Figure 22(b)).
Figure 22. (a) HR-TEM images of rugby-ball shaped polytypic CZTSSe nanocrystals with a central wurtzite core and zinc blend ends; (b) HR-TEM image Cu$_2$Cd$_x$SnSe$_y$ polypods with zinc-blende derived core and wurtzite pods; (c-e) 3-D crystal models of the ellipsoidal, arrow-shaped and bullet shaped polytypic CZTSSe nanocrystals with wurtzite core and zinc-blende derived tips.$^{152,174,31}$

The number of interfaces shared between the two phases i.e., WZ and ZB and their size ratio is also controllable in multinary nanocrystals. We have recently observed that by judicious selection of ligands and metal precursors the shape of linear polytypic nanocrystals can be tuned from ellipsoids to arrow shaped to bullet shaped in Cu$_2$ZnSn(SSe)$_4$ (CZTSSe) nanocrystals (Figure 22(c-e)).$^{31}$
1.9.4 Controlling Factors for the Occurrence and Tuning of Polytypism

Phase selective growth to produce polytypic nanocrystals requires a fine balance between the different control factors involved in the reaction kinetics; specifically the temperature, ligand chemistry, presence of additives and choice of precursors and their reactivity. The influence of each of these factors is detailed in the following section.

1.9.4.1 Temperature

Temperature plays an important role in the colloidal reaction kinetics as it determines the activation energy for the nucleation and growth processes. Most of the colloidal syntheses are carried out between room temperature to 350 °C, with the upper limit dictated by the boiling point of solvent/surfactants that are used.\textsuperscript{66, 131} This range facilitates the separate temperature zones effective for nucleation and growth of nanocrystals.\textsuperscript{175} Nanocrystals can be synthesized by the hot-injection approach (most common) where nucleation occurs on rapid supersaturation or by one pot non-injection methods with nucleation initiators.\textsuperscript{65, 176} A rapid temperature perturbation often instigates polytypism in the growing nanocrystals.\textsuperscript{171} During the formation of II-VI semiconductor branched morphologies, the germination occurs in kinetically favoured ZB phase at low temperature and rapid temperature ramp allows the formation of thermodynamically stable WZ phase.\textsuperscript{143} During the synthesis of multicomponent copper chalcogenides, we have observed that the temperature range for the growth of WZ phase is 220–280 °C and for ZB growth is 255–310 °C.\textsuperscript{172} If the nucleation temperature is higher (>280 °C) than the growth temperature then the resulting nanocrystals tend to have the 3-D morphology with a tetrahedrally
coordinated ZB core and WZ derived arms. Contrary to this, when the nucleation is achieved at a much lower temperature (<220 °C) with the growth at higher temperatures, 1-D linear structures are formed having a WZ core and two ZB derived tips on either ends.

1.9.4.2 Ligand Chemistry

The chemical nature and physical dimension of the ligands used in the colloidal synthesis of nanocrystals have a huge impact on the structure, morphology and stability of the resulting nanocrystals. The understanding of the role of ligands during nucleation and growth is essential to help the system break the inversion symmetry of crystal structure which is an intrinsic requirement for growth of biphasic nanocrystals. One of the most exploited classes of ligands in semiconductor nanocrystal growth via colloidal approach constitutes alkylphosphonic acids. This is mainly due to three reasons: (i) they are the strongest binding ligands among TOPO, amines and fatty acids confirmed by DFT calculations, (ii) The [cation-phosphonate] complexes are stable even at high temperature for hot injection colloidal methods, (iii) The lengths of the alkyl chains associated with them has a strong impact on the equilibrium between the wurtzite and zinc-blend polytypes. Many researchers have reported the effect of alkyl chain length of a phosphonic acid over the formation mechanism during the synthesis of branched morphologies in Cd containing semiconductor nanocrystals. It is widely accepted that the shorter chain phosphonic ligands stimulate the anisotropic growth (WZ) in the II-VI nanocrystals. A simpler explanation is that the complex between the cationic species and the short chain ligands react more rapidly to form nuclei upon reaction with the anionic precursor. Due to the less steric hindrance, diffusion of the nuclei is
faster consequently leading to anisotropic shape evolution. The vice-versa applies to the longer chain phosphonic acids. Hence, mixtures of different chain length phosphonic acids in an optimized molar ratio gives control over length and degree of branching in the synthesized nanocrystals.\textsuperscript{47, 48}

1.9.4.3 Impurities/Additives

Interestingly the growth kinetics of the colloidal nanocrystals can be dramatically influenced by the impurities present in the batch of chemical employed for synthesis. Manna and his co-workers found that when very pure ODPA (99%) was used for synthesizing CdTe, spherical nanocrystals were obtained while when low-purity commercially available ODPA was used, nanorods or tetrapods were formed.\textsuperscript{48} The impurities present in the low-purity ODPA batch were the shorter chain phosphonic acids such as methyl phosphonic acid and propyl phosphonic acids which fostered the branching in CdTe nanocrystals.

For the synthesis of multinary copper based metal chalcogenide such as CIS, CIGS, CZTS, CZTSSe in wurtzite phase, oleylamine (OLA) and hexyldecylamine has been widely due to their dual function as coordinating solvent and ligand. We have observed during the formation of CTS, CZTS and CZTSSe polytypic nanocrystals, that OLA clearly favours the wurtzite phase formation at low temperatures either as nucleating seed or as an extension of zinc blend derived seed in the form of elongated pods.\textsuperscript{171-173}

1.9.4.4 Precursor Chemistry

For synthesizing monodisperse binary, ternary or quaternary semiconductor nanocrystals, the reactivity of the ionic precursors and the ligands should be well balanced. This is best achieved by applying Pearson’s hard and soft acids and bases
(HSAB) principle, originally developed for metal coordination compounds, to the bonding of molecular species to the nanocrystal surface and to identify the ideal precursors for controlling the reaction rate.\textsuperscript{42} The initial syntheses of Cd based polytypic nanocrystal were achieved with alkylcadmium precursors as they are the most reactive cadmium source.\textsuperscript{50,147} With the advancement of colloidal chemistry, the highly toxic precursors were replaced by low toxic CdO having moderate reactivity in the reaction which could be tuned by judicious section of ligands.\textsuperscript{57} The reactivity is best balanced by introduction of the anions in the form of phosphine complexes such as, Trioctylphosphine (TOP)-chalcogen (TOP-Te, TOP-Se) which facilitate the formation of zinc-blende seeds at high temperatures and further interplay of precursors and ligands lead to growth extension in wurtzite phases.\textsuperscript{57,158} For multinary metal chalcogenides, due to the involvement of four or five metal precursors in one system, the HSAB principle cannot be used to predict all possible precursor- ligand exchange routes. From detailed in-situ studies on growth and nucleation of copper based metal chalcogenide nanocrystals, it was found that Cu\textsuperscript{+} is the most reactive species in the colloidal solution.\textsuperscript{140} The reactivity of its precursor and the interaction with the ligand decides the rate of nucleation, and number of nuclei formed during nucleation. Wang \textit{et al.} discovered that the use of copper chloride (highly reactive Cu source) along with tin chloride as metal precursors provided optimal control over separation of nucleation and growth events to form polytypic Cu\textsubscript{2}SnSe\textsubscript{3} tetrapod and linear heterostructures.\textsuperscript{172} Coughlan \textit{et al.} for CZTS polytypic nanocrystals reported that the combination of metal chlorides as precursors along with OLA prompts the growth of biphasic heterostructures.\textsuperscript{173} We have observed lately that by separating out the role of precursor and ligand species, it is possible to tune the shape and phases of complex polytypic structures.\textsuperscript{31} When CuCl
is used as copper precursor it facilitates rapid growth on both (002) facets and the occurrence of large ZB-derived tips to form ellipsoidal shaped crystals. On the other hand, when Cu(I)OAc was used as precursor, growth of zinc-blend tip was localized to only one (001) facet of wurtzite disc. Both Cu(I)Cl and Cu(I)OAc are the combination of a soft acid (Cu\(^+\)) and a hard base (Cl\(^-\)/OAc\(^-\)). However, as the acetate is a softer base than the chloride (0.16 eV vs. 2.49 eV respectively), this makes Cu(I)OAc less reactive than Cu(I)Cl. As the (002) facets of wurtzite terminate in either a row of metal or chalcogen respectively, the opposite ends have different polarity and surface energies and are passivated differently by the available surfactant species. With a less reactive copper precursor, this manifests as a preference for growth at one end most likely the chalcogen terminated as the ligand species are optimized for interaction with the metal ions.

Figure 23. (a-d) Assembly of octapods on a flat substrate following solvent evaporation; (e) schematic of self-assembly of tetrapods by the nanowelding approach and (f) TEM image of nanowelding assembly.\textsuperscript{178,179}
1.9.5 Effect of Polytypism on Properties

The wide range of control parameters and complex chemistry makes polytypes some of the most interesting and challenging structures in colloidal nanocrystal chemistry. Progression in our understanding of polytypism from a random event to a controllable phenomenon is critical to the application of semiconductor nanocrystals. In applications requiring single crystal nanostructures for example, spontaneous polytypism is undesirable as regions of different phases can act as electron traps or recombination centres. A better understanding of polytypism would help control the occurrence when not required but equally significant would allow for design of a wide range of new materials and properties that benefit from polytypic transformations. For example, polytypes are particularly interesting for thermoelectric as the small grain sizes and variation in band structure for different phases allow independent tuning of thermal and electrical conductivity to maximise the seebeck coefficient. Arbiol, Cabot and co-workers reported the 2.5-fold enhancement of thermoelectric figure of merit for ternary Cu$_2$GeSe$_3$ (CGSe) nanocrystals by synthesizing polytypic CGSe nanoparticles with disordered cation positions.\textsuperscript{180}

The branched shape evolution possible also leads to shape dependent properties not attainable with single crystal structures such as tetrapod photovoltaics\textsuperscript{181} where the branches act as antennae for light harvesting or as single electron transistors\textsuperscript{182} where the core acts as a quantum well with the pods providing contacting and gating functionality.

In more complex quaternary polytypes the lack of cation ordering in the branches shrinks the band gap energy and shifts the Fermi energy into the conduction band giving the branches a metallic character that are interesting for surface plasmonic
Organisation of polytypes into superstructures is also interesting (Figure 23 (a-d)). Manna and co-workers showed that hierarchical organization of octapods could be achieved by slowly decreasing the stability of the octapods in solution. Later self-assembly by ‘nanowelding’ approach was also introduced by same authors to allow better electron transport. They showed that coalescence of gold domains tipped at the ends of the branches of tetrapods lead to the formation of disordered 3-D superstructures welded together through gold particles (Figure 23 (e,f)).

Ultimately, controlled polytypic transformations in nanocrystals offer exciting opportunities for materials design where complex branched nanostructures can be defined across a range of material compositions, assembled into superstructures and demonstrate heretofore unachievable material properties defined by their polytypic construct.

1.10 Future Outlook

The synthesis and application of semiconductor nanocrystals especially cadmium and lead based binary nanocrystals, has reached new heights in last two decades. However, research on the advancement of robust synthetic protocols and application of ternary and quaternary metal chalcogenide nanocrystals is still in its infancy. A deeper understanding of the complexity of these materials is highly recommended to improve their synthetic strategies and practical uses. Full investigation of the nucleation and growth of colloidal multicomponent nanocrystals is particularly important. Insights on reaction intermediates, growth kinetics and the nanocrystal evolution in solution will give access to extend the material composition and crystal phases. Since the composition and crystal phases have huge impact on the optical
and electronic properties of the materials, it would help to improve the device applicability of ternary and quaternary semiconductor nanocrystals. Moreover, control over the crystal defects is required to improve their optical and electronic characteristics. By introducing external elements as dopant in these systems, the electronic configuration could be modified. Furthermore, research on making the metal chalcogenide nanocrystals air-stable for longer durations is demanded for the fabrication of nanocrystal based devices. Finally, development of more cost-effective protocols to synthesis stable semiconductor nanocrystals consisting earth abundant elements would increase their demand in real life devices fabrication.
1.11 References


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Chapter 2: Experimental Procedures and Characterisation Techniques

2.1 General Synthetic Strategies

The multinary semiconductor nanocrystals presented in this thesis are synthesized by a bottom-up strategy using colloidal chemistry. One of the key appeals of the colloidal synthetic approach is the ability to control the morphology, composition and crystal structure of the nanocrystals.\(^1\) A wide variety of nanocrystals can be synthesized by this method in which ionic precursors are combined in a solvent/ligands at high temperature.\(^2\) Colloidal chemistry can produce materials with a high yield and on big scale, as compared to the top-down technologies. The investments to start the synthesis by the colloidal approach are much lower than any epitaxial method, which is one of the key reasons for the success of this technology.

The equipment required for a colloidal synthesis include a glass Schlenk line connected to vacuum pump and inert gas, round-bottom flask and temperature controller unit (as shown in Figure 1). The three-necked round bottom flask is connected via a condenser to the Schlenk-line. The remaining two necks of the flask are sealed with rubber septa and serve for the measurement of the temperature of the flask using a thermocouple and for the injection of the reactants. The Schlenk line is connected to the vacuum pump via a tube and through liquid nitrogen cooled trap. A second tube from the Schlenk line is connected to an inert gas supply from one side and via an oil bubble to the exhaust. The reaction is carried under an inert atmosphere as some of the reactants are air sensitive. The mixture of ligands, solvent and the metal precursors are loaded together in the flask and connected to the schlenk line. The temperature of the flask is increased to 100-120 °C in an inert atmosphere.
via using the temperature controller unit. Once the mixture is in a molten form, the flask is evacuated and kept under vacuum for 30-60 minutes to remove all the volatile impurities. The flask is again flushed with inert gas after the evacuation period and temperature is increased further up to 250-300 °C. Once the complex between the ligands and the metal precursors are formed, the chalcogen stock solution (i.e. S, Se or Te precursor) is injected into the flask. Nucleation sets shortly after injection of the chalcogen. The reaction between the metal precursor-ligand complex and the chalcogen is accompanied by a colour change in the flask. The flask is then held at high temperatures for an optimised time period to allow for nanocrystal growth. After the nanocrystals are formed, the temperature is lowered to 100-80 °C and anhydrous toluene is added in the flask to quench any further growth of the nanocrystals. The content of the flask is poured into vials and are washed subsequently by using a mixture of toluene and isopropanol. The washed nanocrystals are stored in toluene for further use.

Figure 1. (a) The Schlenk-line set-up; (b) closer view of the flask equipped with condenser and thermocouple.


2.2 Characterisation Methods

2.2.1 TEM

TEM is a powerful and unique technique for the structural characterization of nanocrystals. It gives access to the real space visualization of the crystal and helps in identifying and quantifying the structure of individual nanocrystals. The first TEM was built by two German scientists, Max Knoll and Ernst Ruska in 1931. They also built the first commercial TEM in 1939. Since then, improvements in design and technological innovations have allowed for real-time observation of chemical reactions at the atomic scale.

Figure 2. Schematic representation of a TEM.
A modern TEM is composed of an illumination system, a specimen stage, an objective lens system, the magnification system, the data recording system, and the chemical analysis system. Figure 2 shows the various components of a TEM. At the top of the column, there is a high electron emitter (also known as electron gun). The electron gun uses either a LaB₆ thermionic emission source or a field emission source which gives a high illumination current that travels down the column. The illumination system is also comprised of condenser lenses that assist in making a fine electron probe. The electron beam passes through the specimen stage carrying the sample and a number of magnifying lenses and is ultimately focused at the viewing screen at the bottom of the column. There are three major lenses that are used to form and magnify an image. The objective lens is the primary lens which determines the limit of image resolution. The magnification system consists of intermediate lenses and projection lenses. They increase the magnification of the image up to 1.5 million and project the image onto the imaging surface. The data recording system consists of a charge coupled device (CCD) which allows for digital quantitative data processing.
2.2.2 STEM

STEM offers a range of different imaging modes for proper investigation of the elemental composition with atomic level resolution. The working principle of STEM is similar to the scanning electron microscope (which will be described in section 2.2.5) in many ways. However, STEM requires a thin, electron transparent specimen while a bulk sample is used in SEM. In STEM, the electron beam is focused into a narrow spot which can be scanned over the sample in a raster pattern by the exciting scanning deflection coils. The scattered electrons are detected and their intensity is plotted as a function of the probe position to form an image. The typical imaging detectors used are the bright-field (BF) detector and dark-field (DF) detector. The highest spatial resolution in STEM is obtained by using the transmitted electrons. Similar to SEM, multiple detectors can be used simultaneously in STEM to achieve maximum information about the sample.

2.2.2.1 Bright Field Imaging in STEM

In bright field mode, the transmitted electrons that have not been scattered at all or have been inelastically scattered (also known as the (000) transmitted beam) contribute to the final image formation. The bright field mode in STEM can be beneficial to obtain more information by using a much larger detector compared to TEM mode. If the size is chosen small enough to exclude all of the diffracted beams, the configuration is called diffraction contrast, which is generally used for low-resolution imaging of defects. In this configuration, the crystalline sample is oriented to give a particular diffracted beam and the image is sensitive to differences in the sample thickness, strain and defects in the crystals which result into distortion of crystal lattices. High-resolution imaging is usually performed in bright-field mode by including a few of the Bragg diffracted beams within the objective aperture. When a
crystal is oriented along one of its low-index zone axes, strong Bragg reflected beams are present. The Bragg reflected beams and the central transmitted beam show interference and form an image in high resolution mode.  

Figure 3. Simulated images of Au clusters on few-layer graphene and the corresponding HAADF and BF images.  

2.2.2.2 Dark Field Imaging in STEM

In the dark field mode, the (000) beam is excluded from the final image. Figure 3 shows the bright-field and dark-field images, along with the simulated images generated by careful analysis of the sample in both imaging modes. The dark-field mode involves tilting the incident beam by a pair of deflection coils to bring the diffracted beam parallel to the optic axis and this reduces the spherical aberration effect. A large objective aperture is used to record the high-resolution images in the dark field imaging mode. Dark field operation offers significant benefits over bright field imaging by giving a clearer view of the shape and construction of the crystal using high angle annular dark field (HAADF) imaging. HAADF images are formed by collecting high-angle elastically scattered electrons that travel close to the atomic
nuclei in the crystalline sample, which are detected by using an annular dark-field detector in STEM instruments. The contrast of HAADF images is not strongly affected by dynamical diffraction effects or by sample thickness variations but is strongly dependent on the average atomic number of the scatterer encountered by the incident probe. The spatial resolution is limited by the size of the focused incident probe. HAADF imaging has possible applications in compositional imaging of the semiconductor interface, quantitative elemental mapping and imaging of surface features. In particular, the use of “Z-contrast” in the HAADF-STEM imaging mode is advantageous for providing directly interpretable, atomically resolved imaging and analysis of nanometre-sized particles, where the scattering cross section is sensitive to the projected sample thickness and the atomic number, Z, of the constituent atoms (in the limit of Rutherford scattering, a $Z^2$ relationship).
2.2.3 Electron Diffraction Techniques

Electron diffraction is a powerful method for analysing the crystal structure, as well as the defects in the crystalline sample. Electron diffraction is very different from X-ray diffraction. In electron diffraction, a single wavelength can produce many diffracted beams. The electrons possess a shorter wavelength and experience more scattering because they interact with both the nucleus and the electrons of the scattering atoms through Coulomb forces. The use of electron diffraction to analyse the crystal structure was established by Vainshtein and co-workers in early 1940s.\textsuperscript{10}

![Figure 4](image)

**Figure 4.** (a) Optical ray diagram with an objective lens showing the principle of imaging process in TEM; (b) HRTEM of a twinned segment of kesterite Cu\textsubscript{2}ZnSnS\textsubscript{4} nanocrystals and the resolved FFT pattern indexed with plane positions; (c) the corresponding SAED pattern with indexed planes.\textsuperscript{11}

The main principles of electron microscopy can be explained by using optical ray diagrams, as illustrated in Figure 4 (a). Diffracted waves scattered by the atomic potential are focused with the objective lens to form diffraction spots on the back
focal plane. On the image plane, the diffracted waves recombine to form an image. The diffracted electrons are focused into a regular arrangement of diffraction spots by electromagnetic lenses and recorded as the electron diffraction pattern. The diffraction pattern forms in the space called reciprocal space; the space at the image plane is called real space. The transformation from the real space to the reciprocal space is mathematically given by the Fourier transform.\(^\text{12}\)

The major advantage of TEM is that both electron microscope images (information in real space) and diffraction patterns (information in reciprocal space) for the same region could be obtained by adjusting the electron lenses. Since the SAED can be recorded from almost every grain in a polycrystalline material, the relationship between the reciprocal lattices and mutual crystal orientation can be easily obtained. For example, Figure 4 (b) and (c) show the TEM image and the corresponding SAED pattern of a Cu\(_2\)ZnSnS\(_4\) nanocrystal, respectively. The HRTEM image is marked with the interplanar spacing values. These values show equivalence to the planes obtained from SAED pattern and further confirm the crystal phase to be kesterite. By using electron diffraction, crystal structure information can even be obtained for materials, where single crystals of the sizes suitable for x-ray or neutron diffraction are unavailable.
2.2.4 EDX

EDX and electron energy loss spectroscopy (EELS) can be used as complementary techniques to quantify the chemical composition of the sample. They are possibly the most accurate microanalysis technique in TEM.\textsuperscript{13} Elemental mapping and line scans are two common approaches used in EDX analysis. Figure 5 (a) shows the accuracy of elemental mapping and line scans in STEM mode which were used to determine the local composition of Cu\textsubscript{2}SnSe\textsubscript{3} nanocrystals.\textsuperscript{14} EDX relies on counting the X-rays emitted from the beam-illuminated region of the sample as a function of the photon energy. When the electron beam hits the sample, the electron from the inner shell of the atoms of the sample are excited to higher energy level or are ejected from the atoms leaving behind an electron hole where the electron was. The excited electrons relax into the holes created by the ejected electrons and release energy in the form of x-rays. Since each element gives particular peaks on its x-ray emission spectrum, owing to its unique atomic structure, the different elements present in the sample are detected. EELS analyses the intensity distribution of the transmitted electrons as a function of their energy loss. It provides not only the chemical information on the specimen but also its electronic structure.

![Figure 5](image_url)

**Figure 5** (a) STEM image and STEM-EDX elemental mappings of Cu\textsubscript{2}SnSe\textsubscript{3} nanocrystals; (b) STEM-EDX line scan of one single Cu\textsubscript{2}SnSe\textsubscript{3} nanocrystals; the inset is the corresponding STEM image.\textsuperscript{14}
2.2.5 SEM

Figure 6. Schematic representation of a SEM.

SEM is widely used for analysing the surface topography and chemical composition of the samples. The image resolution is lower than that of a TEM instrument and so, it is not very suitable for nanoparticle characterization (<10 nm). The main components and the working principle of an SEM are similar to that of a TEM. It is comprised of an electron source, a column (shorted in length than TEM column) equipped with electromagnetic lenses through which the electron beam travels, a sample chamber and computer attached with the camera to display images. Electrons are generated at the top of the column, accelerated down via passing through a combination of lenses and apertures to produce a focused beam of electrons. The electron beam hits the surface of the sample which is mounted on a stage in the
vacuum chamber. Both the column and the chamber are evacuated by a combination of pumps. The interaction between the electron and sample produces a number of signals which are detected by suitable detectors. A schematic representation of an SEM is shown in Figure 6.

The SEM uses a much smaller accelerating voltage that the TEM (3-30 kV) and generates topographical and compositional information about the sample. Figure 7 shows the SEM image of the cross-section of submicrometer-sized vertically assembled CuInGaS₂ nanorods. The image reveals that the nanorods assemble in dense and close packed arrays and stack on top to form multilayer nanorod assemblies. During sample cleaving, the multilayer nanorod film was delaminated, resulting in the dark feature between the layer and the underlying substrate in Figure 7 (a).

Figure 7. (a) SEM cross-section image showing the multi-layered assembly of CuInGaS₂ nanorods; (b) High-resolution SEM image showing the vertical alignment of CuInGaS₂ nanorods.

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2.2.6 XRD

XRD is one of the most common analytical techniques used for confirming the crystal phase and purity of the nanoparticle samples synthesised in this thesis. X-rays are electromagnetic radiation with photon energies in the range of 100 eV - 100 keV. The wavelength of the x-rays is comparable to the size of atoms and so, they are used for detecting the structural arrangement in a wide range of crystalline materials. The technique is based on the constructive interference between the monochromatic x-ray source and the crystal when conditions satisfy Bragg’s Law. This law provides the relationship of the radiation’s wavelength (λ) with the interplanar spacing (d) and diffraction angle (θ):

\[ n\lambda = 2dsin\theta \]

X-rays are produced by x-ray tubes in a XRD instrument when the electron beam bombards a stationary or rotating solid target. The target used in the x-ray tubes of the XRD instrument in this thesis is Cu which emits 8 keV x-rays with a corresponding wavelength of 1.54 Å. When the x-ray photons collide with electrons in the crystal, some photons from the incident beam are deflected in the same direction where they travel. If the wavelength of these scattered x-rays does not change, the process is called elastic scattering. On the other hand, when the x-rays transfer energy to the electrons and the scattered x-rays have different wavelengths, the process is called inelastic scattering. During diffraction experiments, the x-rays scattered elastically are measured as they carry information about the electron distribution. Diffracted waves from different atoms of the sample interfere with each other and control the intensity distribution. When the atoms are arranged periodically, sharp interference peaks are obtained having the same symmetry as in the distribution of atoms which are measured in order to deduce the arrangement of
atoms in the crystal. The set of diffraction peaks obtained from the sample is then used to characterize the crystal structure.

The XRD pattern of an unknown sample is often matched to the known crystal structures by using a Rietveld refinement fit. This software uses the least squares approach to refine a theoretical line profile until it matches well with the measured pattern. It refines various parameters including lattice parameters, the shape and width of the peaks and orientation of the crystal. This technique could be used to obtain the quantitative information, crystal size and site occupancy factors.

In this thesis, Rietveld refinement was used for structural analysis of CZTSSe nanocrystals in Chapter 4 and 6. The simulated pattern used for wurtzite, zinc-blende and kesterite phases of CZTSSe nanocrystals are given below:
Crystal data for Chapter 4

Crystal system Wurtzite

Space group P63mc

Unit cell dimensions $a=b=3.89697 \, \text{Å}$ and $c=6.4257 \, \text{Å}$

Atomic coordinates

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Table S3. Summary of peaks simulated data for wurtzite CZTSSe

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Crystal data for Chapter 4

Crystal system Zinc Blende

Space group F-43m

Unit cell dimensions a=b=c=5.658733 Å

Atomic coordinates

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Table S2. Summary of peaks simulated data for cubic CZTSSe

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Crystal data for Chapter 6

Crystal system Wurtzite

Space group P63mc

Unit cell dimensions \( a=b=3.9933 \, \text{Å} \) and \( c= 6.6003 \, \text{Å} \)

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Table S3. Summary of peaks simulated data for wurtzite CZTSSe

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Crystal data for Chapter 6

Crystal system Zinc Blende

Space group F-43m

Unit cell dimensions a=b=c=5.6455 Å

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Table S3. Summary of peaks simulated data for wurtzite CZTSSe

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Crystal system Kesterite

Space group I-42m

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Table S3. Summary of peaks simulated data for wurtzite CZTSSe

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2.2.7 XPS

XPS is a quantitative technique used for analysing the elemental composition of the sample and the chemical and electronic states of the elements in the surface regions. It works on the principle of photoelectric effect where electrons (photoelectrons) are emitted from a metallic surface when exposed to light. XPS spectra are obtained by irradiating a solid surface with a beam of X-rays while concurrently measuring the kinetic energy and electrons that are emitted from the material. The photo-emitted electrons travel through the vacuum to reach the detector of the instrument and undergo inelastic collisions, recombination and trapping. These effects reduce the number of photoelectrons collected by the detector. Since these effects increase with depth in the sample, XPS is regarded as surface sensitive instrument capable of analysis of the top 1-10 nm of the surface. The main components of an XPS instrument include a source of x-rays, an ultra-high vacuum chamber (attached with high vacuum pumps), a magnetic field shielding and an electron detector system. The vacuum chamber has additional units such as sample mounts, sample stage and stage manipulators.

When an atom or molecule absorbs an X-ray photon, an electron is ejected whose kinetic energy (KE) is related to the photon energy (hv) and the binding energy (BE) of the electron (i.e. the energy required to remove the electron from the surface) by the following equation:

\[ E_{\text{binding}} = E_{\text{photon}} - (E_{\text{kinetic}} + \varphi) \]

where \( E_{\text{binding}} \) is the binding energy of the electron, \( E_{\text{photon}} \) is the x-ray photon energy, \( E_{\text{kinetic}} \) is the kinetic energy of the electron and \( \varphi \) is the work function which is dependent on both the spectrometer and the material.
By measuring the kinetic energy of the emitted electrons, it is possible to determine the binding energy of the electron and the identity of the constituting elements and their chemical states. A photoelectron spectrum is recorded by counting the ejected electrons over a range of electron kinetic energies. This gives rise to peaks in the spectrum as a result of atoms emitting electrons of a particular characteristic energy. The energies and intensities of the photoelectron peaks enable identification and quantification of all surface elements (except hydrogen). XPS is very useful technique in determining element composition of a nanocrystal sample, as well as its phase purity. A representative XPS spectrum (indexed with the constituting elements) of CZTS nanorods sample is shown below:

![XPS survey spectrum for CZTS nanorods](image)

**Figure 8.** XPS survey spectrum for CZTS nanorods.¹⁷
2.2.8 UV-Vis and PL Spectroscopy

UV-Vis and PL spectroscopy are complimentary techniques which are used to characterize the optical properties of semiconductor nanocrystals. In UV-vis spectroscopy, electronic transitions from the ground state to the excited state are measured, whereas photoluminescence deals with the transitions from the excited state to the ground state. When molecules having non-bonding electrons absorb the energy in the form of UV or visible light, the electrons get excited to higher molecular orbitals and absorb a longer wavelength of light. The band gap of II-VI semiconductor nanocrystals is in the UV-visible region which means the minimum energy required to excite an electron from the valence states to the conduction states lies in the UV-visible region. This is also the reason why II-VI semiconductor nanocrystal solutions are coloured. On the other hand, photoluminescence is one of the relaxation processes by which a molecule in its excited state returns back to the ground state and loses this energy in the form of a photon.

In order to characterize the optical properties of nanocrystals, it is important to characterize the sample with both these techniques. In nanocrystals, variation in the atoms (additional or removal of atoms of same elements or different elements) changes their electronic structure. Due to this property, it is possible to change the band-gap of semiconductor nanocrystals by changing their size and composition. The nanocrystals absorb light energy over a range of wavelengths for excitation of the electron and the minimum energy required for excitation of an electron is dependent on the band-gap of the material. Thus, by precise measurements of light absorption at different wavelengths, the relationship between the band gap and size/composition of the nanocrystals can be established.
2.2.9 CV

CV is a dynamic electrochemical method where current-potential curves are recorded at well-defined applied potential. It has been successfully employed in the quantitative evaluation of the HOMO and LUMO levels of electro-active semiconductor nanocrystals such as CdS quantum dots. Detailed information about the confinement of the bandgap of quantum dots could also be obtained by several other techniques such as absorption spectroscopy, PL spectroscopy, XPS and scanning tunnelling microscopy. AS and PS provide only information about the energy of the bandgap whereas XPS and CV methods are capable of measuring absolute energy levels within the band structure. The main advantage of band-gap measurements by CV are the mild experimental conditions at which the measurements are carried out. This makes it especially suitable to study semiconducting nanocrystals for their application in electroluminescent or photovoltaic devices. However, one possible drawback of this measurement technique is that there is a certain subjective about the current onset potential (as seen in the CV response of CZTSeS5 in Figure 9).

Similar to other redox molecular species, semiconductor nanocrystals also possess discrete energy levels and undergo electron transfer along the valence band and the conduction band. The measurements are performed in a three-electrode cell with one working electrode, one reference electrode and one counter electrode. During the measurement, the voltage is scanned several times between the lower and upper limit reversely at a fixed rate. The current is measured between the working and counter electrode and the potential are measured between the working and the common reference electrode and is plotted against each other (as shown in Figure 9, for CZTSSe nanocrystals). The measured oxidation potential of the nanocrystal sample
relates directly with the ionization potential and the reduction potential with the electron affinity. Since the vacuum level potentials of the common reference electrodes can be estimated, the band edge positions of the nanocrystals can be approximated. From the reports on the band-gap measurements of CdSe nanocrystals films using CV, it is known that the calculated band-gap from this technique is lower than the corresponding bulk material.

![Figure 9. CV responses of copper selenide–sulfide (CuSeS), copper tin selenide–sulfide (CTSeS), and copper zinc tin selenide–sulfide (CZTSeS) nanoplates obtained by the cation exchange.](image)

Figure 9. CV responses of copper selenide–sulfide (CuSeS), copper tin selenide–sulfide (CTSeS), and copper zinc tin selenide–sulfide (CZTSeS) nanoplates obtained by the cation exchange.¹⁸
2.3 References


15. Singh, A.; Coughlan, C.; Laffir, F.; Ryan, K. M., Assembly of CuIn$_{1-x}$Ga$_x$S$_2$ Nanorods into Highly Ordered 2D and 3D Superstructures. ACS Nano 2012, 6, 6977.


Chapter 3: Colloidal Synthesis and Self-Assembly of Homogeneous CdSe\(_x\)S\(_{1-x}\) Nanorods with Compositionally Tunable Photoluminescence

The content of this chapter appeared in-


3.1 Abstract

Here, we report the synthesis of homogenously alloyed CdSe\(_x\)S\(_{1-x}\) nanorods with controlled aspect ratios by a hot-injection colloidal route. The optical absorption and photoluminescence emission are compositionally tunable with the chalcogen ratios. The influence of chalcogen composition on the shape control is outlined in addition to the ligand chemistry adopted to retain the desired aspect ratios for each composition. The synthetic protocol is sufficiently robust to allow good control of rod aspect ratios, with low polydispersities, suited for their rational assembly into superstructures with either each rod close-packed and oriented perpendicular to the substrate or into 1D rail-tracks depending on the net charge.
3.2 Introduction

Colloidally synthesised semiconductor nanocrystals are an increasingly important material set, which are finding a range of applications in photovoltaic, thermoelectric and photocatalytic devices.\textsuperscript{1-6} 1-D nanocrystals are particularly suited to applications requiring directional charge transfer either in the solid state photovoltaic or in the solution photocatalysis due to their higher aspect ratio in comparison to pseudo spherical dots.\textsuperscript{7, 8} Recent advances in the directional assembly where each nanorod is vertically aligned and closely packed, allow these properties to be harnessed at a device scale.\textsuperscript{9, 10} One of the major applications of colloidal nanocrystals is the possibility of quantum confinement, when the particle size is below the Bohr radius, allowing a range of band gaps to be tuned by particle size.\textsuperscript{11-15} With nanorods and nanowires, while there is confinement in diameter, the electron is unrestricted along the length largely limiting the possibility of band gap control to very narrow diameter wires that are difficult to synthesise. In applications that require exciton separation (photovoltaic, photocatalysis) as opposed to recombination (photo-emissive tags), nanostructures that show non-confinement derived band-gaps may be equally interesting.\textsuperscript{16} In recent examples with colloidally derived metal chalcogenide nanocrystals,\textsuperscript{17, 18} excellent photovoltaic results were obtained with nanocrystals having the characteristic bulk band-gap where the advantages are the wet chemical synthesis\textsuperscript{19-22} and processing for potentially more scalable applications. In the CdSe,\texttextsubscript{1-x}S\textsubscript{x} system, there are many reports on vapour liquid solid protocols for nanowires and nanobelts with compositionally tunable emission.\textsuperscript{23-25} In these protocols, it is very difficult to control the aspect ratio of the wires making them less suited to applications requiring their directional assembly in high density. The ability to control both the composition and the aspect ratio of this system is very attractive.
as optical and electronic properties can be independently tuned and collectively exploited on a large scale.

Herein, we report colloidal CdSe$_x$S$_{1-x}$ alloyed nanorods with homogeneous composition showing tuned photoluminescence and band-gap between 1.77 and 2.03 eV. The monodispersity of CdSe$_x$S$_{1-x}$ nanorods allows the subsequent assembly of the rods into superstructures where each rod is closely packed and vertically aligned.
3.3 Experimental Details

Materials

All reagents were used as received without any further purification. Cadmium oxide (>99%) (CdO) was purchased from Sigma Aldrich, trioctylphosphine (TOP, 90%), trioctylphosphine oxide (TOPO, 99%), selenium (99.98%), sulphur (99%), tellurium (99.9%) were purchased from Aldrich, n-octadecylphosphonic acid (ODPA), tetradecylphosphonic acid (TDPA) and n-hexylphosphonic acid (HPA) was obtained from PolyCarbon Industries Inc (PCI). All solvents were purchased from Sigma Aldrich.

Synthesis of CdSe$_x$S$_{1-x}$ Nanorods

General synthesis procedure: CdO (0.12 g, 1 mmol), TOPO (1.45 g, 3.87 mmol), HPA (concentration as given in Table 1) and ODPA (0.45 g, 1.35 mmol) were weighed into a three-neck round-bottom flask. The flask was fitted with a condenser, a stainless steel thermocouple and a magnetic stir bar. The apparatus was sealed and brought onto a Schlenk line. Using a heating mantle, the mixture was heated to 120 ºC, evacuated under vacuum for 30 min, refilled with argon, and heated to 300 ºC to form a completely colourless solution. When the temperature reached 300 ºC, TOP (0.84 g, 2.26 mmol) was injected into the flask. When the temperature reached 330 ºC, the Se-S stock solution prepared in 500 µl of TOP (the molar amount of Se/S is given in Table 1) was rapidly injected, causing a gradual colour change. After injection, the growth was allowed to continue for 15 min with continuous stirring. Subsequently, the heating mantle was removed and the reaction vessel was allowed to cool to 80 ºC. A 2-3 mL portion of anhydrous toluene was added initially to quench the reaction. The nanorods were then washed in a 2:1 ratio of toluene to 2-
Propanol and centrifuged at 3000 rpm for 10 min. The washing was repeated three times and the nanorods were stored in toluene for further characterizations.

**Table 1.** Composition and dimensions of CdSe$_x$S$_{1-x}$ alloyed nanorods

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Se/S (mmol)</th>
<th>HPA (mmol)</th>
<th>Length (nm) ±2</th>
<th>Diameter (nm) ±0.5</th>
<th>Band Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.14</td>
<td>0.09</td>
<td>40</td>
<td>7.0</td>
<td>2.03</td>
</tr>
<tr>
<td>2</td>
<td>0.33</td>
<td>0.18</td>
<td>37</td>
<td>7.0</td>
<td>1.97</td>
</tr>
<tr>
<td>3</td>
<td>0.45</td>
<td>0.24</td>
<td>36</td>
<td>7.5</td>
<td>1.95</td>
</tr>
<tr>
<td>4</td>
<td>0.77</td>
<td>0.48</td>
<td>37</td>
<td>8.0</td>
<td>1.9</td>
</tr>
<tr>
<td>5</td>
<td>1.28</td>
<td>0.72</td>
<td>43</td>
<td>8.0</td>
<td>1.87</td>
</tr>
<tr>
<td>6</td>
<td>2.2</td>
<td>0.78</td>
<td>37</td>
<td>8.0</td>
<td>1.825</td>
</tr>
</tbody>
</table>

**Synthesis of Cadmium Sulphide (CdS) Nanorods**

Cadmium Oxide (0.21g), trioctylphosphine oxide (2.73g) and octyldecylphosphonic acid (1.07g) were weighed out in a 25ml 3-neck flask and heated to 120 °C under a flow or argon. The system was degassed for one hour to remove any moisture. It was then heated up to 300 °C and the growth monomer TOP + S were injected in. Growth was continued for 30 minutes before removal of the heating mantel. When the temperature reached 70 °C 3ml of anhydrous toluene was injected in. The nanorods were washed three times in a 1:1 toluene:acetone mix to remove any excess surfactants followed by centrifuging to drop the nanorods out of solution. The nanorods were stored in toluene.

**Synthesis of Cadmium Selenide (CdSe) Nanorods**
CdSe nanorods were synthesized according to previous methods where 710mg TDPA, 160mg HPA, 3g TOPO and 200mg CdO were degassed for 60 minutes at 120 ºC in a 25ml 3 neck flask. The temperature was raised under a flow of argon until the solution turned colourless when 1.5g of TOP was injected in. The temperature was raised to 300 ºC and 73mg of selenium in 416mg of TOP was injected in and growth was allowed to continue for 5 minutes until removal of the heating-mantle.

**Monolayer Assembly of Nanorods**

The self-assembly of nanorods was undertaken by drop casting the nanorod solution with various concentrations ranging from $10^{-8}$ to $10^{-2}$ mol L$^{-1}$ onto carbon supported Cu-TEM grids. The solvent was allowed to evaporate slowly under a constant evaporation rate (in an argon glovebox, with 0% relative humidity).

**Growth of the Superstructure (Hexagon)**

The slow crystallization of CdSe$_x$S$_{1-x}$ nanorod was carried out through a three-layer oversaturation technique. In a typical experiment, we filled a vial with 3 mL colloidal solution ($\approx 10^{-7}$ mol L$^{-1}$) of CdSe$_x$S$_{1-x}$ nanorod in toluene. A buffer layer of 2-propanol ($\approx 0.5$ mL) was carefully added above the colloidal solution of nanorod. Next, a layer of methanol (3 mL) was added above the buffer layer. Extreme care was taken while putting the methanol layer to make sure the vial was not disturbed. The vial was sealed with paraffin film and left in the glove box undisturbed for approximately two weeks. After 12 days, the decolouration of nanorod solution was complete, small sediment was taken out with pipette and dropped on the substrates for SEM, TEM and XRD studies.

**Characterization**

The CdSe$_x$S$_{1-x}$ nanorods and their assemblies were characterized by TEM, DF-STEM by using a JEOL JEM-2011F operating at an accelerating voltage of 200 kV.
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.). The sample for XRD analysis was prepared by drop-casting the nanorod solution on a glass substrate. The analysis was carried out on a PANalytical X’Pert MPD Pro using Cu Kα radiation source (λ = 1.5418 Å) and a 1-D X’celerator strip detector with a 1-D X0Celerator strip detector. UV-vis spectroscopy of the nanorod solutions was performed on Cary 5000 UV-Vis-NIR spectrophotometer operated at a resolution of 1 nm. PL spectra were measured with a Cary Eclipse Fluorescence Spectrophotometer equipped with a photomultiplier detector. PL spectra of the samples (dispersed in toluene) were measured at room temperature excited at a wavelength of 360 nm.
3.4 Results and Discussion

Figure 1. CdSe$_x$S$_{1-x}$ optical properties: (a) change in absorption; (b) change in photoluminescence; (c) photograph of CdSe$_x$S$_{1-x}$ nanorods of varied Se/S compositions dispersed in toluene under normal indoor light (the Se/S ratio increasing from left to right); (d) Band-gap variation with Se molar % in the alloyed nanorods.

The CdSe$_x$S$_{1-x}$ nanorods were synthesised and characterised with a broad range of composition variations of Se: S in order to investigate the full range of band gap tuning. Figure 1(a) shows that the first absorption maxima in the UV absorption spectra of the alloyed nanorods are sequentially red-shifted as the Se content increases. The overlaid spectra clearly indicate a compositional dependence of the Stokes shift for all the CdSe$_x$S$_{1-x}$ alloy nanorods that are independent of size. Figure
1(b) shows the corresponding PL emission spectra of CdSe$_x$S$_{1-x}$ nanorods. The band-edge emission peaks for the selenium containing nanorods shift from 610 to 680 nm incrementally according to the Se/S composition. This narrowing of the optical band gap (Eg) is completely governed by composition as all dimensions are larger than the exciton Bohr radius of both CdS (2.9 nm) and CdSe (5.6 nm). Efforts to synthetically tune the emission wavelength of the nanorods towards the blue region (520–600 nm) of the spectra (S-rich) led to highly polydisperse nanorods with broad emission peaks of low intensity most likely due to surface defects (e.g. CdSe$_x$S$_{1-x}$ nanorods with a Se/S ratio of 0.07 in Figure 1(b)). Ultimately, the synthetic composition control allowed very accurate tuning of band-gap within 2.03–1.77 eV. The colour of the nanorod solutions also changes according to composition, which is in good agreement with the band-gap dependent shift in the absorption maximum occurring in the visible part of the electromagnetic spectrum (as shown in Figure 1(c)). The change in the band-gap with the molar percentage of Se content in the alloyed nanorods is further outlined in Figure 1(d). There is a significant initial drop in band-gap energy from 2.4 to 2.03 eV with the initial introduction of Se into the lattice with a linear trend thereafter as the Se content increases. This can be attributed to the variation in lattice constant which alters the band structure coupled with the changes in electronegativity affecting the electron distribution.$^{12,13}$ Once the more reactive Se anion is introduced into the nanorods, it controls the local structural ordering such that the step-to-step increase in the Se becomes the major influential factor in the gradual linear reduction in the band-gap.
Figure 2. (a) XRD pattern of as-synthesized CdSe$_x$S$_{1-x}$ wurtzite nanorods; (b) details of the XRD pattern near the (103) reflection.

Figure 3. CdSe$_x$S$_{1-x}$ nanorods composition obtained experimentally from elemental analysis and X-ray diffraction plotted against molar concentration of Se in the stock solution.
The crystal structure alteration with the composition variation in the alloyed nanorods was supported by XRD. Figure 2(a) shows the XRD spectra of all the as-synthesized alloyed nanorod samples, CdSe (reference no. 98-002-1476) and CdS (reference no. 98-001-7136) nanorods. Each XRD pattern consists of a single set of 20 peaks corresponding to the hexagonal wurtzite structure. All the CdSe$_x$S$_{1-x}$ nanorods samples with different Se/S compositions show 20 peaks falling between the values of pure wurtzite CdS and CdSe phases as reported earlier. The diffraction peaks shifted gradually toward smaller angles with gradual substitution of the S atoms with bigger and heavier Se atoms, indicating increasing lattice constants of the nanorods, in accord with Vegard’s law. Figure 2(b) shows the shift in d-spacing as calculated from individual XRD peaks of each sample. There is an expected shift in the d-spacing of individual peaks towards higher values as the feed molar ratio of Se is increased in the samples. The compositions of different CdSe$_x$S$_{1-x}$ nanorods samples obtained from XRD and wide area ensemble EDX measurement are given in Figure 3. Both XRD and EDX data confirm that the actual composition of the different CdSe$_x$S$_{1-x}$ nanorods samples was more Se rich in comparison to the injected Se–S stock solution. This strongly indicates the higher reactivity of Se in the growth media in comparison to S.
Figure 4. (a) TEM image of CdSe$_x$S$_{1-x}$ nanorods with Se/S = 1.28 after modifying the HPA concentration; (b) HRTEM image showing the wurtzite CdSe$_x$S$_{1-x}$ nanorods with Se/S = 1.28, elongated in the [002] direction; (c) SAED; (d) HAADF image of the CdSe$_x$S$_{1-x}$ nanorods with Se/S = 1.5.

Figure 4 (a) shows a TEM image typical of the nanorods, here with a Se/S ratio of 1.28 where low polydispersity and aspect ratios of 6 were routinely obtained. This low magnification TEM image shows that the nanorods have a conventional rod shape and are quite mono-dispersed in nature with a narrow size distribution. The continuous lattice fringes (Figure 4 (b)) confirm that the nanorods are homogenous single crystals. The SAED pattern (Figure 4 (c)) is indexed to (002), (101) and (102)
confirming the wurtzite structure. High-angle annular dark field imaging, HAADF-STEM, Figure 4 (d), shows that each individual nanorod appears to be uniformly bright throughout their entire length confirming that S and Se signals were distributed homogeneously. The elemental composition of nanorods was further confirmed by EDX analysis (Figure 5 (a)) and EDX line scan analysis (Figure 5 (b)) further confirmed that Cd, S, and Se spanned the entire length of the rods.

![CdSe<sub>x</sub>S<sub>1-x</sub> EDX](image)

**Figure 5.** (a) EDX of CdSe<sub>x</sub>S<sub>1-x</sub> nanorods; (b) DF-STEM image of the CdSe<sub>x</sub>S<sub>1-x</sub> nanorods with Se/S ratio of 0.45 showing the area where EDX line scan was performed and the EDX line scan graph.

Obtaining similar aspect ratio control for all other CdSe<sub>x</sub>S<sub>1-x</sub> nanorods compositions required judicious modification of reaction conditions as the relative concentrations of chalcogen impacted the morphologies. Figure 6 (a) shows the change in crystal shape as the selenium content increases with all other reagents remaining constant.
As the Se/S ratio increases from 0.14 to 0.45, the aspect ratio reduces dramatically from 6 to 1. Trial and error studies (where the relative concentrations of surfactants were varied) identified HPA as a dominant influence on shape control in this system, which is in good agreement with previous reports on cadmium selenide.\textsuperscript{27-29} Interestingly, a concomitant increase in the HPA concentration in accordance with the selenium was necessary to retain similar nanorod aspect ratios (Figure 6 (b-g)). The alteration of structural composition of the nanocrystals via increasing Se content affects the binding energy of the crystal facets with surfactants, and ultimately influences the growth rate of that particular facet. The progression towards a lower aspect ratio as the Se increases suggests equal growth in all directions. However, the simultaneous increase in the HPA concentration clearly increases the passivation in other growth directions leaving [002] as the preferred growth (least passivated) direction allowing rod formation.\textsuperscript{29}
Figure 6. (a) HRTEM images of single crystals of CdSe$_x$S$_{1-x}$ nanorods with Se/S ratios of 0.14, 0.33 and 0.45; (b-g) TEM images of CdSe$_x$S$_{1-x}$ nanorods synthesized with different Se/S compositions and optimized HPA concentration as given in Table 1.
Figure 7. TEM images of CdSe$_x$S$_{1-x}$ nanorods (with Se/S = 1.28 mmol) synthesized with (a) 0 mmol, (b) 0.3 mmol, (c) 0.6 mmol, (d) 0.9 mmol, (e) 1.2 mmol of ODPA.

The effect of concentration of ODPA was studied via the synthesis of CdSe$_x$S$_{1-x}$ nanorods with varied molar concentration of ODPA (keeping the total ligand concentration constant). It was observed that ODPA has control on the overall morphology of the nanocrystals. When the nanocrystals were synthesized in the absence of ODPA, the crystals were small pseudo-spherical crystals without any defined c-axis of growth (Figure 7 (a)). When low concentration of ODPA (0.1-0.25 mmol) was introduced in the reaction flask as surfactant, the formation of irregularly-spherical, multi-faceted nanocrystals was observed (Figure 7 (b, c)). These nanocrystals were 10-11 nm tri-/tetrapods with short arms. The occurrence of tri-/tetrapods in the flask was observed until there was enough ODPA in the reaction flask to control the growth of the nanocrystals in one particular direction i.e., the c-axis. The formation of nanorods started when the concentration of ODPA was 0.6 mmol (Figure 7d). Increasing the concentration of ODPA gradually resulted into
much longer nanorods with reduced diameters (Figure 7e). This observation strongly supports the influential role of ODPA in the overall shape evolution of the nanocrystals as 1-D nanorods.

**Figure 8.** (a-c) DF-STEM images of perpendicular assembly of CdSe$_x$S$_{1-x}$ nanorods with Se/S ratio of 1.28.

By optimising the ligand chemistry, monodisperse CdSe$_x$S$_{1-x}$ nanorods with high uniformity across the length and diameter were achieved for all compositions, which were used to study various forms of self-assembly such as multilayers 2-d microstructures of vertically assembled nanorods, 1-D rail-track patterns with horizontally assembled nanorods and hexagonal crystallization of closely packed nanorods.
The simplest approach to study assembly in a solution of size monodispersed nanorods that are dispersed in an organic solvent is to take a droplet on a TEM grid and allow it to dry. While this is the routine sample preparation for microscopy analysis, there is actually a multitude of factors at play in this system. The drying droplet represents a slowly changing concentration gradient of the rod dispersion in the reducing solvent volume. The droplet however does not shrink uniformly, with successive pinning of the droplet edge, resulting typically in ring patterns as material is deposited due to fluid flow within the droplet. The fundamentals of this process have been studied for a variety of systems with for example the ring patterns in coffee stains providing the initial conundrum. In contrast to a dispersion of coffee particles which will have significant polydispersity, the uniformity of the rod dimensions and hence uniformity of their interparticle interactions creates a more ideal system despite their shape anisotropy. The interactions between the rods can be simplified to columbic forces with repulsion between like charged particles due to net charge offset by dipole–dipole attractions. This interaction has interparticle distance dependence and is therefore greatly affected by the concentration of the particles in solution. Ultimately, the dipole is fixed for a given system and ranges from 150–600 Debye depending on the rod composition and aspect ratio. With a fixed dipole moment, the behaviour of rods in a drying droplet is influenced by a number of factors: 1: their net charge which can be approximated by zeta potential, 2: their concentration in solution and 3: dielectric constant of the solvent. The self-assembly of CdSe$_x$S$_{1-x}$ nanorods (with a Se/S ratio of 1.28) was investigated by drop-casting solutions of nanorods onto carbon supported Cu-TEM grids. All experiments were performed in a glove box giving a constant evaporation rate. This optimization of the nanorod concentration window ($9.3 \times 10^{-7}$ mol L$^{-1}$) allows
isolation of the critical concentration for achieving 2D and 3D assembly. In Figure 8, DF-STEM images show large scale 2D and 3D assembly of CdSe$_x$S$_{1-x}$ nanorods (with a Se/S ratio of 1.28) in which the closely packed hexagonal ordering is obtained by droplet drying when the nanorod concentration in toluene is $9.3 \times 10^{-7}$ mol L$^{-1}$. Each rod in this layer is perpendicularly aligned from edge to centre. As these discs sediment in the droplet, the deposit on top of each other results in a 3D structure. The resultant Moire Patterns results from a rotational offset between the two hexagonal patterns of each respective disc and the type of pattern ultimately corresponds to the angular offset. Outside of this optimum concentration, nucleation does not occur and the evaporating droplet results in randomly deposited rods. The high degree of hexagonal ordering in the vertical assembly further confirms the monodispersity of CdSe$_x$S$_{1-x}$ nanorods achieved synthetically.

![Image](image.png)

Figure 9. (a-b) Low resolution TEM of rail track 1D assembly of CdSe$_x$S$_{1-x}$ nanorods; (c) HR-TEM image of rail track assembly.

The net charge is also affected by the extent of ligand coverage and can be significantly modulated in our observations with repeated anti-solvent precipitations (excess ligand cleaning steps). Adding to this the solvent polarity that screens columbic interactions creates a complex parameter set for predicting the optimum conditions for assembly. To demonstrate this, CdSe$_x$S$_{1-x}$ nanorods were assembled in the form of 1-D rail-tracks by via droplet drying of TOPO capped nanorods.
suspended in hexane which have been subjected to extensive cleaning steps (Figure 9). Here the net charge is sufficient to prevent aggregation in hexane and rods get trapped at the interface and deposit as fluid flow moves from the volume of the droplet to the pinned edge during drying. These rail-tracks are typically of the order of 500 nm in length.

**Figure 10.** (a) Schematic figure showing the assembly in vial; (b, c) multilayer hexagon crystallization of CdSe,S$_{1.3}$ nanorods.

In comparison to a drying droplet, a closed vial of a nanorod dispersion is a simpler system where solvent evaporation, pinning and fluid flow can be discounted. The behaviour of rods under these conditions gives very interesting insights into the processes involved in assembly. The observations of rod assembly both in a droplet and in a vial as outlined demonstrates the interparticle forces involved can overcome anisotropic considerations for nucleation of supercrystals. Achieving long range and defined order in these crystals requires longer growth times. The most effective way to achieve this is by using a three layer oversaturation technique where the solvent (e.g. toluene) is separated from the appropriate non-solvent (methanol) using an isopropanol buffer layer (Figure 10 (a)). The slow diffusion of the non-solvent into the nanocrystal dispersion allows a very gradual change in particle dispersibility. Allowing this solution to sit for 2–3 weeks in complete isolation (no external perturbation) allows complete crystallisation of the nanorods. The rods organise into
hexagonal faceted discs demonstrating true crystallisation as shown in high resolution SEM images of these faceted hexagonal crystals (Figure 10 (b, c)) show that they consist of nanorods perpendicularly aligned and close-packed in plane either as a single monolayer or extending over several multilayers. A detailed investigation of the crystallisation process found that the supercrystal grows layer by layer, with the start of a new layer of nanorods occurring only after the completion of underlying layer and this growth is continuous until all nanorods in the solution are adsorbed on the growing supercrystal. This manifests as a discoloration of the nanorod solution from orange to colourless. The supercrystal growth process is a two-step event (nucleation and growth) expected for crystallisation processes. The nucleation stage leads to the formation of monolayer hexagon and with further growth of these hexagons in the c-direction rod by rod (in-plane) and layer by layer (out of plane).
3.5 Conclusion

In summary, a range of monodispersed, homogenous, wurzite CdSe\textsubscript{x}S\textsubscript{1-x} nanorods were synthesized via a single injection of a mixture of TOP–S–Se solution into a hot cadmium–phosphonate complex. The aspect ratio of the alloyed nanorods, while affected by the increasing selenium content, can be tuned by altering the HPA concentration. The optical and structural properties of the resulting CdSe\textsubscript{x}S\textsubscript{1-x} nanorods directly correlate with the relative molar amounts of S and Se used. UV spectra showed that the absorption band edge of the CdSe\textsubscript{x}S\textsubscript{1-x} nanorods is sequentially red shifted with increasing Se concentration in the nanorods. Similarly, all compositions show direct band edge photoluminescence emission over a 200 nm range that is tunable according to the selenium/sulphur ratio. Moreover, the self-assembly of these nanorods could be obtained by tuning the assembling conditions, which range from: 1D rail-tracks; to perfectly faceted hexagonal supercrystals of vertically aligned nanorods; to close packed nanorod layers deposits on a substrate. Ultimately, as the colloidal rods are synthesised with band-gap tunability and could be processed from solution they allow for low energy and scalable formation of bulk layers which is very interesting for applications where their exploitable optical properties of absorption or emission can be collectively harnessed.
3.6 References


Chapter 4: Colloidal Cu$_2$ZnSn(SSe)$_4$ (CZTSSe)

Nanocrystals- Shape and Crystal Phase Control to form Dots, Arrows, Ellipsoids and Rods

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


4.1 Abstract

Herein, we report shape control in the CZTSSe nanocrystal system by tuning the occurrence of polytypism between wurtzite and zinc-blende phases. We have isolated the key control factors in this system and showed that the choice of solvents/surfactants and precursors and how they are introduced can allow shape control from dots to ellipsoids to arrows and rods. The shape evolution is dictated by independently controlling the respective growth rates of either the zinc-blende or wurtzite regions in the polytypic system. Moreover, this synthetic control could be extended to eliminate polytypism while retaining anisotropy allowing for single-phase wurtzite nanorods of CZTSSe.
4.2 Introduction

Colloidal semiconductor nanocrystals comprising earth–abundant and low-toxic elements such as Cu$_2$ZnSnS$_4$, Cu$_2$ZnSnSe$_4$ and their alloys Cu$_2$ZnSn(Se)$_4$ have received much consideration due to their significant relevance in solar cells, photo/electro-catalysts and thermoelectrics.\textsuperscript{1-4} The structure–property relationships can be tuned for the desired technological application by affecting composition,\textsuperscript{5-7} size,\textsuperscript{8} shape\textsuperscript{9} or ligand shell.\textsuperscript{10, 11} These can be altered respectively by tuning the cation or anion ratios, crystal phase or the nature of the organic-inorganic interface.\textsuperscript{12} Formation of anisotropic geometries is appealing as the functional properties such as electrical and thermal conductivities, total absorption and photon emission have aspect ratio dependence. When these properties are collectively harnessed in assemblies, they can allow for maximized absorption in photovoltaics, enhanced conductivity in thermoelectric devices, or directional emission in displays.\textsuperscript{13-15} In the colloidal synthesis of compound copper chalcogenide nanocrystals, the wurtzite phase is best suited for switching from isotropic spherical nanocrystal growth to anisotropic growth of 1-D nanorods.\textsuperscript{16} A suitable balance between the type of ligands, nature of metal precursor and temperature suppresses the growth of selective facets in the crystal allowing the elongation of the nanocrystals along the [001] direction.\textsuperscript{9, 17} To date, 1D growth in copper based multi-component nanocrystals in the form of nanorods has been widely reported by different synthetic routes for the systems having sulfur as the anion such as CuIn$_x$Ga$_{1-x}$S$_2$,\textsuperscript{18-20} Cu$_2$ZnSnS$_4$,\textsuperscript{9, 21} CuInS$_2$,\textsuperscript{22, 23} and AgInS$_2$.\textsuperscript{24} Notably, complete or partial anionic substitution by Se to form I$_2$–II–IV–Se$_4$ or I$_2$–II–IV–(Se)$_4$ nanocrystals in the crystals quenches directional growth only allowing the formation of pseudo-spherical nanodots or nanoplates in single phase systems.\textsuperscript{25-28} However, shape control has been achieved by
different research groups in bi-phasic nanocrystals, when the nucleation takes place in one phase and the growth in another phase. Branched Cu$_2$Cd$_x$SnSe$_y$ nanocrystals growing from a tetrahedral core with wurtzite arms via a twinning mechanism has been reported by Zamani et al.$^{29}$ We have reported the complete colloidal synthesis of Cu$_2$SnSe$_3$ nanocrystals occurring either as linear polytypes with a wurtzite core and cubic tips or branched polytypes with cubic cores and wurtzite tips.$^{30,31}$ Yu and co-workers have reported the formation of complex quinary systems such as polytypic Cu$_2$CdSn(S$_{1-x}$Se$_x$)$_4$$^{32}$ and CZTSSe$^{33}$ nanocrystals with wurtzite nucleation and zinc blende growth. In some applications, such polytypism is desirable for example in thermoelectrics where a single particle having different phases with different electrical and thermal characteristics, maximizes the seebeck coefficient.$^{29,34,35}$ In other applications, such as photovoltaics, single phase structures are optimal, as occurrence of phase boundaries in a single particle can act as sites for electron trapping.$^{36-38}$ The ability to control the occurrence of polytypism or eliminate as needed is therefore important to allow optimization for desired applications. Herein, we study one of the most important compound semiconductors CZTSSe for both thermoelectrics and photovoltaics and show that polytypism can be tuned in the heterostructures ranging from ellipsoids (two large zinc blende (ZB) tips on a wurtzite (WZ) disc) to arrow heads (one dominant ZB with small WZ stem) to single phase wurtzite rods.
4.3 Experimental Details

Materials

Copper(I) acetate (Cu(I)Ac >97%), Copper(II) acetylacetonate (Cu(II)(acac)$_2$ >99.99%), Copper(I)chloride (Cu(I)Cl >97%), Tin(IV) acetate (Sn(Ac)$_4$, >99.99%), Tin(II)chloride (SnCl$_2$ >97%), Zinc acetate (Zn(Ac)$_2$, >99.99%), Zinc chloride (ZnCl$_2$>99.99%), Trioctylphosphine oxide (TOPO, 99%), 1-dodecanethiol (1-DDT, 98%), diphenyl diselenide (DPDSe 98%), Oleylamine (OLA, technical grade, 70%), 1-octadecene (ODE, 90% tech) were purchased from Aldrich. n-tetradecylphosphonic acid (TDPA), and n-hexylphosphonic acid (HPA) were obtained from PolyCarbon Industries, Inc. (PCI). All chemicals were used as received without any further purification.

Synthesis of CZTSSe ellipsoidal polytypic nanocrystals (Reaction Scheme R1)

In a typical synthesis, Cu(I)Cl (0.25 mmol), ZnAc (0.125 mmol), SnAc (0.125 mmol), TOPO (1.2 mmol), HPA (0.12 mmol), TDPA (0.26 mmol), OLA (3 mL) were added in a three-neck flask and evacuated at 50 °C for 20-30 min. The
solution was then heated to 270 °C under an argon atmosphere. When the temperature reaches 155 °C, a stock solution made by dissolving DPDSe (0.25 mmol) into 1-DDT (0.5 mL) was injected into the flask. After injection, the reaction was allowed to proceed for 15 min with continuous stirring. The reaction was terminated by removal of the heating mantle and allowed to cool to room temperature naturally. The product was washed using toluene and ethanol two times at 4000 rpm. For obtaining high degree of monodispersity, size selective precipitation was carried out at 1000 rpm for 1 min. The supernatant was collected and washed again at 4000 rpm and the final nanocrystals were dispersed in toluene for further characterization. Different Se/S compositions of CZTSSe arrow shaped nanocrystals were synthesizing by varying the DPDSe amount in the stock solution injections.

**Synthesis of CZTSSe arrow shaped polytypic nanocrystals (Reaction Scheme R2)**

The synthesis strategy is same as CZTSSe arrow shaped nanocrystals with the replacement of Cu(I)Cl with Cu(I)Ac (0.25 mmol).

**Synthesis of CZTSSe bullet shaped polytypic nanocrystals (Reaction Scheme R3)**

Bullet shaped nanocrystals were synthesized by the post-treatment of OLA based wurtzite CZTSSe nanocrystals. For synthesizing wurtzite nanocrystals with OLA, Cu(acac)$_2$ (0.5 mmol), ZnAc (0.25 mmol), SnAc (0.25 mmol), OLA (5 mL) were evacuated in a three-neck flask in a schlenk line at 50 °C for 20-30 min. The temperature of the solution was increased to 270 °C under an argon atmosphere in 10 min. When the temperature reaches 155 °C, a stock solution was made by dissolving DPDSe (0.25 mmol) and 1-DDT (1 mL) into 0.5 mL of OLA and this was injected
into the flask. After injection, the reaction was allowed to proceed for 15 min with continuous stirring. The reaction was terminated by removal of the heating mantle and allowed to cool to room temperature naturally. The product was collected in a vial and kept for further post treatment without washing.

For post treatment, TOPO (1.2 mmol), HPA (0.12 mmol), TDPA (0.26 mmol), OLA (3 mL) were added in a three-neck flask and evacuated at 50 °C for 20-30 min. The solution was then heated to 270 °C under an argon atmosphere. At 90 °C, Se/S stock solution (0.1 mmol of DPDSe into 0.5 mmol of 1-DDT) was injected. When the temperature reaches to 270 °C, crude solution of wurtzite CZTSSe nanocrystals (unwashed) was added into the flask and the reaction was allowed to proceed for next 7 min. The product was washed by toluene and ethanol twice for further characterizations.

**Synthesis of CZTSSe wurtzite nanocrystals (Reaction Scheme R4-8)**

Cu(acac)$_2$ (as given in Table 1), Zn(Ac)$_2$ (1 mmol), Sn(Ac)$_4$ (1 mmol) and TOPO (3 mmol) were mixed with 5 mL of ODE in a three-neck flask and were degassed at room temperature for 30 min. The mixture was then heated to 270 °C under argon flow. When the temperature of the flask increases to 155 °C, Se/S stock solution (DPDSe in 2 ml of 1-DDT) was injected to the flask. After injection the color of solution changes from dark green to light yellow and then finally black. After 15 min, nanocrystal growth was terminated by removal of the heating mantle and allowed to cool to room temperature. The nanocrystals were washed 2-3 times in a 1:1 ratio of toluene to isopropanol and centrifuged at 4000 rpm for 5 min to yield a blackish centrifuged product. After cleaning, the nanocrystals were redispersed in fresh toluene for further characterization. The concentration of Cu(acac)$_2$ and DPDSe has been varied for different reactions (reaction R4-R8) and are reported in Table 1.
Table 1. Precursor concentrations, phase and dimensions for CZTSSe nanocrystals synthesized by using ODE

* 1-DDT is used in excess for the synthesis of CZTSSe nanocrystals as it has dual function of sulfur source and capping ligand.

Characterization Methods

The morphology of CZTSSe nanocrystals was characterized by TEM and angular dark-field scanning transmission electron microscopy DF-STEM using a JEOL JEM-2011F, operating at an accelerating voltage of 200 kV. XRD of drop-cast films of nanocrystals on a glass substrate were carried out on a PANalytical X’Pert MPD Pro using Cu Kα radiation with a 1D X’Celerator strip detector. Rietveld refinement was carried out using X’Pert High Score plus software. XPS measurement of CZTSSe nanocrystals were carried out using a Kratos Axis 165 spectrometer. High resolution spectra were taken using monochromated Al Kα radiation of energy of 1486.6 eV at fixed pass energy of 20 eV. For peak synthesis, a mixed Gaussian-Lorenzian function with a Shirley type background subtraction was used. 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. The crystal modelling was performed by using the CRYSTALMAKER software.
4.4 Results and Discussion

**Figure 1.** (a) Magnified HRTEM image of single nanocrystal showing the d spacing of different facets of each phase with crystal model image in inset; (b) Dark Field TEM image of CZTSSe ellipsoids; (c, d) Corresponding FFT of zinc-blende (ZB) and wurtzite (WZ) segments of single nanocrystal; (e) SAED pattern showing the presence of both ZB and WZ phases.

The colloidal synthesis of quinary copper chalcogenides of CZTSSe is complex as it requires balancing the chemistries of three different metal cation precursors and two different chalcogen precursors during the nucleation and growth process. A common feature of the successful protocols employ a high temperature injection strategy to
combine separate cation (flask) and anion (injection) solutions to allow the threshold
temperature and supersaturation required for nucleation to be achieved
simultaneously (Scheme 1). The variables that have a dramatic effect on the resulting
particles are the wide choice of precursors for the cations, anions, surfactants and
solvents. In our observations, by separating out the contributions of each of these
species it is possible to attain control both of shape and phase in this semiconductor
system. The combination of the coordinating solvent oleylamine (OLA) with
phosphonic ligands plays a key role favoring the occurrence of polytypism. Figure 1
(a, b) shows uniform ellipsoids comprised of a wurtzite core (width of $8 \pm 0.5$ nm)
and two large ZB derived segments ($12 \pm 1$ nm) synthesized according to reaction
scheme R1. The d-spacing values and the angles between the planes are in good
agreement with the theoretical values.\textsuperscript{33} From aliquot studies (Figure 5), it was
confirmed that the nanocrystals first nucleate as mixed phase binary Cu-S that are
pseudo spherical in shape with progression of growth to a disc shape with the
subsequent inclusion of Zn, Sn and Se. As the discs grow, the opposite \{002\} facets
dominate which have a very similar plane spacing to the (111) planes of zinc-blende,
creating the optimum conditions for polymorphism to occur. Two factors are at play
here: (1) as the reaction temperature increases, it supports the formation of the more
thermodynamically favorable zinc blende phase; (2) as CuCl is a reactive precursor
(as compared to other copper precursors) it facilitates rapid growth on both \{002\}
facets and the occurrence of large ZB-derived tips. The majority of nanocrystals
formed by this reaction scheme are ellipsoids with the occurrence of 5-10\% of arrow-
shaped polytypic CZTSSe nanocrystals. The polytypism in these nanocrystals is also
verified by fast Fourier transform (FFT) patterns of the core and tip regions of a
single nanocrystal (Figure 1 (c-d)) marked with plane positions of WZ and ZB
phases. They are further correlated with the selected area electron diffraction (SAED) pattern shown in Figure 1(e) confirming the presence of two distinct phases. As the (111), (220) and (311) planes of cubic phase overlap with (002), (110) and (112) planes of wurtzite phase these rings appear brighter confirming the polytypic structure.

Figure 2. (a) DF-STEM image of arrow shaped nanocrystals, with inset showing the HRTEM image of a single nanocrystal; (b) SAED pattern; (c, d) FFT patterns for corresponding ZB and WZ segments of single nanocrystal; (e) Magnified HRTEM image of the interface marked with the interplanar spacing of different facets; (f) HR-TEM images and the corresponding 3-d crystal models from different angles of the tip of the nanocrystals.
The shape evolution is also affected by the choice of copper precursor (Scheme 1(b)). Both Cu(I)Cl and Cu(I)Ac are the combination of a soft acid (Cu$^+$) and a hard base (Cl$^-$/Ac$^-$). However, as the acetate is a softer base than the chloride (0.16 eV vs. 2.49 eV respectively), this makes Cu(I)OAc less reactive than Cu(I)Cl. Here, we observed that the reactivity difference has a big influence on the morphology of resulting nanocrystals. In the case of the nanocrystals produced by employing Cu(I)Ac as the Cu precursor (reaction Scheme R2), the ZB derived tip location has the preference for only one of the {002} facets giving rise to arrow shaped CZTSSe nanocrystals. As the {002} facets of wurtzite terminate in either a row of metal or chalcogen respectively, the opposite ends have different polarity and surface energies and are passivated differently by the available surfactant species. With a less reactive copper precursor, this manifests as a preference for growth at one end most likely the chalcogen terminated as the ligand species are optimized for interaction with the metal ions. The DF-TEM image (Figure 2 (a)) highlights the good monodispersity in particle size and the HRTEM image of a single nanocrystal (inset of Figure 2 (a)) illustrates the crystal morphology which is comprised of a dominant pyramidal ZB-derived tip over a minor wurtzite segment having a length of 38 nm and maximum width of 30 nm. The SAED pattern (Figure 2(b)) verifies the coexistence of the ZB and WZ phase, which is further confirmed by measurement of the interplanar spacing and the respective angles between the planes as marked in the FFT patterns (Figure 2 (c-e)). To illustrate the exact 3D structure of the arrow shaped nanocrystals, TEM images of nanocrystals lying on the TEM grid in different angles were taken and studied to resolve the 3D crystal structure (Figure 2 (f)). In our study of CZTSSe polytypic nanocrystals, we found that the choice of solvent/ligand is the necessary contributor to the occurrence of polytypism whereas the metal precursor
dictates the extent of the zinc blende to wurtzite ratio and therefore whether the shape occurs as ellipsoids or monopods.

**Figure 3.** (a) Low resolution TEM image of wurtzite CZTSSe nanocrystals synthesized by using OLA in reaction scheme R3; corresponding XRD spectra in the inset, (b) HRTEM image of single nanocrystal.
Interesting morphological variations are also attainable if the separate contributions of TOPO and phosphonic acids are considered in this reaction. TOPO is widely used in colloidal nanocrystal chemistry as it stabilizes the complex formation and as a steric ligand controls overall particle size. The other phosphonic acid species (TDPA, HPA) are the main ligands and subtle differences in their binding energies to different facets allow for selective growth. Here, in the initial stages of polypitic nanocrystal formation, the phosphonic acids (PAs) favor disc formation of the wurtzite structure by initially passivating the (002) facets restricting anisotropic
growth in the wurtzite phase (Figure 5(b, f). When we carried out a synthesis just
using OLA without the TOPO/PA combination, wurtzite nanocrystals are formed
with non-uniform morphologies (Figure 3). However, if nucleation is initiated
without the TOPO/PA ligands but they are subsequently introduced in the growth
phase, structures are obtained with a large wurtzite stem and a small cubic tip
(reaction scheme R3). Here in contrast to the zinc blende dominated polytypes of
Figure 1 and 2, wurtzite now dominates in a 3.5:1 ratio with the order of atom
stacking at the interface having the sequence •••ABC/AB•••AB/CBA•••. Figure 4
(a,d), highlights the uniformity, shape and size of the structures with FFT, SAED and
plane spacing confirming both phases with the 3-D crystal models in different
orientations confirming the morphology (Figure 4 (b-f)). It is therefore possible to
obtain a degree of control of the respective segments by controlling the number and
type of surfactant species present during specific growth stages.
To layout the full reaction mechanism for the growth of different shapes of polytypic
nanocrystals, time and temperature dependent studies were carried out in each type
of nanocrystal synthesis. Aliquots were taken out at each minute during the entire
growth process. The aliquots were washed with toluene and ethanol. TEM, DF-
STEM, EDX and XRD analysis was performed for each sample.
Figure 5. Shape evolution in (a-d) Ellipsoids; (e-i) arrow shaped nanocrystals; (j-l) crystal model for ellipsoidal shape formation.

In the case of arrow shaped nanocrystals and ellipsoids, after injection of the Se/S stock solution, the change of colour from green–yellow–orange–light brown–dark brown occurs in 45-50 seconds. During the nucleation process, the monomers in the growth media produce 5-6 nm pseudo-spherical Cu$_2$S particles capped with S (in the form of thiol) and other surfactants in the first 1–1.5 min (Figure 5 (a, e)). However, the nucleation process is slightly slower in case of arrow shaped nanocrystals due to the higher stability of metal precursor–ligands complex. In the next two min, these particles expand in size and diffusion of other elements (Zn, Sn and Se) with lower reactivity starts (Figure 5 (b, f)). The temperature at this stage is still below 200 °C. In three min of growth time, wurtzite hexagonal plates having well defined edges are formed (Figure 5 (f)). They are rich in Cu and S with low concentrations of Zn, Sn and Se due to their differences in their reactivity. This is supported by the XRD
analysis, showing the appearance of wurtzite peaks in the XRD spectra of aliquot at 5 min (Figure 6). After reaching the optimised diameter of 15 nm, in 4.5-5 min, the plates behaves differently for arrow shaped nanocrystals and ellipsoids. In reaction scheme R1, further growth on both ±(002) facets of hexagonal disc is observed, giving rise to ellipsoidal shape (Figure 5 (j-l)). However, due to the involvement of several controlling reaction factors during the formation of these nanocrystals, 5-10% of arrow-shaped polytypic nanocrystals are also formed in reaction R1 by epitaxial growth of zinc-blend derived tip on one of the (002) facet (inset of Figure 5 (d)). In reaction scheme R2, only one of the (002) facet shows further growth. After 5-5.5 min of growth time, formation of ZB-derived tips occurs on the respective ±(002) planes. The intensity of (111)\textsubscript{ZB} peak which overlaps with (002)\textsubscript{WZ} peak increases, confirming the introduction of zinc-blend derived phase in the nanocrystals (Figure 6). The final structures, i.e., arrow shaped nanocrystals and ellipsoids constitute of all the elements in proper stoichiometric ratios.

Figure 6. XRD Spectra of aliquots collected at different time interval for (a) ellipsoids, (b) arrow-shaped polytypic CZTSSe.
The polytypic bullets evolve from wurtzite nanocrystals via post-treatment process. During the aliquot sample analysis, it was observed that wurtzite nanocrystals develop ZB derived tips, when acted upon OLA-PA-Se/S complex at high temperature. The as-synthesized wurtzite nanocrystals are already covered by one or more layers of surfactants. When these nanocrystals are injected in the flask with ligands having more diffusion rate and binding strength, polytypic bullet shaped nanorods are formed. The introduction of ZB-derived phase in the nanocrystals occurs just after two min of reaction time which is evident in the XRD spectra (Figure 7 (b)). After attaining the proper shape, uniformity along the size of nanocrystals is achieved in the later stage of the reaction time due to the effect of temperature and modified ligand complex surrounding each nanocrystal (Figure 7 (d)).
Figure 8. HR-TEM images of the CZTSSe nanorods formed by reaction scheme – (a) R4, (b) R5, (c) R6, (d) R7 (FFT pattern in inset), (f) R8; (e) SAED pattern of nanorods synthesized using reaction scheme R7.

The occurrence of polytypism could be excluded in CZTSSe nanocrystals when OLA and PA are replaced by a non-coordinating solvent, i.e., ODE with TOPO as the only coordinating species (Scheme 1 (d-f)). When stoichiometric amounts of precursor species of CZTSSe is used under these conditions, nanoparticles (diameter 8 ± 1 nm) are formed in the wurtzite phase (Figure 8 (a)). However, preference for 1-D growth can only be initiated by adjusting the amount of copper ion in the reaction (Table 1). As the ratio of copper to other ion species is progressively decreased, there is a corresponding increase in aspect ratio indicated by a shape evolution from pseudo-spherical to conventional rod shape (Figure 8). The composition remains stable up to a half loading of copper and beyond this other binary and ternary phases occur. Copper poor phases of CZTSSe, are of interest as these have shown the highest photovoltaic efficiencies compared to their stoichiometric analogues. 1, 41, 42 Similar
phenomena have been observed in other systems where a low concentration of copper monomer suppresses the number of nucleation events and favors anisotropic growth on existing crystals.\textsuperscript{43, 44} The XRD patterns of the nanocrystals obtained from reaction R4-R8 (Figure 9), match well with the simulated wurtzite crystal structure. Peaks corresponding to the orthorhombic Sn\textsubscript{2}S\textsubscript{3} (ICSD no 98-000-5989) are detectable when the copper loading is reduced below 1mmol in the reaction flask (reaction R8).

\textbf{Figure 9.} XRD spectra of CZTSSe nanocrystals synthesized by reaction R4-8 with the simulated wurtzite derived CZTSSe and Sn\textsubscript{2}S\textsubscript{3} (ICSD no 98-000-5989)
**Figure 10.** XRD pattern and Rietveld fit for polytypic CZTSSe nanocrystals.

Rietveld refinement analysis of the XRD pattern of ellipsoids, arrow shaped and bullets (Figure 10) show a wurtzite composition of 38.0%, 42.5% and 63.6% respectively, which is in good agreement with the TEM observations (crystal data and atomic coordinates used for simulated patterns are provided in Chapter 2).
Figure 11. XPS Spectra of arrow-shaped polytypic CZTSSe.

To confirm the oxidation states of all the constituent elements of different shaped CZTSSe nanocrystals, X-ray photoelectron spectroscopy (XPS) analysis was performed. XPS survey spectrum of a representative sample of arrow shaped nanocrystals is presented in Fig. 11 (a) (Supporting Information). It shows the presence of Cu, Zn, Sn, Se, S, O, C, N and P. Presence of nitrogen, phosphorus, carbon and oxygen is because of the ligands capping of the nanocrystals and solvent (toluene) used to disperse the nanocrystals. High resolution single element spectra were recorded for individual elements and presented in Fig. 11 (b-f). In the copper XPS spectrum, an intense narrow set of doublet peaks positioned at 951.52 eV (2p$_{1/2}$) and 931.75 eV (2p$_{3/2}$) was observed. The two peaks were noted at a difference of 19.77 eV approximately, which confirmed the presence of copper in Cu$^{+1}$ state. With the difference of 23 eV approximately, doublet peaks of Zn 2p were observed at 1044.63 eV (2p$_{1/2}$) and 1021.46 eV (2p$_{3/2}$) respectively, confirming presence of Zn$^{2+}$. The XPS spectra of Sn shows set of narrow doublet peaks belonging to Sn 3d at 494.46 eV (3d$_{3/2}$) and 486.04 eV (3d$_{5/2}$) having a difference of 8.42 eV. This assures
the presence of Sn$^{+4}$ in the system. Presence of S in the form of sulphide ions was confirmed by set of broad peaks merged to an extent at 162.7 eV (2p1/2) and 161.51 eV (2p3/2). The broad peak at 166 eV belongs to Se 3p. In the Se XPS spectrum, Se 3d doublet for Se 3d$_{3/2}$ and Se 3d$_{3/2}$ was observed at 54.8 eV and 53.9 eV with spin-orbit coupling of 0.9 eV. This is a characteristic feature of selenides. It was revealed from the XPS analysis that the % concentration of S was higher than any other element (Cu, Zn, Sn, S and Se) of the system. This could be due to the presence of S in the capping ligand (1-DDT).

Figure 12 (a). EDX of ellipsoidal shaped CZTSSe nanocrystals
Figure 12 (b). EDX of arrow shaped CZTSSe nanocrystals

Figure 12 (c). EDX of bullet shaped CZTSSe nanocrystals

Figure 12 (d). EDX of wurtzite CZTSSe nanocrystals
Figure 13. EDX spectra and composition table for wurtzite nanorods synthesised by reaction scheme (a) R4, (b) R5, (c) R6, (d) R7 and (e) R8.

EDS analysis and line scan measurements (Figure 12 and 13) further confirmed the presence of the respective metal and chalcogen ions in the different CZTSSe nanocrystals and their homogeneous distribution.
4.5 Conclusion

In summary, a range of synthetic approaches were developed to obtain control over shape and phase of anisotropic CZTSSe nanocrystals. We have shown that a combination of coordinating solvent oleylamine, trioctylphosphine oxide and alkylphosphonic acids allows the evolution of atypical polytypic heterostructures whose shape could be controlled by the nature of metal precursors. Moreover, we have shown that polytypism could be ruled out by replacing oleylamine and alkylphosphonic acids with a non-coordinating solvent (1-octadecene). Single phase Wurtzite nanorods are formed whose aspect ratio could be increased by gradual reduction of Cu concentrations in the initial reaction flask. This study confirms the ability to controllably engineer the anisotropic shape and phase of complex quinary nanostructures and gives better understanding of shape evolution in compound copper based semiconductor nanocrystals. As CZTSSe is of interest for a range of diverse applications, the ability to control both shape and polytypism at the nanoscale in a colloidal process offers a reproducible route to a wide range of geometries and morphologies that can be optimised as needed.
4.6 References


Chapter 5: Copper Based Metal Telluride Nanocrystals—Morphology and Composition Control via Colloidal Approach

Publication in Progress

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5.1 Abstract

In this chapter, colloidal synthesis of a variety of metal telluride nanocrystals via the hot-injection approach is reported. Diphenylditelluride was chosen as the Te precursor due to its optimized reactivity which could be balanced well with the reactivity of the cation precursors (Cu⁺, Zn²⁺ and Sn⁴⁺ precursors) resulting into better control over phase and morphology of the synthesized nanocrystals. By regulating the reaction parameters, a selection of metal telluride nanocrystals were synthesized namely copper telluride, copper tin telluride, copper zinc telluride and copper zinc tin telluride. A diverse range of shape morphologies was obtained including nanocubes, octahedral shaped crystals, and nanowires. In addition, the role of different types of ligands in stabilizing the composition, shape and crystal structure of nanocrystals is extensively detailed.
5.2 Introduction

Copper based semiconductor nanocrystals have attracted significant interest for applications in photovoltaics and thermoelectric devices.\textsuperscript{1-5} Among the different copper based metal chalcogenides synthesised, the main focus has been on the sulphur and selenium based semiconductors such as Cu\textsubscript{2}S, Cu\textsubscript{2}Se, Cu\textsubscript{2}SnSe\textsubscript{3}, Cu\textsubscript{2}ZnSnS\textsubscript{4}, Cu\textsubscript{2}ZnSnSe\textsubscript{4} and Cu\textsubscript{2}ZnSn(SSe)\textsubscript{4}. A considerable degree of control over the size and shape, and hence tunability of the optical and electronic properties has been achieved for these materials.\textsuperscript{6-11} In contrast, tellurium based analogues are relatively unexplored due to the low control over nanocrystal size, shape, composition and phase distribution in the methods reported to-date.\textsuperscript{12} The most studied material among the metal telluride family is copper telluride (Cu\textsubscript{2-x}Te).\textsuperscript{13, 14} It has been used for thermoelectric cooling materials\textsuperscript{15} hetero-junction solar cells (p-Cu\textsubscript{2}Te/n-CdTe),\textsuperscript{16, 17} electro-conductive electrodes\textsuperscript{18} and photo-thermal conversion materials\textsuperscript{19} due to its high thermoelectric properties and ionic conductivity. A variety of synthetic strategies for Cu\textsubscript{2-x}Te nanocrystals have been described in the literature such as solvo-thermal synthesis,\textsuperscript{20,21} microwave-assisted elemental direct reaction route,\textsuperscript{22} sonochemical synthesis,\textsuperscript{23} and the colloidal cation exchange approach\textsuperscript{14}. However, good control over the morphology, size and phase in Cu\textsubscript{2-x}Te nanocrystal synthesis is difficult to achieve due to the deviations of stoichiometry in the Cu–Te phase diagram. This makes the synthesis of multinary metal telluride nanocrystals even more complicated. The main cause of the poor quality of the metal telluride nanocrystals is the uncontrollable reactivity of Te precursors. Among the different Te precursors available such as elemental Te mixed in trioctylphosphine (Te-TOP),\textsuperscript{24, 25} tellurium dioxide (TeO\textsubscript{2}),\textsuperscript{26} 1-naphthalyl telluride; Te-TOP is been the most popular Te precursor in colloidal synthetic protocols.\textsuperscript{27} It is highly reactive precursor which
forms nanocrystals under the time period of 3-4 minutes. It is suitable for synthesizing binary semiconductor nanocrystals but when the chalcogen has to bind with two or more cations having different chemical potentials it fails to incorporate all the elements with definite composition in the final product.

We have investigated diphenylditelluride (DPDTe) as a suitable precursor to generate multicomponent metal tellurides, as it is stable in the solution and have optimized reactivity compared to the cation precursors, we used. Use of DPDTe along with metal salts (for Cu$^{+}$, Zn$^{2+}$ and Sn$^{4+}$) give access to the multinary compositions which are not reported previously such as Cu-Sn-Te and Cu-Zn-Sn-Te. In this chapter, the synthesis of a variety of copper based metal tellurides via colloidal hot-injection route is reported. The differences in the shape and size regime of nanocrystals by incorporating more elements in the crystal lattice is observed and characterized. The effect of different ligands on the morphology, dispersity and composition of the resulting metal telluride nanocrystals is outlined.
5.3 Experimental Details

Materials
Copper(II) acetylacetonate (Cu(II)(acac)$_2$; >99.99%), Tin(IV) acetate (Sn(Ac)$_4$, >99.99%), Zinc acetate (Zn(Ac)$_2$, >99.99%), Triocetylphosphine oxide (TOPO, 99%), oleic acid (OA, >99%), diphenyl ditelluride (DPDTe 98%), Oleylamine (OLA, technical grade, 70%), 1-octadecene (ODE, 90% tech) were purchased from Aldrich. n-tetradecylphosphonic acid (TDPA) were obtained from PolyCarbon Industries, Inc. (PCI). The solvents was purchased from Lennox, Ireland. All chemicals were used as received without any further purification.

Synthesis of copper telluride nanocrystals (Reaction Scheme R1)

Cu(II)(acac)$_2$ (0.5 mmol) was mixed with OLA (3 mL) and OA (1mL) in a three-neck round-bottom flask and evacuated at 50 °C for 30 min. The solution was then heated to 180 °C under an inert atmosphere. Meanwhile, a stock solution was made by dissolving DPDTe (0.125 mmol) into OLA (1 mL) When the temperature reaches 160 °C, the stock solution was injected into the flask. After injection, the colour of the solution in the flask changed rapidly from green to brown. The reaction was allowed to proceed for 5 min with continuous stirring. After that, the reaction was terminated by removal of the heating mantle and allowed to cool to room temperature. The solution of the flask was poured in vials and was washed using toluene and ethanol three times at 4000 rpm. The final nanocrystals were dispersed in toluene for further characterization.

Synthesis of copper tin telluride nanocrystals (Reaction Scheme R2)

For the synthesis of copper tin telluride nanocrystals, Cu(II)(acac)$_2$ (0.5 mmol), Sn(Ac)$_4$ (0.25 mmol), TOPO (1 mmol), OLA (4ml), OA (1mmol) were mixed in a round bottom flask at 50 °C and evacuated for 30 min. After 30 min, the solution was
heated to 220 °C. In a vial, a stock solution of DPDTe (0.375 mmol) in 1 mL OLA was prepared by sonicating the solution for 15 min in a water bath. It was injected swiftly into the flask at 155-160 °C resulting into the colour change of the solution in the flask. The reaction was allowed for next 10 min. the heating mantle is removed to cool down the reaction flask at room temperature. The solution was poured into vials and washed with toluene and ethanol for three times. For obtaining high degree of monodispersity, size selective precipitation was carried out at 1000 rpm for 1 min. The supernatant was collected and washed again at 4000 rpm and the final nanocrystals were dispersed in toluene for further characterization.

**Synthesis of copper zinc telluride nanowires (Reaction Scheme R3)**

The synthesis protocol is similar to Reaction Scheme R2 with one modification. Sn(Ac)$_4$ is replaced by equimolar amount of Zn(Ac)$_2$ in the initial reaction flask.

**Synthesis of copper zinc tin telluride nanocrystals using OLA (Reaction Scheme R4)**

In a typical reaction, Cu(II)(acac)$_2$ (0.5 mmol), Sn(Ac)$_4$ (0.25 mmol), Zn(Ac)$_2$ (0.25 mmol) was mixed with OLA (4 mL) in a three neck round bottom flask at 50 °C and evacuated for 30 min. After 30 min, the solution was heated to 250 °C. Meanwhile in a separate vial, a stock solution of DPDTe (0.5 mmol) in 1 mL OLA was prepared by sonication in a water bath at 80 °C. It was injected swiftly into the flask at 145-160 °C resulting into the colour change of the solution from green to dark orange to brown in the flask. The reaction was allowed for next 15 min. The heating mantle is removed to cool down the reaction flask at room temperature. The solution is poured into vials and washed with toluene and ethanol for three times at 4000 rpm. For obtaining better monodispersity, size selective precipitation was carried out at 1000
rpm for 1 min. The supernatant was collected and washed again at 4000 rpm and the final nanocrystals were dispersed in toluene for further characterization.

**Synthesis of copper zinc tin telluride nanocrystals using OLA, TOPO and TDPA (Reaction Scheme R5)**

The synthesis protocol is similar to reaction scheme R4 with additional chemicals, TOPO (0.5mmol) and TDPA (1.5 mmol) in the initial flask.

**Synthesis of copper zinc tin telluride nanocrystals using ODE and TOPO (Reaction Scheme R6)**

In a typical reaction, Cu(II)(acac)$_2$ (0.5 mmol), Sn(Ac)$_4$ (0.25 mmol), Zn(Ac)$_2$ (0.25 mmol) and TOPO (0.5 mmol) was mixed with ODE (4 mL) in a three neck round bottom flask at 50 °C and evacuated for 30 min. After 30 min, the solution was heated to 250 °C. Meanwhile in a separate vial, a stock solution of DPDTe (0.5 mmol) in 1 mL ODE was prepared by sonication in a water bath at 80 °C for 1 hr. It was injected swiftly into the flask at 145-160 °C resulting into the colour change of the solution from green to dark orange to brown in the flask. The reaction was allowed for next 15 min and cool down to room temperature by taking off the heating mantle. The content of the flask is poured into vials and washed with toluene and ethanol. The supernatant was collected and washed again at 4000 rpm and the final nanocrystals were dispersed in toluene for further characterization.

**Characterization Techniques**

For transmission electron microscopy (TEM) analysis, 2 mL 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 nickel grids (Ted Pella Inc.). TEM and Dark-field scanning transmission electron microscopy (DFSTEM) was
conducted by using a 200 kV JEOL JEM-2100F field 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 the 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.
5.4 Results and Discussion

**Figure 1.** (a) Low resolution TEM image of copper telluride nanocrystals; (b) HR-TEM image of single nanocrystal; (c) EDX line scan through a cluster of copper telluride nanocrystals in DF-STEM mode; (d) EDX spectra of copper telluride nanocrystals.

For the colloidal synthesis of copper based metal chalcogenides reported in this chapter, Cu(II)OAc was used as copper precursor in the initial reaction flask due to its compatible reactivity with different ligands such as alkylamines and alkylphosphonic acids.\(^{28}\) The synthesis of copper telluride nanocrystals was first carried out using only OLA as ligand, which led to the formation of multiple phases and diverse morphologies. For better control over the phase and monodispersity of the synthesized nanocrystal, OA was added along with OLA in the initial reaction flask (reaction scheme R1). Fairly monodisperse copper telluride nanocrystals were
obtained having the diameter of 15-17 nm, as shown in Figure 1 (a, b). Clear lattice fringes are observed in the HRTEM image of a single nanocrystal (Figure 1 (b)). The homogenous distribution of copper and tellurium throughout the nanocrystals were detected by an EDX line scan as shown in Figure 1 (c). EDX analysis was employed to measure the ratio of copper and tellurium in the nanocrystals. Measurement of more than five randomly selected areas on a TEM grid gave an average composition of Cu:Te = 1.43:1.

Figure 2. XRD pattern obtained for as-synthesized copper telluride nanocrystals and the standard patterns of copper telluride nanocrystals with different ratios of Cu and Te.

The structure of the as-synthesized copper telluride nanocrystals was characterized by X-ray diffraction (XRD), as shown in Figure 2. The main peaks obtained in the
XRD pattern are consistent with the XRD pattern of the standard Cu$_{2.8}$Te$_2$ (Cu$_{1.4}$Te$_2$) pattern with JCPDS card no. 18-456, confirming the hexagonal crystal structure (P3m1). For further comparison, the simulated pattern of copper telluride with higher copper content i.e., Cu$_{10.56}$Te$_6$ is also given in Figure 2. No other diffraction peaks were observed indicating that the by-products such as Cu, CuO or Te nanoparticles are not formed during the synthesis of copper telluride nanocrystals.

**Figure 3.** (a-d) Scanning electron microscope (SEM) images of Cu$_2$SnTe$_3$ nanocrystals at different resolution with a crystal model of the crystal in the inset of Figure (c).
Figure 4. (a) XRD pattern of the as-synthesized copper tin telluride nanocrystals; (b) EDS line scan in DF-STEM mode performed across three linearly arranged nanocrystals on the TEM grid; (c) STEM image and STEM-EDX elemental mappings of the copper tin telluride nanocrystals.

For the formation of copper tin telluride, a stoichiometric amount of Sn precursor (Sn(IV)Ac) was added in the initial reaction flask during the synthesis of copper telluride nanocrystals. Phase separation was identified in XRD analysis, with the formation of separate domains of copper telluride, copper tin telluride and tin telluride nanocrystals in the reaction flask. To achieve full control over the single phase formation, the reaction conditions were modified as follows. TOPO was used as ligand along with the combination of OLA and OA. The combination of TOPO and OLA optimized the temperature of thermal decomposition of Cu(II)OAc and Sn(IV)Ac in the reaction flask at 120 °C evident from the color change of the
solution from dark blue to intense green. OA assisted in the stabilization of the complex between the precursors and ligands up to the temperature of injection of Te precursor in the flask i.e., 160 °C. Immediately after the injection of Te precursor, the solution changes the color from dark green to orange to dark brown signaling the onset of nucleation process. Further progress in the reaction leads to the final color change of the solution from brown to black around 220 °C indicating the incorporation of all the constituting elements in the crystals.

The final product obtained is the highly faceted octahedral copper tin telluride crystals with sizes in the range of 275-300 nm as shown in Figure 3. The XRD pattern as shown in Figure 4 (a) shows the presence of major peaks at 27.8°, 40.9°, 50.3° and 58.6° which are in agreement with (111), (220), (311) and (400) planes of the cubic structured copper tin telluride crystals as reported in the literature. There is a slight shift noticed in the peak position of (111) and (220) planes in the experimental data compared to the literature values. The crystal structure belongs to the space group F-43m with Cu⁺ and Sn⁴⁺ occupying the same Wyckoff position (4c) and Te⁴⁻ occupying the 4a Wyckoff position. The EDS line scan on a group of three copper tin telluride nanocrystals as shown in Figure 4(b) confirms the homogenous distribution of all three elements throughout the nanocrystals. The elemental distribution in the octahedral shaped nanocrystals is also supported by the elemental mapping in DF-STEM mode as illustrated in Figure 4(c).

Similar reaction conditions were employed to synthesise copper zinc telluride by replacing the tin precursor (Sn(IV)Ac) with equimolar concentration of zinc precursor (Zn(II)Ac) in the initial reaction flask. Interestingly, instead of the production of highly faceted 3-D nanocrystals, the final product obtained was in the form of 1-D nanowires. The SEM image of the drop cast nanowires on a Si wafer, in
the inset of Figure 5(a) shows the high density of the copper-zinc-telluride nanowires. The DF-STEM images of the nanowires (Figure 5(a-c)) clearly illustrate the high aspect ratio of the nanowires with lengths of over 5 microns and diameters of the order of 150 nm. The synthesised nanowires are predominantly untapered and straight with a minority of the nanowires showing some kinks along their lengths. As highlighted in the DF-STEM image in Figure 5 (c), spherical copper telluride nanocrystals are also formed as a by-product during the colloidal synthesis of the copper zinc telluride nanowires. The lattice fringing observed in the HR-TEM image in Figure 5 (c) shows the highly crystalline nature of the nanowires with the inset FFT pattern indexed for the (111) plane elucidating the <111> growth direction for the nanowires.
The formation of the copper telluride nanocrystals during the synthesis of the copper zinc telluride nanowires could be explained by considering the difference between the reactivities of the copper and zinc ions in the alkylamine or phosphonic acid ligands solution. The order of reactivity as observed by different research groups during the colloidal synthesis of quaternary semiconductor nanocrystals is Cu>Sn>Zn.\textsuperscript{29-31} From the aliquot studies, it was confirmed that copper telluride
nuclei are formed first during the nucleation process and owing to the lower reactivity of zinc, the growth process is delayed allowing for by-product formation.

**Figure 6.** (a-b) STEM image of the end and the middle section of copper zinc telluride nanowires and STEM-EDX elemental mappings of the focused images; (c) EDX line scans in DF-STEM mode performed across the length of the nanowire illustrating the distribution of elements in the tip and stem of the wires.

The elemental map as shown in Figure 6 (a, b) supports the presence of each element (Cu, Zn and Te) in both the tip and along the length of the nanowire. The EDX line profile, indicated by the blue line, across the tip of the nanowire shows an approximate 1:1 ratio of Te and Zn while the Cu signal is approximately half of their value, indicating that the tip of the wires is Cu poor. The orange line along the nanowire length beginning at the tip again confirms the 2:2:1 ratio of the Te, Zn and Cu respectively. However, as the scan continues, it can be noted that the signals for
Te and Zn both decrease while the Cu signal is maintained, suggesting a 1.5:1.5:1 ratio of the elements in the nanowires.

The XRD analysis of the as-synthesised copper zinc telluride nanowires (Figure 7) confirms the presence of peaks which match well with Cu-Zn-Te XRD pattern (JCPDS card no. 00-045-1298). The nanowires have cubic crystal phase belonging to Fm-3m space group. The XRD pattern also shows extra peaks with very low intensity which matches with copper telluride patterns supporting the evidence of formation of copper telluride as by-product during the synthesis of copper zinc telluride nanowires.

![XRD pattern](image)

**Figure 7.** XRD pattern obtained for as-synthesized copper zinc telluride nanowires and the standard patterns of copper zinc telluride.
The colloidal synthesis of quaternary metal tellurides involving all three cations Cu\(^+\), Zn\(^{2+}\) and Sn\(^{4+}\) while utilizing a similar hot injection strategy (as used for the syntheses of earlier described nanostructures), is further complicated as each of these precursors react with the Te precursor at different rates. Modulating the different reaction parameters such as temperature, choice of reactants and ligands became necessary to obtain control over the phase and morphology of the synthesised quaternary nanocrystals. After performing a systematic variation in the key reaction parameters, we found three sets of different reaction conditions suitable to form quaternary CZTTe nanocrystals with good control over phase and morphology (Table 1). The synthesis details are described in the experimental section (reaction schemes R4, R5 and R6). The growth temperature to form quaternary copper zinc tin telluride nanocrystals was 250 °C, which is higher than the growth temperature of copper tin telluride and copper zinc telluride. The main motive for increasing the growth temperature was to provide the optimum activation energy so that all three cations could incorporate together in one crystal structure with Te.
<table>
<thead>
<tr>
<th>Reaction Scheme</th>
<th>Ligands used</th>
<th>Morphology</th>
<th>Zn/Sn ratio in nanocrystals</th>
<th>Dispersity</th>
</tr>
</thead>
<tbody>
<tr>
<td>R4</td>
<td>OLA</td>
<td>Abnormally shaped nanocrystals (150-170 nm)</td>
<td>≈ 1</td>
<td>Narrow size distribution and well dispersed in solution</td>
</tr>
<tr>
<td>R5</td>
<td>OLA, TOPO, TDPA</td>
<td>Highly Faceted nanocrystals (200-250 nm)</td>
<td>&gt;1</td>
<td>Broad size distribution and well dispersed in solution</td>
</tr>
<tr>
<td>R6</td>
<td>ODE, TOPO</td>
<td>Abnormally shaped nanocrystals (170-200 nm)</td>
<td>&lt;1</td>
<td>Narrow size distribution and agglomerated in solution</td>
</tr>
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Table 1. Summary of Reaction Schemes R4, R5 and R6 illustrating the effect of different ligands on the morphology, composition and phase of the as synthesised copper zinc tin telluride nanocrystals.

The TEM images, the EDX line scans and the elemental atomic % table for the nanocrystals synthesized by using reaction scheme R4, R5 and R6 are shown in Figure 8. Highly crystalline CZTTe nanocrystals were formed in each reaction scheme as illustrated in the respective TEM images. The control over the shape evolution was best achieved in reaction scheme R5 which produced highly faceted nanocrystals. However, these faceted nanocrystals showed large size distribution (200-250 nm). On the other hand, reaction schemes R4 and R6 produced abnormally shaped nanocrystals having low polydispersity. The EDS line scans across the nanocrystals formed in each reaction scheme revealed the presence of all the constituting elements i.e., Cu, Zn, Sn and Te in the nanocrystals. Interestingly, the Zn/Sn ratio was different in each reaction scheme. While using OLA as the only
ligand in reaction scheme R4, the Zn/Sn ratio was close to 1, illustrating the equal incorporation of both Zn$^+$ and Sn$^{4+}$ in the crystal lattice. When phosphonic ligands were used along with OLA in reaction scheme R5, the atomic % of Zn was higher than Sn. Preference of Sn over Zn was achieved when the synthesis of CZTTe nanocrystals was performed using non-coordinating solvent (ODE) and TOPO according to the reaction scheme R6.

**Figure 8.** DF and BF-TEM images, EDX line scans in DF-STEM mode and the EDS elemental atomic percentage table for the copper zinc tin telluride nanocrystals obtained by using reaction scheme R4, R5 and R6.
Figure 9. XRD pattern obtained for as-synthesized CZTTe nanocrystals and the standard patterns of copper zinc telluride and copper tin telluride.

Figure 9 shows the corresponding XRD spectra of CZTTe nanocrystals synthesized by reaction scheme R4, R5 and R6. As the XRD pattern for CZTTe is not available in literature, simulated XRD patterns for copper zinc telluride and copper tin telluride nanocrystals for comparison are given in Figure 8. Each copper zinc tin telluride spectrum consists of a single set of 2θ peaks belonging to cubic phase, which falls between the peak values for copper zinc telluride and copper tin telluride patterns.

The results collated in Table 1 summarize the effect of different ligands on the morphology, composition and phase of the as synthesised copper zinc tin telluride nanocrystals. It is evident that the phase control in colloidal syntheses of CZTTe nanocrystals is achievable although requires very fine balance between the key parameters of the reaction. However, due to the hyper reactivity of Te, it is difficult to reduce the over growth of the crystal while trying to maintain the stoichiometry of each nanocrystals nucleating in the flask. Hence, control over the monodispersity in CZTTe nanocrystals remains a challenge.
5.5 Conclusions

In summary, we have developed hot-injection colloidal approaches to form a range of metal tellurides with a fine control over crystal phase. A new Te precursor with optimized reactivity namely DPDTTe is used in our synthetic strategies. By systematically tuning the ligand chemistry and growth temperature, formation of metal tellurides were extended from binary, to quaternary compositions. Monodisperse copper telluride nanocrystals were formed by using the combination of OLA and OA as ligands. For synthesizing copper tin telluride and copper zinc telluride, TOPO was added along with OLA and OA as ligands. Copper tin telluride was formed as 3-D highly faceted octahedral shaped nanocrystals. Whereas, under the same reaction conditions, copper zinc telluride was achieved as 1-D nanowires with high aspect ratios. Additionally, for the synthesis of complex quaternary copper zinc tin telluride nanocrystals, a systematic study of ligand and temperature control on the morphology, composition and crystal phase was carried out. Hopefully, such new synthetic schemes can fill the gap in the gallery of colloidal copper based metal telluride nanocrystals and open new avenues for further shape and phase control of complex metal telluride nanocrystals.
5.6 References


Chapter 6: Structural Phase Transformation Induced in Metastable Multicomponent Copper Chalcogenides

Publication in Progress

6.1 Abstract

Here, we report structural phase transition of metastable wurtzite CZTSSe nanocrystals into more stable phases such as zinc-blende and kesterite. The transition from wurtzite to zinc-blende was achieved via solution based post-treatment method. On the other hand, phase transition from wurtzite to kesterite phase was achieved by the thermal annealing approach. The effect of ligands and temperature in the phase transition of the quaternary nanocrystals is discussed in detail. Moreover, the band-gap of the material in different phases is calculated by cyclic voltammetry.
6.2 Introduction

Phase transition is a common phenomenon related to the change of phase stability of materials with the fluctuation in the system.\(^1\) Mostly for the bulk semiconductor materials, phase transitions take place when the temperature or pressure of the system is varied.\(^2\) In nanocrystals, along with temperature and pressure, other variables such as ligand chemistry, doping, alloying, shell formation or composition variation could also lead to change in Gibbs free energy among different phases.\(^2\), \(^3\) Due to the considerable advancement in the colloidal based synthesis, nanocrystals of desired shapes and sizes are also readily accessible in the meta-stable phases which are not quite stable in the bulk form.\(^4\) The structural phase stability of nanocrystals is not only significantly important from a fundamental point of view and also with respect to their technological applicability.\(^5\), \(^6\)

In our area of interest, complex quaternary and quinary materials such as CZTS, CZTSe or CZTSSe have been synthesized in 0-D, 1-D and 2-D morphologies in wurtzite (WZ), zinc-blende (ZB), kesterite and stannite crystal phases by judicious selection of ligands and precursors.\(^7\)\(^-\)\(^{13}\) The first-principles total-energy calculations show that the wurtzite phase as derived from binary II-VI wurtzite structure featuring ABABAB stacking is the least stable phase.\(^14\) On the other hand, kesterite structure derived from a binary II-VI zinc-blende structure having ABCABC stacking is the most stable crystallographic structure.\(^15\) The windows for the growth of meta-stable wurtzite phase (220–280 °C) and more stable zinc-blende or kesterite phases (255–320 °C) overlap regardless of the reaction conditions being provided during the colloidal synthesis.\(^16\) Any gain of thermal energy by the wurtzite nanocrystals trigger the atom diffusion and phase transitions to sta-
ble phases. Mainz and Singh et al. has shown that within few seconds of exposure to high temperature, wurtzite phased aligned CZTS nanorods are converted into kesterite thin films as the solid-solid phase transition pressure elevates.\textsuperscript{17} Similar phase transition has been observed by Agrawal et al. where high temperature selenization process lead to the conversion of metastable wurtzite CZTS nanoparticles into kesterite CZTSSe thin film.\textsuperscript{18} To precisely fabricate the multi-component materials with phase control, it is necessary to explore different approaches for tuning phase stability and controlling phase transition. Despite the reports on the role of ligands in the shape controlled formation of copper-based multinary semiconductor nanocrystals;\textsuperscript{19-21} the surface-ligand interplay for the stability of particular phase is in its infancy.

Herein, we report for the first time the structural phase transition of wurtzite CZTSSe nanocrystals into more stable zinc-blende and kesterite phases via solution based and thermal annealing post-treatment approaches respectively. The wurtzite nanocrystals were first synthesized using alkylamine as ligand. When these nanocrystals were post-treated with a combination of ligands, they underwent a transformation to form zinc-blende particles. They were first transformed into wurtzite-zinc-blende derived polytypic nanocrystals at lower temperatures and were modified into pure phase zinc-blende particles with the further progression of reaction. On the other hand, when the wurtzite nanocrystals were drop-cast on a silica substrate and annealed at high temperature, they transform into kesterite phase grains. The difference in the final phase type obtained from these two approaches of phase transformation gives important insight about the phase-to-phase relationships in nanocrystal systems under the influence of different conditions such as change in thermal energy or surface-ligand chemistry.
6.3 Experimental Details

Materials
Copper(I) acetate (CuAc >97%), Copper(II) acetylacetonate (Cu(acac)2; >99.99%), Copper(II)chloride (CuCl2 >97%), Tin(IV) acetate (Sn(Ac)4, >99.99%), Tin(II)chloride (SnCl2 >97%), Zinc acetate (Zn(Ac)2, >99.99%), Zinc chloride (ZnCl2>99.99%), Trioctylphosphine oxide (TOPO, 99%), 1-dodecanethiol (1-DDT, 98%), diphenyl diselenide (DPDSe 98%), Oleylamine (OLA, technical grade, 70%), Tetrabutylammonium perchlorate (99%) (TBAP) were purchased from Aldrich. n-tetradecylphosphonic acid (TDPA), and n-hexylphosphonic acid (HPA) were obtained from PolyCarbon Industries, Inc. (PCI). All chemicals were used as received without any further purification.

Synthesis of wurtzite CZTSSe nanocrystals
Synthesis of wurtzite CZTSSe nanocrystals, Cu(acac)2 (0.5mmol), ZnAc (0.25 mmol), SnAc (0.25mmol), OLA (5 mL) were evacuated in a three-neck flask in a schlenk line at 50 °C for 20-30 min. The temperature of the round solution was increased to 270 °C under an argon atmosphere in 10 min. When the temperature reaches 155 °C, stock solution made by dissolving DPDSe (0.25 mmol) and 1-DDT (1 mL) into 0.5 mL of OLA was injected into the flask. After injection, the reaction was allowed to proceed for 15 min with continuous stirring. The reaction was terminated by removal of the heating mantle and allowed to cool to room temperature naturally. The product was collected in a vial and kept for further post treatment without washing.

Solution based post-treatment method for phase transformation
In a typical process, TOPO (1.2 mmol), ODPA (0.3 mmol), OLA (3 mL) were added in a three-neck flask and evacuated at 50 °C for 20-30 min. The solution was then heated to 270 °C under an argon atmosphere. At 90 °C, Se/S stock solution (0.1 mmol of DPDSe into 0.5 mmol of 1-DDT) was added. When the temperature reaches to 270 °C, crude solution of wurtzite CZTSSe nanocrystals (unwashed) was added into the flask. The temperature was increased to 305 °C and the reaction was allowed for next 7 min. The product was washed by toluene and ethanol twice for further characterizations. To obtain only polytypic nanorods, the reaction was carried out at 290 °C for 5 min. Further increase in reaction temperature and time give rises to cubic nanocrystals.

**Synthesis of polytypic CZTSSe arrow shaped nanocrystals**

In a typical synthesis, CuAc (0.25 mmol), ZnAc (0.125 mmol), SnAc (0.125mmol), TOPO (1.2 mmol), HPA (0.12 mmol), TDPA (0.26 mmol), OLA (3 mL) were added in a three-neck flask and evacuated at 50 °C for 20-30 min. The solution was then heated to 270 °C under an argon atmosphere. When the temperature reaches 155 °C, stock solution made by dissolving DPDSe (0.25 mmol) into 1-DDT (0.5 mL) was injected into the flask. After injection, the reaction was allowed to proceed for 15 min with continuous stirring. The reaction was terminated by removal of the heating mantle and allowed to cool to room temperature naturally. The product was washed using toluene and ethanol twice. The final nanocrystals were dispersed in toluene for further characterization.

**Synthesis of CZTSSe ellipsoidal nanocrystals**

The synthesis strategy is same as CZTSSe monopods with the replacement of CuAc with CuCl2 (0.25 mmol).

**Ex-situ/In-situ Annealing of nanocrystals**
Nanocrystals solution in toluene was drop casted on silica substrate and dried in air. For ex-situ annealing, these samples were heated on hot-plate on desired temperature. For in-situ annealing, these samples were heated in a closed furnace under N\(_2\) atmosphere.

**Characterization Methods**

The morphology of CZTSSe nanocrystals was characterized by transmission electron microscopy (TEM) and angular dark-field scanning transmission electron microscopy (STEM) using a JEOL JEM-2011F, operating at an accelerating voltage of 200 kV. The sample was made on Carbon supported TEM grids. Scanning electron microscopy (SEM) analysis was performed on a Hitachi SU-70 system operating between 3 and 20 kV. Energy dispersive spectroscopy (EDS) of CZTSSe nanocrystals on a silicon substrate and Nickel TEM grid was performed using a Hitachi SU-70 and JEOL JEM-2011F equipped with EDS detector (respectively). X-ray diffraction (XRD) of drop-cast films of nanocrystals on a glass substrate were carried out on a PANalytical X’Pert MPD Pro using Cu K\(\alpha\) radiation with a 1D X’Celerator strip detector. Rietveld refinement was carried out using X’Pert High Score plus and MAUD software. XPS measurement of CZTSSe nanocrystals were carried out using a Kratos Axis 165 spectrometer. High resolution spectra were taken using monochromated Al K\(\alpha\) radiation of energy of 1486.6 eV at fixed pass energy of 20 eV. For peak synthesis, a mixed Gaussian-Lorenzian function with a Shirley type background subtraction was used. 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. The electro-chemical measurements were performed using Autolab M101 Potentiostat, in a conventional three electrode cell. A 0.1 M solution of TBAP in acetonitrile, used as an electrolyte, was purged with argon.
prior to the measurements to remove any traces of oxygen and inert blanket of argon was maintained above the solution during the measurements. Glassy carbon disc electrodes (part no. CHI104 by CH instruments) were used as the working electrode. These were polished to a mirror-like finish using alumina powder (0.3 μm particles) and thoroughly rinsed with acetone and dichloromethane. Nanocrystals were deposited onto the electrode by drop-casting from toluene solutions with subsequent drying. Potentials were reported vs Ag/AgCl (Ag wire in 10 mmol AgNO₃ dissolved in 0.1 mol TBAP acetonitrile) CV and for calculations vs NHE. A Pt wire was used as the counter electrode.
6.4 Results and Discussion

**Figure 1.** (a) Scheme for the structural phase transformation route via solution based approach; (b) DF-TEM image of CZTSSe wurtzite nanocrystals; (c) HR-TEM image of single nanocrystal with corresponding FFT pattern in inset; (d) SAED pattern indexed with wurtzite planes.

The pristine CZTSSe nanocrystals were synthesized via a hot-injection route using OLA functioning as the coordinating solvent and ligand. The temperature was maintained below 250 °C to rule out the growth of zinc blende-derived phases during the synthesis. Moreover, choice of 1-DDT and diphenyldiselenide (DPDSe) as the chalcogenide precursors along with the presence of tightly bounding ligand (OLA) facilitates the formation of pure wurtzite phase nanocrystals as shown in Fig. 1(b). HRTEM image of a
single nanocrystal (Figure 1 (c)) further confirms their high crystallinity. The observed d-spacing of 0.668 nm, correspond to (001) plane of the wurtzite phase. The plane positions and the observed angles between them are labelled in the FFT image (inset of Figure 1 (c)) which agrees well with the theoretical values of wurtzite structure. The SAED pattern (Figure 1 (d)) is indexed with the rings corresponding to the wurtzite phase of CZTSSe.

Figure 2 (a) EDX spectrum along with the elemental atomic % table; (b) XPS survey spectrum of wurtzite nanocrystals.

EDX was utilized to measure the composition of the wurtzite CZTSSe nanocrystals. Elemental atomic percentage was measured by selecting five randomly selected areas on the SEM sample. The average atomic composition is given in Figure 2 (a). XPS was used to confirm the chemical states of the constituent elements of the as-synthesized CZTSSe nanocrystal (Figure 2 (b)). The survey spectrum of the as-synthesized wurtzite CZTSSe nanocrystal shows the presence of Cu, Zn, Sn, S, Se, O, N and C.
Figure 3. (a) DFTEM of polytypic bullet-shaped nanocrystals; (b) HRTEM image of single nanocrystal showing the $d$ spacing of different facets of each phase; (c) crystal model of the interface; (d, e) corresponding FFT pattern of zinc blende and wurtzite segments; (f) SAED pattern showing the presence of both wurtzite and zinc blende phases.

When these wurtzite nanocrystals were injected in the post-treatment flask constituting a combination of surfactants along with Se/S stock solution at 270 °C, morphological and structural transformations were observed (Figure 1 (a)). The pristine CZTSSe wurtzite
nanocrystals are capped with copious L-type ligands which are usually involved in a fast and dynamic absorption/desorption equilibrium with the surface.\textsuperscript{23} This equilibrium is shifted when the nanocrystals are exposed to ligands having higher displacement potency (such as phosphonic acids).\textsuperscript{24} At high temperatures, the atomic motion along a transition path is well facilitated by the interplay of these ligands resulting into the change in shape of the unit cell along the surface of the nanocrystal. Since, this unit cell transition is coherent along particular facets; the morphology is modified along those facets. The nanocrystals undergo a rapid structural-shape transformation to form polytypic nanobullets as relatively relaxed zinc blende unit cells are formed along the strained wurtzite facets (002) giving rise to zinc blende tips on a wurtzite stem (Figure 3 (a)). The interplanar spacing values of different wurtzite and zinc blende planes and the angles between different planes as shown in the HRTEM image (Figure 3 (b)), corresponds well with the theoretical model (Figure 3c) and previous reports.\textsuperscript{13} The FFT images as shown in Figure 3d and e, reveals the position and angles between the different planes in zinc blende and wurtzite segments respectively. The brighter rings marked in the SAED pattern (inset, Figure 3(f)) are formed due to the overlap of (002)\textsubscript{WZ}/(111)\textsubscript{ZB} and (110)\textsubscript{WZ}/(220)\textsubscript{ZB} planes which further supports occurrence of polytypism in the nanobullets. The EDX spectrum of the polytypic nanocrystals as shown in Figure 4 (a) confirms the presence of all the constituting elements in stoichiometric ratios after post-treatment experiment. The XPS survey spectrum of the polytypic nanocrystals (Figure 4 (b)) shows the presence of both N and P from amine and phosphonic acid ligands attached to the polytypic CZTSSe nanocrystals.
Figure 4 (a) EDX spectrum along with the elemental atomic % table; (b) XPS survey spectrum of the polytypic nanocrystals.

Figure 5. (a) DFTEM of CZTSSe zinc blende particles with the SAED pattern in the inset; (b) HRTEM image of a section of single particle; (c) Scanning electron microscope (SEM) image of CZTSSe zinc blende particles; (d) XPS survey spectrum of the zinc-blend particles with the elemental atomic % table (measured by EDX in SEM mode) in the inset.
As the temperature is further increased, number of strained facets is created. This increase in surface energy results into complete solid-solid phase transformation of remaining wurtzite domains into less strained zinc blende lattice by attachment and coalescence giving rise to the formation of zinc blende particles. These particles were ~200 nm in size (Figure 5 (a, c)) and zinc blende in nature as the rings corresponding to the planes of wurtzite phase were not obtained in SAED pattern (inset, Figure 5 (a)) of the particles. The continuous lattice fringes in the HRTEM image (Figure 5 (b)) confirms that they are single crystalline (not a superstructure formed by assembled nanocrystals). The interplanar spacing was measured to be 0.328 nm for the (111) plane, and the measured angle between (111) and (200) was found to be 56° as shown in Figure 5 (b). The XPS survey spectrum (as shown in Figure 5 (d)) shows the presence of all the constituting elements along with C, O, N and P. It was observed that as the phase of the CZTSSe nanocrystals shifts from wurtzite to zinc-blende, they become more Se rich in composition. We assume that the reducing concentration of S in the nanocrystal composition with the gradual progression in the post-treatment reaction is due to the replacement of the surface bound thiols with phosphonates. As 1-DDT have a dual role as both S precursor and surfactant, it could be present on the surface of the nanocrystals in the form of thiol ligand. During the shape and phase reconstruction of nanocrystals, the surface bound thiols would have been replaced by the phosphonic acids having higher displacement potency.
Figure 6. (a) DF-TEM of arrow-shaped polytypic CZTSSe nanocrystals; (b) SEM image of zinc-blende particles after chemical post treatment of polytypic arrow-shaped nanocrystals; (c) DF-TEM of ellipsoidal polytypic CZTSSe nanocrystals; (d) SEM images of zinc-blende particles after chemical post treatment of polytypic ellipsoidal nanocrystals.

The transition of metastable wurtzite phase to stable zinc-blende phase in the solution based approach was achieved at 300 °C which is much lower than the reported temperature of phase transition via annealing. We rationalize that this lowering of transition temperature is due to the involvement of alkylamine and phosphonic ligands in the post-treatment process. The ligands decrease the threshold energy for transition and structure relaxation. It was observed that the transition temperature could be further minimized in the solution based approach, if the pristine nanocrystals have zinc-blend phase already induced in the crystal structure. When polytypic nanocrystals with the wurtzite compositi-
tion of 51% by weight (and 49% zinc-blende), the phase transformation is achieved at 270 °C which decreased to 250 °C when the wurtzite composition was lowered to 45% by weight (rest zinc-blende) (as shown in Figure 6 and 7).

Figure 7. XRD patterns of polytypic nanocrystals before and after post-treatment.

Since, solution based phase transformation is a thermo-chemical process, it was essential to identify the role of the ligands in the structure modification of nanocrystals. We performed a detailed ligand variation study by excluding one ligand at a time from the post-treatment flask. The structural and morphological changes were carefully observed via TEM, EDS and XRD characterizations. It was found that fast and controlled transformation could be achieved only when thiol, amine and phosphonic functional moieties are balanced together in the flask. The combination of these ligands not only induces phase transformation at different temperature zones but also controls the morphology of the resulting nanocrystals at each stage. Absence of any of these ligands in the post-treatment flask disturbs the overall phase-to-shape equilibrium in the system (Figure 8).
Figure 9. XRD pattern of nanocrystals after post-treatment excluding one ligand at a time.

The nanocrystals formed at different stages of phase transformation were analyzed further by XRD and are shown in Figure 10. The experimental patterns of nanocrystals were compared with the simulated patterns for wurtzite, zinc-blende and kesterite derived CZTSSe phases via Rietveld refinement analysis performed using the simulated patterns in MAUD program. It was found that peak locations and their relative intensities in the experimental data of as synthesized wurtzite nanocrystals matches well with
the wurtzite-derived CZTSSe simulated pattern constructed by randomly distributing Cu, Zn and Sn atoms based on the cation ratio at the Zn sites in wurtzite ZnS (Figure 10a). The Rietveld refinement analysis of the experimental XRD pattern of the bullets shows a wurtzite composition of 50.56% and zinc-blende composition of 49.44% (Figure 10b). The XRD pattern of zinc-blende particles also corresponds well with zinc-blende phase as shown in Figure 10 (c) and is comprised of 99.5% zinc-blend phase.

**Figure 10.** XRD pattern and Rietveld fit for different stages of solution based phase transformation (a) wurtzite nanocrystals; (b) polytypic CZTSSe nanocrystals; (c) zinc-blende particles.

The high resolution spectra of N and P recorded for each stage of phase transformation (Figure 11 (a, b)). After the peak quantification of the recorded N1s spectra, it was observed that the intensity of the quantified peak positioned at 401.5 eV increases and the
intensity of the quantified peak positioned at 399.2 eV decreases while moving from wurtzite to zinc blende (Figure 11 (a)) signifying the increased concentration of unbound N in the solution. On the other hand, in P 2p spectra, the quantified peak positioned at 132.8 eV becomes intense with increasing zinc-blende phase in the solution (Figure 11 (b)) indicating the increase in the concentration of P bounded to the surface. This suggests that with increasing temperature in the post-treatment flask, the nanocrystals undergo ligand exchange reactions and amine is replaced by phosphonic moieties. OLA and thiol favor the stabilization of meta-stable wurtzite phase at low temperature whereas phosphonic groups stabilize the less strained zinc blende phase at high temperatures. Since, the mechanism of preferential ligand binding or calculations of the involved binding energies is not fully developed; it is difficult to justify the role of each parameter separately in the reaction kinetics of solution based phase transformation.

Figure 11. High resolution XPS spectra for (a) N1s and (b) P 2p.
Figure 12. (a) Schematic of the phase transformation route involving annealing of the nanocrystals at high temperature; (b) SEM image of the kesterite grains produced after annealing process; (c) XPS survey spectrum of the kesterite grains; (d) XRD pattern and the Rietveld fit for the kesterite grains
The second approach to study phase transformation in metastable wurtzite CZTSSe nanocrystals involves thin film annealing as reported earlier by Singh et al.\textsuperscript{17} The solution of wurtzite CZTSSe nanocrystals in toluene was drop-cast on a silica substrate and annealed at 400 °C for 2 min (Figure 12 (a)). When the nanocrystal film was exposed to high temperature, an abrupt increase in the linking nucleus bridges between the closest facets of neighboring crystals enhanced the chances of interparticle growth in crystal. This process relaxed the cell dimensions, transforming into least strained and thermodynamically stable crystal lattice (kesterite phase). The direct solid-state transition of metastable wurtzite phase into kesterite phase via annealing corresponds well with the earlier reports from different groups.\textsuperscript{17,18} The shape control over the final phase formation is completely lost due to the instability of organic surfactants at higher temperatures leading to the formation of grains (Figure 12 (b)). The XPS spectrum of the kesterite thin film reveals the presence of all the constituting elements (Figure 12 (c)). However, the final phase after transition is selenium rich signifying the loss of surface bound thiol during the heating process. Rietveld fitting analysis of the annealed sample reveals that the film is composed of 100% kesterite CZTSSe (Figure 12 (d)).

To measure the lowest temperature at which the phase transition experiments could be performed, high temperature XRD analysis of wurtzite thin film (drop-casting wurtzite nanocrystals suspended in toluene onto a silica substrate) under in-situ conditions was carried out. The XRD pattern for kesterite CZTSSe phase was observed as the temperature of the annealing chamber was increased beyond 340 °C (Figure 13). The XRD data analysis showed that in the absence of ligands in annealing process, the metastable form (wurtzite) is directly transformed into most stable (kesterite) form without intermediate
zinc blende phase formation. Interestingly, when the phase transformation was carried out by solution based approach as described earlier in the chapter, the ligand-surface interaction preferably minimizes the conversion energy barrier between the cubic polymorph and hexagonal polymorph, due to which polytypism is induced in the system resulting into the selective transition from wurtzite phase to zinc blende phase with further progression of reaction.

**Figure 12.** (a) In-situ XRD analysis of wurtzite nanocrystal thin film annealing up to 500 °C with simulated patterns for wurtzite and kesterite phases of CZTSSe; (b) In-situ XRD analysis of wurtzite nanocrystal thin film annealing with recorded spectra after every 10 degrees from 320 °C to 350 °C.
To observe the effect of phase transformation on the electronic structure of the nanocrystals, we measured band gap position and magnitude by employing CV. It is an electrochemical method that can yield direct measurements of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies of nanocrystals, which correspond to the valence and conduction band edges, respectively. CVs, recorded for nanocrystal films of each of the CZTSSe phases deposited on a glassy carbon (GC) electrode, are presented in Figure 5 a. In contrast to the featureless trace yielded by uncoated GC, pronounced oxidation currents are obvious at potentials above 0.5 V for the nanocrystal modified electrodes. These are due to the withdrawal of electrons from the valance band and so, the initial onset potential ($E'_{\text{onset}}$) of rising current
yields marks the band edge. Similarly, conduction band frontiers can be derived from the onset potential ($E'_{\text{red}}$) of reduction currents at potentials below -0.5 V. In common with earlier reports on CdSe, CdTe, CuInS$_2$, Cu$_2$SnSe$_3$ and indeed other CZTSSe nanocrystals these reduction peaks are weaker than the oxidation features. In Figure 5 b, $E'_{\text{ox}}$ and $E'_{\text{red}}$ for each type of nanocrystal have been converted to the commonly used Normal Hydrogen Electrode (NHE) scale, and their differences expressed as the band gap ($E_g$) value. There is a decrease in $E_g$ from 1.51 eV for WZ, through 1.41 eV for polypytic, to approximately 1.20 eV for both ZB and KS. The absolute energies, $E$, of the HOMO and LUMO levels are also incorporated in Figure 5 b. These were calculated according to the formulae;

$$E_{\text{HOMO}} = -(E'_{\text{ox (vs. NHE)}} + 4.5) \text{ eV}$$

$$E_{\text{LUMO}} = -(E'_{\text{red (vs. NHE)}} + 4.5) \text{ eV},$$

and facilitate direct comparison of the band gap positions of these nanocrystals with other semiconductor materials. The shift in the band-gap towards lower eV values from wurtzite to zinc blende and kesterite phases could be due to the increasing Se concentration in these phases. This trend in the band-gap values makes phase transformation approach as an alternative route to achieve band-gap tuning in complex multinary semiconductor nanocrystals.
6.5 Conclusion

In summary, crystal phase transformation in CZTSSe nanocrystal system is achieved via solution based post-treatment and annealing approaches. Shape controlled transformation from meta-stable wurtzite nanocrystals to highly stable zinc-blende phase was performed via a solution based post-treatment method. On the other hand, kesterite grains were produced by annealing WZ nanocrystal based thin films. The effect of ligands and temperature in lowering the barrier for rapid conversion from one phase to another has been discussed. The effect of phase transformation on the band-gap tuning is illustrated via CV measurements. This facile phase transformation routes gives useful insights on the phase-to-phase relationships under extreme conditions and even opens new pathways for band-gap engineering in copper based multicomponent nanocrystals.
6.6 References


Chapter 7: Conclusion and Future Directions

Colloidal synthetic routes to fabricate metal chalcogenide semiconductor nanocrystals have attracted a great deal of attention. Cadmium and copper based semiconductor nanocrystals are potential materials for photo conversion, photoemission and thermoelectric applications, owing to their high optical absorption coefficients and band-gaps that are tunable according to composition and size. This thesis is devoted to the development of novel colloidal approaches to synthesize a wide range of metal chalcogenide nanocrystals. The hot-injection approach, typically of an anion complex into a melted surfactant mixture containing the cation precursors, is used to achieve full control over the morphology, crystal phase and composition of the nanocrystals. The thesis explores the underlying solution phase reactions and the effect of different key parameters on nanocystal nucleation and growth.

Moreover, using the insight gained by experiments, the thesis also puts forth a facile approach to transform the crystal phase of colloidal nanocrystals in solution from the metastable wurtzite phase to thermodynamically stable zinc blende phase.

General conclusions and directions for future study for each of the research chapters are discussed in the following sections.
7.1. Chapter 3- Synthesis and Self-Assembly of CdSe$_x$S$_{1-x}$ Nanorods

In Chapter 3, a range of monodisperse colloidal CdSe$_x$S$_{1-x}$ nanorods were synthesised with homogeneous composition and controlled aspect ratios. To achieve alloyed nanorods, a combined chalcogen precursor was prepared by dissolving elemental S and Se in TOP and this was injected at high temperature into the flask containing Cd-phosphonate complex. The optical absorption and photoluminescence emission were compositionally tunable with the chalcogen ratios. UV absorption spectra showed that the absorption band edge of the CdSe$_x$S$_{1-x}$ nanorods was consecutively red shifted with the gradual increase of Se concentration in the nanorods. Similarly, the different compositions of nanorods showed direct band edge photoluminescence emission over a 200 nm range that was tunable according to the Se/S ratio. The combination of using a longer alkyl chain and shorter alkyl chain in the phosphonic acid ligands (i.e. ODPA and HPA) proved crucial to form the nanorod geometry. The effect of chalcogen composition and ligand chemistry on shape control was extensively studied to maintain the desired length and diameter for each nanorod composition. It was found that the shape of the nanocrystals could be tuned from spherical dots to high aspect ratio nanorods by varying the HPA concentration in the initial reaction flask. Our synthetic protocol was sufficiently robust to achieve good control over the nanorod aspect ratios, with low polydispersities, which makes the nanorods well suited for rational assembly into superstructures. We have demonstrated the self-assembly of nanorods into close-packed structures perpendicular to the substrate and horizontal 1D rail-track depending on the net charge.
Controlled 3-D assembly of these nanorods can be obtained by using external electric fields to push the rods from solution towards a substrate interface that is placed on the appropriate electrode. This can be achieved in the non-polar solvents (e.g. toluene) that are used to store the nanorods after synthesis. The ordered assemblies are more likely to enhance the optical properties of the nanocrystals. Further investigations should examine the optical properties of assemblies of compositionally tunable CdSe$_x$S$_{1-x}$ nanorods for photo-emissive applications.

The assemblies of the CdSe$_x$S$_{1-x}$ nanorods could also be used for solar energy conversion. The band gap alignment could be investigated between the different compositions of the n-type CdSe$_x$S$_{1-x}$ nanorods as the buffer layer and the p-type CZTS or CZTSSe nanorods as the absorber layer.

Metal-semiconductor nanorod hybrid nanostructures would also be an interesting area to explore using the CdSe$_x$S$_{1-x}$ nanorods. Au, Ag or Pt tipped binary CdSe and CdS nanorods have been previously reported by different research groups for applications such as photocatalysis and protein immobilisation.$^{1-3}$ Similarly, CdSe$_x$S$_{1-x}$ nanorods could be tipped with metals such as Au or Pt. Since the optical and electronic properties are dependent on the composition of the nanorods, the heterostructures could be harnessed as photo-catalytic materials for the study of solar-to-chemical energy conversion.
7.2. Chapter 4- Shape and Crystal Phase Controlled Synthesis of CZTSSe Nanocrystals

In this chapter, we have demonstrated an extensive study on the colloidal synthesis of an important compound semiconductor system, CZTSSe. Exquisite control over the CZTSSe nanocrystal shape was achieved by tuning the occurrence of polytypism between wurtzite and zinc blende phases. We have shown that the judicious selection of ligands and precursors and how they are introduced in the reaction flask can tune the morphology of the nanocrystals from dots to ellipsoids to arrows and rods. The shape evolution was dictated by independently controlling the respective growth rates of either the zinc blende or wurtzite regions in the polytypic system. By using a combination of trioctylphosphine oxide and alkylphosphonic acids as ligands and the coordinating solvent oleylamine, polytypic heterostructures having wurtzite cores and zinc blende tips were formed. The shape of these polytypic nanocrystals were controlled by the choice of metal precursors used in the synthesis, preferably the Cu$^+$ precursor producing ellipsoids (two large zinc blende tips on a wurtzite disc), arrow shaped (one dominant zinc blende with small wurtzite stem) and bullet shaped nanocrystals (one dominant wurtzite stem with a small zinc blende tip).

Furthermore, we also showed that polytypism could be eliminated from the system where single-phase wurtzite CZTSSe nanorods could be synthesized by replacing the oleylamine and alkylphosphonic acids with a non-coordinating solvent (1-octadecene). The aspect ratio of these nanorods was increased by gradual reduction of the Cu concentration in the initial reaction flask. Time-dependent aliquot studies were performed to detail the growth mechanism of the differently shaped polytypic and the phase pure nanocrystals reported in this chapter. They were characterized by different microscopic and spectroscopic techniques such as TEM, SEM, XRD and
XPS to confirm the nanocrystal composition, morphology, occurrence of polytypism and the ratio of the wurtzite and zinc blende phases. The systematic study not only confirmed the ability to controllably engineer the anisotropic shape and phase of these multicomponent nanocrystals but also provided useful insights about shape evolution in compound copper based semiconductor nanocrystals.

Figure 1. (a) Low resolution TEM image of CZTSe nanocrystals; (b) HR-TEM image of single nanocrystal; (c) XRD pattern of wurtzite CZTSe nanocrystals.

The synthetic strategies used to synthesize the polytypic and phase pure CZTSSe nanocrystals show significant promise for extension to other materials such as CZTS, CZTSe and CZTGeS. For example, preliminary investigations showed that single phase WZ CZTSe nanocrystals could be synthesised by replacing the S precursor (1-DDT) with OLA in the anionic stock solution. The TEM image and XRD pattern of the as-synthesized CZTSe nanocrystals is shown in Figure 1.

In terms of the future directions for CZTSSe, it would be interesting to investigate the use of polytypic CZTSSe nanocrystals for thermoelectric applications. It has recently been reported that polytypism could be desirable in thermoelectrics as a single particle, having different phases with different electrical and thermal characteristics, maximizes the Seebeck coefficient.\(^4\)

CZTSSe is also an interesting material for photovoltaic applications. Further investigations should examine the incorporation of the CZTSSe nanorods into a
nanocrystal based photovoltaic device, in which the CZTSSe nanorods would be ideally assembled on molybdenum coated ITO glass substrates followed by subsequent assembly of CdSe$_{1-x}$S$_{1-x}$ nanorods and ZnO/ZnO:Al top contacts. Complete testing of the power conversion efficiency of this device architecture should be investigated.
7.3. Chapter 5- Synthesis of Copper Based Metal Telluride Nanocrystals Ranging from Binary to Quaternary Composition

In this chapter, the colloidal synthesis of a series of metal telluride nanocrystals was demonstrated via the hot-injection approach. Diphenylditelluride was chosen as the Te precursor as it showed optimized reactivity which was well balanced with the reactivity of the cation precursors in the reaction flask. By regulating the reaction parameters, such as ligands and growth temperature, a variety of metal telluride nanocrystals were synthesized such as binary copper telluride, ternary copper tin telluride and copper zinc telluride and quaternary copper zinc tin telluride nanocrystals. A combination of solvents such as OLA and OA were used to synthesise binary copper telluride nanocrystals with a hexagonal crystal structure. TOPO was required as an additional ligand, along with OLA and OA in the initial reaction flask, to form the ternary nanocrystals such as copper tin telluride and copper zinc telluride. Under the same reaction conditions, copper tin telluride was formed as 3-D highly faceted octahedral shaped nanocrystals, whereas copper zinc telluride formed as 1-D nanowires with high aspect ratios. Furthermore, the synthetic strategy was extended to form complex quaternary copper zinc tin telluride nanocrystals. A complete systematic study of the effect of key control parameters on the morphology, composition and crystal phase was carried out. Three reaction schemes were selected to tune the shape of the nanocrystals and the ratio between zinc and tin in the final nanocrystals. The variation in the shape, size regime and phase of the synthesized nanocrystals by extending the composition from binary to quaternary was characterized by TEM, STEM, SEM, EDX and XRD measurements.
For future research, the synthesis of quaternary metal telluride reported in this chapter could be improved further by refining the reaction scheme to produce better quality copper zinc tin telluride nanocrystals.

It would be interesting to achieve a better control over the copper zinc telluride nanowires synthesis in the colloidal solution so that kinking in the nanowires could be reduced further. Recently, copper telluride nanowires have been explored as a thermoelectric material and used to fabricate flexible thermoelectric fabrics. It would be interesting to observe how the thermoelectric properties are affected by using nanowires of the copper zinc telluride composition.

Further investigations must be done to explore the effect of both shape and composition on the thermoelectric properties, especially the ternary and quaternary compositions as they are rather unexplored so far due to the difficulties in their synthesis.
Chapter 6 demonstrates the structural phase transition of metastable wurtzite CZTSSe nanocrystals into more stable phases such as zinc-blende and kesterite via solution based and thermal annealing post-treatment approaches respectively. The transition of CZTSSe nanocrystals from wurtzite to zinc-blende phase was achieved via a solution based post-treatment method. The WZ nanocrystals were synthesized using OLA as ligand. When these nanocrystals were post-treated with a combination of OLA, ODPA and TOPO, a two stage phase transformation was observed. They were rapidly transformed into wurtzite-zinc blende derived polytypic nanocrystals of similar size at 270 °C. When the temperature was increased beyond 300 °C, the polytypic nanocrystals were modified into pure phase zinc blende particles (>150 nm). On the other hand, the phase transition from the wurtzite to kesterite phase was achieved by the thermal annealing approach. When the wurtzite nanocrystals were drop-casted on a silica substrate and annealed at high temperature, they transformed into kesterite phase grains. The morphology, composition and crystal phases at the different stages of the phase transformation were characterized by using microscopic, spectroscopic and diffraction techniques such as TEM, SEM, XPS, EDS and XRD. The effect of ligands and temperature in the phase transition mechanism was studied extensively. Moreover, the band-gap of the material in different phases was calculated by CV to observe the effect of phase transformation on electronic properties.

This facile phase transformation route gives valuable insights into the phase-to-phase relationships under chemical and thermal stress in copper based multicomponent nanocrystals. It would be interesting to further investigate if the nanocrystals could
transform from the metastable wurtzite phase to other thermodynamically stable phases such as kesterite and stannite via the solution based phase transformation approach.

![Image](image.jpg)

**Figure 2.** (a) Low resolution DF-TEM image of CZTGSSe nanorods; (b) HR-TEM image of single nanorod; (c) DF-TEM image of CZTGSSe nanorods with the EDS line scan plot; (d) XRD pattern of CZTSSe nanocrystals with the DF-TEM image in the inset and the XRD pattern of CZTGSSe rods with the DF-TEM image of self assembled nanorods in inset.

Preliminary results have indicated the possibility of using the post-treatment method for partial cation exchange in multinary nanocrystals. When the post-treatment of wurtzite CZTSSe nanocrystals is carried out in the presence of Ge precursor along with the same combination of ligands at 270 °C, CZTGSSe nanorods are formed (as shown in Figure 2). The TEM image of the CZTGSSe nanocrystals shows nanorods formed with low aspect ratio ((Figure 2 (a,b)). The polytypic nature of the nanorods is dictated by the HR-TEM image (Figure 2 (b)) and the XRD pattern (Figure 2 (d)). The control over the morphology in this extremely complex system opens new pathways for partial cation-exchange in simpler systems such as copper tin sulphide/selenide and copper zinc tin sulphide/selenide.
7.5 References


