

Development of Cu-based multicomponent quantum nanostructures



Xue Bai

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Summary

The main goal of this project was to develop novel Cu-based multicomponent quantum nanostructures with distinct morphologies and optical properties and explore their potential applications as materials for luminescent solar concentrators.

Chapter 1 presents a literature review and background knowledge on the photophysics, synthesis and applications of Cu-based multicomponent quantum dots, particularly heterostructured quantum dots.

Chapter 2 provides the synthetic and experimental protocols used in this project. The characterization techniques and equipment employed are also detailed.

Chapter 3 presents the synthesis and characterization of Cu-based spherical CIZS/ZnS core/shell and CIZS/ZnS/ZnS core/shell/shell quantum heterostructures. The Cu-In-Zn-S core was prepared using a hot injection technique by injecting the anion precursor solution into the cation precursor solution which loaded in a three-neck round-bottom flask. Then a seeded growth method was employed to coat the first ZnS shell onto the preformed CIZS core to obtain the CIZS/ZnS core/shell heterostructures, and then the second ZnS shell to get the CIZS/ZnS/ZnS QDs with higher quantum yields. The obtained quantum nanostructures were fully characterized by various instrumental techniques.

Chapter 4 describes the synthesis and characterization of a novel, highly fluorescent Cu-based Cu-In-(Zn)-S/ZnS “ice-cream” like nanoheterostructures. The Cu-In-S seeds were prepared with a straightforward heating up technique, which was followed with the shell coating using a seeded growth method. This sample was thoroughly characterized using a range of microscopy and spectroscopic techniques.

Chapter 5 reports the synthesis of the fluorescent Cu-based Cu-In-Zn-Se/Cu-In-Zn-S/ZnS core/shell/shell heteronanonail structures. The hot injection technique was employed to prepare the CIZSe seeds, which was followed by the shell coating of CIZS shell and then ZnS shell with the seeded growth methods. Au particles were deposited onto the surface of the preformed CIZSe/CIZS/ZnS nanonails resulting in the unique Au-CIZSe/CIZS/ZnS nanocomposites.

Chapter 6 is dedicated to the incorporation of highly fluorescent Cu-based QDs into PMMA matrix for the building of luminescent solar concentrators. Four types of Cu-based QDs have been embedded into PMMA polymer block, including (1) CIZS/ZnS heterostructured QDs with relatively thin ZnS shell, (2) CIZS/ZnS/ZnS heterostructured QDs with thicker ZnS shell, (3) CIZS/ZnS/ZnS heterostructured QDs with the thickest ZnS shell and (4) alloyed CIZS/ZnS QDs. Detailed study of the obtained LSCs have been performed.

Finally, chapter 7 outlines the conclusions of the entire work, presents some preliminary studies and future plans for our work.

Publications list

1. **Xue Bai**, Finn Purcell-Milton, Yurii K. Gun'ko, Near-infrared-emitting CIZSe/CIZS/ZnS colloidal heteronanonail structures. *Nanoscale* **2020**, 12 (28), 15295-15303.
2. **Xue Bai**, Finn Purcell-Milton, Yurii K. Gun'ko, Optical Properties, Synthesis, and Potential Applications of Cu-Based Ternary or Quaternary Anisotropic Quantum Dots, Polytypic Nanocrystals, and Core/Shell Heterostructures. *Nanomaterials* **2019**, 9 (1), 85.
3. **Xue Bai**, Finn Purcell-Milton, Yurii K. Gun'ko, Controlled synthesis of luminescent CIZS/ZnS/ZnS core/shell/shell nanoheterostructures. *CrystEngComm* 2021.
4. **Xue Bai**, Finn Purcell-Milton, Daniel K. Kehoe and Yurii K. Gun'ko, Photoluminescent, “Ice-cream Cone” like Cu-In-(Zn)-S/ZnS Nanoheterostructures. Under review in *ACS Nano*.
5. **Xue Bai**, Finn Purcell-Milton, Yurii K. Gun'ko, Macro matrix for quantum dots. In submission.

Declaration

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Xue Bai

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Abbreviations

ASE – Amplified spontaneous emission	LSC – Luminescent solar concentrator
CGeS – Cu-Ge-S	MA - Myristic acid
CGS – Cu-Ga-S	MPA - Mercaptopropionic acid
CIGS - CuIn _{1-x} Ga _x S	MRI - Magnetic resonance imaging
CH - Chalcopyrite	NC - Nanocrystal
CIS – Cu-In-S	NIR – Near-infra red
CISe – Cu-In-Se	NPL - Nanoplatelet
CIZS – Cu-In-Zn-S	NR – Nanorod
CIZSe – Cu-In-Zn-Se	OA – Oleic acid
CTS – Cu-Sn-S	OAm - Oleylamine
CTSe – Cu-Sn-Se	ODE – Octadecene
CZTS - Cu ₂ ZnSnS ₄	PL – Photoluminescence
CZTSe - Cu ₂ ZnSnSe ₄	PLQY – Photoluminescence quantum yield
DAP - Donor-acceptor pair	QD – Quantum dot
DDT - Dodecanethiol	ST - Stannite
DMF - Dimethylformamide	TOA - Trioctylamine
EL - Electroluminescence	TOP – Trioctylphophine
FWHM – Full width half max	TOPO - Trioctylphosphine oxide
GSH - Glutathione	TP – Tetrapod
HDA – Hexadecyl amine	WZ - Wurtzite
HWHM – Half width half max	XANES - X-ray absorption near-edge structure
KS -Kesterite	ZB – Zinc blende
ZnEX - Zinc ethylxanthate	

Chapter 1 Introduction

An entitled talk “There’s Plenty of Room at the Bottom” was delivered by Physics Nobel Laureate Richard Feynman on 29 December 1959 at the annual American Physical Society meeting, which is the first lecture referring the applications for nanoscale materials. The term “nanotechnology” was initially introduced by Norio Taniguchi at the International Conference on Precision Engineering (ICPE). Afterwards, this area has been advanced greatly along with the fast development of the sophisticated instrumentation that enable the characterization of materials on nanoscale. Quantum dots (QDs) also known as inorganic semiconductor nanocrystals have emerged and been explored for decades.

QDs are very important light emitting nanomaterials which have been intensively explored for many decades¹⁻⁴. The most well investigated systems are the II-VI Cd-based QDs⁵⁻⁶, and corresponding Cd-based core/shell heterostructures⁷⁻⁹. More recently, Cu-based multicomponent (ternary, quaternary and quasi-quaternary) QDs have attracted great attention due to their advantages over its Cd-based counterparts and a range of other unique and important properties. Firstly, the absence of toxic heavy metals (e.g. Cd or Pb) shows particular advantages due to reduced environmental impact and increased ease for biological applications. Secondly, Cu-based multicomponent QDs show even greater absorption and emission tunability relative to Cd-based systems since they not only display a size-dependent bandgap they also display the property of non-stoichiometry. It means that the optical properties of Cu-based multicomponent QDs can also be tuned *via* varying the ratio of cations that compose the QDs in addition to the size of the sample. Thirdly, Cu-based multicomponent QDs possess enhanced stability against external environment (oxygen, moisture and photoirradiation), especially after inorganic shell coating with large band gap

semiconductors such as ZnS¹⁰⁻¹². Thus, Cu-based multicomponent QDs are very promising candidates to replace the traditional Cd-based systems.

It is well known that the optical properties of QDs are not only size and composition dependent but also determined by the resulting shape and morphology, with several morphologies demonstrating this, including spherical QDs, nanorods (NRs), and tetrapods (TPs). Especially NRs and TPs, showing increased electrical conductivity compared to quasi-spherical nanoparticles, and therefore are very appealing for applications requiring efficient charge transfer¹³. CdSe/CdS dot in rods and rod in rods have shown polarized emission for use in a liquid crystal display, acting as optical funnels, absorbing across a significant range of unpolarised wavelengths and then emitting strongly linearly polarised emission at a specific wavelength depending on the specific nanostructure¹⁴⁻¹⁵. There are many other applications based on the special properties like intrinsic polarized emission, decreased Auger recombination rate and large Stokes shift and so forth^{16 17 18-19}.

The best way to produce these particular morphologies is to coat a shell onto the preformed core to prepare heterostructures using the controlled reaction conditions (core with specific crystal structures, long-chain ligands, reaction temperature, addition rate of the shell materials to the core solution and so forth). The synthesis of nanoheterostructures is well explored for Cd-based systems^{7, 20-25}. In order to prepare and make the best of high quality (regarding optical properties and morphologies) Cu-based multicomponent heterostructures with particular morphologies, it is important to know the commonly used synthetic techniques and photophysics of Cu-based multicomponent QDs.

1.1 Unique photophysical properties of Cu-based multicomponent QDs

1.1.1 Emission mechanism

The general fundamental photophysical processes in a QD are presented in Figure 1.1. An electron can be promoted to a certain energy level in the conduction band and is termed as a hot carrier and it leaves a hole in the valence band at the same time upon photon excitation. Then there are two pathways for the hot carriers to release energy. The first way is relaxing to the band edge position to form excitons, and the other possibility is being trapped by the surface defects. For the first case (formation of excitons), the formed excitons also have two potential channels to further release the energy, the first way is giving emission through radiative decay, the other one is producing heat *via* non-radiative decay. As for the trapped hot carriers, there is still a chance for them transfer back to regenerate excitons.

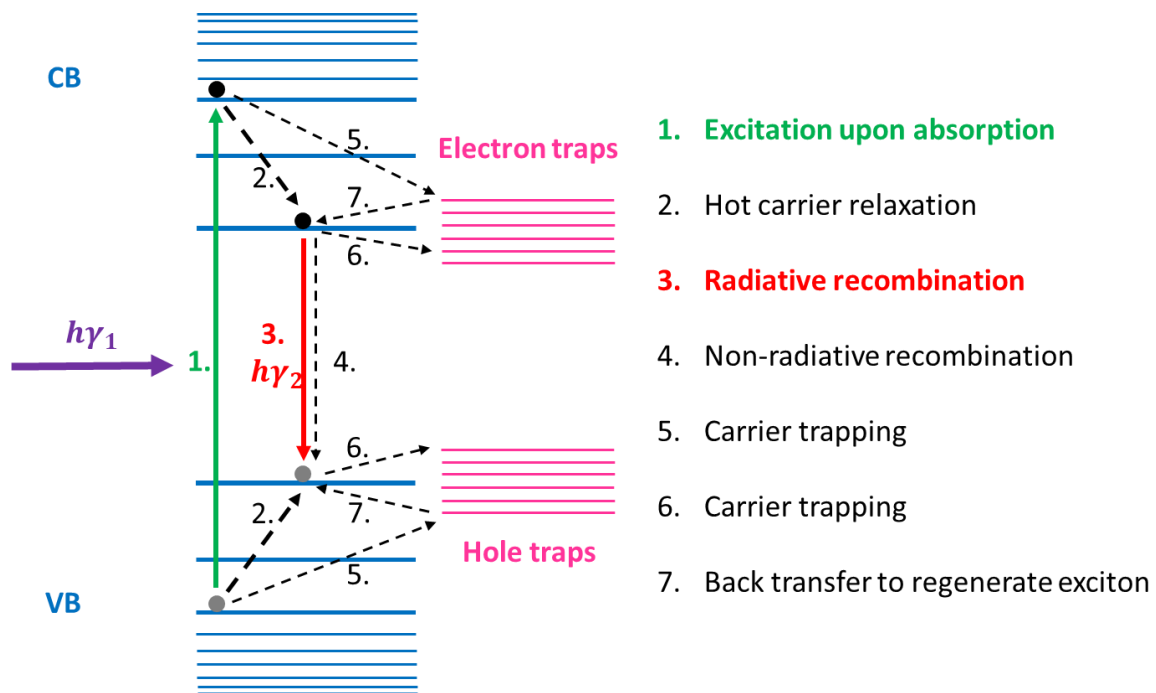


Figure 1. 1 Basic photophysical processes in a QD upon photoexcitation.

For Cu-based multicomponent nanocrystals (NCs), the emission mechanism is still under debate. Several photoluminescence mechanisms have been proposed due to the complexity of the different crystal structures and a large range of non-stoichiometric compositions. Among the proposed mechanisms, there are two widely accepted possible luminescence mechanisms, one is DAP (donor-acceptor pair) recombination, which was established in the early 1950s²⁶⁻²⁷, and the other one is free-to-bound recombination (Figure 1.2). The DAP recombination involves a deep acceptor level and a relatively shallow donor level. Among ternary Cu-based QDs, CIS is the most investigated system. Castro *et al.*²⁸, Chen *et al.*²⁹ and Kraatz *et al.*³⁰ suggested that the presence of a donor–acceptor pair was a plausible reason, due to their faster relaxation pathways, as compared to band edge recombination. DAP recombination involved a deep acceptor level identified as either a copper vacancy (V_{Cu} , formed under In^{3+} rich growth conditions) or indium vacancy V_{In} that formed under Cu^{1+} rich growth conditions, and a relatively shallow donor level identified as sulfur vacancy V_S ³¹⁻³⁴. When describing free-to-bound recombination, one of the carriers is delocalized in the conduction band or valence band and the other carrier is localized at a defect³⁵⁻³⁷. For CIS, the electron is in the conduction band and the hole is localized³⁸⁻⁴⁰. It also has been proposed that the DAP and free-to-bound mechanisms coexist as a competitive recombination pathway^{35, 41-42}, with the dominant mechanism determined by the QD stoichiometry and whether the QD is shelled.

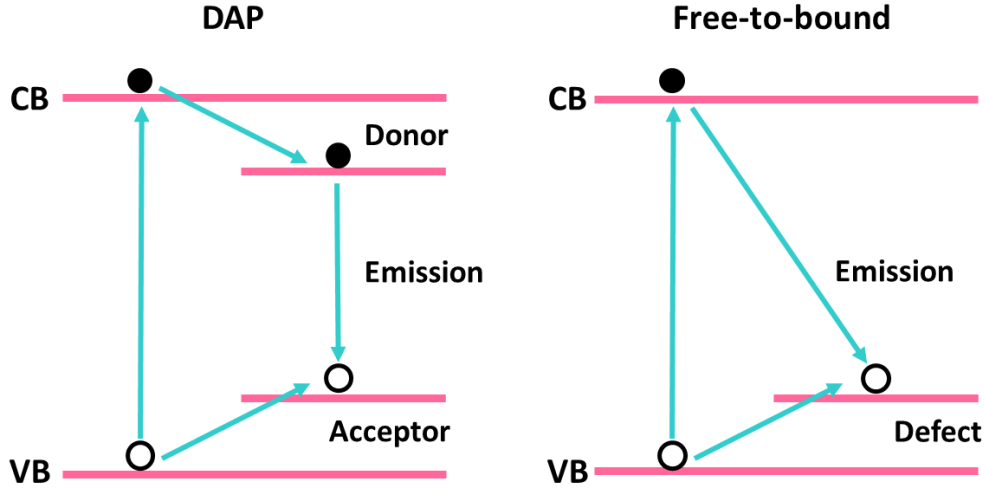


Figure 1. 2 Schematics showing DAP and free-to-bound recombination pathways in Cu-based multicomponent QDs.

1.1.2 Size-dependent PL

The emission energy of quantum dots can be calculated using the Brus equation⁴³:

$$\Delta E(R) = E_g(R) + \frac{h^2}{8R^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - 1.8e^2/4\pi\epsilon_0\epsilon_\alpha R$$

In this equation, E is the new band gap energy due to quantum confinement, E_g is the bulk band gap energy, R is the radius of the sample, m_e^* is the electron effective mass and m_h^* is the hole effective mass, ϵ_0 is the permittivity of a vacuum, ϵ_α is the high frequency dielectric constant and R is the radius of the sample.

QDs show size-dependent band gap energy with smaller QDs showing increased band gap energy (Figure 1.3), which is also known as quantum confinement effect (the confinement effect can be observed when the exciton distance is smaller than the Bohr radius of the semiconducting material). The emission region can be tuned upon the varying of the sample size, which can be done by modifying certain reaction conditions (increase reaction temperature, prolong reaction time and so forth).

For example, quantum confinement effects can be observed in CIS NCs up to a size of approximately 8 nm, since the Bohr radius of CIS semiconductor is 4.1 nm. The absorption and emission can be tuned from visible up to the near infrared region by changing the sizes of CIS QDs⁴⁴. An excellent example of this size dependent behaviour has been demonstrated by Zhang and Xie using CIZS that was synthesized with a hot injection method⁴⁵. QDs with a range of different diameters have been obtained using different reaction temperatures (180, 210 and 240 °C), with the corresponding emission of the sample tuned from 620 to 750 nm by increasing the size of the NCs from 2.0 to 7.0 nm. In addition this behaviour has also been demonstrated *via* variation of the reaction time⁴⁶. The sizes of the CIGS particles increased from 2.9 to 4.3 nm with prolonged reaction time and it was observed that the resulting bandgaps of CIGS QDs moved from 1.83 to 1.64 eV⁴⁷. In addition, the same trends were observed for CZTS QDs⁴⁸ and CZTSe QDs⁴⁹.

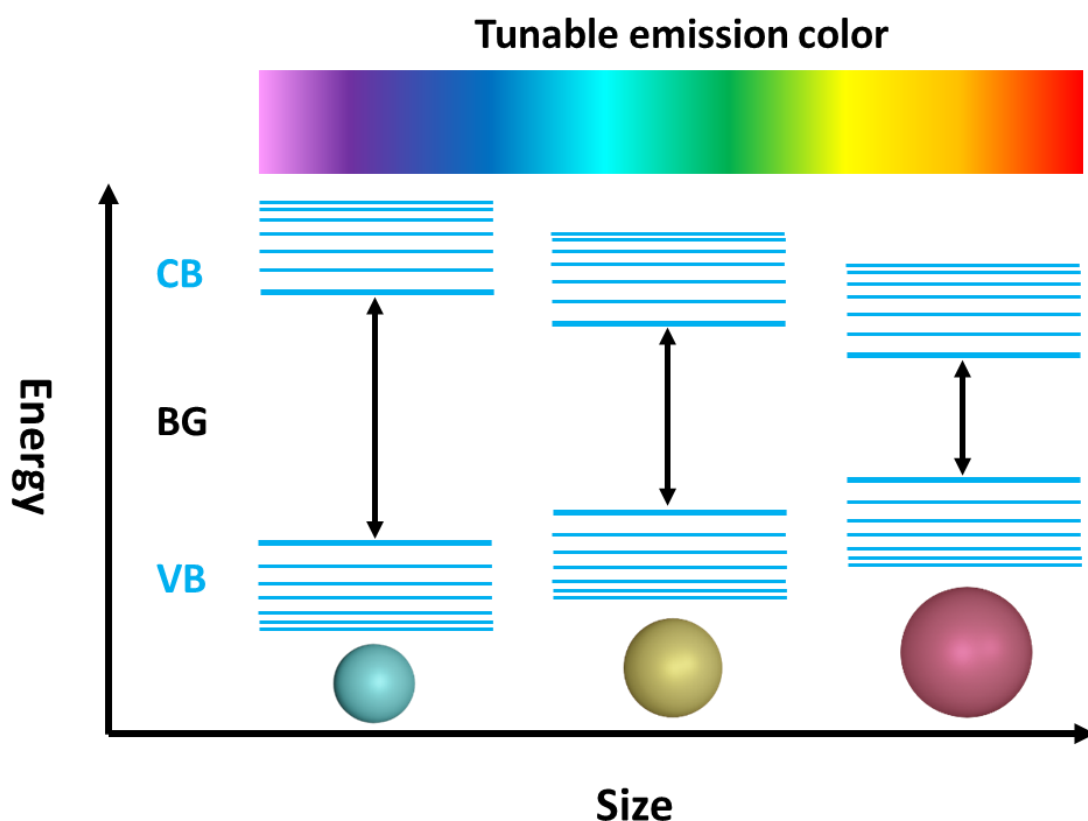


Figure 1. 3 Size-dependent band gap in Cu-based multicomponent QDs.

1.1.3 Composition-dependent PL

According to Zunger's theoretical model on defects, Cu-based multicomponent QDs can bear larger stoichiometrically tunability compared to traditional binary Cd- and Pb-based QDs⁵⁰. In this way, changing the composition is another effective way to tune the emission in addition to varying the size of Cu-based multicomponent QDs (Figure 1.4). This can be done by changing the ratio of the precursors used in certain reactions. Generally, the blue shift of the absorption and emission spectra can be observed upon incorporation of Zn into Cu-based ternary systems. The emission peak of the as-prepared highly luminescent CIZS/ZnS showed great contrast to that of CIS/ZnS NCs²⁹ and has demonstrated that the emission further blue shift with more Zn incorporated in the Cu-based multicomponent NCs⁵¹⁻⁵³. In addition, this composition tunability has been demonstrated in heterostructured QDs also, with Sing *et al.* having tuned the composition and therefore band gap of CIZS NRs. It has been revealed that absorption onset blue shifted due to increasing Zn concentration in CIZS NRs¹³.

Ga has the same effect as Zn on the band gap of Cu-based ternary or quaternary systems. It has been found that the band gaps of the quaternary CIGS QDs systematically increased with a higher Ga concentration between 2.15 (CIS QDs) and 2.60 eV (CGS QDs) by Song *et al.*⁵⁴. Changing the ratio of Cu and In in Cu-based ternary or quaternary QDs can also induce blue shift or red shift of the optical spectra⁵⁵⁻⁵⁶. The photoluminescence spectra of CIZSe QDs displayed a slight blue shift with the decrease of the Cu/In ratio with the absorption onset of this sample also exhibiting the same trend as the Cu/In ratio decreased. It is concluded that decreasing the Cu concentration in the CIZSe QDs leads to the increase of the band gap⁵⁷ and is consistent with the observations from other previous reports^{29, 58-59}. The same type of behaviour has also been demonstrated in CZTS QDs, with the bandgap

also being able to be tuned from 1.56 to 1.83 eV by varying the compositional ratios of Cu and Zn⁶⁰.

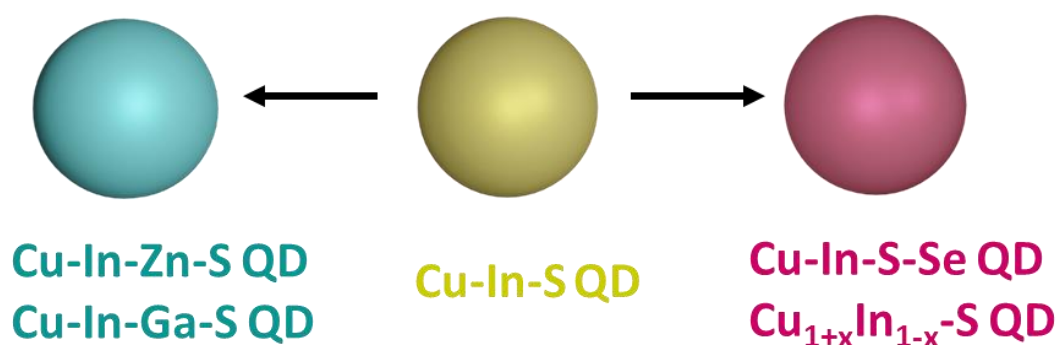


Figure 1. 4 Schematic presentation of the composition dependent band gap of Cu-based multicomponent QDs.

1.1.4 Emission range

For binary Cd- or Pb-based QDs, if the size distribution is narrow, the emission range can be characterized by a small HWHM (half width at half maximum), while this is more complicated for Cu-based multicomponent QDs. Many works have been carried out to explore the reasons for the broad emission of Cu-involved NCs with the PL bandwidths having been investigated by optical microscopic studies of Cu-doped (Cu⁺:CdSe) QDs⁶¹, also luminescence line narrowing in ensembles of copper-doped ZnSe/CdSe core/shell NCs has been carried out by Brovelli *et al.*⁶². In addition, size-selective precipitation has been performed on the CIS QDs, aiming to narrow the size distribution. It turned out that overall shape of the UV-Vis absorption and photoluminescence spectra did not change upon the size-selective precipitation²⁸. All the experimental results demonstrate that copper-involved photoluminescence is NCs intrinsically broad. For the Cu-based ternary or quaternary multicomponent core/shell heterostructures even with quite narrow size distribution, it is still challenging to achieve narrow HWHM.

There are several reasons that can account for this broad emission range based on the previous reports. The first one is that it is hard to balance the reactivity of all the precursors in the reaction, which easily results in compositional difference among different particles from the same batch. The compositional differences give rise to a distribution of the donor-acceptor distances, which is the reason for the broad emission⁶². The second cause is dependent upon the strong electron-photon coupling, which leads to a large nuclear distortion around Cu in the luminescent excited state⁶¹. It also has been reported that the differences in local environments of Cu-based core/shell heterostructures, especially at the core/shell interface relate to the broad emission range⁶².

1.1.5 Featureless absorption spectra

Except for the broad emission spectra, another traditional trait of Cu-based multicomponent QDs is the absence of distinct excitonic absorption peak in UV-Vis absorption spectra. This trend is more obvious in Cu-based multicomponent QDs prepared with a cation precursor ratio of Cu:In = 1:1. It is believed that this trait is because the excitation of an electron from Cu¹⁺ state to CB is allowed due to the specific electron configuration of Cu⁶³. This particular electron transition gives rise to the extending of the absorption spectra to the lower energy region, resulting in the UV-Vis absorption spectra without distinct excitonic absorption peak.

1.1.6 Large Stokes shift

The Stokes shift is referred to the energy difference between the first exciton absorption peak and the emission peak of QDs. Cu-based multicomponent QDs exhibit large Stokes shifts (0.2-0.6 eV) compared to Cd-based QDs demonstrate (0.1-0.2 eV).

It was found that it is the intrinsic optical property for the CIS NCs to have significant Stokes shift by A. Shabaev using their developed theoretical study of the band structure of small

CH CIS NCs based on the multiband effective-mass approximation⁶⁴. It was suggested by Li *et al.* that the large Stokes shift between the PL band and the band-edge absorption feature was not in accordance with either band-edge recombination or the recombination between two localized states, instead it involved a transition from a conduction-band state to an intra band state³⁸. The transition from a conduction-band state to an intra band state is consistent with the free-to-bound emission mechanism. Differently, Castro *et al.* proposed that the distinct energy shift between the excitation and emission peaks is consistent with the DAP recombination mechanism²⁸.

No matter the DAP or free-to-bound mechanism, the typical broad emission is related to the various types of intrinsic defects (lattice vacancies or other point defects) that are present in Cu chalcogenide systems, which not only leads to possibilities of compositional inhomogeneities within QDs but also consolidates many kinds of defect-based, nonradiative decay pathways in their luminescence. For type I Cu-based core/shell heterostructures, they readily produce the large Stokes shift, since the shell with a larger bandgap can dominate the absorption spectrum, while the emission originates from the core with a narrower band gap, therefore the energy difference gives rise to a large Stokes shift. Doped Cu-based QDs also possess large Stokes shift due to the intra-band energy level introduced by this dopant. The large Stokes shift of Cu-based multicomponent core/shell heterostructures helps eliminate the reabsorption problem when talking about the application in LSCs.

1.1.7 Long PL lifetime

Cu-based ternary or quaternary, core/shell heterostructures possess relatively long-lived emission, in the order of several hundred nanoseconds. Several theories have been proposed for this observation. It is believed that the relatively long decay time is typical for defect related emission of Cu-based systems⁶⁵. Li and Pandey prepared CIS-based core/shell

structures³⁸, and a very long PL lifetime (ca. 500 ns) was observed for the core/shell NCs. The authors attributed the long-lived emission to a large disparity in localization volumes of the electron and the hole, which would lead to slowed radiative decay, though still further study needs to be done to elucidate this question more clearly.

This increased lifetime is suitable for certain important applications, especially for bioimaging, since when using Cu-based NCs, long PL lifetimes help reduce the background signals from autofluorescent biological tissue, *via* time gating approaches.⁶⁶ It has been found that the elongated PL lifetime favours the electron extraction in QDs based photovoltaics, which helps to enhance the device efficiency⁶⁷⁻⁶⁹.

1.2 QD Synthesis techniques

The techniques for the preparation of high-quality QDs have been improved over many years. For the synthesis of colloidal QDs in organic solvents, there are three commonly used methods: hot injection, heating up and seeded-growth method especially for the core/shell heterostructures. To discuss these methods, we need to understand some basic concepts such as: (1) Free monomer. Free monomer is the chemically reactive species needed for nucleation to take place. (2) Precursors. Precursors are the complex of monomer and long chain ligands. Upon a thermodynamic driving force, the long chain ligands de-attach to give free monomer for nucleation to happen.

1.2.1 Hot injection

Hot injection is the most developed synthetic method to prepare colloidal QDs by injecting anion (cation) precursor solution into the cation (anion) precursor solution that loaded in a reaction vessel with a syringe at quite high reaction temperatures. This technique was

popularised for the preparation of Cd-based QDs by Bawendi and Alivisatos and their co-workers over 20 years ago⁷⁰ on the basis of previous works⁷¹⁻⁷⁵.

As shown in Figure 1.5, there are following distinct stages involved in this classic synthetic technique: (1) Burst nucleation. Since the cation and anion precursor solutions mix at quite high reaction temperatures that crossing of thermodynamic energy barriers for homonucleation to occur, which results in the formation of a large number of nuclei in the reaction solution. Since the formation of free monomer happen at this high temperature, this process happens dramatically faster compared with other processes, so not shown in the schematic. (2) Growth. After the nucleation burst, the active monomers left in the reaction vessel attached to the formed nuclei, the size of the particles increase as the reaction proceeds, while the monomer concentration decrease continually. (3) Ostwald ripening. At the end of this reaction, active monomers are barely left, this drives the dissolution of the tiny, less stable particles with larger surface energy in the solution to reform active monomers, which will attach to the larger formed particles with lower surface energy. This process helps to reduce the size distribution of the QDs. Since the distinct separation of the nucleation and growth processes with the hot injection method, it can be employed to prepare high quality QDs with quite narrow size distribution, which indicates higher purity of the emission of the QDs which are therefore suitable for many applications.

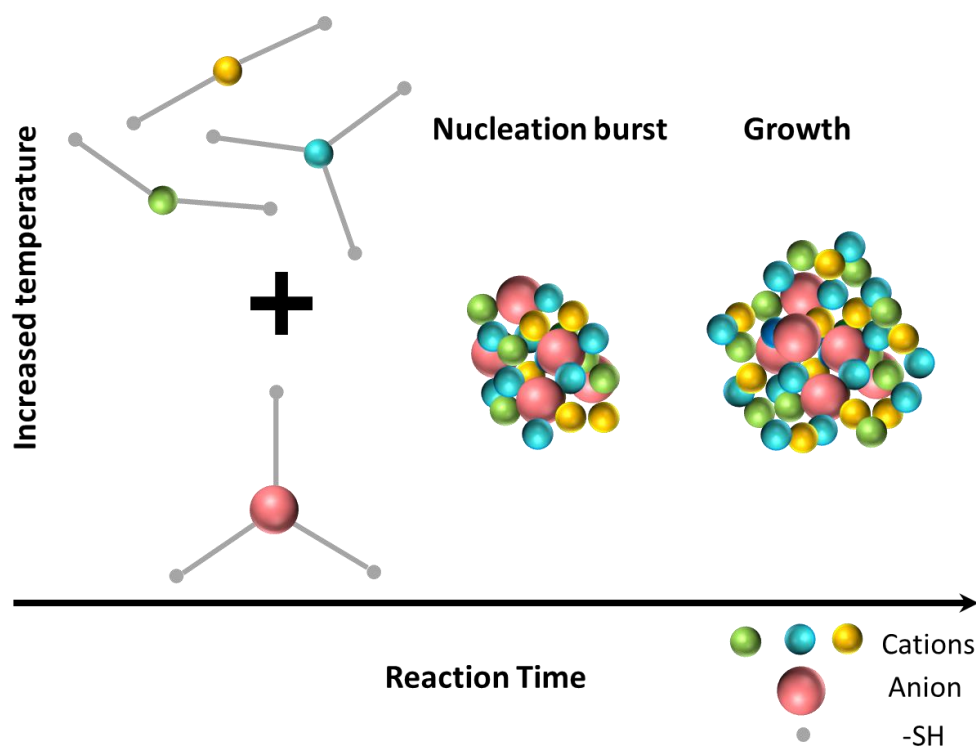


Figure 1. 5 Distinct stages in classic hot injection technique.

1.2.2 Heating up method

Heating up is a straightforward technique to synthesize colloidal QDs, which is done by mixing all the precursors, ligands and solvents needed for particular reactions together in one reaction flask and heating the reaction mixture to a certain high reaction temperature after degassing to remove oxygen and moisture. Compared with hot injection, it is possible to make large batch QDs synthesis with the heating up method. There are several publications that discussed this synthetic method in detail⁷⁶⁻⁷⁷.

The essential stages of the heating up method are shown in Figure 1.6. The cation and anion precursors are normally mixed together in one reaction vessel at RT, which is followed by the thermodynamically driven formation of monomer (reactive species) as the reaction solution is heated. The continued heating helps to conquer the critical homonucleation energy barrier and induce the nucleation process. Eventually, the formed nuclei grow into

mature QDs *via* the consumption of the remaining monomers. As the reaction solution is heated up progressively, it is hard to separate the nucleation and growth processes, which gives rise to wide size distribution.

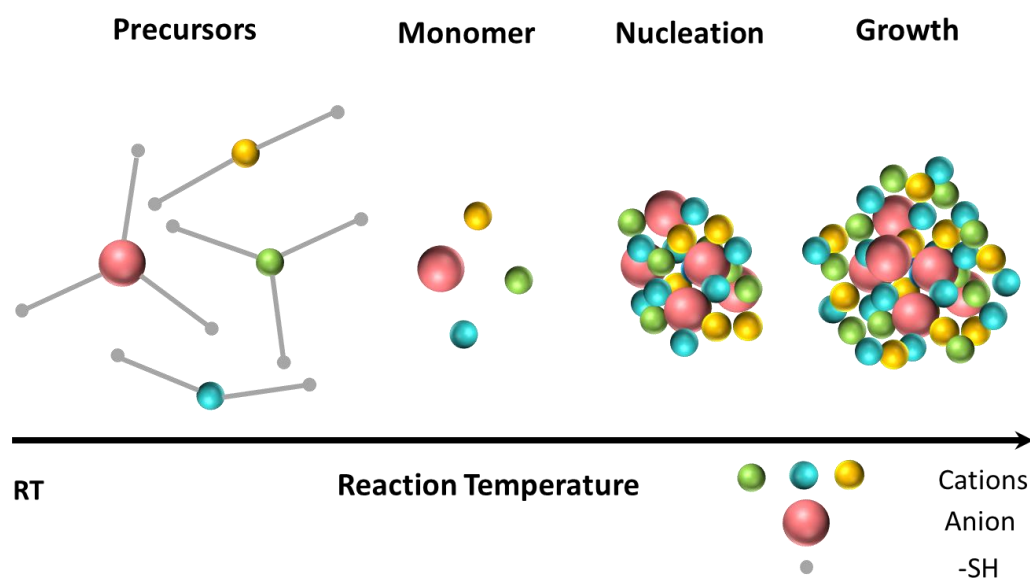


Figure 1. 6 Distinct stages in typical heating up method.

1.2.3 Seeded growth method

The seeded growth method to prepare core/shell nanoheterostructures involves the addition of shell material precursor solutions into the reaction vessel which is loaded with the pre-made colloidal solution of core nanoparticles. It is an essential way to improve the optical performance of the QDs by coating a shell onto the formed QD, especially the shell materials with wider band gaps, since it helps to confine the excitons in the core from moisture, oxygen and surface defects which can act as nonradiative pathways to release the energy. In addition, seeded growth is the most practiced way to achieve the most effective shell coating process. As shown in Figure 1.7, this synthetic technique involves the heterogeneous nucleation of the nuclei of the shell material onto the existing core. The heterogeneous nucleation process

is more favourable than the homonucleation if the lattice mismatch between the core and shell materials are not dramatically large^{1, 77-79}.

Syringe pumps are normally employed to complete the seeded growth. In this way, the injection rate can be well controlled, and one can stop the injection of the precursor solution at any time point, thus shell thickness can be tuned precisely. It is also very convenient to investigate the evolution of certain reactions and development of particular morphologies, which is of great importance for the understanding of growth mechanism of Cu-based multicomponent anisotropic nanostructures (dot-in-rod and tetrapod nanostructures).

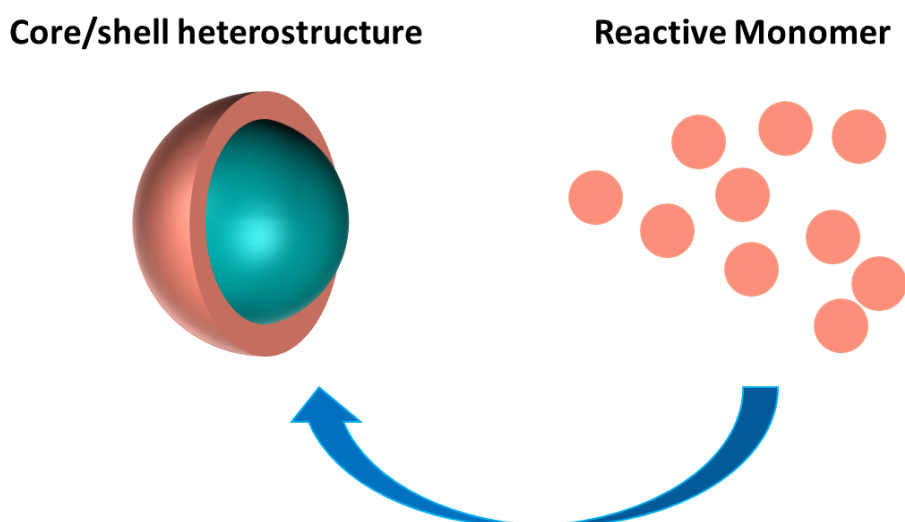


Figure 1. 7 Illustration of seeded growth technique to prepare core/shell heterostructures.

1.3 Synthesis of Cu-based multicomponent nanoheterostructures

Heterostructured NCs can be produced by coating a core semiconductor with a shell of an alternative semiconductor regarding to composition and crystal structure. Using this approach, not only can the morphology be profoundly modified; the photophysical properties can be finely controlled also through the electronic band alignments between the core and shell semiconductors.

1.3.1 Classification of Cu-based multicomponent heterostructures

As illustrated in Figure 1.8, based on the relative bandgaps and positions of the bandgaps of the involved semiconductors (materials that have been chosen to build core/shell structure), the heterostructures can be divided into four types, termed type I, quasi-type II, reverse type I and type II⁸⁰.

Type I heterostructures are the most commonly utilised, since this type can have hugely enhanced PL properties by passivating surface defects which can act as non-radiative pathways, also by confining the formed excitons from the external environment (oxygen and moisture)⁸¹, since the excited electrons and holes are both confined in the core.

Quasi-Type II refers to the relative same level of CB between the core and the shell semiconductors, which indicates that the exciton confinement effect is not very obvious. In this case, the excited electrons evenly distributed in the core and the shell. While the energy level of the VB of the core is higher than that of the shell, therefore the excited holes are confined in the core.

In reverse Type I heterostructures, the energy level of the CB of the core is higher than that of the shell, the excited electrons are confined in the shell. The higher energy level of VB of the shell results the holes also confined in the shell.

As for type II band alignment, due to the staggered band alignment, the energy level of CB of the core is lower than that of the shell and the excited electrons are confined in the core, while the energy level of VB of the core is lower than that of the shell, therefore the holes are confined in the shell. Or the energy level of CB and VB of the core are higher than that of the shell, which results the electrons are confined in the shell, and the holes are confined

in the core. Normally, the enlarged spatial distance between the excited electrons and holes gives relatively longer PL lifetime of the core/shell heterostructures.

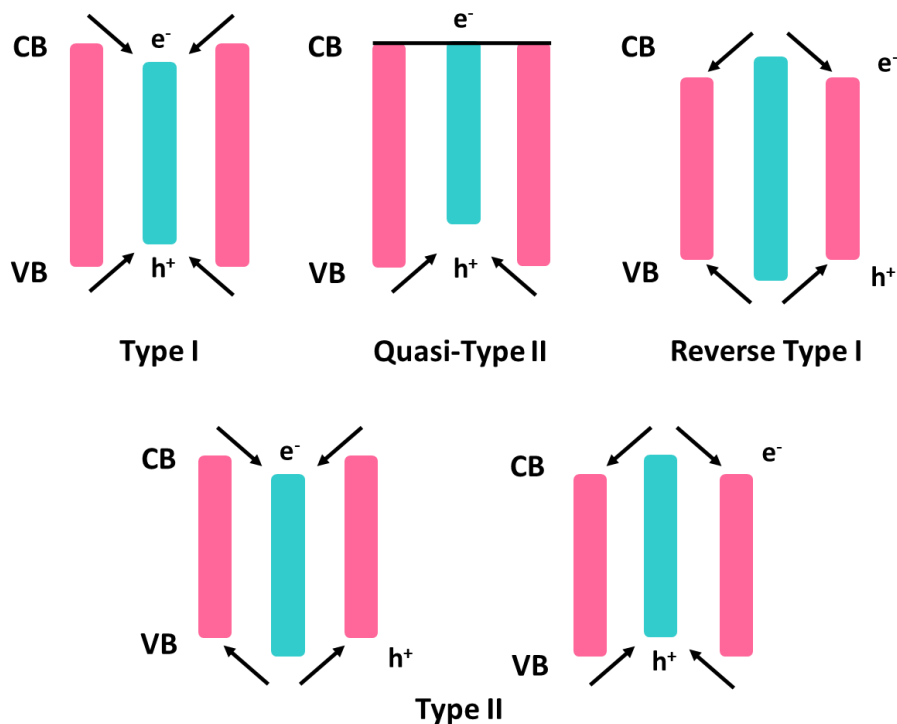


Figure 1. 8 Schematic presentation of three types of band alignments in Cu-based multicomponent core/shell heterostructures. The pink bars refer to the CB and VB of the shell, while the blue bars refer to the CB and VB of the core.

1.3.2 Crystal structure of Cu-based multicomponent QDs

There are three distinct and important types of Cu-based multicomponent heterostructures that will be discussed here: Cu-based multicomponent spherical core/shell, dot-in-rod and tetrapod heterostructures.

For ternary or quaternary Cu-based nanocrystals, there are three main crystal structures that can be produced in colloidal synthesis, including chalcopyrite (CH), wurtzite (WZ) and zinc blende (ZB). For ternary Cu-In-E (E = S, Se) materials, the bulk form is in CH phase at room temperature, WZ and ZB can only exist at high temperature. As for structures in nanoscale, all three crystal structures can be obtained at RT. Most of the synthesis results in chalcopyrite,

while wurtzite and zinc blende can be obtained upon fine control of the reaction temperature and the ligands that used in the reactions⁸². Understanding the nature of different crystal structures is of great importance for the preparation of core/shell or even core/shell/shell heterostructures. CH is the most common crystal structure for Cu-based QDs. This crystal structure can be deduced from cubic zinc blend by replacing zinc with one cation in higher valency (In^{3+}) and one cation in lower valency (Cu^{1+}) in an ordered way. The occurrence of anisotropic polytypic nanostructures are commonly observed with ZB and WZ. ZB has 8 crystalline facets that allows for the heterogeneous nucleation, four of them exhibit higher reactivity. In 3D, the atoms arrange in a pattern of “ABCABCABC” in ZB crystal structure. If the heteronucleation of the shell precursors on the four facets with higher reactivity, then tetrapod nanostructures can be obtained. If all of the eight facets are available for the nucleation to happen, then octapod nanoparticles can be prepared. This mechanism has been well investigated and applied for Cd-based QDs. However, fluorescent Cu-based tetrapod nanostructures without any heavy metals has not been prepared until now, even though it is quite feasible in theory. Referring to WZ, it has two opposite polar sides of the crystal structure due to the specific elements arrangements. Therefore, it is particularly employed to prepare elongated anisotropic nanorod nanocrystals⁸³. In 3D, the elements occupy the sites in a “ABABABAB” pattern, so there is vacant C sites in WZ crystal structure. The growth mechanism for the well-known nanorod nanostructures has been well investigated and applied for both Cd-based and Cu-based QDs.

1.3.3 Synthesis of Cu-based multicomponent spherical nanoheterostructures

The preparation of Cu-based multicomponent spherical heterostructures is a quite well-developed field regarding the control of size and composition. An important consideration

when producing heterostructures, is related to difference in the lattice constants of core and shell material, which can produce distinct lattice strain at the interface of the core and shell which increases as the thickness of the shell grows, resulting in crystal defects, and reduced PLQY of the core/shell structures. In addition, if crystal structures are distinctively different it may prove impossible to produce uniform growth and instead the formation of polytypic crystals takes place, with shell material only growing in specific areas upon the original core material⁸⁴. ZnS is normally the optimal choice for the shell coating to Cu-based multicomponent QDs, due to the minor lattice difference between them and the production of a type I band alignment, which helps to confine the excitons in the core from the surface defects and external oxygen and moisture, therefore enables outstanding photophysical properties (Figure 1.9). It is also important to note that the seeded growth method is the most common means to prepare Cu-based multicomponent spherical core/shell heterostructures.

The typical examples of Cu-based ternary heterostructures are CISE- and CIS-based core/(ZnS)shell structures, because they constitute non-toxic elements, display the bright emission in the near infrared region, have high absorption coefficients and relatively long photoluminescence lifetimes (the decay can be as long as 500 ns³⁸). All these factors render them the most promising candidate for a range of applications.

CIS-based QDs is the most well studied system in this category. Detailed studies on the shell coating process have been carried out by Berends and Stam through seeded growth strategy⁸⁵. The effects of low and high reaction temperatures, various reactive and unreactive Zn- and S-precursors have been checked in their work. It was found that low reaction temperatures favour etching, cation exchange and alloying. Reactive S-precursors combined with unreactive Zn-precursor resulted primarily in etching, while the use of reactive S- and Zn-precursors resulted in a combination of etching and ZnS deposition, followed by alloying.

High reaction temperatures and less reactive precursors promote cation exchange followed by alloying. Amine ligands are the most commonly used ligands in the synthesis of CIS/ZnS core/shell heterostructures. The effects of varying amine ligands used in the reaction solution on the optical properties and morphology of the CIS/ZnS QDs have been explored by Michalska *et al.*⁸⁶. All these works paved the way towards the fine design of improved synthesis methods of high-quality CIS/ZnS core/shell heterostructures. The main reported results of the synthesis of CIS/ZnS core/shell nanostructures are summarised in the Table 1.1 below.

Table 1. 1 Examples of typical synthesis and PLQY of CIS/ZnS core/shell nanoheterostructures.

Materials	Precursors for core	Ligands and solvent for core	Precursors for shell	Ligands and solvents for shell	Dia of core/shell structure(nm)	PLQY (%)	Ref
CIS/ZnS	CuOAc, In(Ac) ₃ , DDT	DDT, ODE	Zn(Ac) ₂ , DDT	DDT/TOP, ODE	/	80	⁸⁷
	CuI, In(Ac) ₃ , DDT	DDT	ZnO	OA, ODE	4	/	⁸⁸
	CuCl ₂ , InCl ₃ , Na ₂ S	H ₂ O, GSH	Zn(Ac) ₂ , CH ₄ N ₂ S	H ₂ O	1.8±0.4	/	⁸⁹
	CuCl ₂ ·2H ₂ O, InCl ₃ ·4H ₂ O, Na ₂ S	H ₂ O, MPA	Zn(Ac) ₂ , Na ₂ S	H ₂ O	10.3	/	⁹⁰

CuI, In(Ac) ₃ , DDT	DDT, ODE	ZnEX, Zn(St) ₂	ODE, DMF, toluene	2.8	50	⁴²
CuCl ₂ , InCl ₃ , Na ₂ S	L-GSH, water	Zn(Ac) ₂ ·2H ₂ O, CH ₄ N ₂ S	L-GSH, H ₂ O	4.8	22-43	⁹¹
CuI, In(Ac) ₃ , DDT	DDT, ODE	Zn(Ac) ₂ , DDT	DDT	4.65-5.7	74	⁹²
Cu(NO ₃) ₂ , InCl ₃ , Na ₂ S	GSH, water	Zn(Ac) ₂ , Na ₂ S	GSH, water	3.3	24	⁹³
CuI, In(Ac) ₃ , DDT	MA, ODE	Zn(Ac) ₂ ,	MA, ODE	4.2	65	⁹⁴
CuI, In(Ac) ₃ , DDT	DDT, ODE	Zn(St) ₂ , ZnEX,	ODE, DMF, toluene, H ₂ O	2.4-3.6	65	⁵¹
In(Ac) ₃ , CuI, S	OA, DDT, ODE,	Zn(Ac) ₂ ,	OAm, ODE	/	56	⁹⁵
CuI, In(Ac) ₃ , DDT	DDT	Zn(CH ₃ COO) ₂ · 2H ₂ O, DDT	DDT, OA, ODE	3.0-3.4	86	⁹⁶
CuAc, In(Ac) ₃ , DDT,	DDT, ODE	Zn(Ac) ₂ , DDT	DDT, ODE	4.3	80	⁹⁷

CuI, In(Ac) ₃ , DDT	DDT	Zn(St) ₂ , DDT	OA, ODE	5-10	60	⁹⁸
CuI, In(Ac) ₃ , DDT	OA, DDT, ODE	Zn(Ac) ₂ ,	OAm, ODE	3.0	35-74	⁹⁹
Cu(NO ₃), In(NO ₃) ₃ ·xH ₂ O, Na ₂ S	GSH, H ₂ O	Zn(Ac) ₂ , Na ₂ S,	H ₂ O	3.5±0.5	26	¹⁰⁰
CuI, In(Ac) ₃ , DDT	DDT	Zn(St) ₂ , DDT,	DDT, ODE	3.2-4.0	68-78	¹⁰¹
In(St) ₃ , CuAc, S	OA, DDT, ODE	Zn(Ac) ₂ , Zn(St) ₂ , DDT	OAm, ODE, OA	12.5	50±5	¹⁰²
In(Ac) ₃ , CuI, DDT	DDT	Zn(St) ₂ , S	TOP, ODE,	/	80	³⁸
CuI, In(Ac) ₃ , DDT	DDT, OAm	S, Zn(St) ₂	TOP, ODE	/	60	¹⁰³

Abbreviations: Dodecanethiol (DDT), Octadecene (ODE), Trioctylphosphine (TOP), Oleic acid (OA), Glutathione (GSH), 3-mercaptopropionic acid (MPA), Zinc ethylxanthate (ZnEX), Trioctylamine (TOA), Dimethylformamide (DMF), Myristic acid (MA), and Oleylamine (OAm).

The CISE/ZnS core/shell structure was prepared by Li and Pan for applications in QD sensitized solar cells. In this work, CISE_{0.8}/ZnS_{0.2} and CISE_{0.7}/ZnS_{0.3} NCs have been prepared by using different amounts of Zn(OAc)₂ and sulphur powder in the shell coating step. A large-scale synthesis of water-soluble CISE/ZnS core/shell QDs have also been demonstrated by Kang and Yang¹⁰⁴, giving the obtained samples a PLQY as high as 23.3% with a straightforward preparation method. Recently, near-infrared emitting CISEs/ZnS colloidal NCs were reported by F.L. Lox and Dang¹⁰⁵. Firstly, CISE NCs were prepared by cation exchange on the preformed Cu_{2-x}Se NCs through hot-injection. Subsequently, a ZnS shell was coated to get the core/shell structure with a seeded-growth method. Interestingly, it was found that in the shell coating step, a partial cation and anion exchange took place, producing the novel CISES/ZnS core/shell structure. In another approach, ZnSe_{1-x}S_x shell was coated onto the CISE cores through the similar mechanism by Moser and Yarema¹⁰⁶. It was found that Zn cations could only diffuse into the outermost atomic monolayer of the CISE core at reaction temperatures below 100 °C, although when the temperature was raised above 100 °C, the second monolayer also became thermally accessible and, therefore, could be filled with Zn cations.

For Cu-based quaternary core/shell structures, the techniques to synthesize CIZS/ZnS core/shell heterostructures have been much more developed than that for the synthesis of corresponding CIZSe and CZTS because of its superior stability and photophysical properties. Non-blinking (Zn)CIS/ZnS QDs with high PLQY of 74% was prepared by Zhang and Dong through an in situ interfacial alloying approach¹⁰⁷. CIZS/ZnS spherical heterostructure with tuneable emission can also be prepared using the seeded growth method by tuning the ratio between Cu / (Zn + In)¹⁰⁸. Highly stable CIZS/ZnS/ZnS core/shell NCs with thick shells were also prepared by Wu and Wang¹⁰⁹. It is worthy to note that the blue shift of PL commonly occurs during the ZnS shell-coating process, which is either due to

the etching of the core or the incorporation of Zn ions into the core. Interestingly, Guo *et al.* has developed an approach to address this unexpected blue-shift issue during the reaction for CIZS/ZnS core/shell structures¹¹⁰, eliminating the majority of this effect.

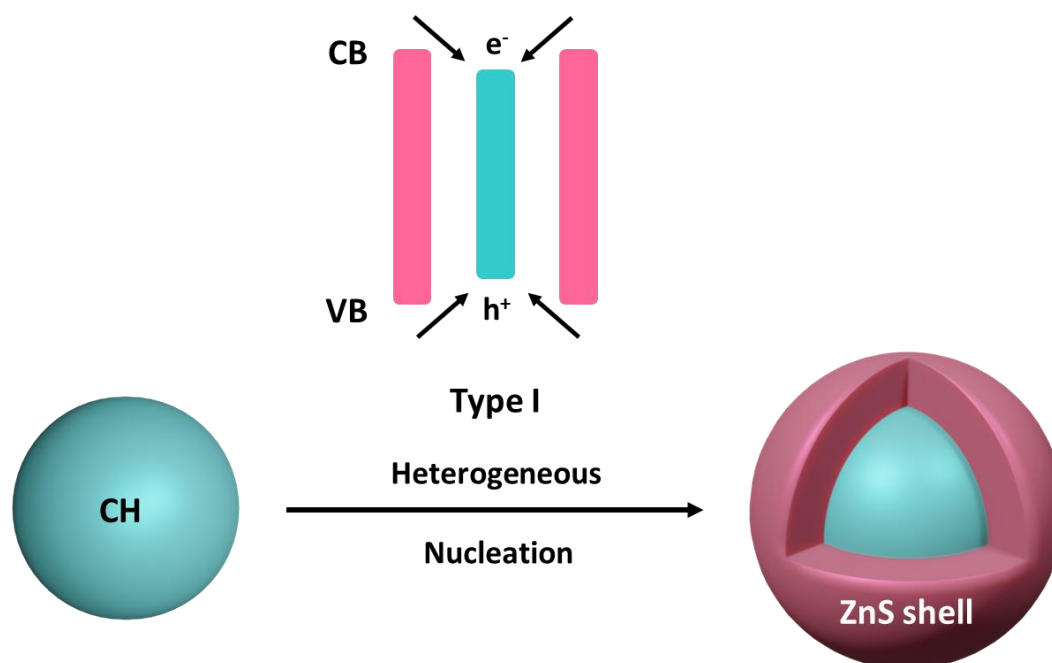


Figure 1. 9 Schematic presentation for the preparation and band alignment of spherical core/(ZnS)shell heterostructure.

1.3.4 Synthesis of Cu-based multicomponent dot-in-rod heterostructures

This specific morphology is based upon the incorporation of a core QDs in a shell of another semiconductor of rod shape, with the position of the core in this rod variable. Generally, seeds with the hexagonal WZ crystal structure is the infrastructure for the preparation of a dot-in-rod nanostructure⁸³. As for WZ seeds, there are only two opposite reactive $\{002\}$ facets that allow for the epitaxial growth of zinc blend tips. The shell material can nucleate either on both $\pm \{002\}$ facets or only on more reactive $- \{002\}$ facet depending on certain reaction conditions¹¹¹. Since the reactivity of $+ \{002\}$ facet differs from that of $- \{002\}$ facet, this therefore gives access to localize the ZB tips selectively on one or both WZ ends or

unequally localize on both ends as illustrated in Figure 1.10, which ending different core locations.

The most well-known structure of this type is the CdSe/CdS dot-in-rod heterostructures with the growth mechanism, the optical properties and applications of this specific NR structure have been studied intensively. However, in contrast, there are only a limited number of reports on the synthesis of Cu-based multicomponent dot-in-rod structure, therefore it is of great importance to understand the growth mechanism of this dot-in-rod structure in order to obtain Cu-based counterparts.

Stam *et al.* proposed the first work describing the synthesis of Cu-based multicomponent CISE/CIS dot-in-rod nanoheterostructure¹¹². However, the reaction process involved Cd-based precursors since the reaction proceeded *via* cation exchange on an initial CdSe/CdS dot-in-rod structure. A Cu₂Se/Cu₂S dot-in-rod QDs were obtained through complete cation exchange in which the resulting Cd was completely replaced by Cu. Following this, luminescent CISE/CIS was obtained by a partial cation exchange with the incorporation of indium into the rod structure. ZnSe/ZnS dot-in-rod QDs also have been achieved through similar procedure, with complete cation exchange taking place to convert from CdSe/CdS to Cu₂Se/Cu₂S NRs, which was then followed by complete cation exchange to produce the final ZnSe/ZnS dot-in-rod nanostructure¹¹³.

Except for the cation exchange technique, Xia and Winckelmans are the first group that have produced CIS/ZnS dot-in-rod heterostructure *via* a seeded growth method which was done by growing the ZnS tips onto the preformed WZ CIS seeds¹¹⁴. In this work, the growth mechanism for this particular Cu-based multicomponent heterostructure is similar to that of Cd-based dot-in-rod structures, with HAD (hexadecylamine) used as a coordinating ligand.

The obtained colloidal CIS/ZnS dot-in-rod heterostructures showed PL in the near infrared region with PLQYs of 20%, with emission being assigned to the CIS core.

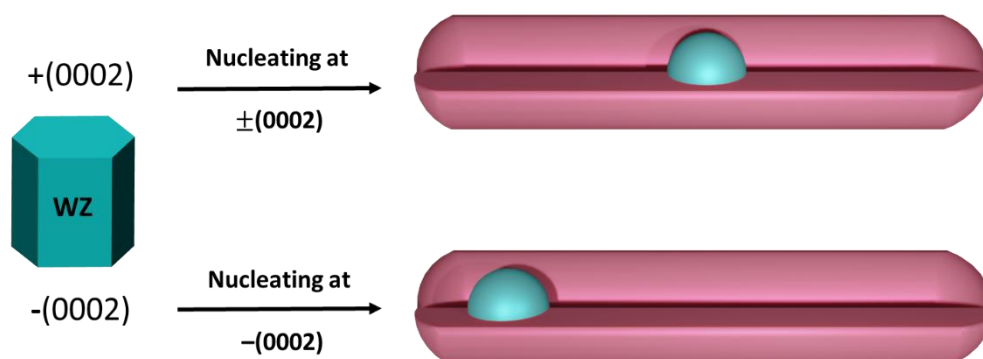


Figure 1. 10 Schematic showing the dot-in-rod heterostructure growth with different core location.

1.3.5 Synthesis of Cu-based multicomponent tetrapod heterostructure

According to the established theory, for the preparation of this particular anisotropic structure, a ZB core is the basis to build up these TPs. As shown in Figure 1.11, the ZB core has eight $\{111\}$ crystalline facets with each serving as a nucleation point for the growth of WZ arms. When the nucleation takes place at all of the eight crystalline facets, octopods can be obtained¹¹⁵⁻¹¹⁶, while when only four more reactive facets act as nucleation spots, this allows for epitaxial growth of WZ arms enabling the growth of TPs¹¹⁷⁻¹¹⁹.

Several Cd-based nano TP structures have been successfully developed^{120 7}. Unfortunately, as with other Cd based structures, the presence of highly toxic heavy metals greatly impedes the practical application of these quantum nanostructures, so the obtaining of its Cu-based counterparts is imperative.

As for Cu-based multicomponent counterparts, the Sakamoto group was the first group which reported incorporating Cu-based core (CIS) into a TP heterostructure¹²¹. It was done by first forming the CIS seeds, and then the CIS/CdS TPs was prepared *via* a seeded growth method. They found that this TP structure possessed a quasi-type II band alignment giving

them a longer-lived charge. A particularly novel point of this work is that the CIS seeds possessed a CH crystal structure instead of a ZB core, which is not consistent with the proposed growth mechanism above and in fact remains an issue to be explained. Two years later, a similar CIS/CdS TP heterostructure with pretty high PLQY (40%) was obtained using a ZB CIS core by the Kim group¹²².

Unfortunately, at present, absolute Cd-free Cu-based multicomponent TP heterostructures have not been achieved yet, though in theory this structure should be readily accessible. Since the ZB structure of Cu-based cores such as CIS and CIZS can be synthesized, also the small lattice spacing mismatch between ternary CIS or quaternary CIZS and ZnS is quite small, which favours the epitaxial shell growth to achieve TP heterostructures. More synthetic and theoretical work should be devoted to this area to make the versatile Cu-based multicomponent tetrapod or even octapod nanoheterostructures possible for certain applications.

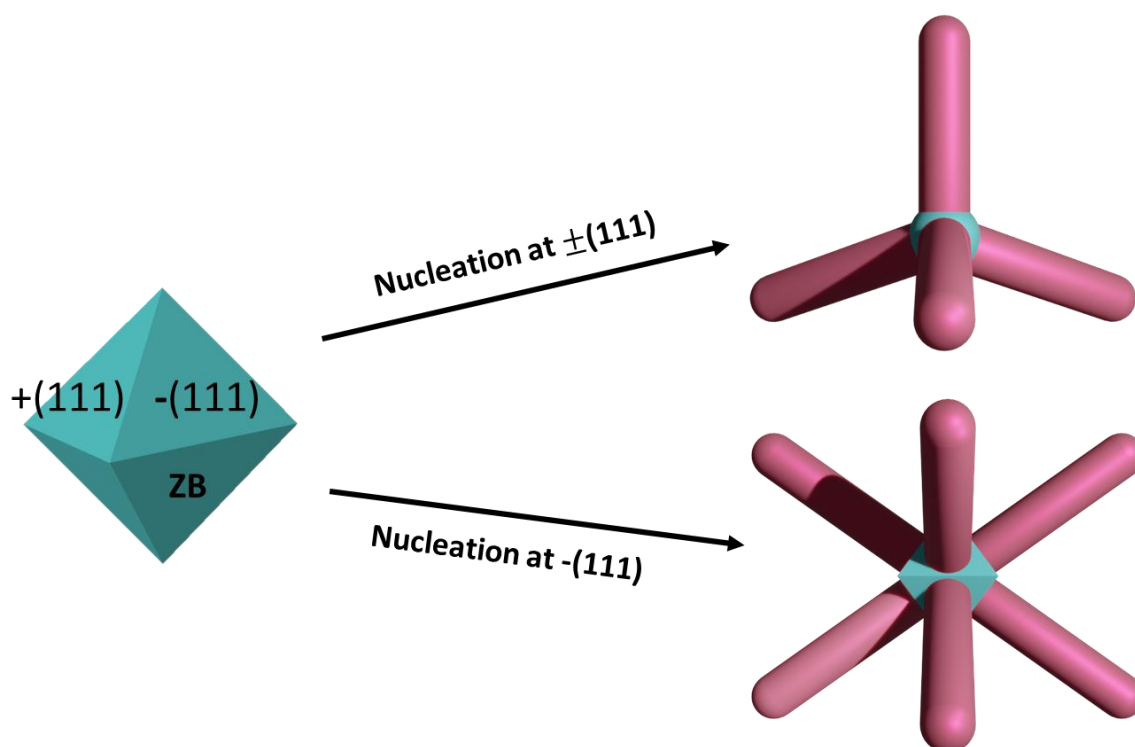


Figure 1. 11 Schematic illustration of the growth of tetrapod and octapod heterostructures based on ZB core.

1.4 Post-synthetic modifications of QDs

After the QDs are obtained through the conventional synthetic methods (heating up, hot injection and seeded growth), some post-synthetic techniques can be carried out to modify the binding ligands on the surface, the chemical composition of the QDs and so forth for certain application purposes.

1.4.1 Cation exchange (CE)

Cation exchange (CE) is one of the typical post-synthetic method that can be performed to fine tune the chemical composition of the preformed colloidal QDs. This technique can be applicable to Cd-, Pb- and Cu-based QDs^{94, 113, 123}. As shown in Figure 1.12, the CE process involves the discharging of the cations in the host lattice (Cu^{1+} , In^{3+}) and incorporating of the new cation species (Zn^{2+}) that presenting in the solution environment. The facets on the

QD where the CE take place are denoted as “reaction zone”. Normally the size of the host QD is much larger than that of the reaction zone, in which case, the anion framework can be preserved during the CE process, and the ratio among the cations can be tuned and the morphology of the QD can be maintained. This is mainly due to the much larger size of the anions and their low diffusion coefficient in solution¹²⁴⁻¹²⁵. Based on the level of the CE takes place, it can be divided into partial CE (only certain amount of cations in the host QD being replaced) and complete CE (the present cations in the host QD completely substituted by the new cation species). This technique is of great importance for the achievement of certain Cu-based QD nanostructures which are not readily accessible through conventional colloidal synthetic methods due to the complexity in the balancing of all the reactivities of the cation precursors. According to Pearson’s hard and soft acids and bases (HSAB) theory, the affinity between the soft (hard) acid and soft (hard) base are much higher than that between the soft and hard species. Ionic complexes can be formed through the reaction between hard acids and hard bases, while covalent complexes are accessible *via* the interaction between soft bases and soft acids. Therefore, the CE process on Cu-based multicomponent QDs can be facilitated by adding soft bases for example TOP (tri-n-octylphosphine) and TBP (tri-n-butylphosphine) to prompt the release of the soft acids Cu^{1+} and replaced by hard ones Zn^{2+} .

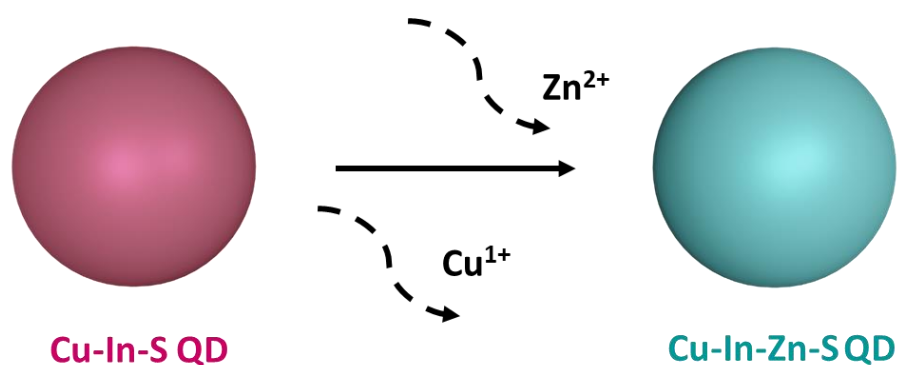


Figure 1. 12 Schematic presentation of CE process for Cu-based multicomponent QDs.

1.4.2 Phase transfer

Phase transfer is a post-synthetic surface modification method that can be used for phase transfer of the nanoparticle sample from nonpolar to polar media, or vice versa, to meet the requirements for certain applications¹²⁶.

The obtained QDs prepared with the above mentioned traditional synthetic methods are soluble in nonpolar solvents due to the binding of long-chain ligands on the surface. While the colloidal QDs are not suitable for applications which require hydrophilic luminophores, e.g. biological uses. Therefore, frequently it is important to transfer the QDs from nonpolar solvent to aqueous phase (Figure 1.13). There are two commonly used methods to achieve this goal. One is done by ligand exchange, which is normally done by replacing the original long chain ligands with hydrophilic short chain ligands¹²⁷. The other way is over coating a second bimodal layer onto the original long chain ligands. One end of the second layer ligands interacts with the original long chain ligands on the surface of the QDs, the other end of the second layer ligands is hydrophilic, that can drag the nanocomposite into the aqueous phase.

Cu-based QDs are commonly capped with ligands with a thiol group, and it turns out that this thiol ligands are not be easily removed from the surface of the QDs and replaced by other ligands^{67, 128-129}. Therefore, the above mentioned second method is more favourable in this case. Presently, CTAB is the most practically used ligands to over coat onto the obtained colloidal QDs to complete phase transferring from nonpolar to polar solvent, with the over coating of CTAB, this approach maintaining the optical performance of the QDs, which is due to the lack of direct modification to the original QD surface¹³⁰.

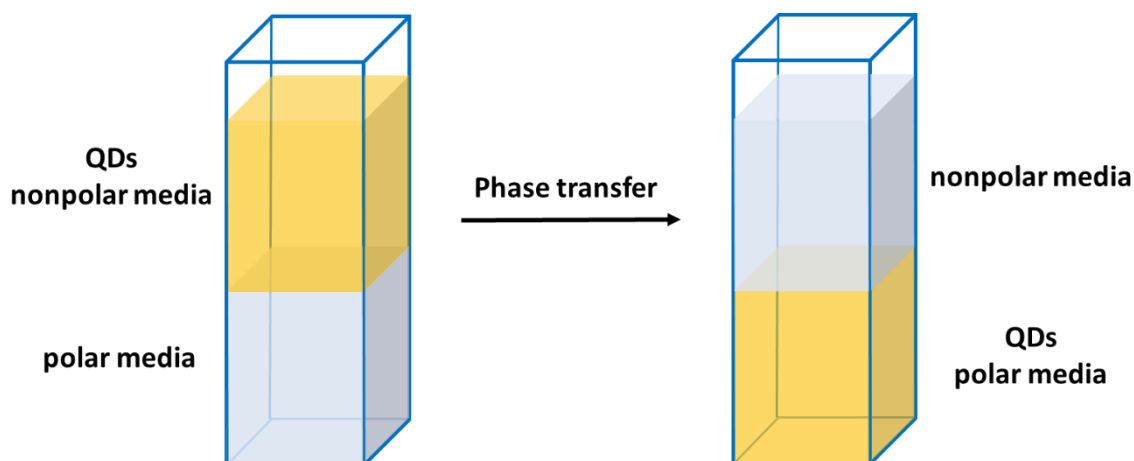


Figure 1. 13 Schematic showing phase transfer process of QDs.

1.5 Applications of Cu-based QDs

1.5.1 Bioimaging

Bioimaging refers to the visualization of biological tissues and processes (Figure 1.14). QDs have been studied extensively as fluorescent probes because of their unique optical properties compared with traditional fluorescent dyes. Among them, Cu-based multicomponent NCs are more promising than the Cd-based counterparts due to the following reasons: (1) Cu-based multicomponent QDs demonstrate less toxicity than Cd- or Pb-based QDs¹³¹⁻¹³³; (2) the emission range of Cu-based multicomponent NCs are normally located at near infrared region, which is more appropriate for many bioimaging applications^{112, 134}. In the visible spectra region, light scattering in biological tissues is distinct, which would restrict the spatial resolution and penetration depth of fluorescence imaging performance in that region; (3) they possess relatively long PL lifetimes, which would help to improve the “signal to noise ratio” to obtain a better contrast⁶⁶.

To best take advantage of these properties of Cu-based QDs, it is also necessary for the fluorescent materials to have improved stability in aqueous phase and against photobleaching. This can be done by coating with a ZnS shell onto the core to create a type I core/shell structure with the aim to improve the effectiveness of the QDs. The evaluations of the chemical stability and cytotoxicity of CIS and CIS/ZnS have been done by Chen *et al.*¹³⁵. They found that the intensity of photoluminescence has been enhanced by approximately 16 times after growing a ZnS shell around the surface of the CIS QD. In the cytotoxicity assay, the cell viability is more than 90% when the QD concentration ranged from 1 to 250 $\mu\text{g/mL}$, which is nontoxic to HeLa and OECM⁻¹ cells. The X-ray absorption near-edge structure (XANES) results demonstrated the high chemical stability of CIS and CIS/ZnS QDs in *Caenorhabditis elegans* for a range of exposure times. Speranskaya *et al.* has studied the photostability and cytotoxicity of CIS/ZnS heterostructures¹³⁶. It was found that photostability of CIS/ZnS core-shell structures under constant UV illumination depends on the Cu/In ratio used for CIS core synthesis. Among them, CIS/ZnS with Cu/In equal to a 1: 4 ratios, showed high photostability under UV illumination both in toluene and aqueous solutions. The as-prepared QDs were transferred to aqueous solutions by amphiphilic polymer encapsulation, with the CIS/ZnS QDs showing only slight cytotoxicity with all three polymeric shells. Confocal microscopy confirmed the penetration of CIS/ZnS NCs inside the cells, and indicated the low toxicity of the CIS/ZnS core/shell structures in general.

Highly luminescent, non-stoichiometric CIS/ZnS QDs have been synthesized for near infrared fluorescence bioimaging¹³⁷. In this work, using *in vitro* and *in vivo* imaging sensitivity tests, the QDs were detectable to the depth of a few millimetres in an imaging phantom and in an intramuscular section of a mouse. This work demonstrated the feasibility of the bioimaging applications of the less-toxic, near infrared-emission CIS/ZnS system in deep biological tissues. Kim *et al.* prepared a CIS/ZnS core/shell structure¹³⁸ and the

obtained QDs could be transferred into the aqueous phase. The authors claimed that the CIS/ZnS QDs were fabricated to an appropriate size for bioimaging (140 nm), which had the potential application in vivo imaging. As for the quaternary core-based core/shell structure, Guo *et al.* carried out a one-pot synthesis of hydrophilic CIZS/ZnS QDs for vivo imaging¹³⁹ and the synthesis of CIZS/ZnS with inhibited blue-shift emission for tumour targeted bioimaging¹¹⁰. The as-prepared hydrophilic CIZS/ZnS QDs showed low cytotoxicity and offered a great opportunity for a direct in vivo imaging application without phase transfer. As for the obtained CIZS/ZnS with inhibited blue-shift photoluminescence, these were transferred into aqueous phase by a polymer coating technique and coupled with cyclic Arg-Gly-Asp peptide (cRGD) peptides. Following this, these QDs were injected *via* the tail vein into nude mice bearing U87 MG tumour. The results indicated that the signals detected in the tumour region were much more distinguishable when injected with CIZS/ZnS-cRGD rather than CIZS/ZnS QDs. All of these works demonstrated the advantages of Cu-based multicomponent core/shell structures for bioimaging application.

Aside from luminesce, the application of multimodal particles is an emerging concept in bioimaging, and of great importance, enabling additional properties such as a magnetic modality in the same nanoprobe. The addition of paramagnetic functionalities, therefore, enable these nanoprobes to function as magnetic resonance imaging (MRI) contrast agents. Generally, there are three popular ways to combine QDs with magnetic resonance imaging (MRI) contrast agents, including combining them with magnetic nanoparticles, paramagnetic ion doping, or conjugating them with paramagnetic complexes, and have been previously demonstrated in Cd-based based QDs¹⁴⁰.

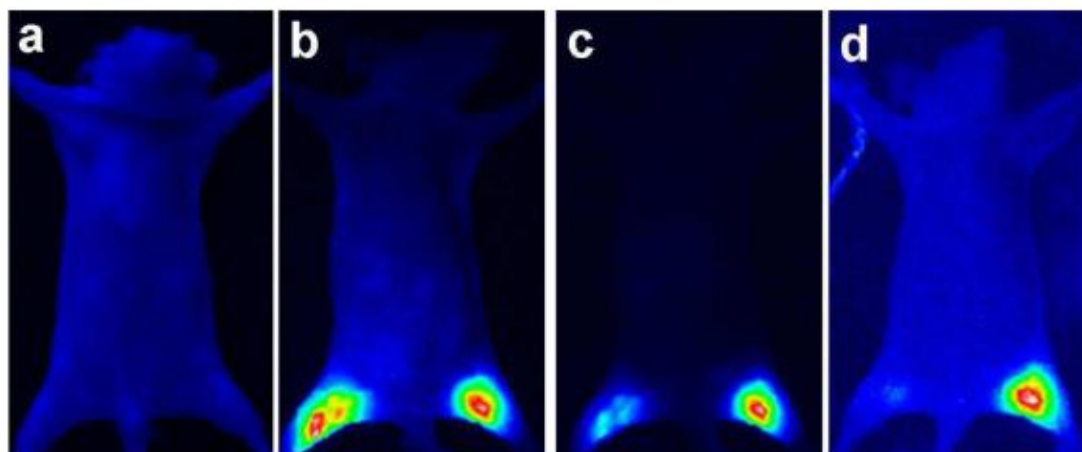


Figure 1. 14. Multiplex NIR fluorescence imaging of mouse administered with two different NIR-emitting QDs-loaded micelles by subcutaneous injection (the right leg, 720 nm-emitting NCs; the left leg, 800 nm-emitting NCs): (a) before injection, (b) $\lambda_{ex} = 600$ nm, a 700 nm long pass filter, (c) $\lambda_{ex} = 660$ nm, an 800 nm long pass filter, (d) $\lambda_{ex} = 766$ nm, an 800 nm long pass filter. Reproduced with permission from ¹⁴¹. Copyright American Chemical Society, 2012.

Recently, multimodal imaging has also been achieved in Cu-based multicomponent core/shell heterostructures. A method of Gd paramagnetic ion doping was explored by Yu *et al.* using CIS/ZnS NCs¹⁴². In their work, high quality bimodal bioimaging nanoprobe based on Gd (gadolinium)-CIS/ZnS were prepared by a simple hot-injection method. The incorporation of Gd³⁺ into CIS/ZnS QDs led to a stable structure of Gd-CIS/ZnS, which produced enhanced MRI contrast, while still showing strong PL emission. Cheng *et al.* produced dual-modality Poly(maleic anhydride-alt-1-octadecene) (PMO) coated CIS/ZnS QDs by conjugating the PMO coated CIS/ZnS QDs with diethylenetriaminepentaacetic acid gadolinium(III) dihydrogen salt hydrate (Gd(III)-DTPA)¹⁴³. A clear, positive and increasing contrast enhancement of magnetic resonance signals were observed as increasing Gd (III) concentration. This dual-modality nanoprobe also demonstrated excellent biocompatibility and negligible cytotoxicity. A bimodal contrast agent was successfully developed by chelation of the gadolinium ion to DTDTPA-modified CIS/ZnS QDs by Yang *et al.*¹⁴⁴. It was proved that the as prepared CIS/ZnS QDs conjugating Gd(III) chelates had excellent

capability to enhance the NIR fluorescence and MR imaging. These works are excellent examples of possible approaches to take full advantage of Cu-based multicomponent core/shell QDs for biological in vitro and in vivo studies.

NC heterostructures such as rods, tetrapods and plate morphologies, are greatly appealing to a range of bioimaging applications. For example, NRs demonstrate a unique interaction with polarized light due to the electron and hole being polarized along the long axis, producing linearly polarized light emission that can be used to detect particle orientation and particle location *via* fluorescence polarization spectroscopy. NPLs are a family of QDs that are nearly planar and atomically flat, possessing narrow excitation and emission bands¹⁴⁵, making them an excellent candidate for multiplexed bioimaging applications, due to the enhanced capability to detect multiple signals. It has also been determined that rod like structures diffuse faster through porous media than dot shaped particles when measuring per weight and have a lower nonspecific cellular uptake, properties which are ideal for improving imaging of cell plasma membranes.¹⁴⁵ This range of properties related to the anisotropic nature of NPs make them intriguing for a wide range of bioimaging applications.

1.5.2. Light emitting diodes

Due to the wide tuneable emissive range and high quantum yields, quantum dots are an excellent candidate for a range of architectures of lighting emitting diodes (LEDs), which either utilise QDs as down converters of a blue emitting conventional LED termed a QDLED in the design or through the use of QDs in an electroluminescence (EL) device design creating an EL QD-LED.

In addition, as with other applications discussed previously, this field initially developed with the use of Cd based QDs, and then progressed towards the elimination of toxic metal

use, and so the field has found huge success in recent times through the use of a range of Cu based ternary and quaternary QDs. Cu ternary and quaternary quantum dots are an excellent fit for a range of LED applications due to their tunability across the entire visible range, while achieving high quantum yields. A range of excellent reviews have covered this important field in the past number of years in great detail.¹⁴⁶⁻¹⁴⁸

Down converter LEDs are an area which has matured exceptionally, with Cu based QD devices showing excellent performance at present. In these designs, a blue emitting LED is used as the light source, upon which is placed a transparent matrix, typically a form of SiO₂ resin, which is doped with variable concentrations of QDs. In this design, the blue LED emits, short wavelength photons, some or all of which are absorbed by the overcoated QD doped resin depending on the design, these QDs then reemit light upon excitation giving the emission colour of the specific QDs utilised. For these designs, a range of Cu based QDs have been tested including, CuInS₂/ZnS,^{98, 101, 149-151} CuGaS₂,¹⁵²⁻¹⁵³ and CuInZnS₂/ZnS,¹⁵⁴ along with CuSnInS¹⁵⁵ and Mn doped CuInZnS.¹⁵⁶ The performance of these devices heavily relies upon the PLQY of the utilised QDs, which ranges between 70-80 % in these QD based systems and whether there is a loss upon incorporation into the transparent matrix used, or if this PLQY is reduced overtime due to photobleaching effects. Another important characteristic is the question of reabsorption, which lowers the efficiency of the devices, therefore some work has explored the use of dopants to increase the Stokes shift significantly, with Mn doped CuInZnS being an excellent fit for this.¹⁵⁶

In contrast to down converted QD LEDs, the field of electroluminescent QD LEDs, remains still a field full of potential with the designs showing significant progress, while still with many challenges remaining to be tackled for commercialisation to take place. The devices take full advantage of the use of a semiconducting fluorescent nanoparticle, by using the

inherent property of electroluminescence of fluorescent QDs. These devices are based upon the injection of charge carriers into the emissive layer, the QDs, at which point the charge carriers recombine, releasing the excess energy in the form of emitted light. This design allows for in theory much greater efficiency in comparison to down converter LEDs and allows for more easily miniaturization of the QD-LED. Unfortunately, disadvantages or at least complications come with this design also, since the device must be carefully designed so as charge carriers can be efficiently combined in the emissive layer, avoiding recombination *via* non-radiative routes, or loss of charge carriers while transporting them. This all means, as with solar cell designs, that multiple layers of different semiconductors must be chosen so as to drive this process to best take place at the highest efficiency, with the QD sandwiched between two charge transport layers at least. Currently, the most effective designs incorporate a layer to transport holes efficiently, typically a p-type organic semiconductor typically composed of poly(ethylenedioxythiophene): polystyrene sulfonate (PEDOT:PSS), and another layer to transport electrons efficiently, a n-type semiconductor metal oxide, typical examples would be ZnO, with the QD layer sandwiched in-between these.

A range of Cu based QDs to have been tested in these designs including Mn doped CuInZnS,¹⁵⁷ CuInS₂/ZnS,^{29, 158-160} CuInSe₂/ZnS,¹⁶¹ CuInZnS/ZnS¹⁶² and CuInGaS/ZnS.¹⁶³ In addition mixed systems exist using CuInS₂/ZnS and ZnCdSe/ZnS QDs¹⁶⁴ or CdZnS/ZnS¹⁶⁵ have also been reported. A common trend in these systems is the use of synthesis which optimise for high PLQY systems, with the dominant approach synthetically being to produce a type band alignment using ZnS on the core, therefore increasing the PLQY and the resistant to photobleaching. In addition, the use of Cu poor reactions, in which In is in large excess is also very commonly applied to achieve the highest performing results.²⁹

White light LEDs are an important class of LEDs aiming to produce emission as close as possible to blackbody emission at $\approx 6,000$ K, and therefore simulate sunlight and so to act as replacement for a range of lighting sources used at present (Figure 1.15). A number of Cu based white light sources have been demonstrated,^{98, 101, 149-152, 154, 156-157, 164, 166-169} either *via* the use of down converting^{101, 149-156, 166-168} or electroluminescence,^{157, 164-165} QD based LEDs. These devices are achieved by either combining a number of luminescent sources, or *via* the use of a single broad emission sources. Cu based QDs are an excellent fit for this type of light source due to the inherent broadness of the QD emission relative to other QDs, in addition upon the inclusion of dopants into the structure the emission can be even further broadened, using Mn,¹⁵⁶⁻¹⁵⁷ Sn¹⁵⁵ or Ga¹⁵² for example. In addition, the alternative approach of multiple luminescent dyes, can be easily achieved *via* either varying the stoichiometry of the QDs or *via* the size of the QDs.

The application of nano-heterostructures is widely presented in the field of QDLED with the use of core/shell structures of type I band alignments showing significant success. In contrast, the effects of varying heterostructure morphology is only now gaining attention as a novel approach to further improve upon these exciting devices. As with many areas of QD applications, Cd-based QDs have led the way in this investigation of anisotropic structures with a number of studies showing some exciting results through the use of dot in rod structures of CdSe/CdS,¹⁷⁰⁻¹⁷¹ CdSe NPLs,¹⁷²⁻¹⁷⁵ and CdSe/CdS TP¹⁷⁶ in a number of LED designs. The unique advantages gained from the use of heterostructures have been very effectively covered in a recent review of QD LED designs¹⁴⁷, with polarization, alignment and narrow emission being some of the highlights with some examples detailed below to illustrate this point. CdSe/CdS dot in rods have been aligned to the surface of water to then enable the production of an emissive layer in a polarised electroluminescent device.¹⁷⁰ A CdSe_{1-x}S_x NPL based LED has also been demonstrated showing the narrowest emission

spectrum (FWHM of 12.5 nm) for any colloidal semiconductor LED.¹⁷² Also dual wavelength electroluminescent has been demonstrated using CdSe/CdS tetrapods, with two peaks associated with the core and arms of the heterostructure originating from distinct peaks, a property at present which seems unique to this specific morphology.¹⁷⁶

In addition, to these core shell anisotropic heterostructures, some very interesting results have recently been reported on the use of a relatively novel nanoparticle, CdS/CdSe/ZnSe, termed a double heterojunction nanorod for the design of some of the highest performing EL QDLEDs to date.¹⁷⁷⁻¹⁸⁰ In which a CdS nanorod is initially grown, then CdSe is grown at two tips of the formed CdS nanorod, which is followed by the shell coating of ZnSe, forming two heterostructures at the each end of the nanorods. Due to the morphology and the band alignments these have demonstrated excellent performance.

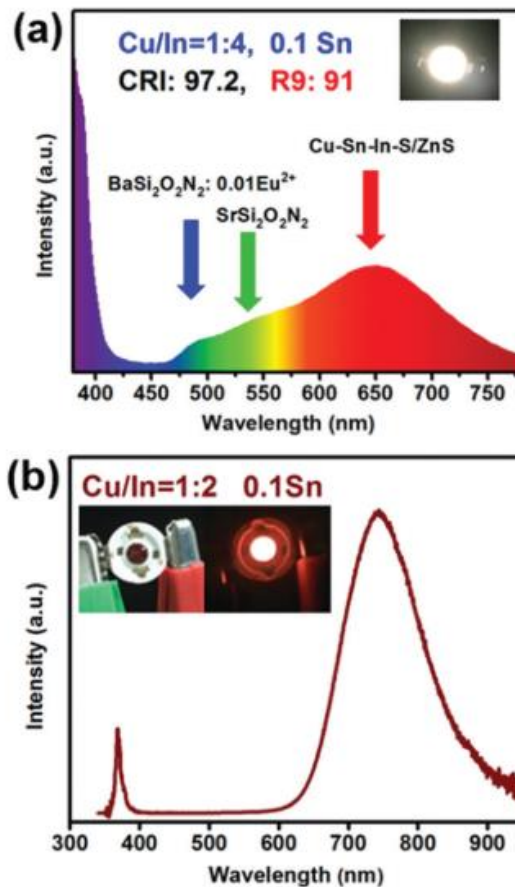


Figure 1. 15. Electroluminescence (EL) spectra of (a) wLED and (b) NIR LED devices combined with CTIS/ZnS QDs (0.1 mmol Sn) with the Cu/In molar ratios of 1/4 and 1/2 respectively. Reproduced with permission from ¹⁸¹.

1.6 Applications of QDs in luminescent solar concentrators

Great concerns about environmental sustainability and global warming, have evoked intensive worldwide efforts which focused on the use of “green” renewable energy sources such as solar power. Under these circumstances, photovoltaics have received increased attention in the past decades, however, it is still a challenge to achieve high efficiency with limited fabrication cost at present. One of the approaches to tackle this issue is the employment of Luminescent Solar Concentrators (LSCs). The major role of the LSCs is to concentrate solar radiation over a large area waveguide onto a small area of attached solar cells to enhance the efficiency of photovoltaics and lower the cost of solar energy. As shown in Figure 1.14, a typical LSC is comprised of a planar waveguide containing embedded fluorescent materials with photovoltaics attached to the waveguide edges. In addition, sometimes Bragg mirrors are also incorporated into LSCs to enable better lateral light propagation. Fluorescent materials absorb a certain fraction of solar radiation and re-emit this energy as luminescence in lower energy region, with the re-emitted radiation trapped due to total internal reflection. There are essentially three pathways for energy loss during this working process, the first possible pathway is that a fraction of the light exits through top surface of LSCs, termed the escape cone and is dependent on the refractive index of the used matrix. The second possibility is the reabsorption of the photons by the embedded fluorescent materials. In addition, mirror losses is the third energy loss pathway if the Bragg mirror is far from perfect. Due to the larger lateral area of the LSC to the edge area for solar

cells, the photon density can be increased considerably which is also known as the concentrator effect.

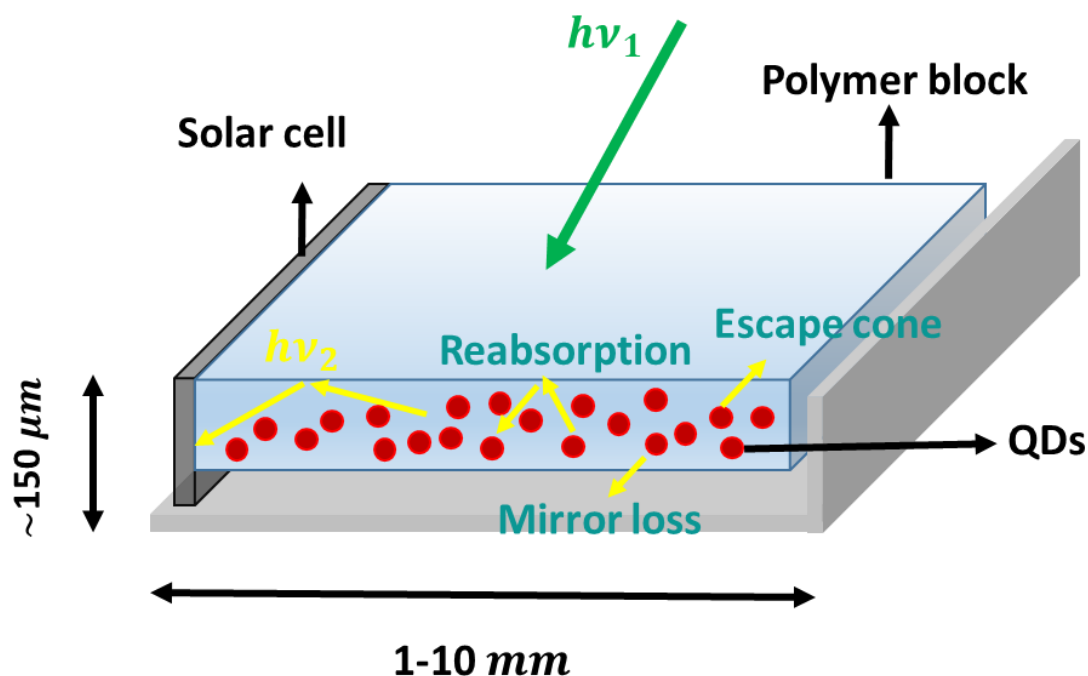


Figure 1. 16 Scheme showing the structure and the energy loss pathways in a LSC.

A number of advantages render QDs as a very promising fluorescent material for the application in LSCs over traditional dyes. High quality QDs can be produced due to the fast development of the colloidal synthesis techniques, enabling QDs to possess high luminescence quantum yields (even above 90%), tuneable absorption and emission based on the obtained size, composition and morphology. Type I core/shell heterostructures would be the optimal choice regarding the requirement for the fluorescent materials of great resistance to photobleaching. Some core QDs might be sensitive to the environment due to the potential oxidation under solar irradiation, therefore this can be improved by coating the final NC in an inorganic shell (ZnS) producing a core/shell structure. In this case, the shell of ZnS, shows excellent stability and therefore protects the core from the external environment, greatly enhancing photostability. Large Stokes shift is another typical

characteristic of Cu-based multicomponent QDs that favours its application in LSCs, since the undesired reabsorption because of the small Stokes shift¹⁸², which causes energy loss, can be eliminated *via* the use of Cu-based multicomponent QDs. Also, *via* design of a specific optimal heterostructure design, Cu- based QDs can be designed with an even larger Stokes shift, *via* a core-shell structure. In addition, the application of doped Cu-based QDs also possess large Stokes shift ideal for LSC applications with the dopants (Mn^{2+} , Co^{2+} , Ni^{2+}) producing an intraband energy level¹⁸³. All these factors make Cu-based multicomponent heterostructures meet many of the criteria for ideal fluorescent materials for LSCs and make them a much better choice than Cd- or Pb-based QDs considering the inherent environmental issue of heavy metal use.

In spite of all the advantages of Cu-based heterostructures, there are still few reports in literature related to their application in this area, though some excellent examples have been reported. Bright CIS/CdS phosphors have been tested for LSCs applications by Knowles and Kilburn¹⁸⁴. The colloidal CIS/CdS QDs they prepared possessed large solar absorption, high PLQYs and only moderate reabsorption, which lead to CIS/CdS QDs outperforming CdCuSe QDs. But this sample still contained toxic heavy metal Cd. Meinardi *et al.* demonstrated that the use of Cu-based multicomponent heterostructures allow us to overcome many limitations of both organic dyes and more traditional Cd- or Pb-based QDs, including incomplete coverage of the solar spectrum, toxicity and strong colouring of the LSC¹⁸⁵ (an optical power conversion efficiency of up to 3.27%). Li and Chen synthesized CIS/ZnS heterostructures for LSCs¹⁸⁶. In their work, the as-prepared heavy metal free CIS/ZnS QDs possessed advantages of high PLQYs of 81% and a large Stokes shift of more than 150 nm. The optical efficiency of CIS/ZnS QDs-LSC reaches as high as 26.5%, with the power conversion efficiency of the QD-LSC-PV device reaching more than 3-fold than that of a pure PMMA-PV device. Nearly reabsorption-free CISE/ZnS quantum dots were

synthesized by Wu and the performance of this heterostructure checked in a tandem LSCs¹⁸⁷. They found that the power conversion efficiency improvement versus single-layer devices can exceed 50% (with bandgap-matched PVs).

All the above results indicate that highly effective performance can be achieved with these environmental-friendly, low-cost, easy solution-processable Cu-based multicomponent heterostructures in standard or even tandem LSCs.

The use of anisotropic morphology also offers some unique advantages when designing a LSC using heterostructured nanocrystals. For example, it has been simulated that if CdSe-CdTe NRs are aligned in the LSC with their long axis perpendicular to the top surface in the LSC, they emit anisotropic luminescence parallel to the top surface, thus reducing the escape of emitted light from the LSC¹⁹. A range of techniques including such as solvent effect¹⁸⁸⁻¹⁸⁹, thermal annealing¹⁹⁰, controlled drying¹⁹¹ and electric field¹⁹² that have been developed for the alignment of NRs in solution and corresponding matrix. As for Cu-based multicomponent polytypic or heterostructured rod and TP structures, they have excellent light absorption abilities due to their large absorption cross section and carrier-guiding directions, all these unique morphology-dependent optoelectrical properties make them even more promising in LSC applications, although they have not been applied to this application at present and therefore remain a unique opportunity to further leverage the advantages of QD based LSC designs. One of the challenges is that there are only a very limited number of reports on the achievement of the Cu-based anisotropic multicomponent heterostructures so far, despite there is a great interest in the development of the Cu-based anisotropic multicomponent QDs with better photophysical performance.

1.7 Aims of the project

It is well known that the optical properties of QDs are not only size and composition dependent, but are also strongly determined by the resulting shape and morphology, with several morphologies demonstrating this, including spherical QDs, nanorods (NRs), nanoplatelets (NPLs) and tetrapods (TPs). These nanoheterostructures exhibit unique optical properties, spherical core/shell heterostructures show great stability and large Stokes shift, while NRs and TPs, showing increased electrical conductivity compared to core, quasi-spherical nanoparticles, and therefore are very appealing for photovoltaic applications. Their synthesis is well explored for Cd-based systems. However, reports on luminescent Cu-based multicomponent heterostructured nanocrystals especially anisotropic nanoheterostructures are currently very limited. Therefore, the main aims of this project include the development and characterization of novel Cu-based multicomponent nanoheterostructures with various morphologies and distinct optical properties. The main research and technical objectives of this project are as follows:

- To prepare highly fluorescent CIZS and CIZSe -based core/shell heterostructures with isotropic morphologies and study their photophysical properties.
- To develop and investigate novel, fluorescent CIZS and CIZSe -based multicomponent core/shell nanoheterostructures with anisotropic morphologies.
- Selected, some of the obtained highly fluorescent, stable CIZS/ZnS core/shell nanoheterostructures to explore their potential applications in luminescent solar concentrators.

I believe that this research will contribute to further advancement of research and technology of copper-based quantum nanostructures and their applications in Energy Science.

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Chapter 2 Experimental

2.1 Chemicals, starting materials and general procedures

All chemicals were purchased from Sigma-Aldrich and used as received without any further purifications. All solvents were obtained from the Trinity College Dublin Solvent and Hazardous Waste facility.

Syringe pump that used was from KD Scientific, Model No: KDS-100-CE

Centrifugation was done using Hermle Z233 M-2 centrifuge for TEM, EDX, XRD and AFM samples and Hettich Zentrifugen Universal 32 centrifuge for the samples for optical characterizations.

Ultrasonic equipment was Ultrawave model U100H bath with sonication power of 35 W.

Millipore water was produced using a Millipore filtration system operating at 18 M Ω .

Quartz cuvettes for the characterization of UV-Vis, PL, PLQYs, PL lifetime are purchased from Sigma Aldrich.

Copper TEM grids were purchased from TED PELLA for TEM and STEM.

Gold TEM grids were purchased from TED PELLA were used for EDX and line scanning to determine the compositions of the obtained Cu-based multicomponent QDs.

2.2 Experimental protocols

2.2.1 Experimental details for chapter 3

Materials. S powder (99.9%), indium acetate ($\text{In}(\text{Ac})_3$, 99.99%), 1-dodecanethiol (1-DDT, $\geq 98\%$), 1-octadecene (ODE, $\geq 95\%$), zinc stearate ($\text{Zn}(\text{St})_2$, technical grade), copper iodide (CuI , 99.99%), trioctylphosphine (TOP, 90%), oleic acid (OA, $\geq 99\%$), oleylamine (OAm, $\geq 98\%$), Copper(II) acetylacetonate ($\text{Cu}(\text{acac})_2$, 99.9%) were purchased from Sigma-Aldrich . All the reagents were used as received without further purification.

2.2.1.I Synthesis of CIZS QDs

Preparation of precursor solution. 1.2 mmol (0.0384 g) of sulphur powder was dissolved in 2 mL of OAm under sonication.

Synthesis. The synthesis of CIZS QDs was carried out according to a previously reported method¹. In a typical synthesis of CuZnInS_3 QDs, 0.4 mmol (0.253 g) of $\text{Zn}(\text{St})_2$, 0.4 mmol (0.1168 g) of $\text{In}(\text{Ac})_3$, 0.4 mmol (0.1047 g) of $\text{Cu}(\text{acac})_2$, 2 mL of 1-DDT, and 1 mL of OA were mixed with 16 mL of ODE in a three-neck round-bottom flask. The mixture was degassed under vacuum for 30 min, then the atmosphere was switched to argon. The flask was heated to 225 °C (injection temperature) until a clear solution was formed, then 2 mL of the S precursor solution was quickly injected into the reaction flask. After which the reaction vessel was kept at 240 °C (growth temperature) for 15 min. Let the reaction vessel cool to RT.

Purification. Toluene and ethanol were used to clean the QD sample. The purified CIZS QDs were stored in toluene in the fridge at +4 °C.

2.2.1.II Preparation of CIZS/ZnS core/shell QDs

The CIZS/ZnS core/shell heterostructures were prepared with a seeded growth method.

Preparation of precursor solution. 2 mmol (1.26 g) of $\text{Zn}(\text{St})_2$ was dissolved in 5 mL of OA, 5 mL of 1-DDT and 10 mL of ODE at RT. The mixture was degassed for 20 min, then the atmosphere was switched to argon.

Synthesis. 3 mL of the preformed CIZS QDs solution, 5 mL of OAm and 10 mL of ODE were loaded in a three-neck round-bottom flask. The reaction mixture was degassed for 30 min at 90 °C and then flashed with argon. Then the reaction temperature was increased to 230 or 260 or 280 °C respectively for each experiment. When the temperature reached 200 °C, the precursor solution was injected into the reaction vessel drop wisely with a syringe pump (Vol = 20 mL, injection rate = 5 mL/h). After the injection was finished, then heating mantle was removed and the reaction vessel was let to cool down to RT.

Purification. Toluene and ethanol were used to wash the sample. The purified CIZS/ZnS QDs were stored in in toluene in the fridge (+4 °C).

2.2.1.III Preparation of CIZS/ZnS/ZnS QDs

Preparation of the precursor solution. 4 mmol (2.529 g) of $\text{Zn}(\text{St})_2$ was dissolved in 10 mL of OA, 10 mL of 1-DDT and 20 mL of ODE. The mixture was degassed for 30 min at RT.

Synthesis. 4 mL of the preformed CIZS/ZnS QDs solution, 5 mL of OAm and 10 mL of ODE were mixed in a three-neck round-bottom flask. The mixture was degassed at 100 °C for 30 min, and flashed with argon. The reaction temperature was increased to 230 °C

(reaction temperature). When the temperature reached 200 °C (injection temperature), the precursor solution was injected into the reaction vessel drop wisely with a syringe pump (Vol = 10/20/40 mL, injection rate = 5 mL/h), with the injection being 2/4/8 h. When the injection was finished, the heating mantle was removed and let the reaction vessel was cooled to RT.

Purification. Toluene and acetone were used to clean the sample and the clean CIZS/ZnS/ZnS QDs were stored in the fridge (+4 °C).

2.2.2 Experimental details for chapter 4

Materials: CuI (Copper iodide, 99.99%), In(Ac)₃ (indium acetate, 99.99%), 1-DDT (1-dodecanethiol, ≥ 98%), ODE (1-octadecene, ≥ 95%), Zn(St)₂ (zinc stearate, technical grade), OA (oleic acid, ≥ 99%), OAm (oleylamine, ≥ 98%) were purchased from Sigma-Aldrich . All the reagents were used as received without further purification.

2.2.2.1 Synthesis of Cu-In-S QDs

Synthesis. CIS seeds were prepared with a heating up technique according to a previously reported method with minor modifications².

0.5 mmol (0.0952 g) of CuI, 0.5 mmol (0.041 g) of In(Ac)₃, 10 mL (8 mmol) of 1-DDT and 10 mL of ODE were mixed in a 100-mL three-neck round-bottom flask. The mixture was degassed at 30 °C for 30 min after which it was heated to 210 °C under argon flux. The reaction temperature was kept at 210 °C for 2 h. Then the reaction vessel was allowed to cool to RT.

Purification. Ethanol was used to remove excess organic materials and precipitate the QDs by centrifugation. The purified Cu-In-S QDs were stored in toluene in the fridge (+4 °C).

2.2.2.II Preparation of Cu-In-(Zn)-S/ZnS “ice-cream cone” like nanoheterostructures

The synthesis of the Cu-In-(Zn)-S/ZnS core/shell heterostructures was carried out using a seeded growth method.

Preparation of precursor solution. 1 mmol (0.6323 g) of $\text{Zn}(\text{St})_2$ was dissolved in 2.5 mL of OA, 2.5 mL (2 mmol) of 1-DDT and 5 mL of ODE in a 100-mL three-neck round-bottom flask. The mixture was degassed at RT for 20 min under stirring then the atmosphere was switched to argon.

Synthesis. 3 mL of the clean Cu-In-S QDs solution, 5 mL of OAm and 10 mL of ODE were loaded in a 100-mL three-neck round-bottom flask and degassed at 100 °C for 30 min to remove solvents with low boiling points. Under argon atmosphere, the temperature was increased to 230 °C (growth temperature). When the temperature reached 150 °C (injection temperature), the precursor solution was injected into the reaction vessel using a syringe pump (KD Scientific, Model No: KDS-100-CE, volume = 10 mL, injection rate = 5 mL/h) with the injection taking 2 h. Aliquots were taken out from the reaction mixture at certain time intervals (30 min, 60 min, 120 min) for further studies. The aliquots that were taken from the reaction vessel at these certain time intervals are denoted as Cu-In-(Zn)-S/ZnS30, Cu-In-(Zn)-S/ZnS60 and Cu-In-(Zn)-S/ZnS120, respectively. After the injection was completed, the heating mantle was removed, and the reaction vessel was allowed to cool to RT.

Purification. Acetone and toluene were used as the polar and nonpolar solvents to clean the sample with centrifugation and the purified sample was stored in toluene in the fridge (+4 °C).

2.2.3 Experimental details for chapter 5

Materials: Se powder (Selenium, $\geq 99.5\%$), DPP (diphenylphosphine, 98%), CuI (copper (I) iodide, 99.999%), In(OAc)₃ (indium acetate, 99.99%), Zn(OAc)₂ (zinc acetate, 99.99%), Zn(St)₂ (zinc stearate, technical grade), Cu(acac)₂ (copper(II) acetylacetonate, 99.9%), AuCl₃ (gold(III) chloride, 99%), 1-DDT (1-dodecanethiole $\geq 98\%$), OA (oleic acid, $\geq 99\%$), ODE (1-octadecene, $\geq 95\%$), OAm (oleylamine, $\geq 98\%$) were purchased from Sigma-Aldrich. All of the reagents were used as received without further purification.

2.2.3.I Synthesis of CIZSe QDs

The CIZSe QDs were prepared *via* a hot injection method that has been reported previously.³

Preparation of precursor solution. Se precursor solution was prepared in a separate flask. 1.2 mmol of (0.0947 g) of Se powder was added to 1 mL of OAm in a 10 ml vessel followed by gassing for 10 min at RT. Under argon atmosphere, 1.2 mL of DPP was injected into the mixture, which was followed by sonication under argon atmosphere to dissolve Se powder.

Synthesis. 0.4 mmol (0.076 g) of CuI, 0.4 mmol (0.116 g) of In(OAc)₃, 0.16 mmol (0.0293 g) of Zn(OAc)₂, 9 mL of OAm and 7 mL of ODE were loaded into a 100 mL, 3-neck, round-bottom flask and were degassed at 30 °C for 30 min. Then the mixture was heated to 130 °C and was kept at 130 °C for 5 min until colour change of the solution to straw yellow was observed. Then the temperature was increased to the target temperature of injection, which was 175 °C (It should be noted that the injection temperature should not be heated above 180 °C due to the degradation of metal complex formed in the vessel at higher temperature, which is indicated by the colour change from light yellow to black). When the temperature reached the target temperature, the preformed Se precursor solution was injected into the reaction vessel swiftly using a syringe. The growth time was allowed to proceed for 5 min.

Following this, the heating mantle was removed, and the reaction vessel was allowed to cool to RT.

Purification. Ethanol and toluene were used as the polar and nonpolar solvents to clean the sample by centrifugation. The clean Cu-In-Zn-S QDs were stored in toluene in the fridge at +4 °C.

2.2.3.II Preparation of Cu-In-Zn-Se/Cu-In-Zn-S core/shell heterostructures

The CIZSe/CIZS core/shell heterostructures were prepared with a seeded growth method.

Preparation of cation precursor solution (cation ratio of Cu:In:Zn = 1:2:3). 0.2 mmol (0.052 g) of Cu(acac)₂, 0.4 mmol (0.1168 g) of In(OAc)₃, 0.6 mmol (0.11 g) of Zn(OAc)₂, 4.4 mL of OA and 5.6 mL of ODE were mixed in a 100 mL 3-neck flask. The mixture was degassed at 30 °C for 30 min, which was followed by heating the mixture to 130 °C until the solution became clear. This cation precursor solution was then allowed to cool to RT.

Preparation of anion precursor solution. The preparation of the anion precursor solution was then carried out by adding 0.4 mmol (0.5 mL) of 1-DDT into 9.5 mL ODE at RT in a separate 25 mL flask. The mixture was sonicated for 20 min under vacuum and then flashed with argon.

Synthesis. For a typical synthesis of CIZSe/CIZS QDs, 1 mL of the purified CIZSe QDs solution, 10 mL ODE and 5 mL OAm were added into a 250 mL four-neck round-bottom reaction flask and the mixture was degassed for 30 min at 80 °C to remove the solvents with low boiling points. The atmosphere was then switched to argon and the reaction mixture was heated to 220 °C (growth temperature). When the temperature reached 150 °C (injection temperature), the cation and anion precursor solutions were injected into the reaction vessel

with two syringe pumps (KD Scientific, Model No: KDS-100-CE, volume = 10 mL, injection rate = 10 mL/h) with the injection time of 60 min. When the injection finished, the reaction was kept at 220 °C for an additional 10 min. Then the heating mantle was removed, and the reaction vessel was cooled to RT. The obtained crude solution was then used for the next step.

2.2.3.III Cu-In-Zn-Se/Cu-In-Zn-S/ZnS core/shell/shell heteronanonail structures

This CIZSe/CIZS/ZnS core/shell/shell heteronanonail structure was prepared with a seeded growth method.

Preparation of precursor solution. 2 mmol (1.2646 g) of Zn(St)_2 was dissolved in 5 mL of OA 5 mL (4 mmol) of 1-DDT and 10 mL of ODE at RT in a flask. The mixture was then degassed for 30 min at RT under sonication, which was followed by switching the atmosphere to argon.

Synthesis. For a representative synthesis of CIZSe/CIZS/ZnS HNNs, the CIZSe/CIZS QDs solution was degassed at 120 °C for 30 min to remove volatiles that were produced during the previous step of the reaction. Following this, under an argon atmosphere, the temperature was increased to 220 °C (growth temperature). When the temperature reached 200 °C (injection temperature), the injection of the above precursor solution with a syringe pump was started (injection rate = 4 mL/h), with a total injection time of 5 h. Aliquots were taken out from the reaction mixture at certain time intervals (1, 2, 4 and 6 h) for further studies. After the injection finished, the solution was stirred for another 60 min at 220 °C to ensure complete reaction of precursors. Following this, the heating mantle was removed, and the reaction vessel was allowed to cool to RT.

Purification. Acetone and toluene were used as the polar and nonpolar solvents to clean the sample with centrifugation. The purified heteronanonail structures were stored in toluene in the fridge (+4 °C).

2.2.3.IV Au-Cu-In-Zn-Se/Cu-In-Zn-S/ZnS nanocomposites

Synthesis. In a separate 5 mL flask, 0.1 mL of CIZSe/CIZS/ZnS HNNs solution was dispersed in 1 mL of degassed OAm. 3 mL of degassed OAm was injected into the reaction vessel which was loaded with 0.05 mmol (0.015 g) of AuCl₃ at 60 °C. Following this, the mixture of CIZSe/CIZS/ZnS HNNs and OAm was injected into the reaction vessel using a syringe. Upon injection of CIZSe/CIZS/ZnS HNNs into the Au(Cl)₃/OAm mixture, the solution was heated to 110 °C (heating rate = 2 °C/min) and held at that temperature for 10 min. Following this, the reaction vessel was cooled to RT.

Purification. Acetone and toluene were used as the polar and nonpolar solvents to clean the sample with centrifugation. The purified nanocomposites were stored in toluene in the fridge (+4 °C).

2.2.4 Experimental details for chapter 6

Materials. Copper iodide (CuI, 99.99%), indium acetate (In(OAc)₃, 99.99%), 1-dodecanethiol (1-DDT, 98%), zinc stearate (technical grade), 1-octadecene (ODE, ≥ 95%), trioctylphosphine (TOP, 97%), diphenylphosphine (DPP, 98%), oleic acid (OA, ≥ 99%), methyl methacrylate (MMA, 99%), 2,2'-Azobis(2-methylpropionitrile) (AIBN, 98%), lauroyl peroxide (LP, 98%), polytetrafluoroethylene (PTFE) film with 2 mm thickness, glass slides (width*length = 2 cm*5 cm), silicone glue. All chemicals were purchased from Sigma-Aldrich and used as received without any further purification.

2.2.4.I Synthesis of fluorescent alloyed CIZS/ZnS QDs

The typical synthesis of colloidal CIZS/ZnS QDs was carried out according to previously reported method⁴.

Synthesis of colloidal CuInS QDs. 0.2 mmol (0.0358 g) of CuI, 0.6 mmol (0.1168 g) of In(OAc)₃ and 20 mL of 1-DDT were mixed in a 100 mL 3-neck flask. The flask was degassed for 30 min at 80 °C, and then the atmosphere was switched to argon. Under argon flux, the reaction temperature was increased to 215 °C, and kept at this temperature for 10 min. Then the heating mantle was removed and the reaction vessel was cooled to RT naturally. Without purification, the crude solution was ready for the synthesis of CuInZnS alloyed QDs.

Synthesis of colloidal CuInZnS QDs.

Preparation of Zn cation exchange solution. The Zn precursor solution was prepared by dissolving 0.6 mmol (0.3768 g) of zinc stearate in 8 mL of ODE. 2 mL of TOP was injected into the flask under argon. The mixture was heated to 100 °C until clear precursor solution was obtained.

Synthesis of CIZS QDs. CIZS QDs were prepared through *in situ* cation exchange of the preformed CIS QDs. The crude CuInS QD solution was degassed at 115 °C for 30 min to remove volatiles that produced during the reaction. Then the atmosphere was switched to argon and the temperature was set at 120 °C (injection temperature). When the temperature reached to the target temperature, the zinc precursor solution was added drop wisely with a syringe which was set on a syringe pump over 30 min (injection rate = 20 mL/h) to the reaction vessel. When the injection was finished, the temperature was increased to 200 °C

and maintained at that temperature for 90 min before cooling to RT. Without cleaning, the sample was ready for ZnS shell coating.

Synthesis of colloidal CuInZnS/ZnS QDs

Preparation of Zn and S precursor solution. 4 mmol (2.52932 g) of zinc stearate was dissolved in 10 mL of OA, 10 mL of 1-DDT and 20 mL of ODE. The mixture was degassed for 2 h at 30 °C under stirring and then the reaction vessel was flashed with argon.

Synthesis of CIZS/ZnS QDs. The crude CIZS QD solution in the reaction vessel was degassed for 30 min at 120 °C to remove volatiles that produced during the reaction. Under argon atmosphere, the temperature was increased to 220 °C (reaction temperature). When the temperature reached 200 °C (injection temperature), above precursor solution was injected into the reaction vessel with a syringe pump (injection rate = 4 mL/h, volume = 40 mL), the injection taking 10 h. After the injection, the solution was stirred for another 1 h at 220 °C. Then the heating mantle was removed and the reaction vessel was cooled to RT naturally. Hot ethanol and toluene were used to clean the sample. The obtained clean CIZS/ZnS QDs were stored in toluene in the fridge (+4 °C).

2.2.4.II Synthesis of CIZS/ZnS/ZnS core/shell/shell QDs

Preparation of CIZS QDs by hot-injection technique

Preparation of S precursor solution. 1.2 mmol (0.0384 g) of S powder was dissolved in 2 mL of OAm under sonication.

Synthesis. The synthesis of CIZS QDs was carried out according to a previously reported method¹. In a typical synthesis of CuZnInS₃ QDs, 0.4 mmol (0.0734 g) of Zn(St)₂, 0.4 mmol (0.1168 g) of In(Ac)₃, 0.4 mmol (0.1047 g) of Cu(acac)₂, 2 mL of 1-DDT, and 1 mL of OA

were mixed with 16 mL of ODE in a three-neck round-bottom flask. The mixture was degassed under vacuum for 30 min, then the atmosphere was switched to argon. The flask was heated to 225 °C (injection temperature) until a clear solution was formed, then 2 mL of the S precursor solution was quickly injected into the reaction flask. After which the reaction vessel was kept at 240 °C (reaction temperature) for 15 min. After which the reaction vessel was cooled to RT. Toluene and ethanol were used to clean the sample, with cleaned CIZS QDs stored in a fridge (+4 °C).

Preparation of CIZS/ZnS QDs

Preparation of ZnS precursor solution. 2 mmol (1.26 g) of Zn(St)₂ was dissolved in 5 mL of OA, 5 mL of 1-DDT and 10 mL of ODE at RT. The mixture was degassed for 20 min, then the atmosphere was switched to argon.

Synthesis. 3 mL of the preformed CIZS QDs solution, 5 mL of OAm and 10 mL of ODE were loaded in a three-neck round-bottom flask. The atmosphere was switched to argon after 30 min degassed at 90 °C. Under argon atmosphere, the temperature was increased to 230/260/280 °C. When the temperature reached 200 °C (injection temperature), the ZnS precursor solution was injected into the reaction vessel drop wisely with a syringe pump (Vol = 20 mL, injection rate = 5 mL/h). After the injection was finished, the heating mantle was removed, and the reaction vessel was cooled to RT. Toluene and ethanol were used to clean the sample with cleaned CIZS/ZnS QDs stored in the fridge (+4 °C).

Preparation of CIZS/ZnS/ZnS QDs

Preparation of the ZnS precursor solution. 4 mmol (2.529 g) of Zn(St)₂ was dissolved in 10 mL of OA, 10 mL of 1-DDT and 20 mL of ODE. The mixture was degassed for 30 min at RT.

Synthesis. 4 mL of the preformed CIZS/ZnS QDs solution, 5 mL of OAm and 10 mL of ODE were mixed in a three-neck round-bottom flask. The mixture was degassed at 100 °C for 30 min, and then the reaction vessel was flashed with argon. The reaction temperature was increased to 230 °C. When the temperature reached 200 °C (injection temperature), the precursor solution was injected into the reaction vessel drop wisely with a syringe pump (Vol = 10/20/40 mL, injection rate = 5 mL/h), with differing injection time of 2/4/8 h. When the injection was finished, the heating mantle was removed, and the reaction vessel was cooled to RT. Toluene and acetone were used to clean the sample and the cleaned CIZS/ZnS/ZnS QDs were stored in the fridge (+4 °C).

2.2.4.III Incorporation of QDs into PMMA block

The polymerization of PMMA block was conducted based on a precious report⁵.

Preparation of solid QDs

Solid QDs were used to building of LSCs, which were prepared using the Schlenk line to evaporate the original solvent (toluene) that employed to disperse the obtained QDs at RT.

Pre-polymerization

First, the so-called “syrup” was prepared. The 40 g of MMA monomer was heated in a beaker to 80 °C. When the MMA temperature was stabilized, 0.004 g of AIBN (100 ppm wt/wt with respect to MMA) was added. At the point, pre-polymerization took place and the monomer temperature increased to the MMA boiling temperature (95 °C). When the monomer achieved the stage of vigorous boiling, the syrup was quenched and cooled to RT.

Mixture of QDs and initiator

Here, the above obtained three types of QDs (the first one is the alloyed CIZS/ZnS QDs, the second one is CIZS/ZnS core/shell QDs and the third one is CIZS/ZnS/ZnS core/shell/shell QDs.) In a separate vial, 0.008 g of the obtained solid QDs were dispersed in 4 ml of MMA monomer solution, which was followed by the addition of 0.0016 g of lauroyl peroxide (LP) under sonication at RT.

Polymerization

The mixture of the QDs and LP in MMA monomer solution was mixed with the prepolymer syrup under stirring at RT.

The obtained solution was introduced into our home-made reaction chamber, where the polymerization reaction proceeded. The casting mould was made from two glass plates sealed with a PEFT gasket (to preserve the inert atmosphere) and clamped together. After that, the reaction chamber was put in the oven for 24 h for the polymerization to complete. The polymerization temperature was set 60 °C.

2.2.5 Experimental details for chapter 7

Materials. Copper iodide (CuI, 99.99%), indium acetate (In(OAc)₃, 99.99%), 1-dodecanethiol (1-DDT, 98%), zinc stearate (technical grade), 1-octadecene (ODE, ≥ 95%), Trioctylphosphine (TOP, 97%), diphenylphosphine (DPP, 98%), oleic acid (OA, ≥ 99%), Cetyltrimethylammonium bromide (CTAB, 99%), SUC (sucrose, technical grade), D-(+)-TRD (Trehalose dihydrate, technical grade). All chemicals were purchased from Sigma-Aldrich and used as received without any further purification.

2.2.5.I Synthesis of CIZS/ZnS QDs

The typical synthesis of colloidal CIZS/ZnS QDs was carried out according to previously reported method⁴.

Synthesis of colloidal CuInS QDs. 0.2 mmol (0.0358 g) of CuI, 0.6 mmol (0.1168 g) of In(OAc)₃ and 20 mL of 1-DDT were mixed in a 100 mL 3-neck flask. The flask was degassed for 30 min at 80 °C, and then the atmosphere was switched to argon. Under argon flux, the reaction temperature was increased to 215 °C, and held at this temperature for 10 min. Then the heating mantle was removed and the reaction vessel was cooled to RT naturally. Without purification, the crude solution was ready for the synthesis of CuInZnS alloyed QDs.

Synthesis of colloidal CuInZnS QDs.

Preparation of Zn cation exchange solution. The Zn precursor solution was prepared by dissolving 0.6 mmol (0.3768 g) of zinc stearate in 8 mL of ODE. 2 mL of TOP was injected into the flask under argon. The mixture was heated to 100 °C until clear precursor solution was obtained.

Synthesis of CIZS QDs. CIZS QDs were prepared through *in situ* cation exchange of the preformed CIS QDs. The crude CuInS QD solution was degassed at 115 °C for 30 min to remove volatiles that produced during the reaction. Then the atmosphere was switched to argon and the temperature was set at 120 °C (injection temperature). When the temperature reached to the target temperature, the zinc precursor solution was added drop wisely with a syringe which was set on a syringe pump over 30 min (injection rate = 20 mL/h) to the reaction vessel. When the injection was finished, the temperature was increased to 200 °C

and maintained at that temperature for 90 min before cooling to RT. Without cleaning, the sample was ready for ZnS shell coating.

Synthesis of colloidal CuInZnS/ZnS QDs

Preparation of Zn and S precursor solution. 4 mmol (2.52932 g) of zinc stearate was dissolved in 10 mL of OA, 10 mL of 1-DDT and 20 mL of ODE. The mixture was degassed for 2 h at 30 °C under stirring and then the reaction vessel was flashed with argon.

Synthesis of CIZS/ZnS QDs. The crude CIZS QD solution in the reaction vessel was degassed for 30 min at 120 °C to remove volatiles that produced during the reaction. Under argon atmosphere, the temperature was increased to 220 °C (reaction temperature). When the temperature reached 200 °C (injection temperature), above precursor solution was injected into the reaction vessel with a syringe pump (injection rate = 4 mL/h, volume = 40 mL), the injection taking 10 h. After the injection, the solution was stirred for another 1 h at 220 °C. Then the heating mantle was removed and the reaction vessel was cooled to RT naturally. Hot ethanol and toluene were used to clean the sample. The obtained purified CIZS/ZnS QDs were stored in toluene in the fridge (+4 °C).

Phase Transfer.

Phase transfer was carried out according to previously reported method with minor modifications⁶.

1 mL of CIZS/ZnS QD solution was added into 1 mL of chloroform. 0.2 g of CTAB was dissolved in 10 mL of water. Mix the two solutions and stir it vigorously at 35 °C for 3-4 h until opaque microemulsion solution was formed. Then the opaque solution was transferred to a heating mantle and heated to 70 °C and kept at that temperature for 10 min to evaporate

the chloroform and induce the interaction between the hydrophobic chains of the CTAB and the hydrophobic chains of the ligands that bind to the surface of the CIZS/ZnS QDs. Then the heating mantle was removed and the flask was cooled to RT. The solution was kept in the fridge (4 °C) for 72 h, which was followed filtration of the cold solution with 0.25 µm syringe filter to remove excess CTAB to get clean CTAB-costed CIZS/ZnS water solution.

2.2.5.II Preparation of sugar glasses

The preparation of sugar glasses was done according to previously reported method with minor modifications⁷.

2 g of TRD and 2 g of SUC were dissolved in 4 mL of water to get the mixture solution in a sample tube. Then 0.1/0.2/0.5 mL of CTAB-coated CIZS/ZnS QD solution was dispersed in the sugar solution under sonication. After that the mixture was transferred to a plastic cuvette and was dehydrated in the oven at 70 °C for 72 h to make sugar glasses that loaded with CTAB-coated CIZS/ZnS QDs.

2.3 Instrumentation and sample preparation

2.3.1 Spectroscopy

2.3.1.I UV-Vis absorbance spectroscopy

UV-Vis is the measurement of the attenuation of a beam of light after it passes through a sample. The absorption peak arises from the transition of electrons from the valence band to conduction band in a quantum dot. In this project UV-Vis absorption spectra were measured using a Varian Cary 60 UV-Vis spectrometer. UV-Vis-NIR absorption measurements were recorded with a Perkin Elmer LAMBDA 1050 UV/Vis/NIR spectrometer. The samples for absorption characterization are prepared by dispersing the QDs in certain solvent (toluene,

chloroform and so forth) in a 1 cm path length quartz cuvette, and the same solvent is used as the reference. As shown in Figure 2.1, the radiant source goes through the monochromator, then was being split into sample beam and reference beam, passes through the sample and the reference, then it is collected by the photodetectors. After the signal was processed, the spectra can be observed.

Based on the obtained UV-Vis absorption spectra, we can get specific information of the QD sample, for example, size estimation can be made based on the position of the excitonic absorption peak, size distribution estimation can be made based on the hwhm of the absorption spectra (small hwhm indicates narrow size distribution). It can also be used to determine the concentration of Cd-based and Pb-based QDs as reported in literature⁸⁻⁹. Recently, it was reported that it can also be used to determine Cu-In-S QDs concentration¹⁰. It is also a convenient way to monitor synthesis.

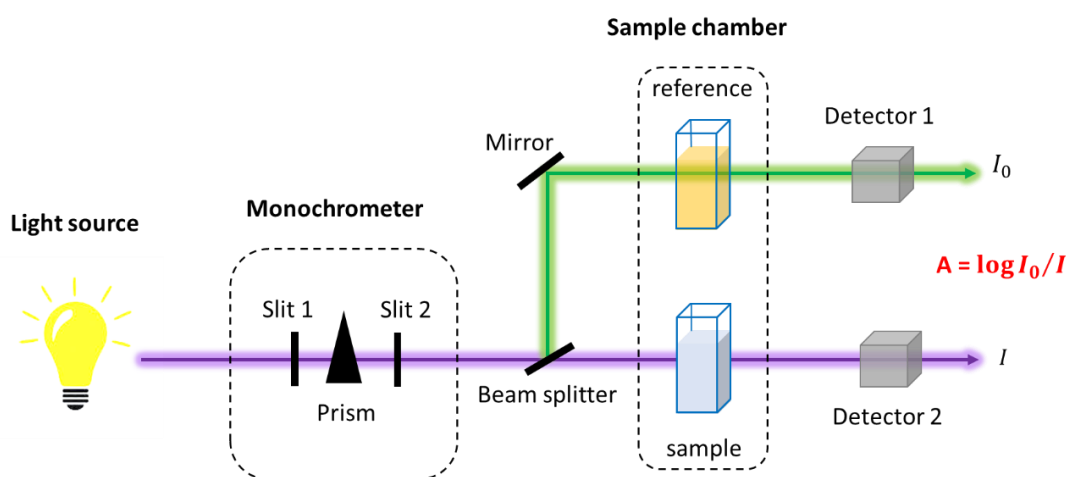


Figure 2. 1 Diagram of the operation of a dual beam UV-Vis absorption spectrometer.

2.3.1.II PL spectroscopy

PL spectroscopy is one of the most important characterization techniques for QDs. In this project UV-Vis photoluminescence spectra were recorded using a Varian Carly Eclipse fluorescence spectrometer, while NIR fluorescence measurements were measured with a

Horiba Jobin Yvon Fluorolog-3 using a Hamamastu InP/InGaAs photomultiplier (R5509-7-3) cooled to -80°C using liquid nitrogen. Samples for PL measurements were prepared by dispersing the QD sample in certain solvent (toluene, chloroform and so forth) in a 1 cm path length quartz cuvette. The operating basics are shown in Figure 2.2. The excitation light with certain wavelength (normally below 20 nm than the absorbance peak) was used to record the PL spectra. Upon excitation, the excitons (the excited electron and hole) in QDs give emission through radiative recombination and the emitted photons reached the photo sensor. PL spectra can be obtained after the process of the data being collected by the photodetector.

The exact excitation wavelength used for the PL characterization of each sample can be found in Table A 13 in Appendix (Chapter 8).

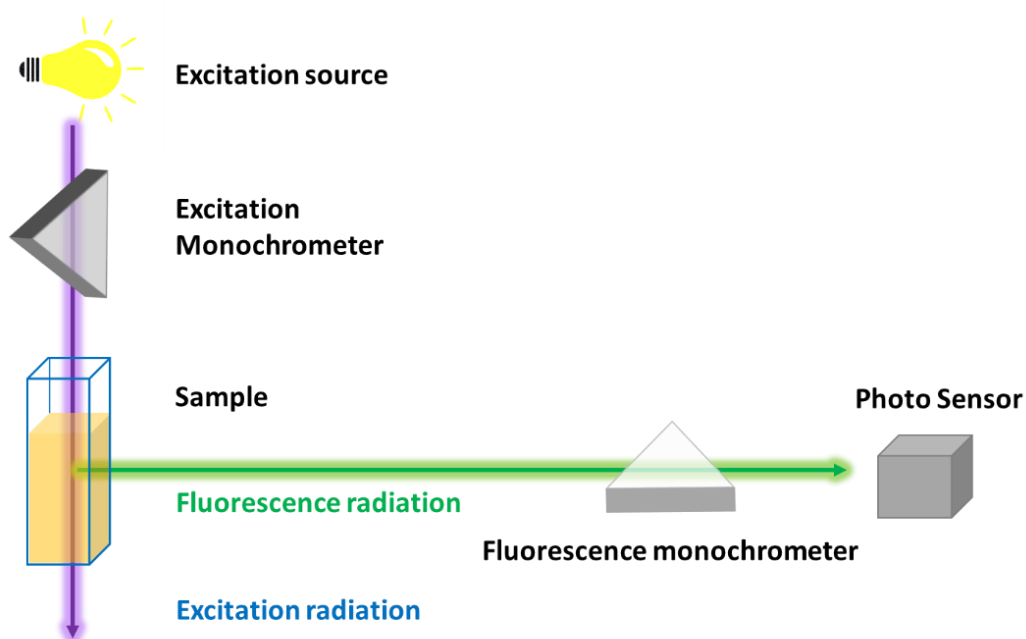


Figure 2. 2 Diagram of the operation of a photoluminescence spectrometer.

2.3.1.III Relative PLQYs

Relative PLQY is the most common way to determine the optical properties of QDs, which was done by comparing the PL intensity between the QDs and a standard dye with known QY. Certain dyes for the measurements was chosen based on the overlap of the UV-Vis absorption spectra and the emission range between the sample and the dye. It is important to control the concentration of the QD sample and the standard dye low enough (absorbance below 0.05) to avoid the reabsorption of the fluorescence. During the measurement, the PL spectra of the sample and the chosen dye are measured under the exact same conditions, including excitation with the same wavelength, the slit value for the excitation light to reach the sample and the dye, the same range of PL and so forth. After the PL spectra were obtained, the integral of the obtained PL spectra can be obtained. Then the relative PLQY of the QD sample can be calculated using the following equation 2.1:

$$\Phi_x = \left(\frac{A_s}{A_x}\right) \left(\frac{F_x}{F_s}\right) \left(\frac{n_x}{n_s}\right)^2 \Phi_s$$

Here, Φ = quantum yield, A = absorbance, F = integrated fluorescence, n = solvent refractive index and subscript s is for standard dye and x is for QD sample.

2.3.1.IV Absolute PLQYs

Absolute PLQY is another way to evaluate the optical performance of the QDs, which involves using integrating spheres instead of standard dyes. Integrating spheres manage to count all the emission that comes out from the QD sample. In this way, this determination method is based on the comparison of the number of the photons that absorbed and emitted by QDs.

In this method, the blank sample (the solvent that used to disperse the QDs in) should be measured using the integrating sphere first in order to determine the exact number of the photons that absorbed by the QDs.

2.3.1.V PL lifetime

In this project a time correlated single photon counting (TCSPC) spectrometer (Fluorolog 3 Horiba Jobin Yvon) and a range of different semiconductor diode lasers with different wavelength (340 and 370 nm “Nano LED” – HORIBA Jobin Yvon) with pulse duration shorter than 1 ns as excitation were used to perform the photoluminescence lifetime measurements.

In general, the behaviour of an excited population of fluorophores is described by a familiar rate equation 2.2:

$$\frac{dn^*(t)}{dt} = -kn^*(t) + f(t)$$

Here, $n^*(t)$ is the number of excited elements at time t , k is the rate constant of all the deexcitation processes, $f(t)$ is an arbitrary function of the time.

If the excitation is switched off at time $t=0$, it gives equation 2.3,

$$\frac{dn^*(t)}{dt} = -kn^*(t)$$

Integration gives equation 2.3,

$$n^*(t) = n^*(0)\exp(-kt)$$

The lifetime τ is equal to k^{-1} .

If a population of fluorophores are excited, the lifetime is the time it takes for the number of the excited elements to decay to $1/e$ or 36.8% of the original population according to equation 2.4,

$$\frac{n^*(t)}{n^*(0)} = e^{-t/\tau}$$

The fluorescence intensity $I(t) = k_f n^*(t)$ is proportional to $n^*(t)$ and vice versa.

Therefore, the measurement of the PL lifetime of QDs can be done by measuring the decay of the fluorescence intensity after the QDs are excited by a very short pulse at $t = 0$.

$$I(t) = I(0)\exp(-t/\tau)$$

The PL lifetime decay can be single-exponential decay:

$$I(t) = I(0)\exp(-t/\tau)$$

It can also be multi-exponential decay:

$$I(t) = I(0) \sum_i \alpha_i \exp(-t/\tau_i)$$

Here, τ_i is the lifetime component, and α_i is the fraction of this lifetime component.

As for Cu-based multicomponent QDs, the PL lifetime can normally be fitted to 2 or 3 exponentials due to the existence of different defects, which corresponds to 2 or 3 pathways that contribute to the PL lifetime of the sample.

Normally there are two ways to calculate the average PL lifetime of one sample, one is intensity average lifetime and the other way is amplitude average lifetime. As for QDs,

amplitude average lifetime is the standard way to calculate the average PL lifetime of the samples.

2.3.1.VI EDX (Energy dispersive X-ray spectroscopy)

EDX technique was employed to identify the elements that presented in the obtained QDs based on the interaction between the electron beam and the sample. As shown in Figure 2.3, upon the excitation of the electron beam, the inner electron is “kicked out” from the sample, the electron on the outer layer delocalizes to fill the blank position accompanying the release of the radiation. Since the energy gap between the electron layers is like “finger print” for each element, it can be used to identify the presented elements in the sample. In this project, measurements for all the samples were performed at 300 kV using an Oxford instruments X-max silicon Drift Detector on Titan. The data were analysed with AZtechEnergy EDX software, allowing for point scans, line scans and mapping scans to be carried out and interpreted.

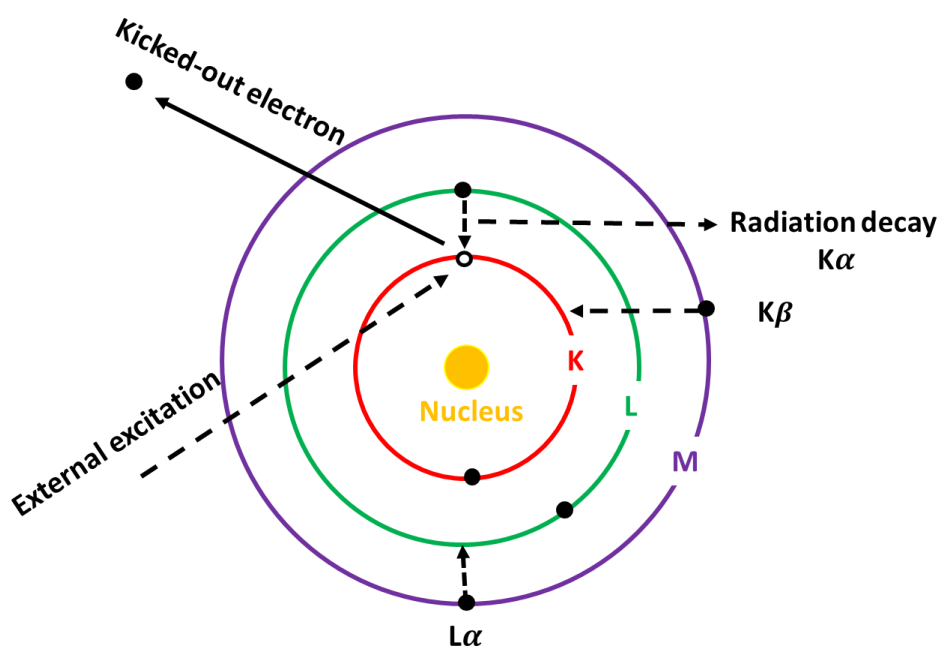


Figure 2. 3 Basic principles in EDX.

2.3.2 X-ray diffraction analysis (XRD)

This technique can be used to determine the crystal structure on the obtained QD samples through the interaction between the X-ray and the crystalline planes in the sample. A collimated beam of X-ray is generated and strikes onto the powder sample. When the Bragg's law has been satisfied, then the scattered secondary waves interfere constructively to give diffraction peaks at certain angles (Figure 2.4).

Powder X-ray diffraction (XRD) patterns were acquired on a Bruker D2 phaser in a 2θ range of $10\text{-}70^\circ$ using Cu K α radiation ($\lambda = 1.548 \text{ nm}$) as the X-ray source. The samples for XRD analysis were prepared by drying the clean sample solutions in toluene under vacuum for 2 h to get dry powder.

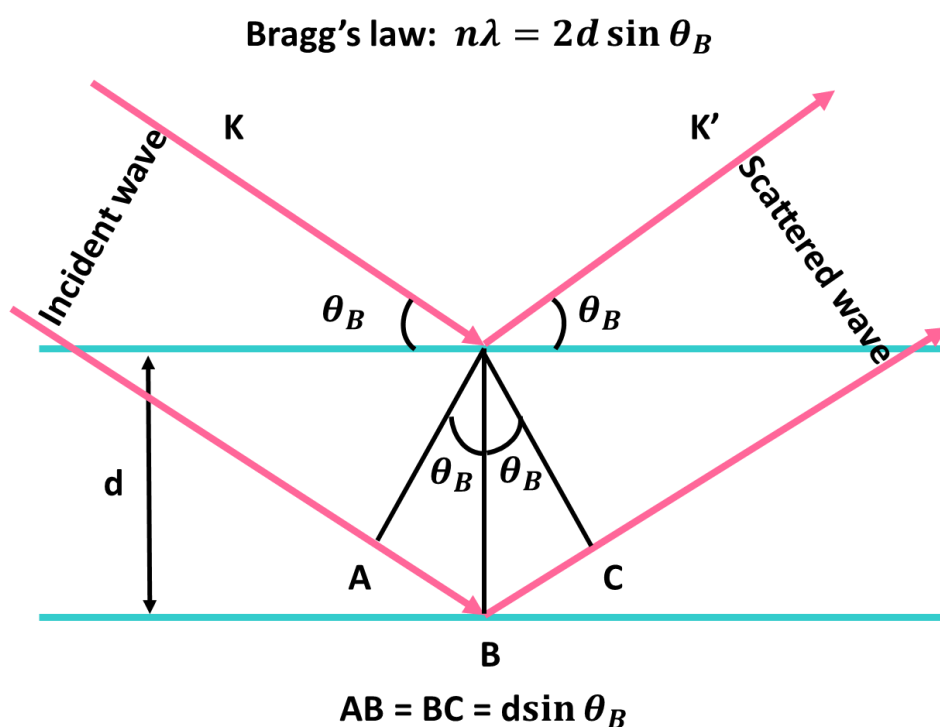


Figure 2. 4 Schematic showing Bragg's law.

2.3.3 Microscopy techniques

2.3.3.1 TEM (Transmission electron microscopy)

In this project the morphology referring to the shape and size of the obtained QDs were characterized with transmission electron microscopy (TEM) by using a Titan operating at an accelerating voltage of 300 kV. As shown in Figure 2.5, all the lenses were adjusted to give parallel electron beam onto the TEM grids that loaded with QDs. The samples for TEM characterization were prepared by dropping dilute QD solution in toluene or hexane on copper or gold TEM grids with 300 mesh, which was followed by the evaporation of the solvent for 24 h at RT.

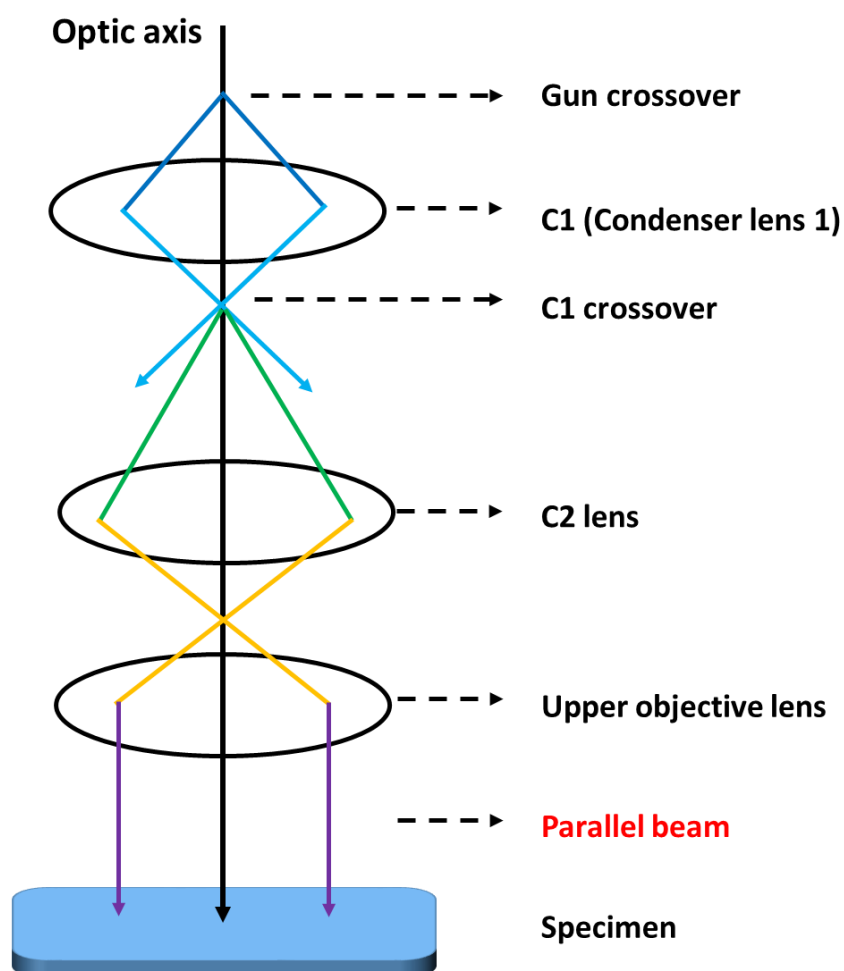


Figure 2. 5 Diagram showing the basic working principles of TEM.

2.3.3.II STEM

In this project the morphology of the obtained QDs was confirmed with scanning transmission electron microscopy (STEM) by using Titan operating at an accelerating voltage of 300 kV. The basic working principles of STEM mode of Titan are shown in Figure 2.6. The basic difference between STEM and TEM working modes is that convergent electron beam is generated onto the TEM grids under STEM working mode instead of parallel beam. Since I am working on the preparation and characterization of Cu-based multicomponent QDs, gold grids instead of copper grids were chosen to perform STEM characterization to ensure the high intensity of the sample on the grids.

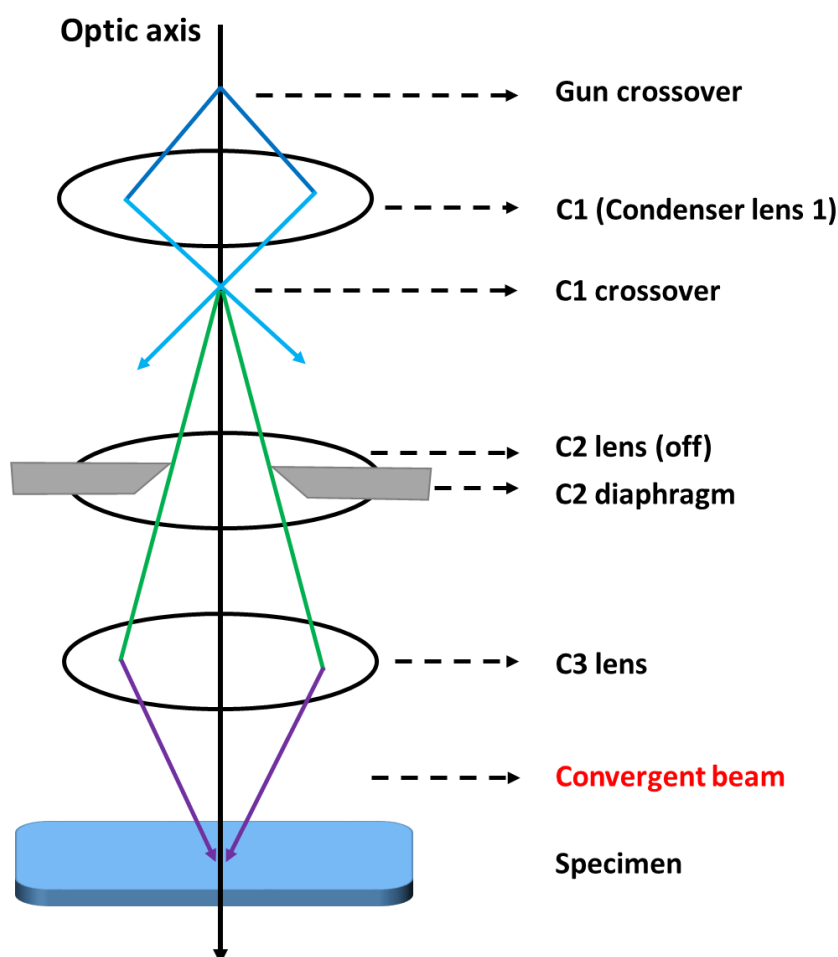


Figure 2. 6 Diagram showing the basic working principles of STEM.

2.3.3.III AFM (Atomic Force Microscopy)

AFM is a powerful technique that commonly used in material science. As shown in Figure 2.7, the tip (probe) is set to move across the sample surface with constant force using piezoelectric motors, and the system that consists of laser, mirror and detector is employed to measure the position of the tip. The physical properties of the sample including morphology, size and surface roughness can be obtained after processing the information of the position of the tip.

In this project the samples for AFM measurements were prepared by dispersing the QDs in toluene and dropping the sample solution onto the silicon wafers (1 cm*1 cm), which was followed by the evaporation of the solvent. The silicon wafers were washed with ethanol under sonication for 5 min beforehand. The measurement was done using AFM Asylum MFP-3D under soft tapping mode. Tips from NANOSENSORS (Type: PPP-NCST-50, S/N: 89310F7L1333) was used to do this measurement.

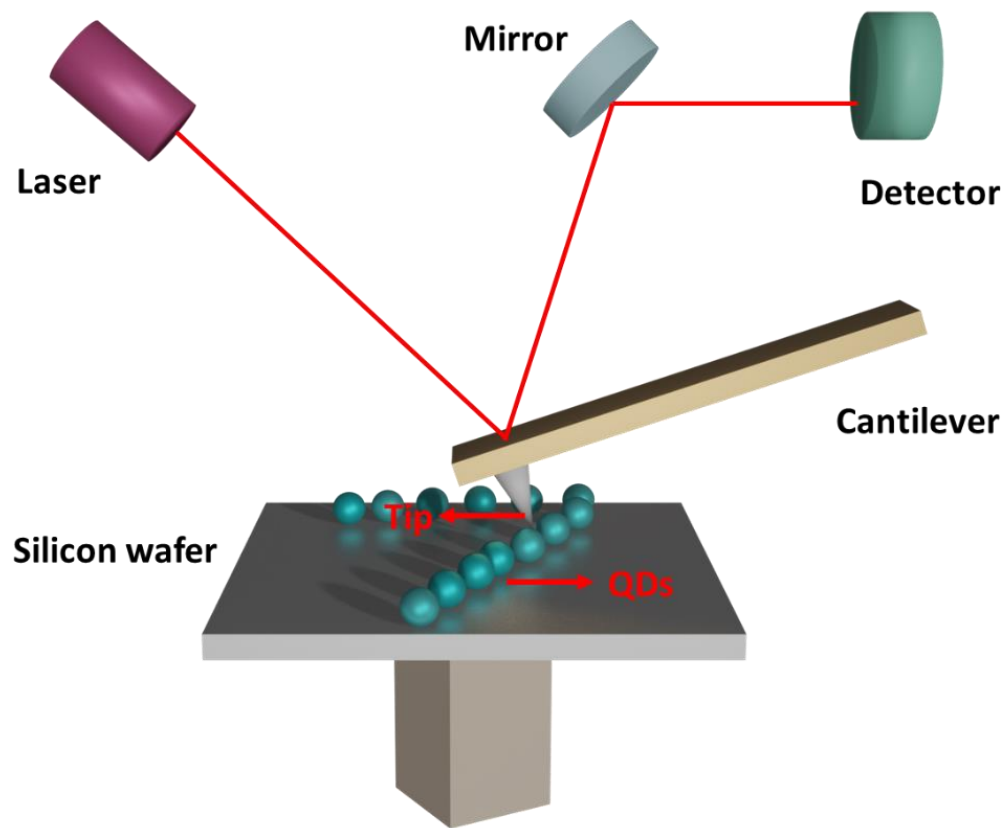


Figure 2. 7 Diagram showing the working principle of AFM.

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Chapter 3 Controlled synthesis of luminescent

CIZS/ZnS/ZnS core/shell/shell QDs

3.1 Introduction

Quantum dots (QDs) are inorganic nanocrystals and have been under continuous investigation for decades. As inorganic fluorophores, QDs outperform traditional dyes due to their significantly larger absorption cross-section¹⁻³ and higher photostability⁴. Cu-based multicomponent QDs have become some of the most promising semiconductor nanocrystals due to their low toxicity and distinctive photophysical properties compared to traditional Cd- or Pb- based quantum dots⁵⁻⁷. The optical properties of Cu-based multicomponent QDs are not only size and morphology dependent (quantum confinement effect)⁸, but also related to their elemental compositions⁹⁻¹³, which gives them even higher tunability in relation to the absorption and emission range. Emission peak shift of more than 100 nm (510-620 nm) can be achieved by changing the ratio of Cu/(Zn+In) ranging from 2.5% to 20% for the synthesis of CIZS QDs¹⁴.

High photoluminescence quantum yields (PLQYs) are the basic requirements for practical applications, including bioimaging and photovoltaic applications. It is well known that one of the most effective ways to enhance the optical properties of a quantum dot is to coat it in a shell of a wider band gap semiconductor than that of the core and therefore form a type I core/shell or even core/shell/shell heterostructured QDs. The shell helps passivate the defects on the surface of the core which can act as nonradiative recombination sites, also the excitons can be confined to the core away from the surface defects and the external micro-environment (oxygen and moisture)¹⁵⁻¹⁹. For Cu-based QDs, a ZnS shell is the best option

as the passivating shell due to the small lattice mismatch between the Cu-based core and the ZnS shell²⁰⁻²². In addition, these shells can be used to further tune the morphology of the nanocrystal with recent reports of several anisotropic morphologies that have been obtained with distinct fluorescence²³⁻²⁴.

To date, there are a number of important reports on the preparation of CIZS/ZnS QDs^{11, 14} and CIZS/ZnS/ZnS QDs²⁵ examining in detail the many reaction conditions including injection temperature, precursor choice, growth time etc. Aside from these, a key element in CIZS/ZnS QDs synthesis is ligand choice with dodecanethiol (DDT) being by far the most successful and commonly used option, due to its ability to act as solvent, ligand and S source. During a reaction, long chain ligands bind to the surface of QDs, and are also key to the formation of reactive precursors, usually in the form of metal complexes, which have a chosen stability so as to enable decomposition at a target temperature, enabling the formation of monomer and therefore nanocrystal nucleation to take place. Hence, the ligands present in the reaction system play an important role in making the reaction more controllable. If the reaction temperature is too high, the reaction is too rapid due to faster precursor decomposition. In addition, ligands help to passivate the dangling bonds that exist on the surface of the QDs (which can act as the nonradiative centers to lose energy) thus helps to enhance the PL intensity.

In the work of Jia *et al.*, the effects of the different reaction temperatures is examined (200/220/240/260 °C) on the optical properties of the obtained CIZS/ZnS QDs¹⁴, with higher reaction temperatures (260 °C) found to be detrimental to PLQYs due to the degradation of DDT ligands on the surface of the QDs and therefore resulting in a decrease in PL intensity. Higher reaction temperature induced the physical separation of the labile ligands from the surface of the QDs, which results in under- or unpassivated QDs. In another piece studying

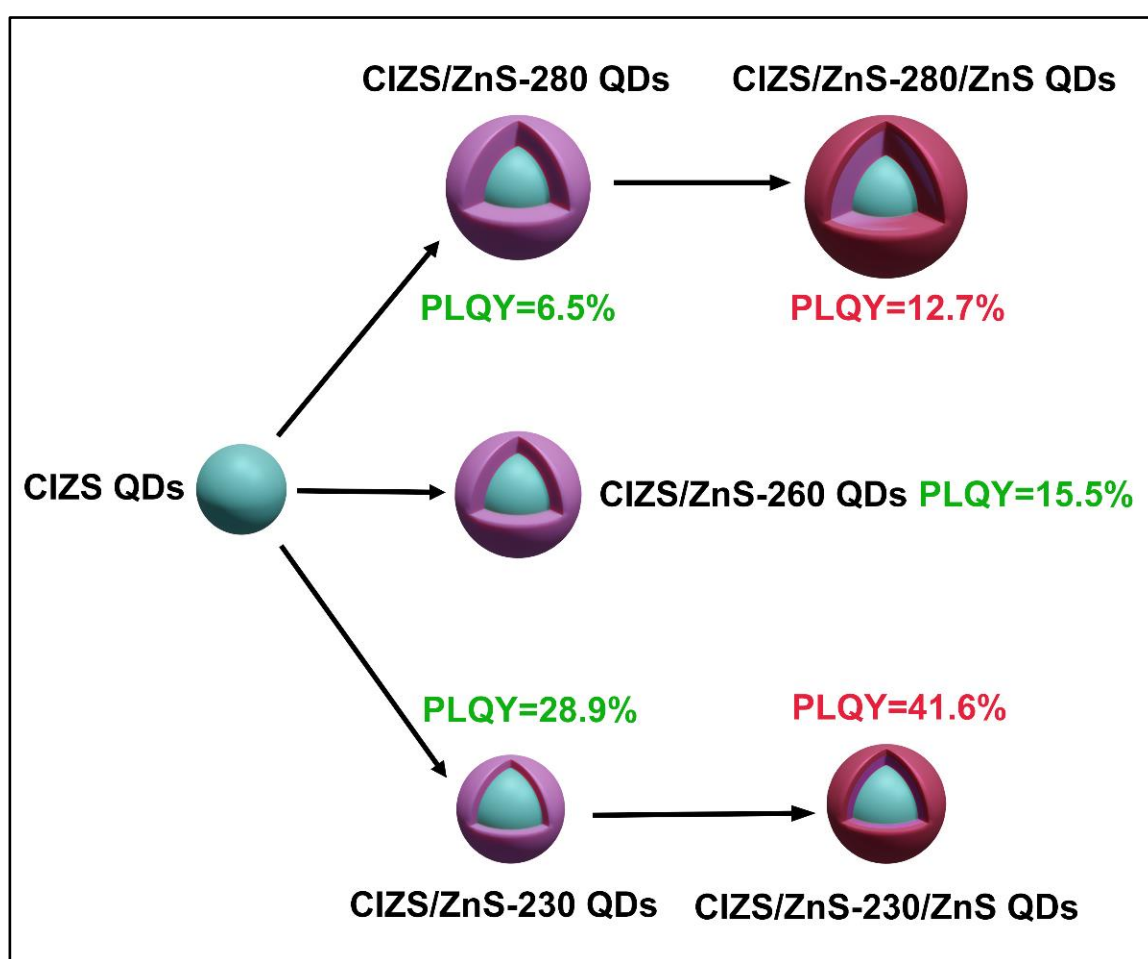
CuInS QD formation in the presence of DDT and octadecene (ODE), this decomposition product was identified as thioether dodecyloctadecylsulfide.²⁶

It has been reported that the negative effects of ligand decomposition due to higher reaction temperature can be lessened by coating with an inorganic shell with a wider bandgap²⁷. Therefore, the decreased PLQYs of CIZS/ZnS QDs formed at higher reaction temperature could be mitigated by the deposition of a second ZnS shell. This is key parameter I aim to verify experimentally.

Aside from this, the category of “Giant” shelled QDs have distinct uses due to the presence of an increased size of the QD shell, which produces non-blinking, high absorption cross-sections and strong resistance to photobleaching and other quenching process²⁸⁻²⁹. Therefore, the growth of a thick ZnS shell on a CIZS QDs is a desirable target nanomaterial. In spite of this, CIZS/ZnS QDs with relatively large diameters (≥ 10 nm) have not been obtained so far to the best of my knowledge, a fact probably due to the low reactivity of the commonly used ZnS shell precursors (zinc stearate, zinc acetate and 1-dodecanethiol). For the synthesis of QDs, either extending the growth time or increasing the reaction temperature promotes the formation of the QDs with larger sizes generally. It has been verified that larger CIZS/ZnS QDs have not been obtained even when the reaction time has been extended longer than 10 h^{11, 25}, which makes the case that increasing the reaction temperature is the sensible direction worth exploring in order to achieve fluorescent CIZS/ZnS QDs with larger sizes. (≥ 10 nm). In addition, it has been shown that by separating the shell deposition phases and forming a shell/shell NC, a larger total shell can be more easily obtained with CIZS/ZnS QDs.³⁰

Therefore, this work has been designed to investigate the effects of different reaction conditions to optimise the growth of the first ZnS shell and the second ZnS shell on the

morphology and optical properties of CIZS/ZnS QDs and CIZS/ZnS/ZnS QDs (Schematic 3.1). Through this I determine the actual reasoning for decreased PLQYs at higher reaction temperatures and explore the reaction conditions to prepare CIZS/ZnS QDs or CIZS/ZnS/ZnS QDs with larger sizes (≥ 10 nm) and optimal reaction conditions to produce highly fluorescent CIZS/ZnS QDs and CIZS/ZnS/ZnS QDs. Therefore, this work is key to the design and control of Cu-based multicomponent heterostructured QDs synthesis with optimal optical and morphological properties.



Schematic 3 1. Illustration of strategies for the preparation of the CIZS/ZnS QDs and the CIZS/ZnS/ZnS QDs.

3.2 Preparation of CIZS QDs by hot injection

The CIZS QDs were prepared using a hot-injection technique according to a previous report with minor modifications⁹. In the synthesis, S precursor solution was injected into the mixture of Cu, In and Zn precursors at 210 °C, with the total growth time of 15 min at 240 °C (see details in Experimental part). The sample was characterized with microscopy as shown in Figure 3.1A, the CIZS particles display a spherical shape and quite narrow size distribution with a 3.2 ± 0.4 nm diameter (Figure 3.1B). Figure 3.1C shows the UV-Vis absorption and PL spectra, the obtained QDs absorb light from the ultraviolet to the visible range of the spectrum. The sample is fluorescent in the visible region with the emission peak at approximately 670 nm, while the emission intensity of the CIZS QDs is too low to determine their PLQY.

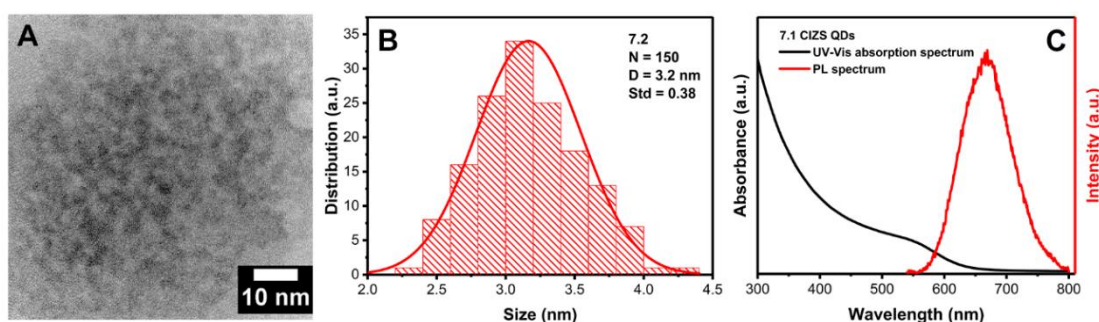


Figure 3. 1 (A) TEM images, (B) the size distribution histogram, (C) UV-Vis absorption spectrum (black line) and PL spectrum (red line) of the obtained CIZS QDs.

3.3 Preparation of CIZS/ZnS QDs

After cleaning the obtained crude CIZS QDs, the sample was dispersed in 20 mL of toluene and 4 mL of the sample solution was used to produce CIZS/ZnS QDs. The synthesis was designed to investigate the effects of different reaction temperatures on the morphology and

photophysical properties of the CIZS/ZnS core/shell heterostructured QDs. The preparation of CIZS/ZnS core/shell QDs was done with a seeded growth method using a syringe pump. The precursor solution of the shell material was injected into the reaction vessel drop wisely at three different reaction temperatures (230/260/280 °C, respectively.). This therefore produced three batches of samples, denoted as CIZS/ZnS-230 (230 °C), CIZS/ZnS-260 (260 °C) and CIZS/ZnS-280 (280 °C), respectively.

TEM and STEM images are shown in Figure 3.2A-B, with sample CIZS/ZnS-230 (prepared at 230 °C) demonstrating a branched tetrahedron shape, with the size of the sample increasing to 5.1 ± 0.8 nm (Figure 3.2C) from 3.2 ± 0.4 nm (Figure 3.1B). The fringes observed in Figure 3.2A indicate the high crystallinity of the sample. When the reaction temperature was increased to 260 °C, the particles become more branched as shown in the TEM image (Figure 3.2D), this morphology was also confirmed using STEM as shown in Figure 3.2E. The size of the sample prepared at 260 °C was determined to be 7.8 ± 1.1 nm (Figure 3.2F). When the reaction temperature was fixed at 280 °C, the morphology of the obtained CIZS/ZnS QDs display a more uniform tetrahedron shape as shown in the TEM and STEM images (Figure 3.2G-H). The size of the sample increased further to 10.3 ± 1.7 nm (Figure 3.2I).

As for the coating of the first ZnS shell, higher reaction temperature (280 °C) encourages the growth of larger CIZS/ZnS QDs, while relative mild reaction temperature (230/260 °C) boosts the formation of branched CIZS/ZnS core/shell quantum nanostructures. All three batches of samples demonstrate a narrow size distribution.

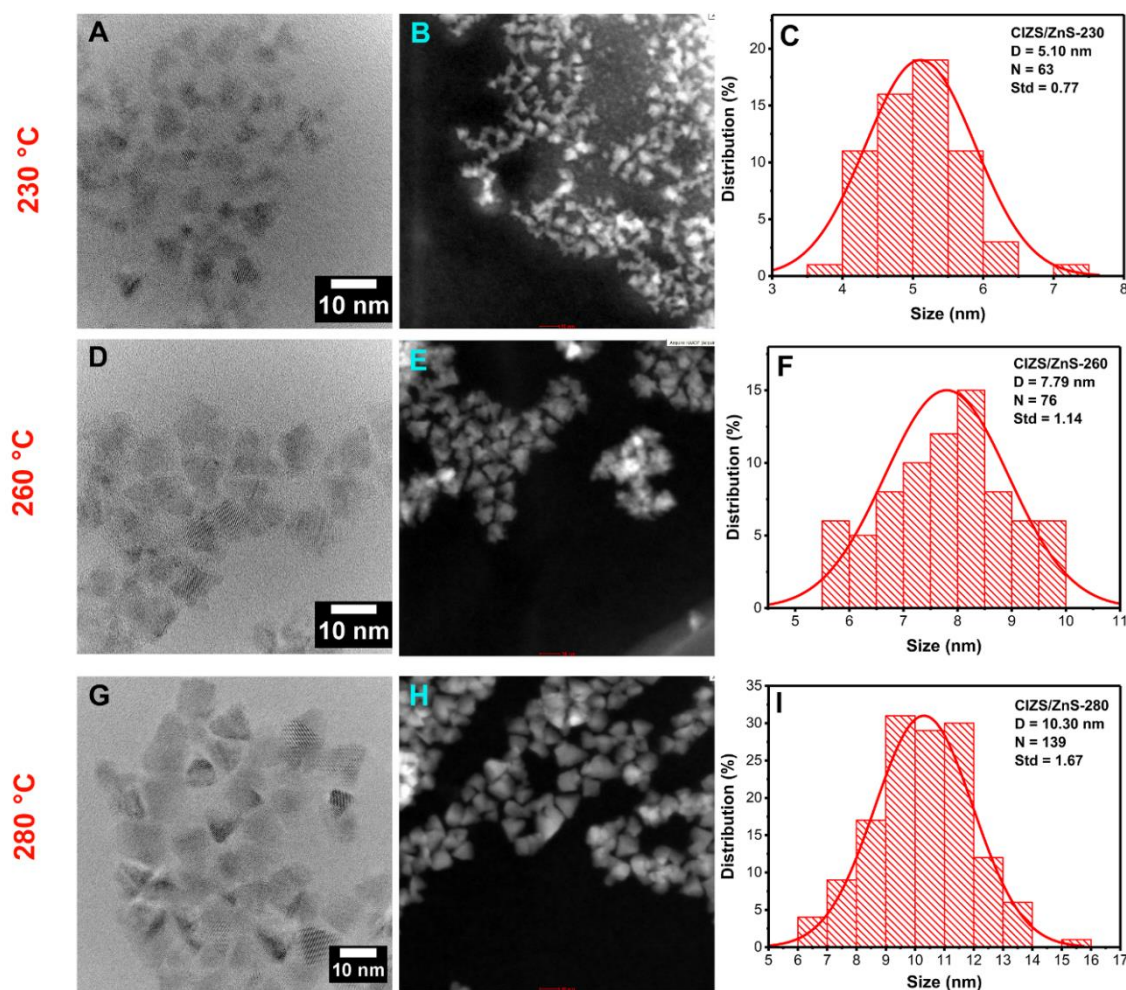


Figure 3. 2. TEM images, STEM images and size distribution histograms of CIZS/ZnS-230 (A-C), CIZS/ZnS-260 (D-F) and CIZS/ZnS-280 (G-I) QD samples.

The optical properties of the obtained three samples have been investigated (Figure 3.3), with the colour of the CIZS/ZnS QDs became lighter as the reaction temperature increased from 230 to 280 °C (Figure 3.3A). Under UV illumination, the emission brightness of the samples lowers relative to reaction temperature (Figure 3.3B). Figure 3.3C shows the UV-Vis spectra of the three samples, with all three spectra featureless with no observable excitonic absorption peak, which is a traditional trait of Cu-based multicomponent QDs, especially for core/shell nanostructures³¹⁻³³. This is due to the electron transition from the Cu^{1+} state to the conduction band being allowed upon excitation, which extends the absorption to the lower energy region and results in the featureless absorption spectra³⁴⁻³⁵.

As shown in Figure 3.3D, photoluminescent spectroscopy confirms that all three samples are fluorescent in the visible range of the spectrum, with CuInZnS/ZnS-230 displaying the highest PL intensity, with the PL intensity reducing as the reaction temperature increases. The emission range for all three samples is broad and is consistent with previous reports^{31, 36-37}. In addition, the higher reaction temperature induced a more significant blue shift, with the emission peak shifted from 700 to 665 then further to 650 nm as the reaction temperature increased from 230 to 260 then to 280 °C. Blue shifting is commonly observed regarding the synthesis of Cu-based multicomponent QDs which involve Zn³⁸⁻³⁹. Rhodamine 6G was chosen as the standard dye to determine the PLQYs of the obtained QDs. The PLQYs of the three samples were calculated to be 28.9±2.9% (CIZS/ZnS-230), 15.5±1.6% (CIZS/ZnS-260) and 6.5±0.7% (CIZS/ZnS-280), respectively. These experimental results are consistent with the observation from Figures 3.3B and 3.3D.

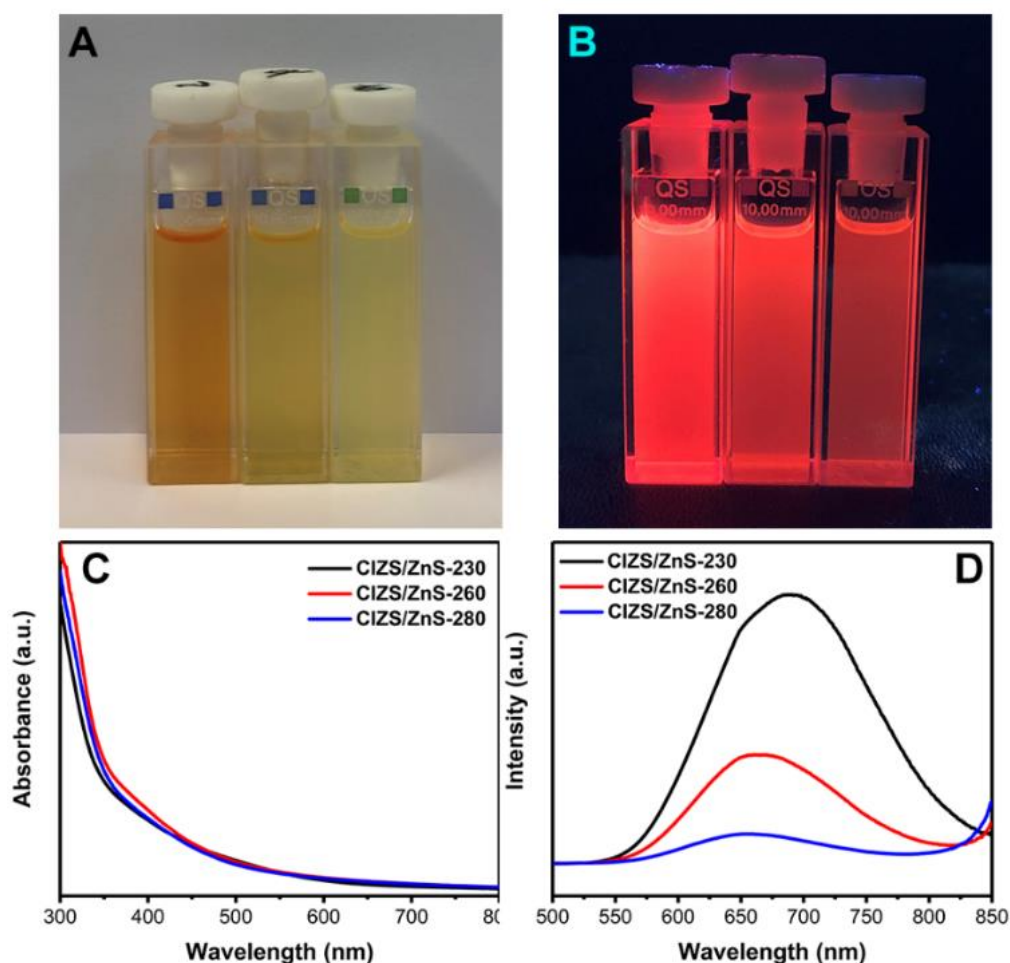


Figure 3. 3. (A-B) photographs of the samples under daylight and UV lamp (sample CIZS/ZnS-230, CIZS/ZnS-260, CIZS/ZnS-280 from left to right), respectively. (C) UV-Vis and (D) PL spectroscopy of the samples that prepared at 230(black)/260(red)/280(blue) °C.

The PL decay curves of the three samples are shown in Figure 3.4. The average PL lifetimes of the samples are determined to be 4.2×10^{-7} s, 4.38×10^{-7} s, and 5.26×10^{-7} s, respectively (See details in Table A1-A3 in Appendix). The PL lifetimes of all the three samples are long, which is a well-known trait of Cu-based QDs⁴⁰⁻⁴¹, which relates to the proposed emission mechanism of Cu-based QDs^{12, 42-44}. This long PL lifetime of non-toxic Cu-based quantum dots renders them an excellent potential candidate in bioimaging and photo-voltaic applications⁴⁵⁻⁴⁶.

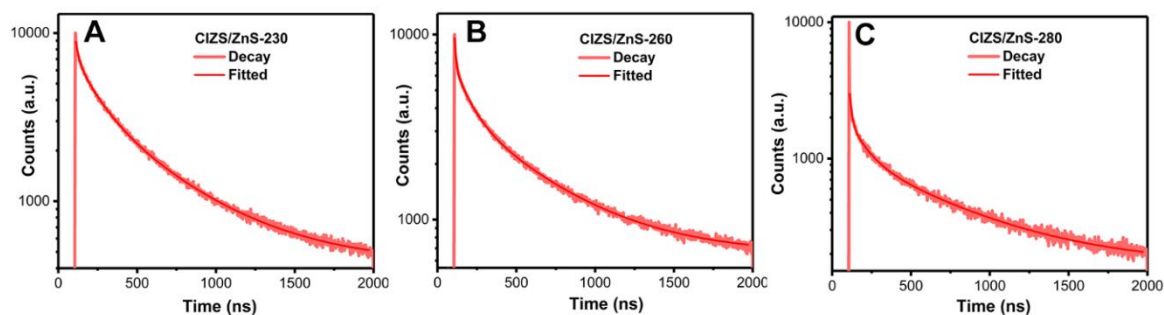


Figure 3. 4. PL lifetime curves of sample (A) CIZS/ZnS-230, (B) CIZS/ZnS-260 and (C) CIZS/ZnS-280, respectively.

3.4 Preparation of giant shell CIZS/ZnS/ZnS QDs

CIZS/ZnS/ZnS QDs with giant shell were obtained by depositing a second ZnS shell onto CIZS/ZnS-280 QDs, with the aim to enhance their optical properties further. As for the reaction conditions, the reaction temperature was set at 230 °C based on the experimental fact that relative mild reaction temperature benefits better optical properties of the obtained QDs, as demonstrated in the previous section.

The second ZnS shell was deposited using a seeded growth technique at 230 °C (see details in Experimental), utilising 4 ml of the obtained sample CIZS/ZnS-280, the reaction time was varied from 2 h to 4 h to 8 h. These samples were respectively assigned as CIZS/ZnS-280/ZnS-2h, CIZS/ZnS-280/ZnS-4h and CIZS/ZnS-280/ZnS-8h. As shown in Figure 3.5A-C, after 2 h, the shape of the obtained sample did not change significantly while the size has increased from 10.3 ± 1.7 nm to 11.3 ± 1.4 nm. When the reaction time prolonged to 4 h, the shape of the sample has been maintained and the size has increased to 12.3 ± 1.8 nm as shown in Figure 3.5D-F. The same trend has been observed with the sample after 8 h, with similar shape and larger size (13.0 ± 2.0 nm) being achieved as shown in Figure 3.5G-I.

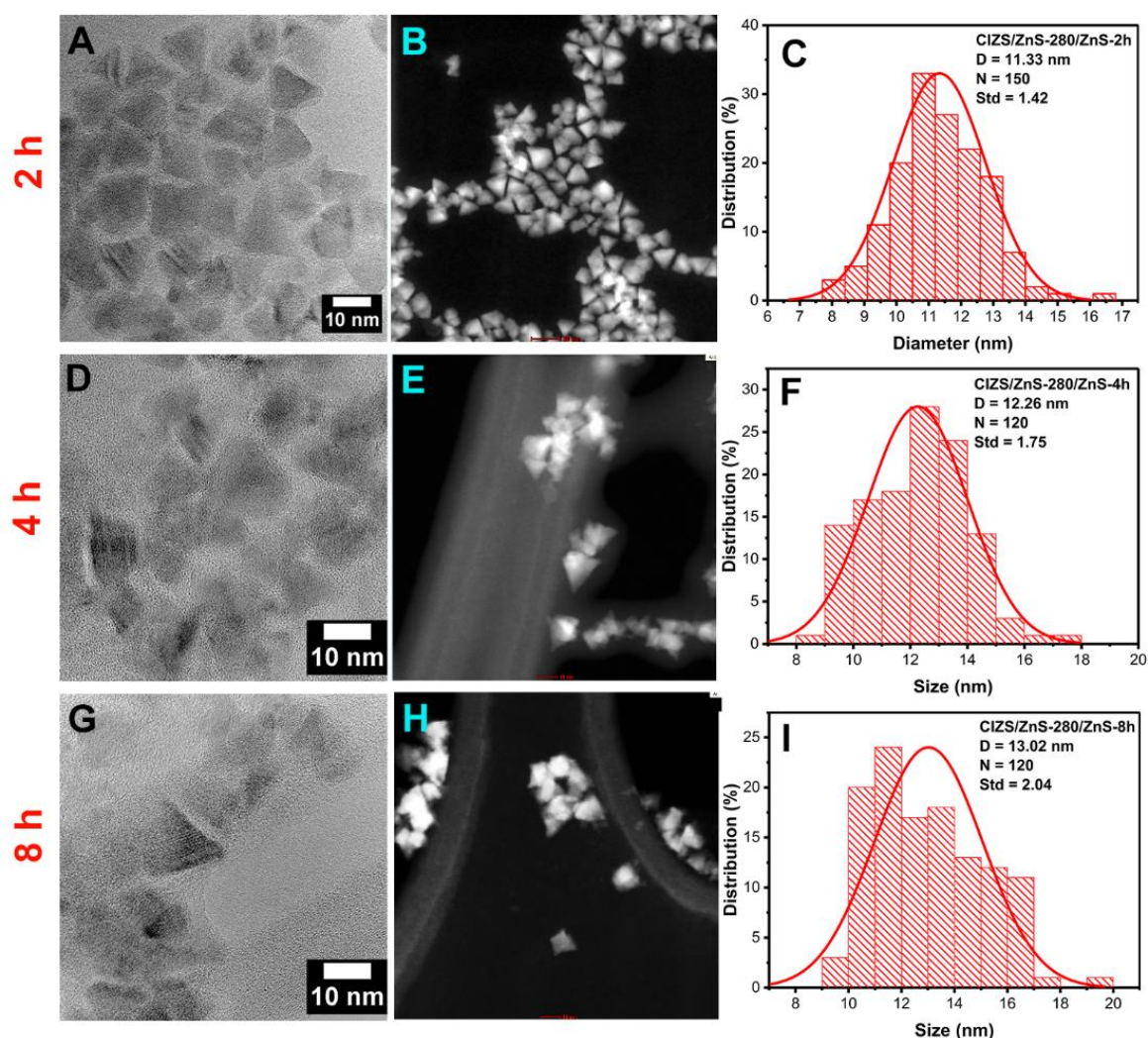


Figure 3. 5. (A-C) TEM images, STEM images and size distribution histograms of the CIZS/ZnS-280/ZnS-2h (A-C), CIZS/ZnS-280/ZnS-4h (D-F) and CIZS/ZnS-280/ZnS-8h (G-I) QD samples.

The optical properties have also been studied to investigate the effect of the second ZnS shell. As shown in Figure 3.6A, no big change of the colour of the samples from 2 h to 8 h has been observed. While the sample becomes more fluorescent as shown in Figure 3.6B as the reaction time proceeds as revealed under UV illumination. The UV-Vis absorption spectra of the three samples are shown in Figure 3.6C, it can be observed that the absorbance in the higher-energy region (≤ 400 nm) has increased as the reaction time prolonged from 2 h to 4 h. However, this trend has stopped as I prolonged the reaction time from 4 h to 8 h, with the absorbance in the high-energy region staying relatively similar. As shown in Figure 3.6D, the PL intensity of the sample has increased significantly from 2 h to 4 h, this trend

continued from 4 h to 8 h, but the degree of PL enhancement was not as high, with the PLQYs of the three samples determined to be $7.9 \pm 0.8\%$, $10.4 \pm 1.0\%$ and $12.7 \pm 1.3\%$, respectively. The increased PLQYs indicates that coating a second ZnS shell significantly enhances the optical properties of the QDs obtained.

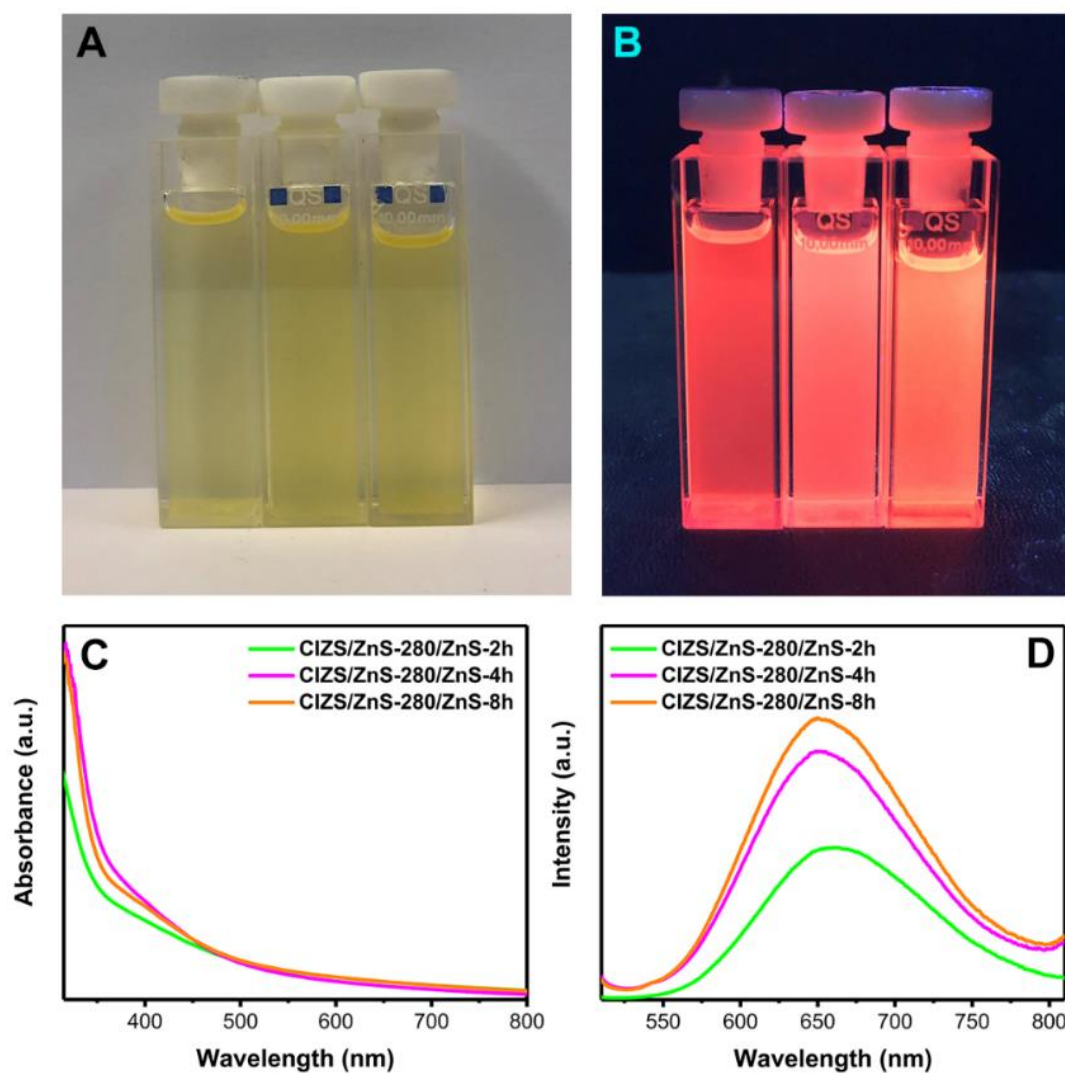


Figure 3. 6. Pictures of the samples under daylight and UV lamp, respectively. (C) UV-Vis spectra and (D) PL spectra of the CIZS/ZnS-280/ZnS QDs.

Figure 3.7A-C show the PL decay curves of the above three samples. The average PL lifetimes were calculated to be 5.86×10^{-7} s, 6.22×10^{-7} s and 6.08×10^{-7} s, respectively (See details in Table A4-A6 in Appendix). The PL lifetimes of the three samples with a second ZnS shell are longer than that of the starting sample CIZS/ZnS-280 which is $5.26 \times$

10^{-7} s. Again, the lifetime results support the earlier conclusion that coating a 2nd ZnS shell helps to prolong the PL lifetimes of the obtained QDs.

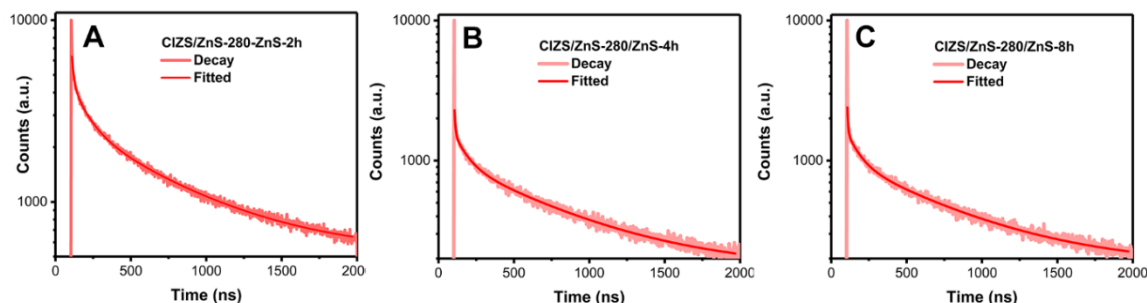


Figure 3. 7. The PL decay curves of the CIZS/ZnS-280/ZnS samples.

3.5 Preparation of highly fluorescent CIZS/ZnS/ZnS QDs

Based on the above study, it was found that the relatively mild reaction temperature to coat the first ZnS shell and coating of a second ZnS shell help to enhance the optical properties of the QDs. Herein, sample CIZS/ZnS-230, the most fluorescent CIZS/ZnS QD sample, was coated with a second ZnS shell with the time of ZnS growth being carefully controlled, with the aim to achieve highly fluorescent CIZS/ZnS/ZnS core/shell/shell heterostructure QDs.

Figure 3.8A shows the UV-Vis absorption spectra of the aliquots taken from the reaction vessel, the samples absorb light from the ultraviolet to the visible region of the spectrum, and the spectra lack the existence of any distinct excitonic absorption peak. The corresponding PL spectra of the aliquots are shown in Figure 3.8B. A slight decrease of the PL intensity can be observed after 2 h at 230 °C, which can be explained by the thin ZnS shell that formed on the CIZS, at this temperature the DDT ligands on the surface of the QDs detached, while the thin ZnS shell that formed was not enough to protect and preserve the original PL intensity of the QDs. After 4 h at 230 °C a significant increase of the PL intensity can be noticed, which is due to the continuous growth of ZnS. Interestingly after

this, the PL intensity started to decrease when grown for 8 h, which could be attributed to strain formed in the core/shell heterostructure. The most fluorescent sample was fully characterised, with the PLQY of sample CIZS/ZnS-230/ZnS-4h determined to be $41.6 \pm 4.2\%$ (with Roahdamin 6G as the standard dye), and the average PL lifetime of sample CIZS/ZnS-230/ZnS-4h was determined to be 4.26×10^{-7} s (Figure 3.8C, see details in Table A7 in Appendix). As shown in Figure 3.8D and Figure 3.8E, a branched morphology has been obtained after deposition of the second ZnS shell at 230 °C for 4 h, the size of the sample was measured to be 6.1 ± 0.9 nm (Figure 3.8F).

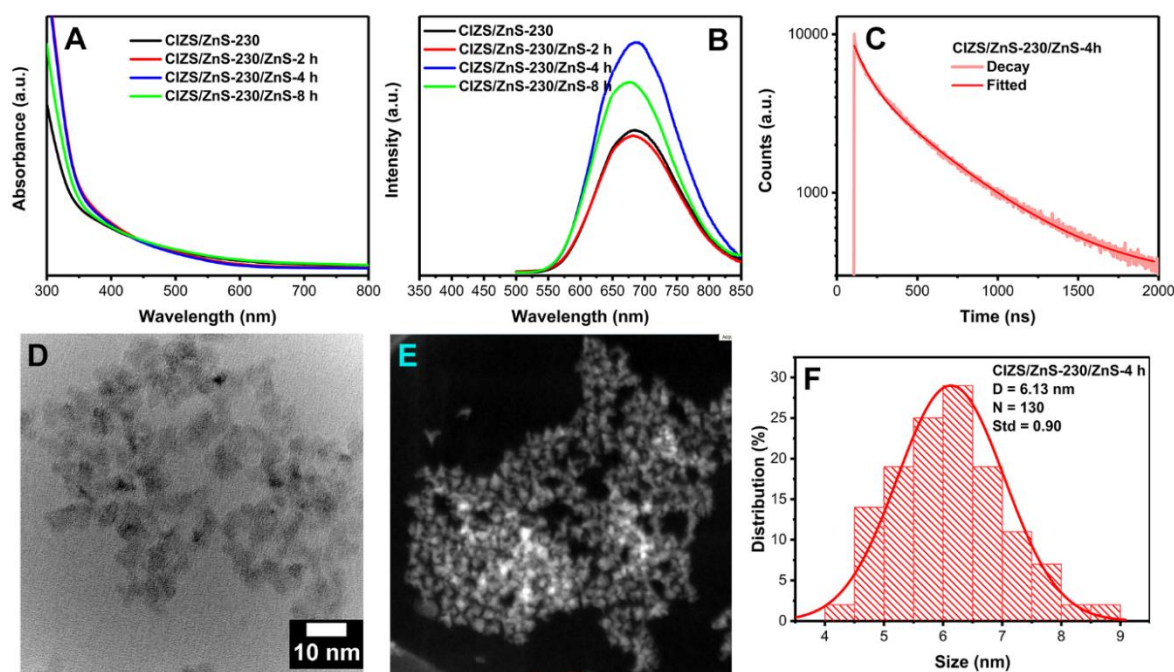


Figure 3. 8. (A) UV-Vis absorption spectra, (B) PL spectra and (C) PL decay curve, (D) TEM image, (E) STEM image and (F) size distribution histogram of sample CIZS/ZnS-230/ZnS-4h.

3.6 Discussion of Trends

A number of changes in properties of the CIZS/ZnS samples relative to reaction temperature are clear, resulting in an evolving morphology from a branched type of shape to the defined tetrahedron, a distinct increase in NC size, a strong blue shift in UV-Vis absorption and a

decrease in PL intensity. These trends are key to understanding the effect that change in temperature has upon the reaction.

The blue shift of the emission peak observed as the growing of the ZnS shell can be attributed to the combined effects of (1) the filling up of the intra-bandgap states,⁴⁷⁻⁴⁸ and (2) the widening of the bandgap by the entrance of the Zn ions.⁴⁹ Band gap widening by the entrance of Zn ions into the lattice⁴⁹ can take place *via* diffusion of them into the pre-existed Cu-based seeds. This induces a widening of the band gap, which is quite similar to the doping of Zn into CIS thin films.⁵⁰ In addition, due to the growth of the second ZnS shell, certain surface defects have been passivated, making direct recombination of the electron from the conduction band with the hole from valence band more likely, thus this also gives rise to emission with higher energy, and hence a blue shift of the PL peak.

The ZnS shell precursors have higher reactivity at increased reaction temperatures. This has given rise to larger CIZS/ZnS QDs being formed as the reaction temperature increased. Unfortunately, due to the faster ZnS deposition at higher reaction temperature and therefore a more kinetic controlled growth process, I postulate that a substantial increase in stacking defects and/or interfacial defects in the ZnS shell occurs, which act as non-radiative sites.⁵¹ This therefore I propose is the reason for decreased PLQYs of the obtained core/shell heterostructured CIZS/ZnS QDs as temperature is increased.

Aside from the stacking faults and interfacial defects, the degradation of DDT ligands that bind to the surface of the CIZS/ZnS QDs at higher reaction temperature (260 °C) also give rise to the decreased PLQYs of the QDs.¹⁴ Generally, coating of a second inorganic shell can counteract this negative effect and enhance the optical properties of the QDs dramatically. To verify this a second ZnS shell was deposited on the preformed CIZS/ZnS QDs. Due to this, the PL intensity of the sample CIZS/ZnS-280/ZnS increased as the coating

of the second ZnS shell increased. However, it has been found that the PLQY of sample CIZS/ZnS-280/ZnS only reached a maximum of $12.7 \pm 1.3\%$ and therefore was not as high as that of sample CIZS/ZnS-230, which reached $28.9 \pm 2.9\%$. Therefore, I propose that higher reaction temperature not only cause ligands degradation, but also promotes the formation of defects during the fast deposition of the shell materials onto the preformed cores and therefore defects formed due to the fast deposition of the first ZnS shell materials can only be alleviated to a certain level *via* the deposition of a second shell.

In this work, I have carried out the synthesis of heterostructured CIZS/ZnS QDs and CIZS/ZnS/ZnS QDs and investigated the effects of various reaction conditions (reaction temperature and growth time) on the morphology and photophysical properties of the obtained Cu-based multicomponent heterostructured QDs. It has been found that relative mild reaction temperature is key in obtaining more fluorescent heterostructured QDs. Aside from this the coating of a second ZnS shell enhances the optical properties of the core/shell QDs further (increased PLQYs and prolonged PL lifetimes). It has been verified that the decreased PL intensity of the QDs at relatively high reaction temperature is not only the result of the ligand degradation but is also due to stacking defects/interfacial defects formed due to the fast deposition rate of the precursors at higher reaction temperature, which can only be alleviated to a limited level by coating a second layer of ZnS. Additionally, increasing the reaction temperature, does enable the formation of CIZS/ZnS heterostructured QDs with relatively large sizes (≥ 10 nm). Overall, I believe that this work is of great significance paving the way to Cu-based heterostructured QDs with ever improving photophysical properties.

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Chapter 4 Novel “ice-cream cone” like Cu-In-(Zn)-S/ZnS nanoheterostructures

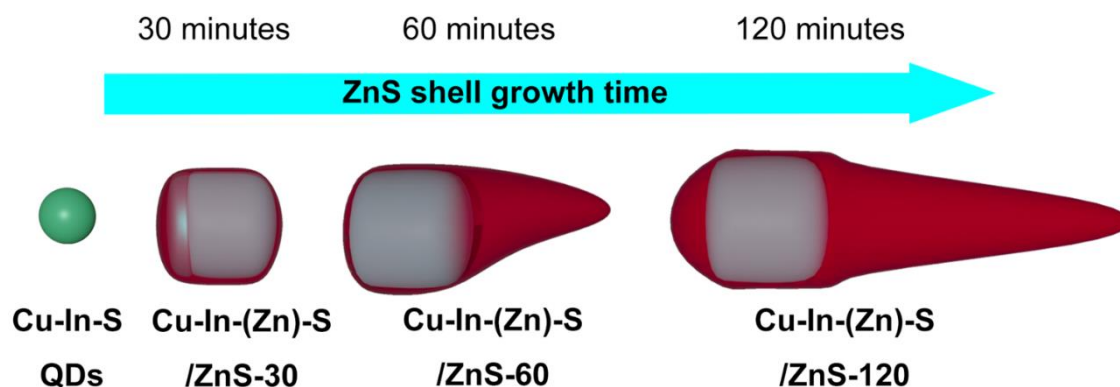
4.1 Introduction

Controlling the morphology of nanocrystals has always been a very important area because the optical properties of QDs are strongly dependent on their morphologies¹⁻². Much effort has been focused on the investigating of the growth mechanisms for anisotropic geometries³⁻⁸. Fluorescent Cd-based QDs with nonspherical shapes have been widely investigated^{3, 9-12} even rod-in-rod structures¹³ or dot-in-rod structures with circularly polarized luminescence¹⁴. Based on the previous work, it is widely accepted that WZ (Wurtzite) seeds are necessary for the formation of 1D nanorod structure and ZB (zinc blende) core is the basis for the preparation of branched nanostructures¹⁵⁻¹⁶. In contrast, the manipulation of the morphology of Cu-based quantum dots has been developed to a limited level with some nonspherical shapes being acquired (including ternary or quaternary nanoplatelets¹⁷⁻²⁰, nanorods²¹⁻²⁶ and tetrapods²⁷). Only several of these papers reported the preparation of fluorescent nanocrystals. For example, Ward van der Stam prepared NIR emitting CuInSe₂/CuInS₂ dot-in-rod structure through quite complex cation exchange technique²⁸. Two groups prepared fluorescent CuInS₂/CdS heterotetrapod nanocrystals²⁹⁻³⁰. However, these two tetrapod nanostructures still contain highly toxic element Cd, which hinders their practical applications. Importantly, the growth mechanisms that proposed for these two similar tetrapod structures are different, one is composed of a CH (chalcopyrite) CuInS₂ core and WZ CdS arms²⁹, while the other one involved the growth of WZ CdS arms on the ZB CuInS₂ core³⁰. Normally, the growth mechanisms that proposed for Cu-based multicomponent anisotropic nanostructures are consistent with the ones that proposed for much more

explored Cd-based counterparts. The above case is an exception, which indicates that the growth mechanisms for Cu-based multicomponent anisotropic geometries have not been fully understood. Therefore, there is an emerging interest to further explore the synthesis of environmental friendly, highly fluorescent Cu-based multicomponent nanocrystals with elongated or branched morphologies due to their unique optical properties and a broad range of potential applications³¹⁻³⁵.

In order to achieve better optical performance of QDs, CdS or ZnS shell can be deposited onto the preformed bare seeds³⁶⁻³⁸. The quite wide band gap (3.7 eV)³⁹, low toxicity and small lattice spacing mismatch between ZnS and the multicomponent Cu-based core (ternary or quaternary)⁴⁰ renders it the best option to passivate the bare Cu-based core and give the nanocrystals high QYs and better photostability. The two-step seeded growth technique is the most useful one to prepare core/shell heterostructures⁴¹. It is possible for us to better manipulate the synthesis with this technique being employed by tuning the addition rate of the shell precursors and quenching the reaction at any time point (better control the thickness of the shell that grown onto the core), especially for the delicate reactions to make Cu-based multicomponent anisotropic heterostructures.

Here, highly fluorescent Cu-based multicomponent Cu-In-(Zn)-S/ZnS anisotropic “ice-cream” like nanoheterostructures have been prepared using a straightforward seeded growth approach (Schematic 4.1). The growth mechanism and optical properties of the obtained “ice-cream” like nanoheterostructures have been investigated. This work presents a further step to the development of highly luminescent Cu-based multicomponent anisotropic nanostructures as well as their potential applications.



Schematic 4 1. Schematic presentation of the synthesis of the “ice-cream cone” like heterostructures.

4.2 Synthesis of ZB Cu-In-S QDs

The ZB Cu-In-S QDs were prepared using the established heating-up technique, heating a mixture of CuI, In(Ac)₃, 1-DDT and ODE to 210 °C for 2 h (see Experimental part for details)³⁰. Here, 1-DDT was used as both the sulfur source and the ligand in this reaction and ODE was used as the solvent.

Figure 4.1A shows the TEM image of the as prepared Cu-In-S QDs, which display a spherical shape with an average diameter of 2.7 ± 0.3 nm (Figure 4.1B) and a limited size distribution. The crystal structure of the Cu-In-S QDs was determined to be ZB by XRD analysis (Figure 4.1C). As shown in Figure 4.1D, the UV-Vis absorption spectrum is essentially featureless, lacking presence of any well-defined exciton absorption peak, which is a traditional trait of Cu-based multicomponent quantum dots⁴²⁻⁴⁴. It is believed that this intrinsic trait can be attributed to the existence of Cu¹⁺-related defects, especially for the Cu-based QDs that are prepared with cation ratio of Cu:In $\approx$ 1:1. That is because the optical transition of an electron from Cu¹⁺ to conduction band is allowed upon excitation besides the excitonic transition from valence band to conduction band, which results in the extended tails reaching lower energy regions in the UV-Vis absorption spectra⁴⁵⁻⁴⁶. The sample is

fluorescent in the visible/NIR region with an emission peak centred on 770 nm with a fwhm of 150 nm. The PLQY of the sample was determined to be 2.7 % using HITCI as the standard dye.

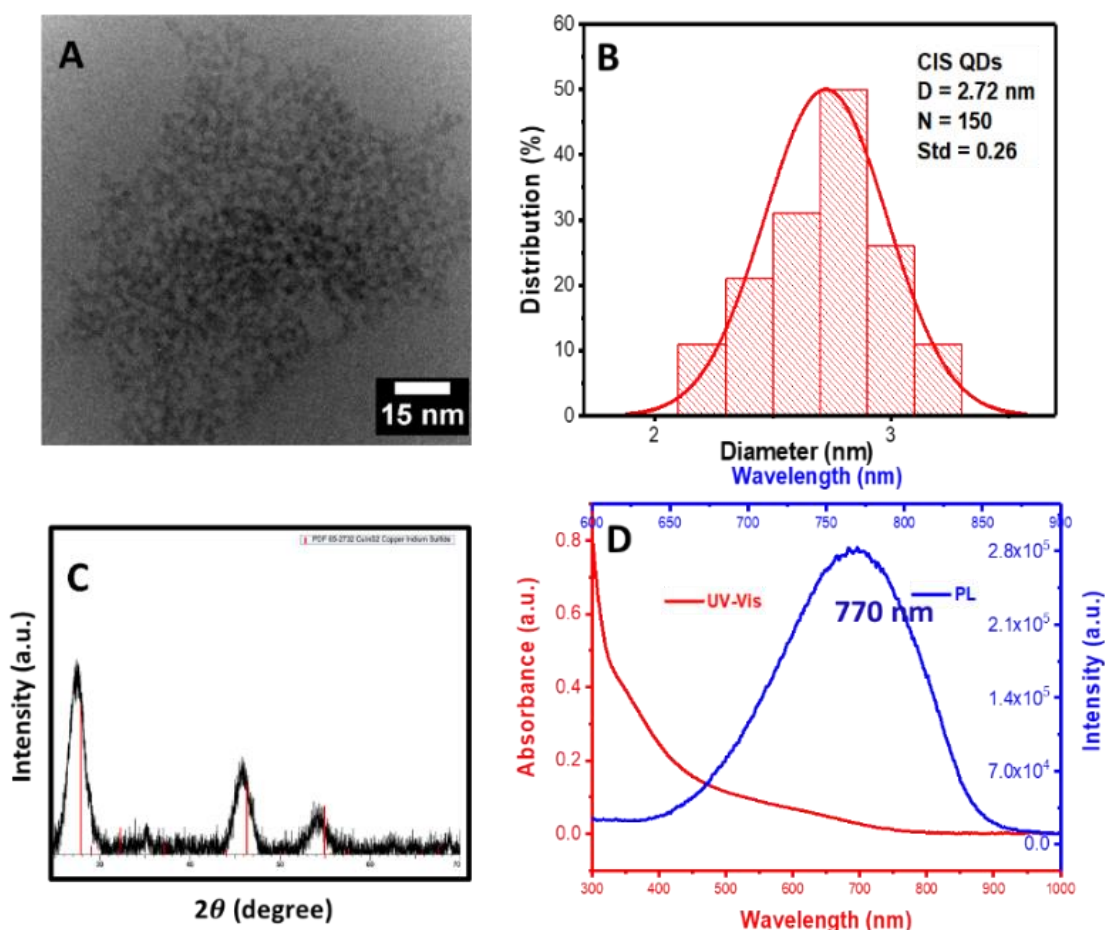


Figure 4. 1 (A) TEM image, (B) diameter histogram, (C) XRD diffraction pattern and (D) UV-Vis spectrum (red line) and PL spectrum (blue line) of the obtained Cu-In-S QDs.

4.3 Investigation of products after 30 min reaction

After Cu-In-S QDs were prepared, a ZnS shell was deposited onto the Cu-In-S seeds to improve the optical properties and stability of the sample, which was done by employing a seeded growth method (see Experimental part for details). The ZnS shell precursor solution consisted of Zn(St)₂ in a solution of OA, DDT and ODE, and was injected into the reaction

vessel loaded with the Cu-In-S seeds with total injection time of 120 min. In order to monitor the evolution of the nanostructures over the reaction time and investigate the growth mechanism of their formation, I have taken aliquots from the reaction mixture for further studies after 30, 60 and 120 min.

The sample aliquot taken out at 30 min was denoted as Cu-In-(Zn)-S/ZnS-30. As shown in Figure 4.2A-C, after 30 min the majority of the particles display short cylindrical morphology with the diameter increasing to $\approx 30.2 \pm 3.8$ nm (Figure 4.2D) from $\approx 2.7 \pm 0.3$ nm for the Cu-In-S seeds (Figure 4.1B), and the length being calculated to be 30.3 ± 4.4 nm (Figure 4.2E). The clear lattice fringes indicate the high quality of the crystal structure. A small amount of cone-like structures have been observed at this time point as shown in Figure 4.2B-C. The crystal structure of Cu-In-(Zn)-S/ZnS-30 is also determined to be the ZB phase (Figure 4.2F) by XRD analysis. The morphology of the sample was verified further with STEM images and is shown in Figure 4.2G and Figure 4.2I (more STEM images of Cu-In-(Zn)-S/ZnS-30 can be found in Figure A1 in Appendix).

EDX line scanning has been performed on Cu-In-(Zn)-S/ZnS-30 to determine the elemental distribution along two different directions, parallel to the top and bottom surfaces of the cylindrical structure and perpendicular to the top and bottom surfaces, respectively. Interestingly, different elemental distribution trends can be observed along the two different scanning directions. The line scanning spectra shown in Figure 4.2H were carried out along the direction parallel to the top and bottom surfaces of the cylinder (marked with orange line in Figure 4.2G). It was found that elements Cu and In are distributed evenly along the scanning direction instead of being confined in a small spot in this structure, considering the small size of the Cu-In-S core compared to the much larger size of Cu-In-(Zn)-S/ZnS-30. It is expected that elements Zn and S can be found along the whole scanning range since the

two elements are from the ZnS shell, while the even distribution of elements Cu and In instead of being confined in one small spot is an excellent indication that in fact an alloyed Cu-In-(Zn)-S/ZnS structure was formed at this stage, which is a common phenomenon during ZnS shell coating.⁴⁷⁻⁵² The interdiffusion between the core and the shell was also reported by Min Fu *et al.* using inductively coupled plasma-optical emission spectroscopy and X-ray photoelectron spectroscopy.⁵³ Here, the high reaction temperature (230 °C) and the similar size of elements Zn, Cu and In facilitated Zn diffusion into the Cu-In-S core, which induced the formation of the alloyed Cu-In-(Zn)-S/ZnS structure. The intensities of elements Zn and S are much higher than that of elements Cu and In (Figure 4.2H), which is due to the large volume ratio between the much larger Cu-In-(Zn)-S/ZnS-30 (diameter $\approx$ 30 nm) core/shell structure and the original small Cu-In-S seeds (diameter $\approx$ 3 nm). In contrast, it is a completely different case when the line scanning was carried out along the direction perpendicular to the top and bottom surfaces of the cylinder (indicated by the orange line in Figure 4.2I). As shown in Figure 4.2J, the intensities of Zn and S are higher due to the much greater size of nanostructures upon the incorporation of the elements. Interestingly, the intensity of Cu is much higher at one side (1/4 of the total length of the cylinder) than the opposite side (the remaining 3/4) of the cylinder, and indicates that more Cu is located in this 1/4 part of the cylindrical structure than the amount of Cu in the remaining 3/4 parts (line scanning has been carried out upon multiple particles as shown in Figure A2A-D in Appendix). In addition, two adjacent Cu-In-(Zn)-S/ZnS-30 nanoparticles were scanned at the same time, resulting in a relatively symmetrical distribution of Cu intensities. Additionally, the heavier distribution of Cu at one side of the cylinder accounted for the intensity contrast that is shown in the TEM images (Figure 4.2A-C, darker side of the cylinder) and STEM images (Figure 4.2G and Figure 4.2I, brighter side of the cylinder). The occurrence of Zn and S outside the alloyed Cu-In-(Zn)-S part observed in Figure 4.2H and

Figure 4.2I indicates that an alloyed Cu-In-(Zn)-S structure has been obtained with a thin ZnS shell forming on the outside after 30 min of the reaction.

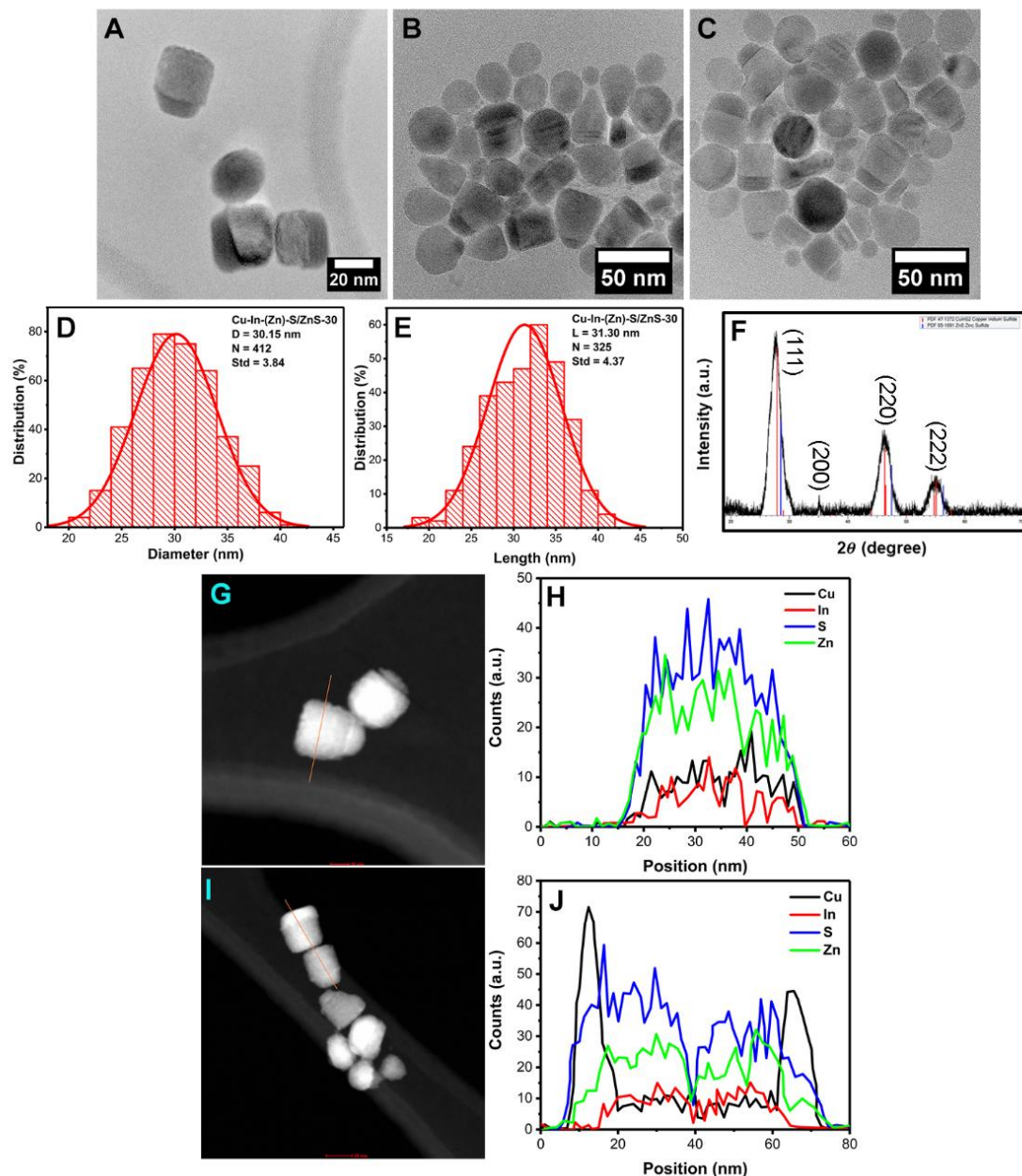


Figure 4. 2 (A-C) TEM images, (D) Diameter histogram, (E) Length histogram and (F) XRD diffraction pattern of the sample Cu-In-(Zn)-S/ZnS-30. (G-H) STEM image and corresponding line scanning spectra following the direction of the orange line in Figure 4.2G. (I-J) STEM image and the corresponding line scanning spectra of the orange line in Figure 4.2I.

4.4 Investigation of products after 60 min reaction

An aliquot after 60 min was also taken out from the reaction vessel for characterization, which is denoted as Cu-In-(Zn)-S/ZnS-60. Figure 4.3A-C shows the TEM images demonstrating that the nanoparticles with the cone-like morphology clearly dominated in occurrence as the reaction proceeds. The diameter of the structure maintained the same relative value ($\approx 30.0 \pm 3.9$ nm, Figure 4.3D), while the length of Cu-In-(Zn)-S/ZnS-60 increased to 44.8 ± 12.2 nm (Figure 4.3E) from 31.3 ± 4.4 nm of Cu-In-(Zn)-S/ZnS-30 (Figure 4.2E). The crystal structure was determined to be WZ of Cu-In-(Zn)-S/ZnS-60 (Figure 4.3F). In addition, the intensity contrast across particles observed for Cu-In-(Zn)-S/ZnS-30 are not clearly observable for Cu-In-(Zn)-S/ZnS-60. EDX line scanning has been performed on Cu-In-(Zn)-S/ZnS-60 to verify the observation from TEM images. As shown in Figure 4.3G, the intensity contrast can hardly be observed. The line scanning spectra (Figure 4.3H) of the two adjacent particles along the direction indicated with the orange line in Figure 4.3G confirmed the even distribution of elements Cu and In in both particles along this direction. The line scanning spectra displayed in Figure 4.3J along the direction indicated with the orange line in Figure 4.3I demonstrates that elements Cu and In are confined in the “head” of the “ice-cream cone” like structure. These two elements can also be observed to distribute throughout this “head” part evenly, in contrast to the uneven distribution of Cu and In after 30 minutes. The “cone” part of the “ice-cream cone” like structure consists of elements Zn and S, while elements Cu and In can scarcely be detected.

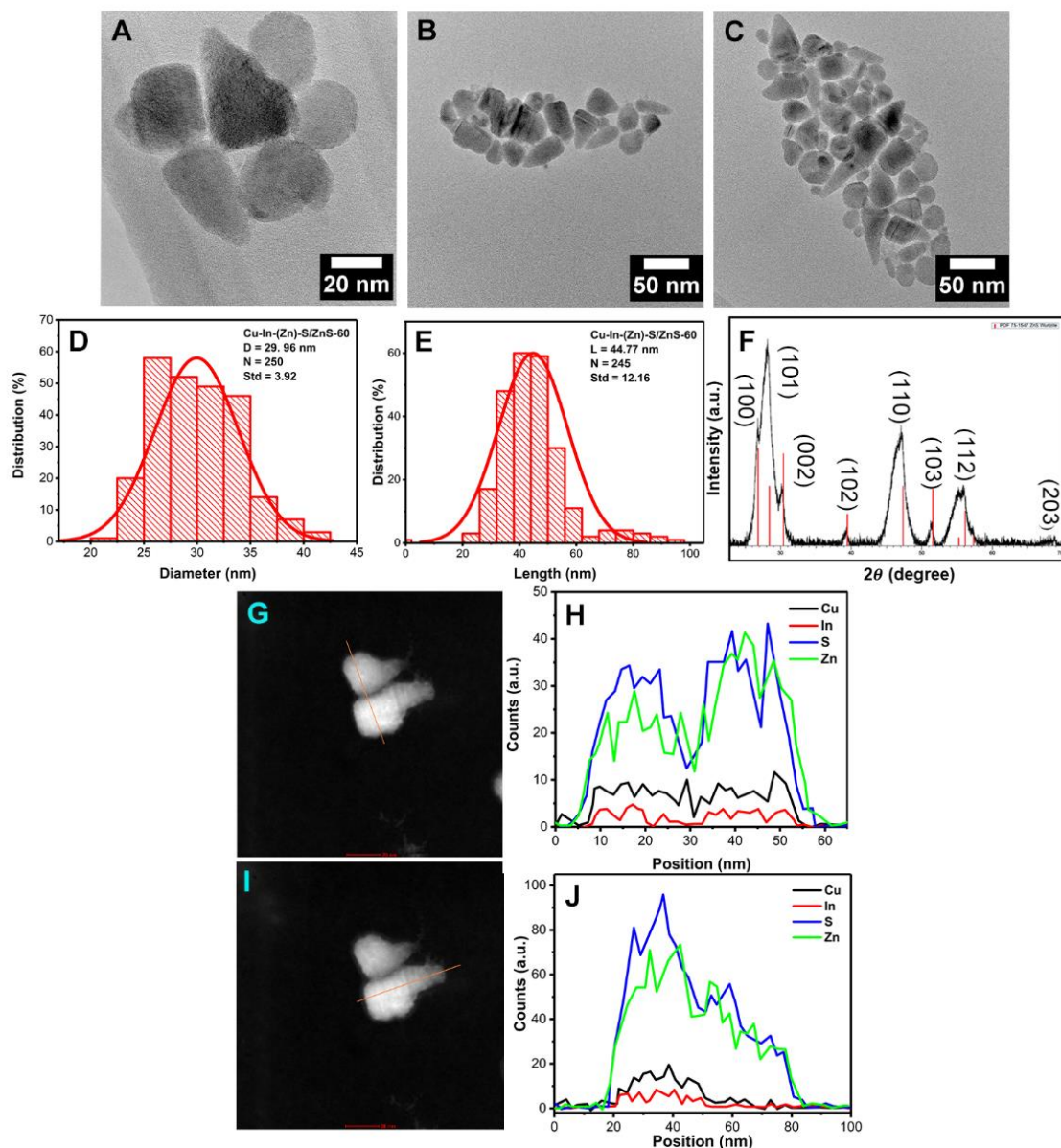


Figure 4. 3 (A-C) TEM images, (D) Diameter histogram, (E) Length histogram and (F) XRD diffraction pattern of the sample Cu-In-(Zn)-S/ZnS-60. (G-H) STEM image and corresponding line scanning spectra following the direction of the orange line in Figure 4.3G. (I-J) STEM image and the corresponding line scanning spectra of the orange line in Figure 4.3I.

4.5 Investigation of Cu-In-(Zn)-S/ZnS “ice-cream” like nanoheterostructures

Injection of the mixture of $\text{Zn}(\text{St})_2$ and 1-DDT as the ZnS shell precursor solution was completed after 120 min, and the sample Cu-In-(Zn)-S/ZnS-120 has been characterized by

electron microscopy and spectroscopy techniques. The nanostructures with a cone-like morphology observed in Cu-In-(Zn)-S/ZnS-60 have been transformed into the final “ice-cream cone” like nanostructures according to the TEM images shown in Figure 4.4A-C (more TEM images can be found in Figure A3A-D in Appendix). The diameter remained relatively similar to Cu-In-(Zn)-S/ZnS-60 ($\approx 31.4 \pm 4.5$ nm, Figure 4.4D), while the length of the “ice-cream cone” like nanostructure significantly increased and was determined to be $\approx 107.2 \pm 17.8$ nm (Figure 4.4E). In addition, using XRD it was revealed that the “ice-cream cone” like nanostructures demonstrate the WZ crystal structure (Figure 4.4F).

The morphology and size of this structure was confirmed by STEM imaging (Figure 4.4G, and Figure 4.4I, more STEM images can be found in Figure A4 in Appendix), while also EDX line scanning was conducted to determine the elemental distribution in this unique nanostructure (Figure 4.4H and Figure 4.4J). Firstly, all the expected elements (Cu, In, Zn and S) can be easily detected in the structure, with the intensities of Cu and In significantly lower than that of the other elements detected, which is due to the small volume of the original Cu-In-S core relative to the shell. In addition, the even distribution of Cu and In are confined to the “head” of the “ice-cream cone” like nanostructure. Therefore, this clearly indicates the position of the alloyed Cu-In-(Zn)-S core. Observing the trends of the shell material, Zn and S, they presented from the “head” part to the “cone” part of the structure. In total, the final “ice-cream cone” like nanoheterostructure consists of the Cu-In-(Zn)-S/ZnS “head” part and the ZnS “cone” part.

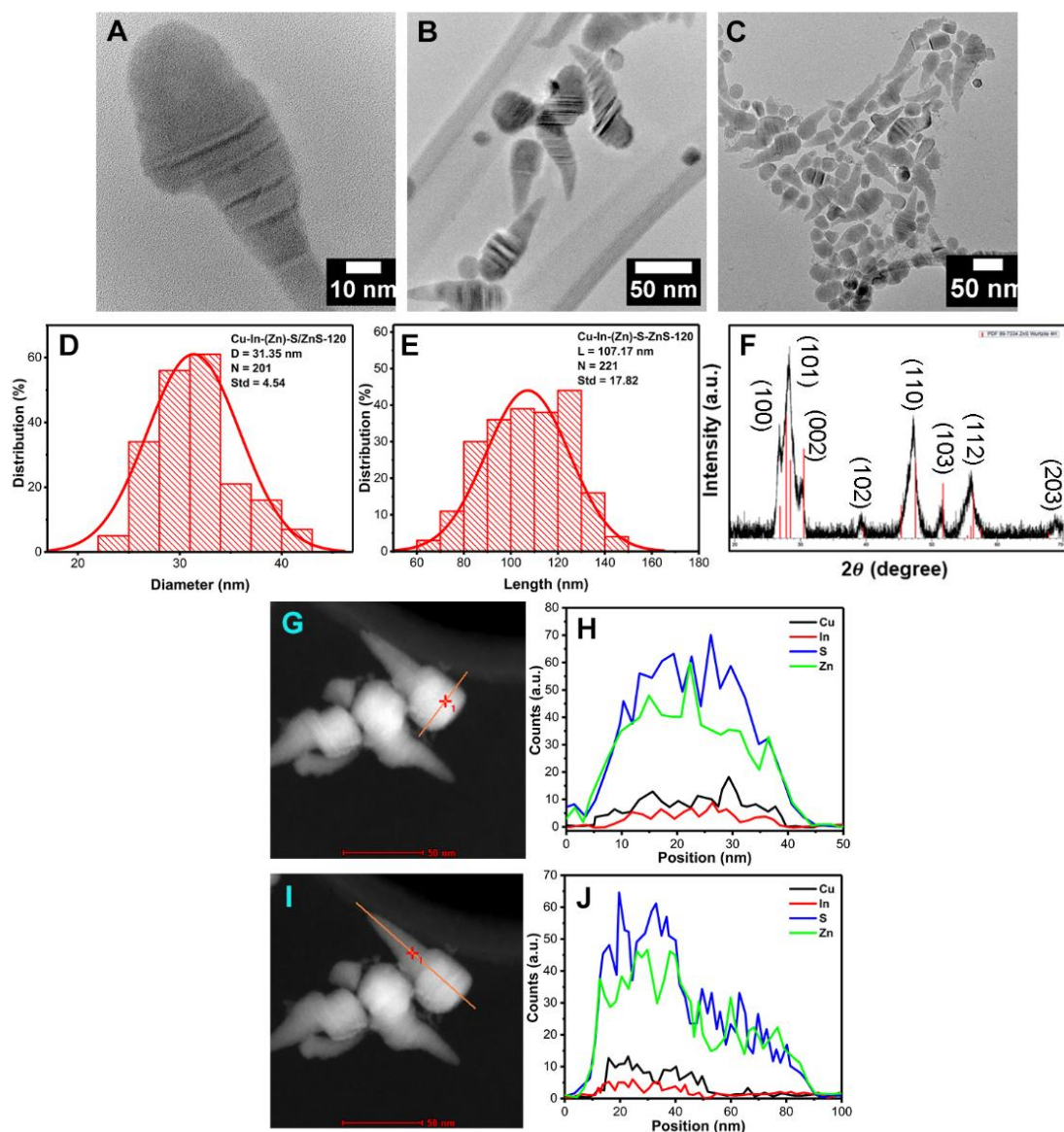


Figure 4. 4 (A-C) TEM images, (D) Diameter histogram, (E) Length histogram and (F) XRD diffraction pattern of the sample Cu-In-(Zn)-S/ZnS-120. (G-H) STEM image and corresponding line scanning spectra following the direction of the orange line in Figure 4.4G. (I-J) STEM image and the corresponding line scanning spectra of the orange line in Figure 4.4I.

The final “ice-cream cone” like nanoheterostructures have also been studied using AFM. The phase and topography images confirmed the morphology of the “ice-cream” like geometry laying on the silicon wafer (Figure 4.5A-C). The average length ≈ 110 nm, measured from the elongated “ice-cream cone” like structure in AFM image (Figure 4.5D) was consistent with the lengths obtained from TEM images.

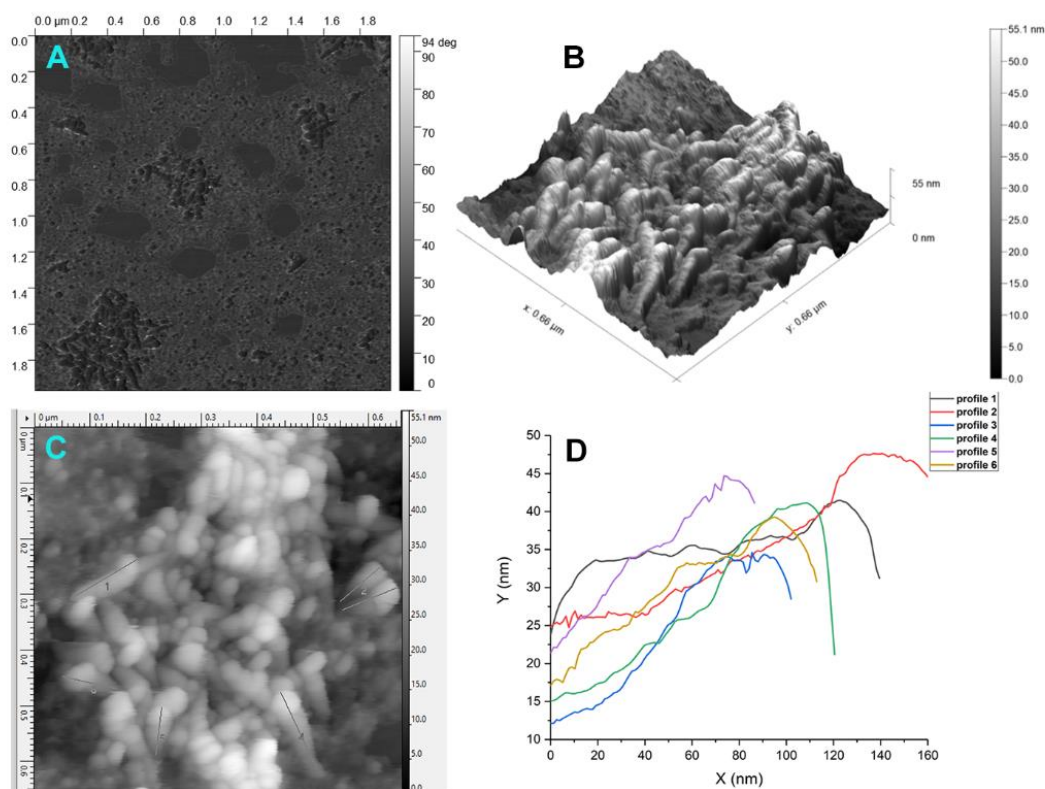


Figure 4. 5. (A) Phase image and (B) the corresponding topography image, (C) enlarged Phase image of the final Cu-In-(Zn)-S/ZnS “ice-cream” like nanostructure, (D) the morphological information (length and thickness) measured from the structures shown in Figure 4.5C.

4.6 Optical properties of the “ice-cream” nanostructures

A series of spectroscopic characterizations have been carried out on 4 aliquots (after 10, 30, 60 and 120 min of the reaction process). As shown in Figure 4.6A, the color of the aliquots changed from brown (10 min) to bright orange (120 min) under daylight. Under a UV lamp, the sample shows increasing luminescence with the reaction time (Figure 4.6B). Figure 4.6C shows the UV-Vis spectra of the Cu-In-S QDs, the sample Cu-In-(Zn)-S/ZnS-60 and the sample Cu-In-(Zn)-S/ZnS-120. Due to the traditional trait of multicomponent Cu-based quantum dots, these UV-Vis spectra are featureless without any observable well-defined exciton absorption peaks for all three samples.⁴²⁻⁴⁴ The enhanced absorbance and the blue shift of the onset of the absorption before 400 nm can be observed as the reaction proceeds,

which is due to the increased absorption cross-section upon coating with ZnS, a wide band gap semiconductor. Therefore, the Cu-In-(Zn)-S/ZnS “ice cream cone” heterostructures represent an effective down-converting luminescent NC.

The corresponding photoluminescence (PL) spectra of the three samples are shown in Figure 4.6D. The Cu-In-S QDs are emissive in the NIR region (770 nm) with relatively low PLQY (2.7 %). After 60 min of ZnS shell precursor solution injection, a substantial blue shift (125 nm) can be observed, shifting the emission peak from 770 nm for the Cu-In-S core to 645 nm for Cu-In-(Zn)-S/ZnS-60. When the reaction reached completion, the emission peak of Cu-In-(Zn)-S/ZnS-120 showed a further minor blue shift (7 nm) from 645 nm to 638 nm. Such an observed blue shift of PL peaks have commonly been reported during the synthesis of Cu-based quantum dots^{39, 54} particularly for Cu-based ternary or quaternary core/shell nanostructures involving Zn.⁵⁴⁻⁵⁹ It was found that Zn(St)₂ was the most effective precursor for achieving a blue shift among a range of Zn precursors for the preparation of CuInS₂/ZnS core/shell quantum dots, including zinc chloride, zinc acetylacetonate and zinc acetate reported by Jaehyun Park and Sang-Wook Kim.⁴⁹ The mechanisms underlying this PL blue-shift phenomena during the synthesis are not clearly established, with several pathways having been proposed such as: (1) Filling up of intra-bandgap defect states,^{53, 60} (2) Core size reduction by cation exchange^{47-49, 61} and (3) Band gap widening by the entrance of Zn ions.⁶² The first mechanism is mainly about passivation by means of ZnS shelling, which facilitates the reduction of the fraction of donor-acceptor recombination pathways with lower energy levels; thus the band-edge or band to donor/acceptor emission with higher energy levels becomes the dominant emissive deexcitation pathway, leading to the observed blue shift. Core size reduction by cation exchange^{47-49, 61} is proposed to occur due to the similar sizes of the metal cations present of Cu, In and Zn. Since the reaction takes place at high temperatures, Zn²⁺ can diffuse into the Cu-based ternary or quaternary core lattice

structure and can replace the Cu^{1+} and In^{3+} ions, therefore reducing the size of the core and resulting in core-size dependent blue shift. Finally, band gap widening by the entrance of Zn ions into the lattice⁶² can take place *via* diffusion of them into the pre-existed Cu-based seeds. This induces a widening of the band gap, which is quite similar to the doping of Zn into CIS thin films.⁶³

In this work, it was verified that alloyed Cu-In-(Zn)-S core formed through the entrance of Zn into the original Cu-In-S seeds (Figure 4.2D and Figure 4.2F) as the reaction proceeds. In addition to the formed alloyed structure, ZnS shell has been deposited onto the alloyed core part. Thus, it can be proposed that the combined effects of above mentioned factors (1) and (3) induced this dramatic PL blue shifting as the reaction proceeds at high reaction temperature (230 °C) for significant reaction time (120 min).

As the ZnS shelling proceeds, the intensity of the emission greatly increases, giving a significant increase in PLQY of the final Cu-In-(Zn)-S/ZnS “ice-cream cone” like structure up to $27.7 \pm 2.8\%$. The gradually improved PL properties can be interpreted to be due to the surface passivation effect of the ZnS shell upon the surface defects which can act as a nonradiative pathway.³⁶⁻³⁸ PL decay curve of the final Cu-In-(Zn)-S/ZnS “ice-cream cone” structure, which was biexponentially fitted is shown in Figure 4.6E and the average PL lifetime was found to be 366 ns (see the two lifetime components in Table A8 in Appendix). Noteworthy is the distinct advantage of such a long PL lifetime which could be potentially suitable for bioimaging.⁶⁴

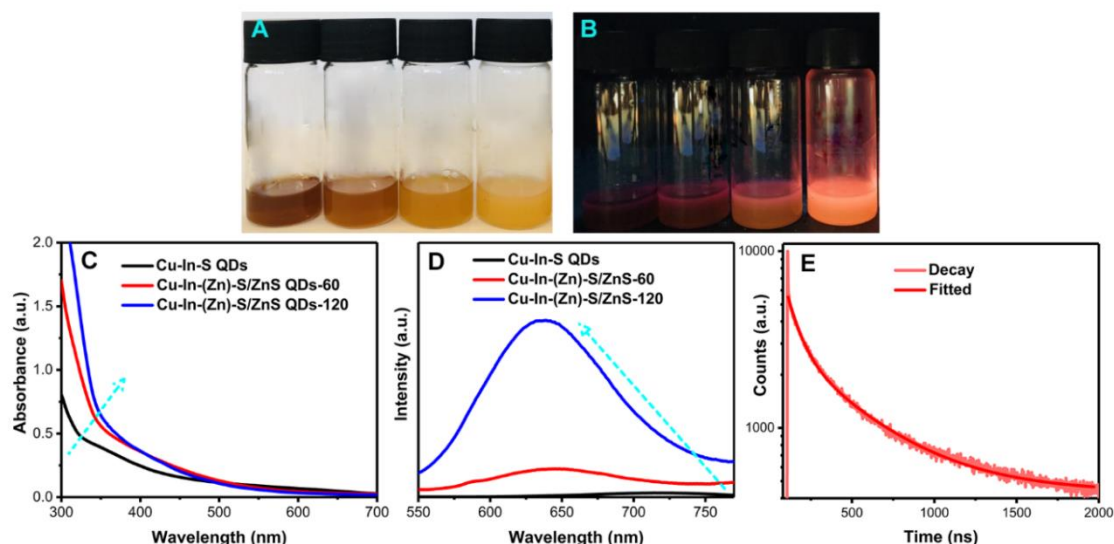


Figure 4. 6 (A-B) Photographs of aliquots taken from the reaction vessel at different time intervals (from left to right, 10 min, 30 min, 60 min and 120 min) under daylight and UV lamp. (C-D) UV-Vis spectra and PL spectra of Cu-In-S QDs, Cu-In-(Zn)-S/ZnS-60 and Cu-In-(Zn)-S/ZnS-120, respectively. (E) PL decay curve of Cu-In-(Zn)-S/ZnS-120.

The EEM (Excitation Emission Matrix) of CuInZnS/ZnS -120 is shown in a contour map and as a 3-dimensional plot in Figure 7A and B respectively. These spectra were adjusted with a correction factor so as to take account of the inner filter effect (calculated using Equation S1 and S2 in Appendix). The resulting spectra of Figure 7 A and B shows a distinctive behaviour of the material, showing a strong maximum emission intensity in the range of 630-640 nm upon excitation of approximately 400-410 nm and a general decrease in emission intensity with lower energy excitation. In addition, no peak maximum red shifting is found to occur upon excitation variation, which again supports the lack of a broad size distribution of the “ice-cream cone” sample.

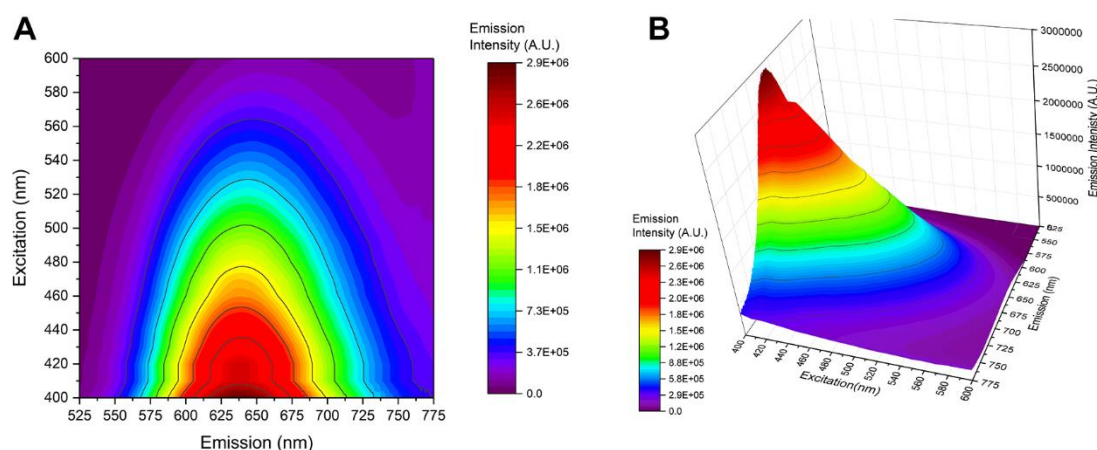


Figure 4. 7 EEM (Excitation Emission Matrix) of CuInZnS/ZnS-120.

4.7 Investigation of the Mechanism of Morphological Development of the “Ice-Cream Cone” Nanoheterostructures

It is widely reported that the energy barrier for heterogeneous nucleation is much lower than homonucleation, if the lattice mismatch between the seeds and the nuclei is not substantial.^{8, 65-67} Therefore, under these conditions, homonucleation of the shell material precursors will be unfavorable and instead heteronucleation will dominate, enabling the controlled growth of heteronanostructures in this case. The seeded growth technique takes full advantage of this approach and has been widely used to synthesize both Cd-based and Cu-based ternary or quaternary core/shell heterostructures with various morphologies (spherical, dot-in-rod, tetrapod or even rod-in-rod structures).^{12-13, 68-69} Therefore, this technique has been employed here to prepare the unique “ice-cream cone” nanoheterostructures.

The preformed ZB Cu-In-S QDs (≈ 3 nm) served as the seeds for heterogeneous nucleation and heteroepitaxial growth (Figure 4.8A) of the “ice-cream cone” nanoheterostructures. The size of the sample increased progressively as the reaction proceeds, with a spherical

morphology present after 5 minutes ZnS shell growth, measuring 20.8 ± 2.1 nm in diameter progressing to 29.4 ± 2.9 nm diameter after 15 minutes growth (see Figure A5 in Appendix for details of the samples that taken out from the reaction vessel at 5 and 15 min).

After 30 min of ZnS shell growth, the NC transformed from a spherical morphology to a cylindrical core/shell structure and size increased significantly as shown in Figure 4.8B. While the crystal structure remained the same (ZB crystal structure) for the sample at 30 min. Interestingly, the EDX line scanning spectra (Figure 4.2D and Figure 4.2F) showed that the elements Cu and In were distributed unevenly along the direction perpendicular to the top and bottom surfaces with more Cu located at the first 1/4 and In distribution at the remaining 3/4 part of the cylindrical structure. In fact the seeded growth method is known to prepare core/shell heterostructures, in which the cation precursors of the shell can enter the pre-existing cores through interdiffusion/substitution processes, with the rate of this highly dependent on reaction conditions.^{28, 62, 70} In this case, the higher reaction temperature (230 °C) and similar sized metal cations (Cu, In and Zn, cation radius = 60-62 pm in a four coordinate system)^{49, 54} promote the interdiffusion process giving rise to the formation of the alloyed Cu-In-(Zn)-S/ZnS structure as opposed to the Cu-In-S/ZnS core/shell structure.

It has been found that after 60 minutes of shell growth, the sample became cone-like (Figure 4.8C) and the crystal structure transformed from ZB to WZ. While after 120 minutes, the sample consisted nearly entirely of the “ice-cream cone” like structures (Figure 4.8D). The EDX line scanning spectra (Figure 4.4F) revealed that elements Cu and In were detected at the top part of the “ice-cream cone” nanoheterostructure, which indicates that the Cu-In-(Zn)-S core is located at the “head” of the “ice-cream cone”. The extended growth of a ZnS shell results in the formation of this unique nanostructure.

The formation of the elongated “ice-cream cone” like structure can, thus, be interpreted by considering the evolution of the crystal structure from ZB to WZ as the reaction proceeds. The ZB crystal structure was maintained from the Cu-In-S seeds to the sample Cu-In-(Zn)-S/ZnS-30, which was followed by the transformation of the crystal structure from ZB to WZ. Then the “ice-cream cone” like structure started to occur. The wurtzite QDs have two polar facets $\pm\{002\}$ that terminated with metal elements and S^{2-} , respectively. With the 1-DDT and OAm being used as ligands in the reaction, the $+\{002\}$ facet that terminated with metal elements are highly passivated. The opposite facet $-\{002\}$ is terminated with Lewis base S^{2-} is less passivated because of its low affinity to the presented ligands (also Lewis bases), which results in higher reactivity of this face. The growth of the ZnS shell was proceeded *via* the addition of the [ZnS] monomer onto the facet (it was also claimed for the Cd-based anisotropic nanorod structure),^{8, 41, 68, 71-73} maintaining the polarity of the growing facet and resulted in the elongated “ice-cream cone” like nanoheterostructures. The higher growth rate of ZnS shell on the $-\{002\}$ facet resulted in the top positioning of the Cu-In-(Zn)-S core.

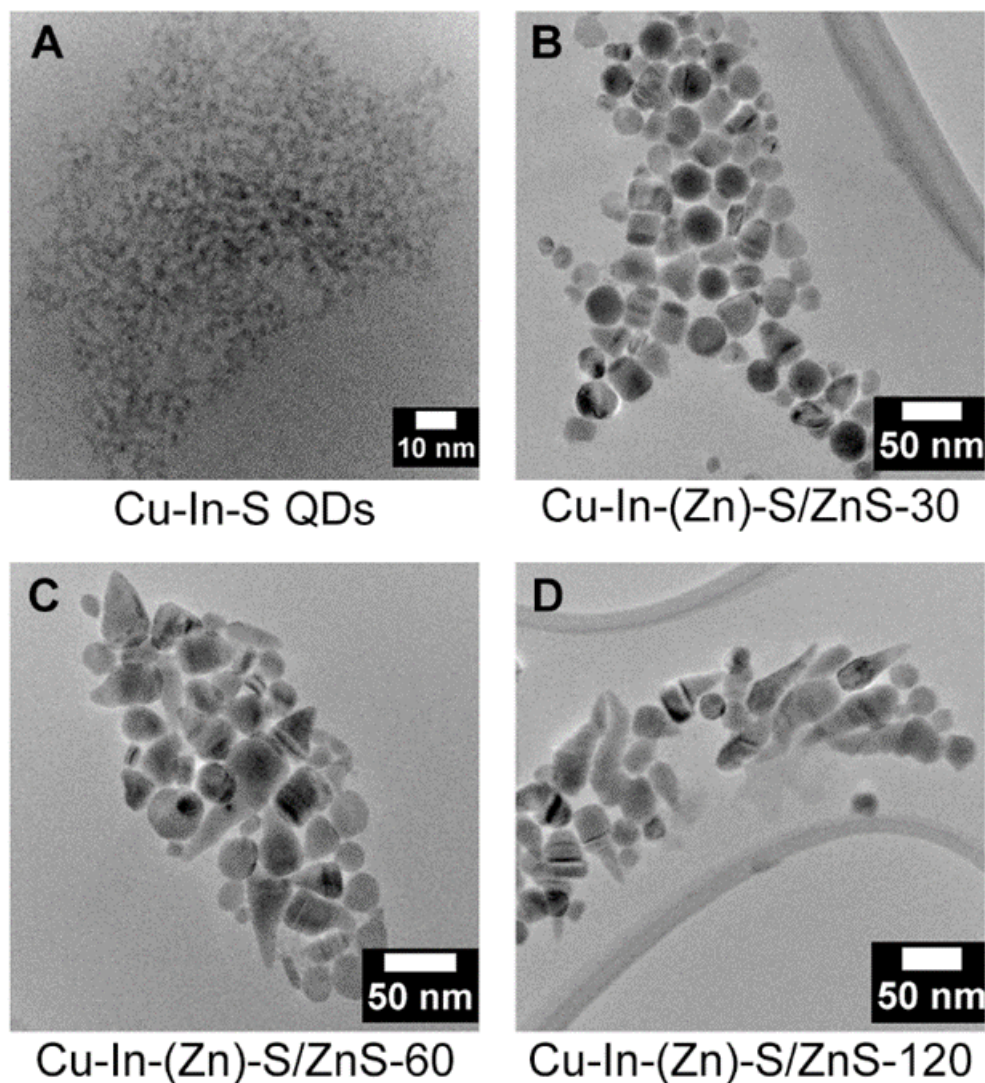


Figure 4. 8 (A-D) TEM images showing the morphology development of the Cu-In-(Zn)-S/ZnS “ice-cream” like nanostructures.

Thus, the seeded growth method was employed to produce at unique Cu-based multicomponent Cu-In-(Zn)-S/ZnS “ice-cream cone” nanoheterostructures with emission in the visible region and excellent PLQY (27%). The combination of several effects (band gap widening by the entrance of Zn ion into the core, the passivation of the intragap defect states and core size reduction through cation exchange) caused the impressive blue shift of the PL peak from the NIR region (770 nm) of the Cu-In-S core to visible region (638 nm) of the final Cu-In-(Zn)-S/ZnS “ice-cream like” structure. The growth mechanism of this particular “ice-cream” like structure involves the crystal structure evolving from ZB to WZ as the

reaction proceeds and eventually results in the elongated “ice-cream cone” structure. I believe that these findings open up new possibilities to prepare even more interesting and highly fluorescent non-toxic Cu-based multicomponent heteronanostructures, while also offering a distinctive insight into the design of bespoke Cu-based nanoheterostructures.

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Chapter 5 Near-infrared-emitting CIZSe/CIZS/ZnS core/shell/shell heteronanonails

5.1 Introduction

Recently, Cu-based multicomponent (ternary, quaternary and quasi-quaternary) especially core/shell heterostructured quantum dots (QDs) have attracted great attention due to their advantages over the well-explored binary Cd-based systems¹⁻⁶. The absence of toxic heavy metal Cd shows particular advantages referring to reduced environmental impact and increased ease for various applications⁷⁻¹⁰. In addition, Cu-based multicomponent QDs bear high level of off-stoichiometry, indicating even greater absorption and emission tunability compared to Cd based QDs, meaning the photophysical properties of Cu-based ternary or quaternary QDs can simply be tuned *via* varying the ratio of cations that composed the QDs, except the size and morphology of the sample¹¹⁻¹³. What's more, excellent stability against external environment (oxygen, moisture and photoirradiation), especially after inorganic shell coating with large band gap semiconductors (ZnS), can be achieved for Cu-based multicomponent QDs^{6, 14-15}. Thus, Cu-based multicomponent QDs are very promising to replace Cd-based QDs.

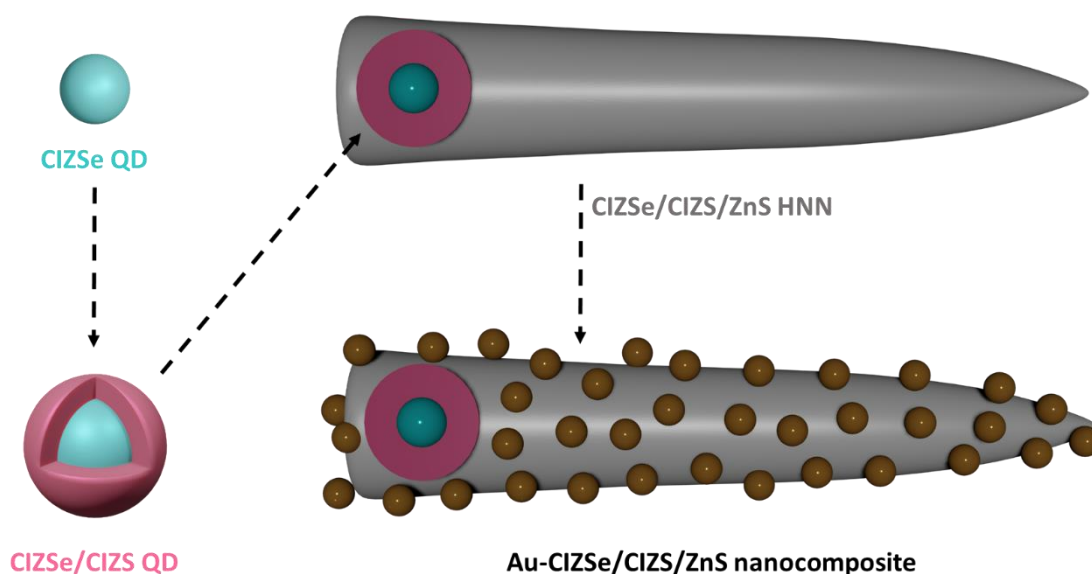
It is well known that the properties of QDs are not only size and composition dependent, but also strongly determined by the resulting morphology, for example, nanorods (NRs), which show increased electrical conductivity compared to spherical nanoparticles, and therefore are very appealing for applications requiring efficient charge transfer¹⁶⁻¹⁸. Also the polarized emission from the particular NR morphology favours the their applications in luminescent solar concentrators and liquid-crystal-display applications¹⁹⁻²⁰. At present, the synthesis of

Cd-based (heteronanorods) HNRs has been well explored with the most well-known structure of this type being CdSe/CdS dot-in-rod HNRs²¹⁻²⁴. In contrast, there are only limited reports regarding the synthesis of Cu-based dot-in-rod heterostructures. Stam *et al.* proposed the first work referring to the synthesis of CIZSe/CIS dot-in-rod nanostructure²⁵. However, the synthesis was complex and involved the use of Cd-based precursors. Since the reaction proceeded *via* an initial CdSe/CdS dot-in-rod which was prepared first, which was followed by a complete cation exchange to obtain Cu₂Se/Cu₂S dot-in-rod structure, resulting Cd was replaced by Cu. At the final step, luminescent CIZSe/CIS was obtained *via* a partial cation exchange process with indium being incorporated into the rod structure. A CIS/ZnS dot-in-rod heterostructure *via* a straightforward seeded growth method was prepared by Xia and Winckelmans²⁶. WZ CIS seeds were synthesized first, which was followed by growth of ZnS tips. In their work, the growth mechanism for the growth of this particular Cu-based multicomponent anisotropic dot in rod heterostructure is similar to that for the growth of Cd-based dot-in-rod structures, with HDA (hexadecylamine) used as the coordinating ligand. However, no further work have directly followed up since their report.

Cu-based multicomponent heterostructured nanorods have large absorption cross-sections and carrier-guiding effect, all of which make the unique morphology-dependent optoelectronic properties even more promising in various applications³. In addition, even greater functionality can be introduced *via* metal nanoparticle deposited onto the NR structure, creating a perfect candidate for a number of photocatalysis applications²⁷. To the best of my knowledge, no such studies have been performed for Cu-based multicomponent systems.

Here, I have carried out a multistep colloidal synthesis and photophysical studies of the unique CIZSe/CIZS/ZnS core/shell/shell heteronanonail-like structures (HNNs) with

emission in the near infrared region (≈ 850 -1000 nm). I have also prepared Au-CIZSe/CIZS/ZnS nanocomposites by growing Au nanoparticles on the obtained HNN surface (Scheme 5.1). This study presents a further step of morphological control of Cu-based multicomponent systems and the first example of metal nanoparticle inclusion to these complex structures.



Schematic 5 1. Schematic illustration of the development of the “nanonail” like heterostructures.

5.2 Synthesis of CIZSe QDs

The CIZSe QDs were prepared *via* a hot-injection method following previously reported procedures with minor modifications²⁸ (see Experimental Section for details). It was found that the CIZSe QDs display a spherical shape (Figure 5.1A) with a diameter of $\sim 4.1 \pm 0.4$ nm and a narrow size distribution (Figure A6 in Appendix) using TEM. The wide-angle powder X-ray diffraction (XRD) pattern (Figure 5.1B) of the representative CIZSe QDs exhibits the characteristic diffraction pattern for CH crystal structure²⁸. UV-Vis absorption spectrum was recorded for the CIZSe QDs showing a first exciton peak at 700 nm (Figure 5.1C). As shown in Figure 5.1D, the resulting sample is fluorescent with an emission range

in the NIR region centered at ~ 804 nm, and a fwhm (full width at half maximum) of 100 nm. The cleaning of the sample was done using ethanol and toluene, then the clean CIZSe QDs are ready for the next step, which is coating the CIZSe core with CIZS shell to get the CIZSe/CIZS core/shell heterostructures.

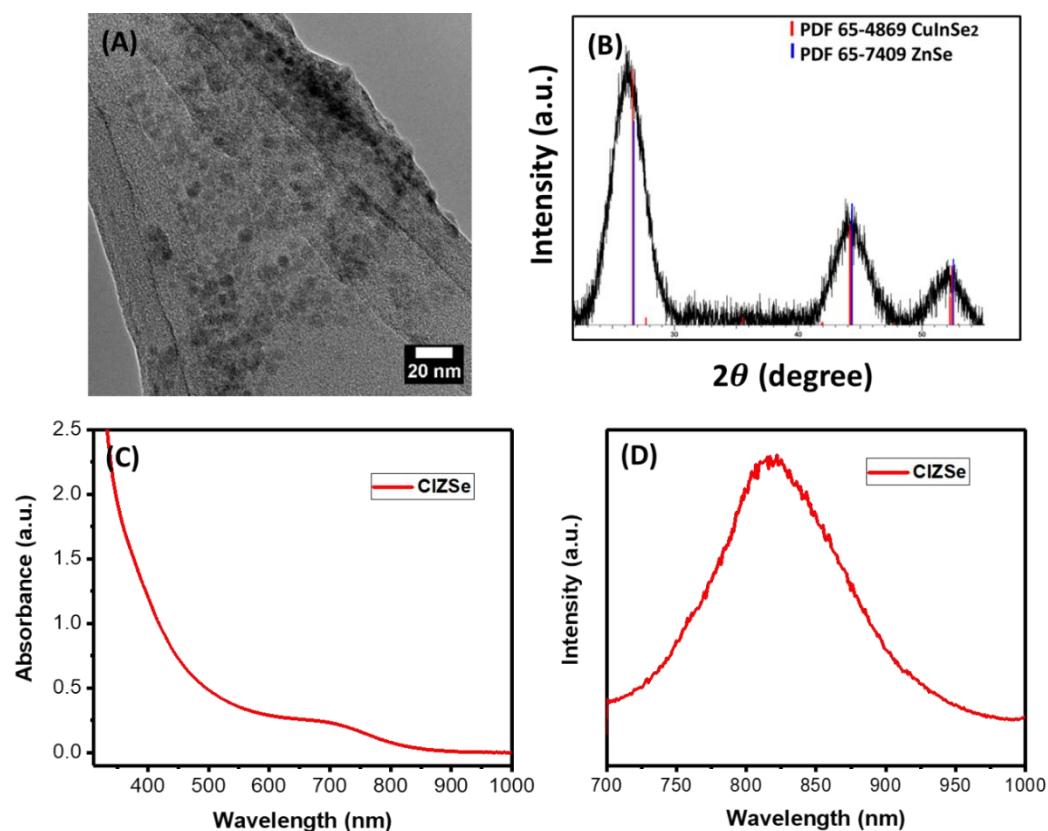


Figure 5. 1 (A) TEM image of CIZSe QDs. (B) X-ray diffraction pattern of CIZSe QDs, the red line corresponds to bulk chalcopyrite CIZe and the blue line corresponds to zinc blende ZnSe. (C) UV-Vis spectrum and (D) PL spectrum of the obtained CIZSe QDs.

5.3 Synthesis of CIZSe/CIZS QDs

The cation (Cu, In and Zn) and anion (1-DDT) precursor solutions were injected into the reaction vessel that loaded with 1 mL of the CIZSe seeds dropwise using a syringe pump at 220 °C (see Experimental Section for details). The reaction was designed to proceed at this temperature for 70 min. It is revealed that the CIZSe/CIZS QDs display spherical shape (Figure 5.2A and Figure 5.2B) with a diameter of $\sim 9.2 \pm 1.9$ nm and narrow size distribution

(Figure A7 in Appendix) by using TEM. The clear lattice that observed indicated the high quality crystalline of the obtained sample. The XRD pattern of the sample exhibits WZ crystal structure with the representative peaks of the WZ crystal structure being labelled in Figure 5.2D. The overlap of the representative XRD peaks of the core and the corresponding peaks of the shell can be observed, due to the relatively small volume ratio of the CIZSe core and the CIZS shell. The STEM image (Figure 5.2C) verifies the uniform morphology of the CIZSe/CIZS core/shell heterostructure. EDX has also been performed on the obtained CIZSe/CIZS QDs as displayed in Figure 5.2E, which demonstrates the presence of all the expected elements (Cu, In, Zn, Se from the core and Cu, In, Zn, S from the shell) in the core/shell heterostructure.

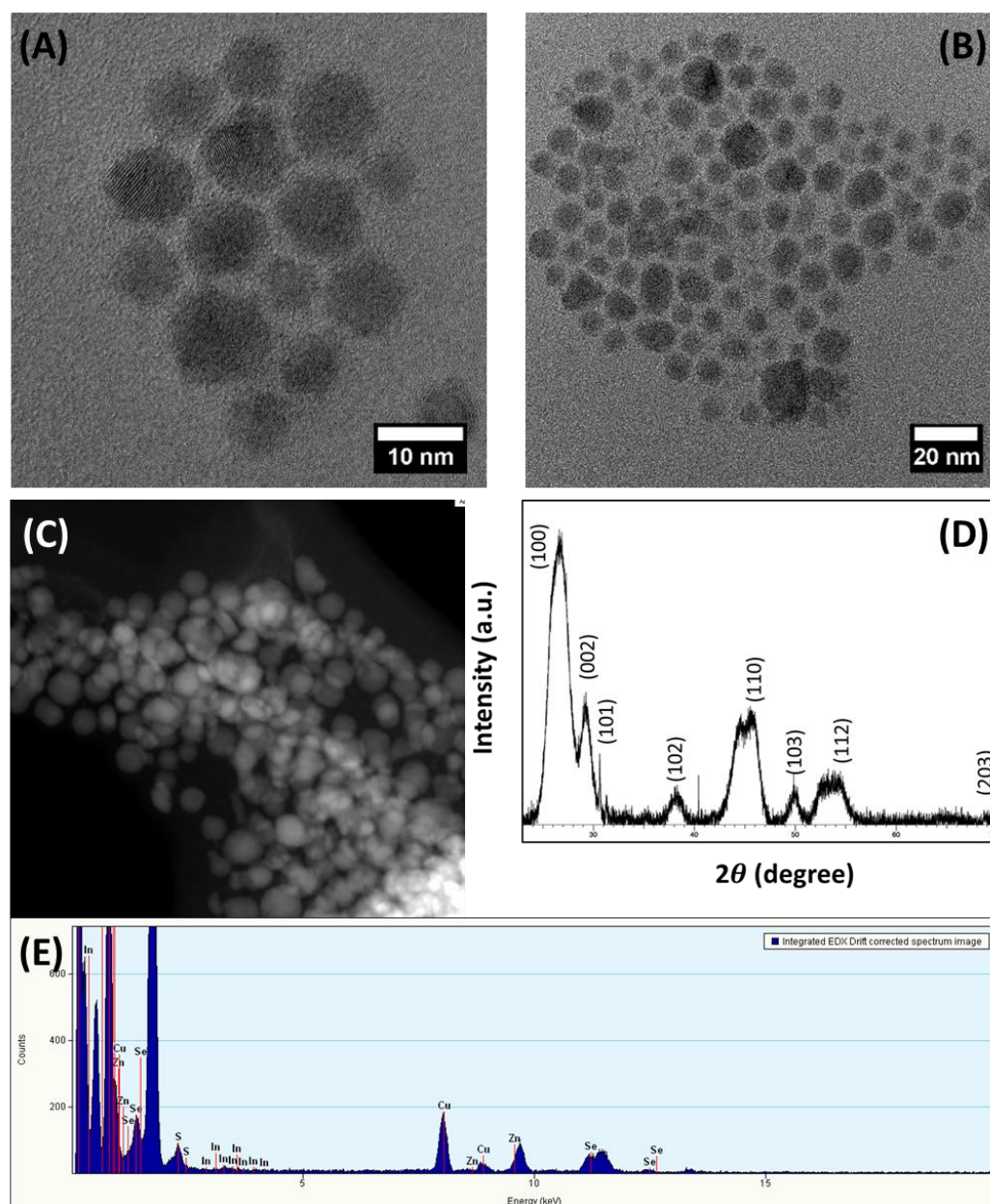


Figure 5. 2 (A, B) TEM images of CIZSe/CIZS QDs, (C) STEM image of the CIZSe/CIZS QDs, (D) XRD diffraction pattern and (E) EDX spectra of CIZSe/CIZS QDs.

After CIZS shell coating onto the CIZSe core, the UV-Vis absorption spectrum of the resulting CIZSe/CIZS QDs is essentially featureless (Figure 5.3A) which is common for Cu-based multicomponent nanocrystals²⁹, while the emission peak is centred on 853 nm with a fwhm of 155 nm (Figure 5.3B). Interestingly there is a red shifting of the emission peak from 820 nm of the CIZSe core to 853 nm of CIZSe/CIZS core/shell structure. This can be explained by the type II band gap alignment which I propose is formed between the core and

the shell (such as in CdTe/CdSe QDs³⁰ or ZnTe/ZnSe QDs³¹). In this case, the holes are located in the valence band of the core, while the electrons are delocalized to the conduction band of the shell, producing an effective bandgap which is a function of this staggered band alignment, this induces a red shifting of the emission of CIZSe/CIZS core/shell nanostructure.

The size increases from ~ 4.1 nm of the CIZSe core to ~ 9.2 nm of the CIZSe/CIZS core/shell QDs, the presence of all the elements (Cu, In, Zn, Se and S) and the red shifting of the emission peak (from 820 nm to 853 nm) confirm the effective coating of CIZS shell onto the CIZSe core.

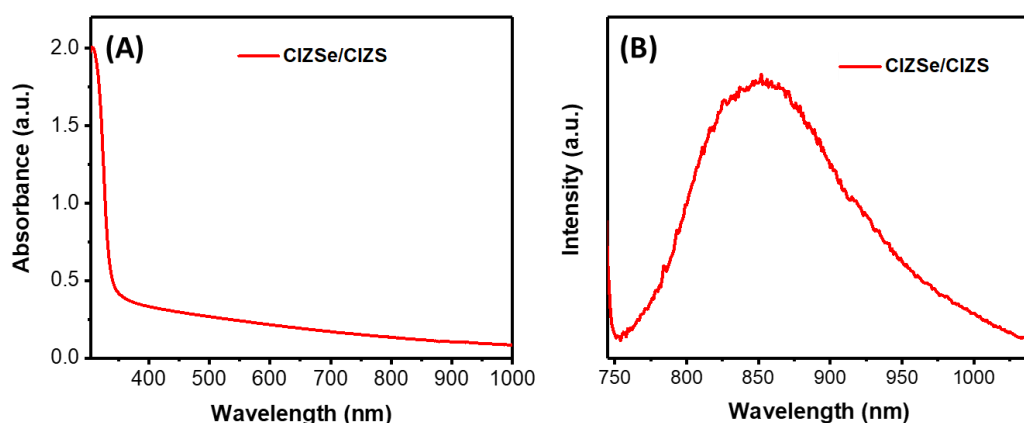


Figure 5. 3 (A) UV-Vis spectrum and (B) PL spectrum of the CIZSe/CIZS core/shell heterostructures.

5.4 Synthesis of CIZSe/CIZS/ZnS HNNs

The CIZSe/CIZS/ZnS heteronanonails have been prepared with a seeded-growth method in the third step without cleaning of the CIZSe/CIZS QDs from the second step (see Experimental Section for details) to further enhance the optical properties *via* careful control of ZnS shell growth. As shown in Figure 5.4A, QDs in nanonail morphology have been produced, with a diameter of $\sim 15.8 \pm 2.4$ nm (“head” of the HNN structure, Figure A8A in Appendix) and length of $\sim 101.1 \pm 29.3$ nm (Figure A8B in Appendix). In addition, the

unique HNN morphology is also confirmed by STEM images (Figure 5.4B). The XRD diffraction pattern indicates that the HNN structure displays WZ crystal structure, with the representative peaks labelled in Figure 5.4C. Unlike the XRD diffraction pattern of CIZSe/CIZS core/shell structure (Figure 5.2D), the overlap of the representative peaks of the CIZSe core, the CIZS shell and the ZnS shell cannot be easily observed because of the much larger volume ratio between the ZnS shell and the CIZSe/CIZS core. The corresponding HRTEM image (Figure 5.4D) of the HNN structure reveals lattice spacing in the CIZSe/CIZS/ZnS HNN of 0.32 nm that match the (002) plane of the WZ structure, confirming the CIZSe/CIZS/ZnS HNN growth in $[000\bar{1}]$ direction.

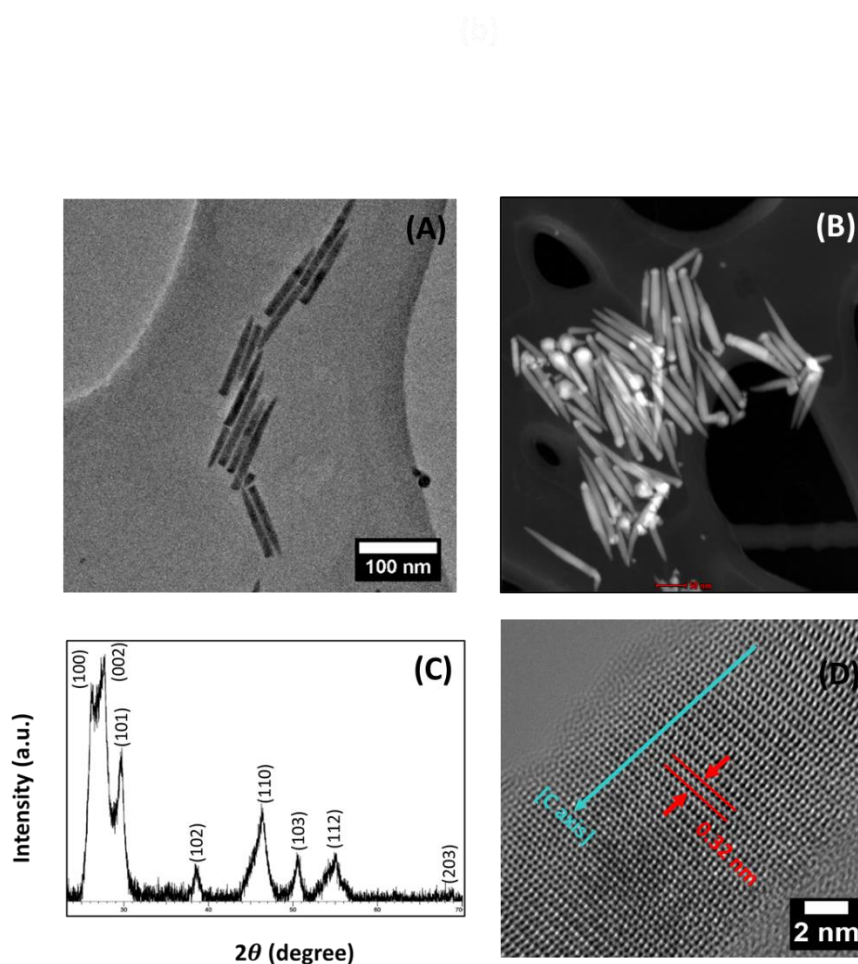


Figure 5. 4 (A) TEM image, (B) STEM image, (C) XRD diffraction pattern, (D) HRTEM image of CIZSe/CIZS/ZnS HNNs, the blue arrow indicates the c-axis direction, d is the measured lattice spacing along (002).

EDX was carried out at three positions from the tip to the tail (position 1 on the tip of the HNN (Figure 5.5A), position 2 at the central part of the HNN (Figure 5.5B) and the position 3 at the tail of the HNN structure (Figure 5.5C)) with spectra of the HNN heterostructure are shown in Figure 5.5. All the expected elements (Cu, In, Zn, Se and S) can be detected in the obtained HNN structure. The element of Se is confined in the “head” of the HNN, which indicates the position of the CIZSe/CIZS core. Elements including Zn and S are the components of the CIZSe core, CIZSe/CIZS core/shell seed and CIZSe/CIZS/ZnS HNN and are detected from position 1 to the position 3 along the HNN. Referring to elements Cu and In, they are the components of the CIZSe seed and CIZSe/CIZS core/shell structure, they should be detected only at position 1 of the HNN but this is not the case. I propose that the crude CIZSe/CIZS QDs from the second step without cleaning was used in the third step to coat the ZnS shell, that in fact not all of the precursors (Cu and In) have been fully reacted, which therefore were left in the reaction vessel, and hence being incorporated into the HNN structure in the third step. That is the reason why both Cu and In can also be found at position 2 and position 3 of the structure.

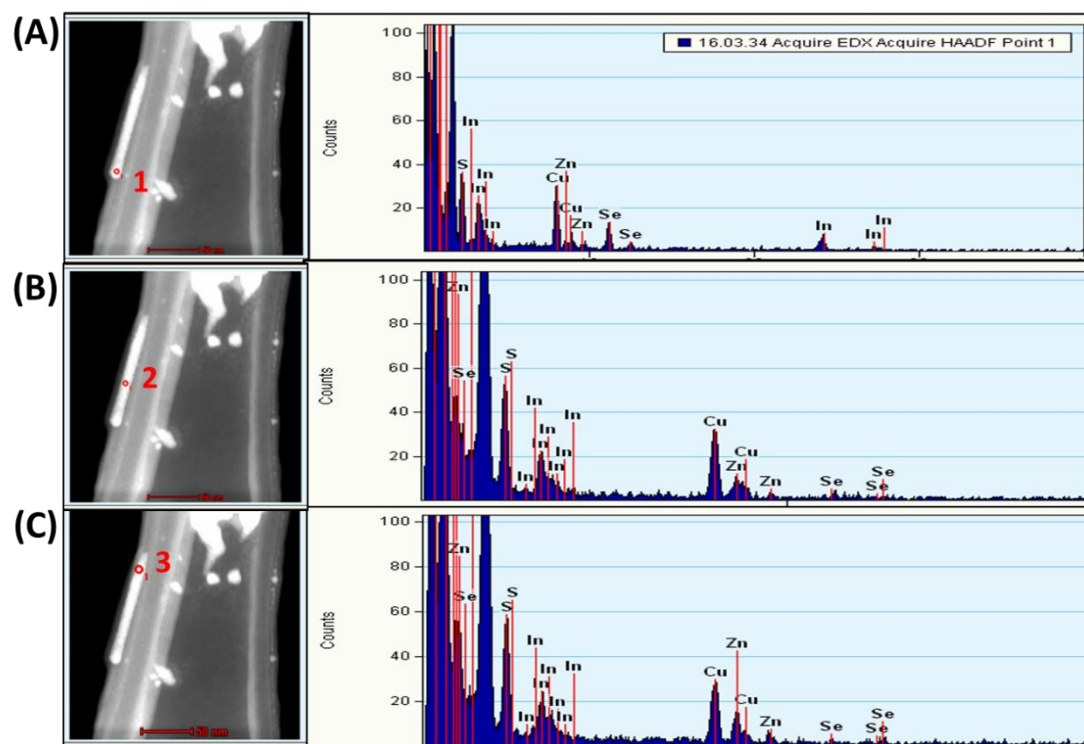


Figure 5. 5 (A-C) STEM images and EDX spectra of CIZSe/CIZS/ZnS HNN structure at 3 different positions.

Optical properties of the obtained 1D HNNs have been characterized with UV-Vis-NIR and NIR PL spectroscopy. The CIZSe/CIZS/ZnS HNNs absorb light from the ultraviolet-to-near-infrared regions of the spectrum (Figure 5.6A), with an emission peak centred approximately at 850 nm (Figure 5.6B). The emission peak of the CIZSe/CIZS/ZnS HNNs is at the same region as the CIZSe/CIZS QDs without any blue or red shift, which indicates that the emission of the final HNN structure comes from the CIZSe/CIZS seed.

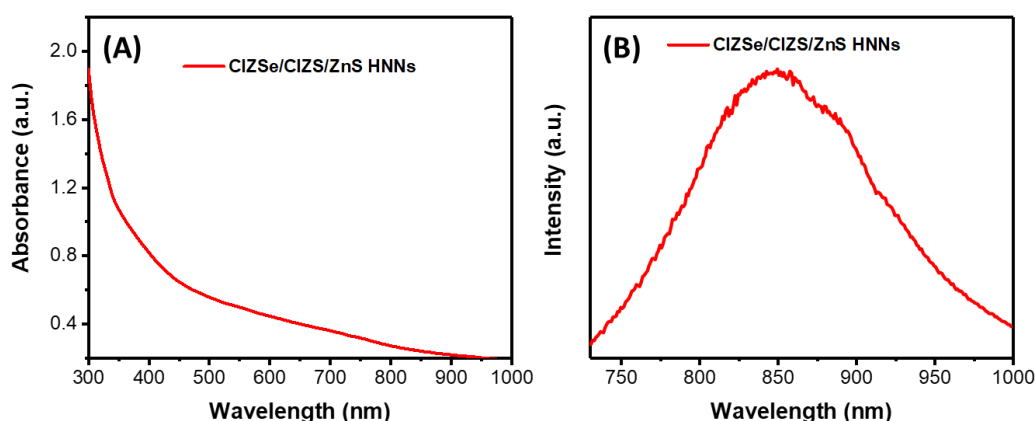


Figure 5. 6 (A) UV-Vis spectra, (B) PL spectra of the CIZSe QDs, CIZSe/CIZS QDs and the CIZSe/CIZS/ZnS HNNs.

Initially the intensity of emission has improved after coating of the CIZS shell onto the CIZSe core. This trend continued with the ZnS shell coated of the CIZSe/CIZS QDs during the third step (Figure 5.7). This shell coating is the most important way to improve the optical properties of quantum dots due to the elimination of possible defects on the surface that can act as the origin of non-radiation pathways³²⁻³⁵. What's more, the ZnS shell exhibits a wider band gap than the CIZSe QDs and CIZSe/CIZS QDs and forms a type I band alignment. Thus, the formed excitons upon excitation can be confined in the CIZSe/CIZS core effectively from the surrounding environment (oxygen and moisture), which is key to achieving a high photoluminescence quantum yield. In addition, the emission range for the CIZSe core, CIZSe/CIZS QDs and CIZSe/CIZS/ZnS HNNs are quite broad, which is consistent with previous findings³⁶⁻³⁸. The samples from the core, to the core/shell and to the final core/shell/shell structures are colloiddally stable as shown in picture of the 3 samples that kept in the fridge at +4 °C for 3 months (Figure 5.8).

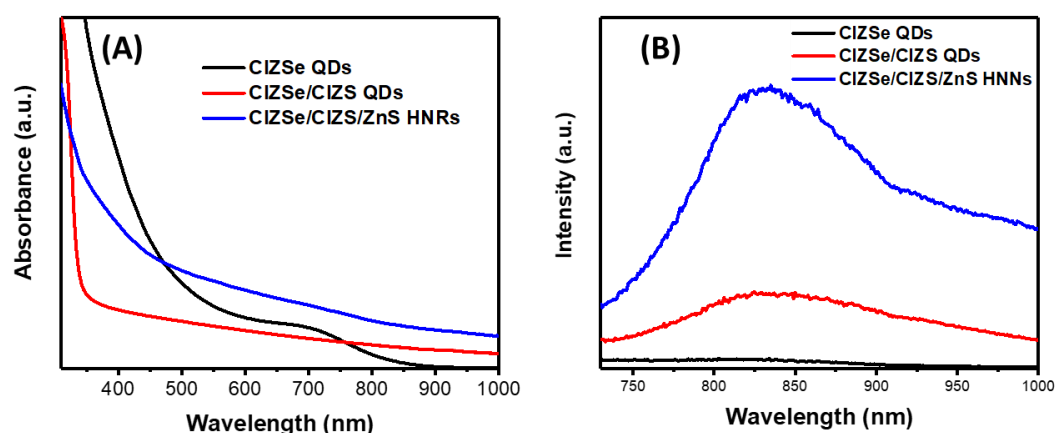


Figure 5. 7 (A) UV-Vis spectra, (B) PL spectra of the CIZSe QDs, CIZSe/CIZS QDs and the CIZSe/CIZS/ZnS HNNs.

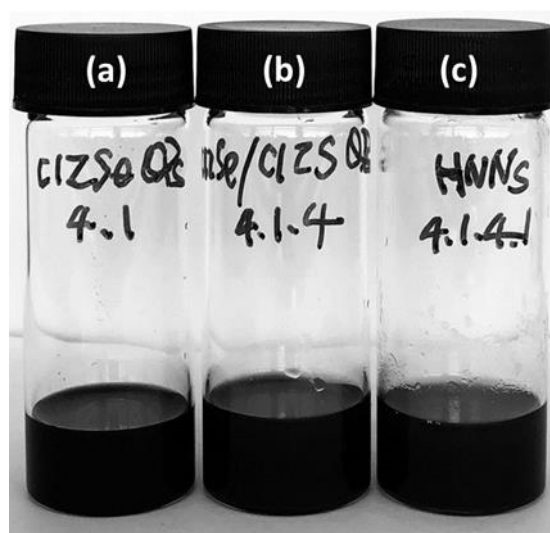


Figure 5. 8 Pictures of the obtained (a) CIZSe QDs, (b) CIZSe/CIZS QDs and (c) CIZSe/CIZS/ZnS HNNs after kept in the fridge for 3 months.

5.5 CIZSe/CIZS/ZnS HNNs morphology control

The morphology of the CIZSe/CIZS/ZnS HNNs can be tuned by adjusting the molar ratio of the Cu, In and Zn precursors used in the second step to make CIZSe/CIZS QDs with three distinct examples of this effect shown in Figure 5.9. Firstly, adjusting the Cu:In:Zn molar ratio to 1:2:3, produced a HNN shaped nanocrystals (Figure 5.9A) measuring 101.1 ± 29.3

nm in length (Figure A9 in Appendix) with a minor tapering. In contrast, changing the ratio to 1:3:2 produced a more nail shaped CIZSe/CIZS/ZnS structure (Figure 5.9B), measuring 86.9 ± 11.5 nm in length (Figure A10 in Appendix). The morphology of corresponding CIZSe/CIZS QDs (1:3:2) can be found in Figure 5.10(A-B), producing a larger seed of 11.5 ± 2.3 nm (Figure 5.10(C)). However, adjusting the ratio to 1:1:3 formed a CIZSe/CIZS/ZnS HNN structure measuring 99.8 ± 48.4 nm (Figure A11 in Appendix) as in the case of 1:2:3, but with a much broader size distribution (Figure 5.9C). The morphology of corresponding CIZSe/CIZS QDs (1:1:3) can be found in Figure 5.10(D-E) which showed a diameter of 5.7 ± 0.8 nm (Figure 5.10(F)).

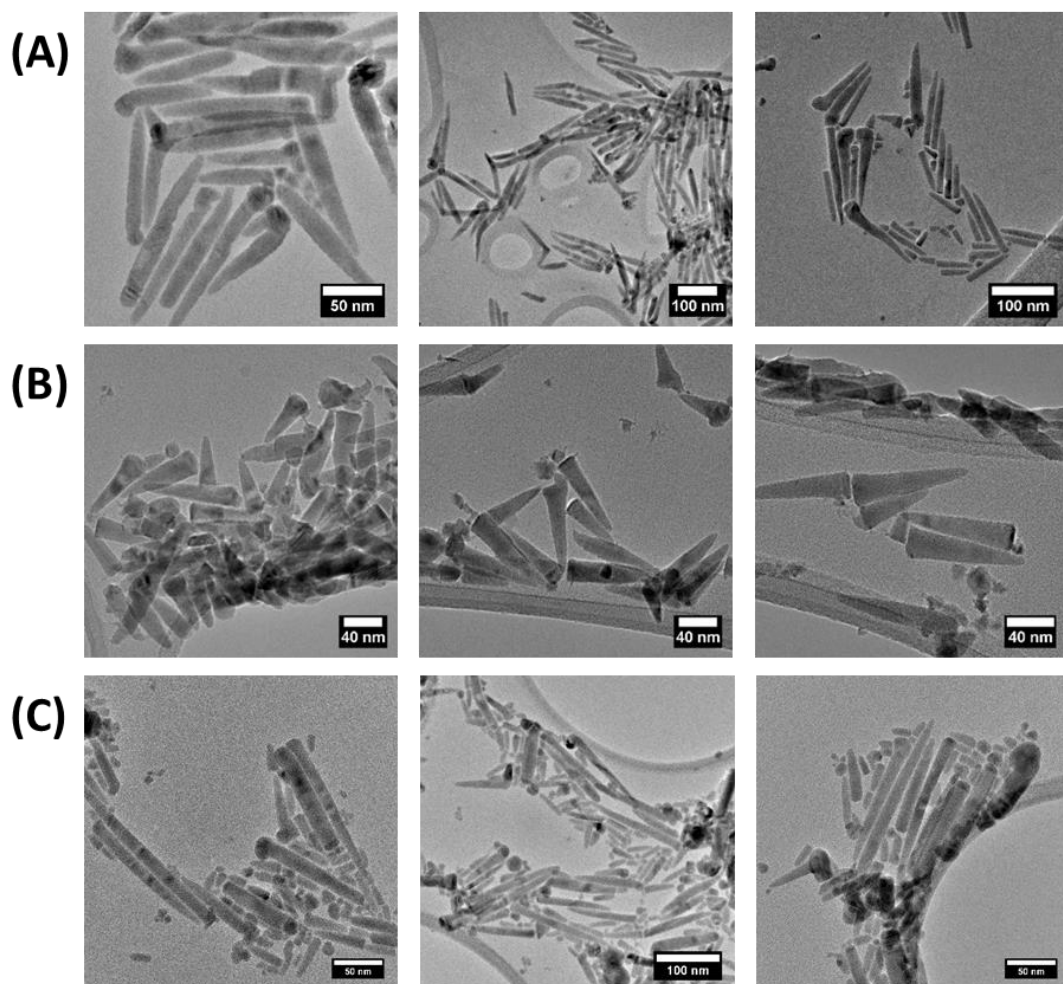


Figure 5. 9 (A) TEM images of CIZSe/CIZS/ZnS HNNs (1:2:3). (B) TEM images of CIZSe/CIZS/ZnS HNNs (1:3:2). (C) TEM images of CIZSe/CIZS/ZnS HNNs (1:1:3).

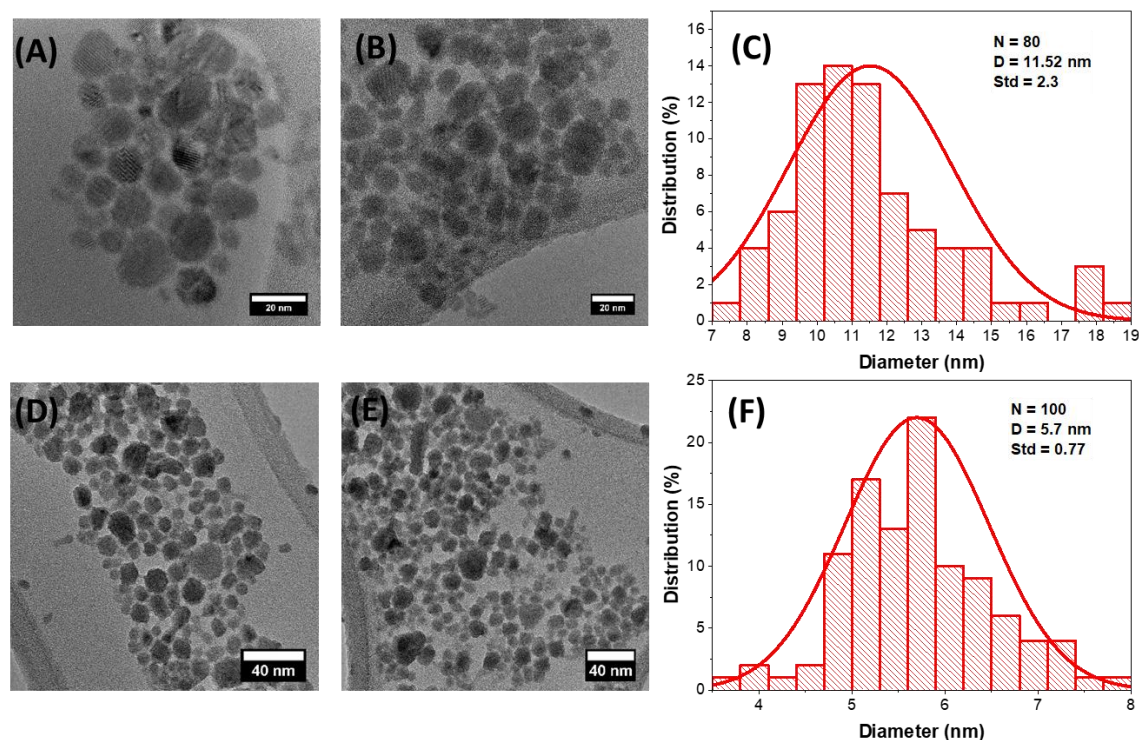


Figure 5. 10 (A-B) TEM images of CIZSe/CIZS QDs (Cu:In:Zn = 1:3:2) and (C) Diameter histogram of the sample. (D-E) TEM images of CIZSe/CIZS QDs (Cu:In:Zn = 1:1:3) and (F) Diameter histogram of the sample.

5.6 Growth mechanism of the distinct HNN nanostructure

It is well known that the optical properties of QDs are not only size and composition dependent but also strongly determined by the resulting shape. HNNs demonstrate increased electrical conductivity compared to quasi-spherical nanoparticles, and therefore are very appealing for applications requiring efficient charge transfer¹⁶. Their synthesis was well established for Cd-based systems. The most well-known structure of Cd-based NR structure is the CdSe/CdS dot-in-rod heterostructure, the growth mechanism of which has been studied intensively^{24, 39-40}. Therefore, core NCs with WZ crystal structure need to be firstly prepared as seeds for the preparation of a dot-in-rod nanostructure. This is due to the WZ nanocrystal seed possessing two polar opposite reactive facets $\pm \{002\}$ that allow for the transition to epitaxial growth of the shell materials and lateral nonpolar facets⁴¹. Regarding

Cd-based QDs, the $\{002\}$ facet is cation (Cd^{2+}) terminated, while the $\bar{\{002\}}$ facet is anion (Se^{2-} or S^{2-}) terminated. The shell materials therefore will preferentially nucleate either on both $\pm\{002\}$ facets or only on the $\bar{\{002\}}$ facet depending on certain reaction conditions.

In order to investigate the growth mechanism of the particular Cu-based multicomponent CIZSe/CIZS/ZnS core/shell/shell HNNs, aliquots were taken out from the reaction vessel and were studied by TEM (Figure 5.11A-F). The chalcopyrite CIZSe core has been made at the very beginning in this work, which was followed by the coating of CIZS shell *via* the seeded-growth method. The diameter increased from 4 nm CIZSe QDs to 9 nm CIZSe/CIZS QDs (Figure 5.11A and Figure 5.11B), indicating the effective coating of a thick CIZS shell onto the CIZSe cores. The WZ crystal structure of the obtained CIZSe/CIZS QDs was verified by the XRD diffraction analysis. In the early stage of the synthesis, the ZnS shell forms on all facets in an epitaxial way, but the growth of WZ ZnS in the S terminated direction is faster than in the opposite metal elements terminated direction and the 6 lateral directions, therefore the aspect ratio of the HNN structure continues to increase (Figure A12 in Appendix). The WZ CIZSe/CIZS QDs have two $\{002\}$ and $\bar{\{002\}}$ polar facets, which have different chemical compositions and polarities ($\text{Cu}^+/\text{In}^{3+}/\text{Zn}^{2+}$ terminated and S^{2-} terminated, respectively)⁴¹. As discussed above, the nucleation and epitaxial growth of ZnS shell on the polar facets are favoured, especially considering the small lattice spacing mismatch (2.8%) between the $\{002\}$ planes of WZ CIZS and WZ ZnS. I propose that the preferred facet is the anion (S^{2-}) terminated facet, which is poorly passivated under the chosen experimental conditions. The ligands present in the reaction medium (including OA and 1-DDT) are hard and soft Lewis bases and therefore have lower affinity to S^{2-} anions (which are hard Lewis bases). In contrast, the ligands can bind readily to the $\text{Cu}^{1+}/\text{In}^{3+}/\text{Zn}^{2+}$ cation (which are soft and hard Lewis acids) terminated facets and therefore this almost fully

passivated facet is hardly accessible for the nucleation of ZnS shell. Therefore, the anion terminated facet is accessible for the nucleation and heteroepitaxial growth of the ZnS shell.

The fact that ZnS HNN growth remains axially asymmetric implies that growth proceeds by addition of [ZnS] monomer unites to the anion terminated $-(002)$ facet, so that the polarity of this facet is preserved throughout the reaction, consistent with the growth mechanism proposed for other heterostructures⁴²⁻⁴⁴. In addition, it is possible that even the successive ion layer adhesion and reaction (SILAR) method, occurs by molecular attachment of shell material units instead of cation and anion in subsequent steps^{43, 45-46}.

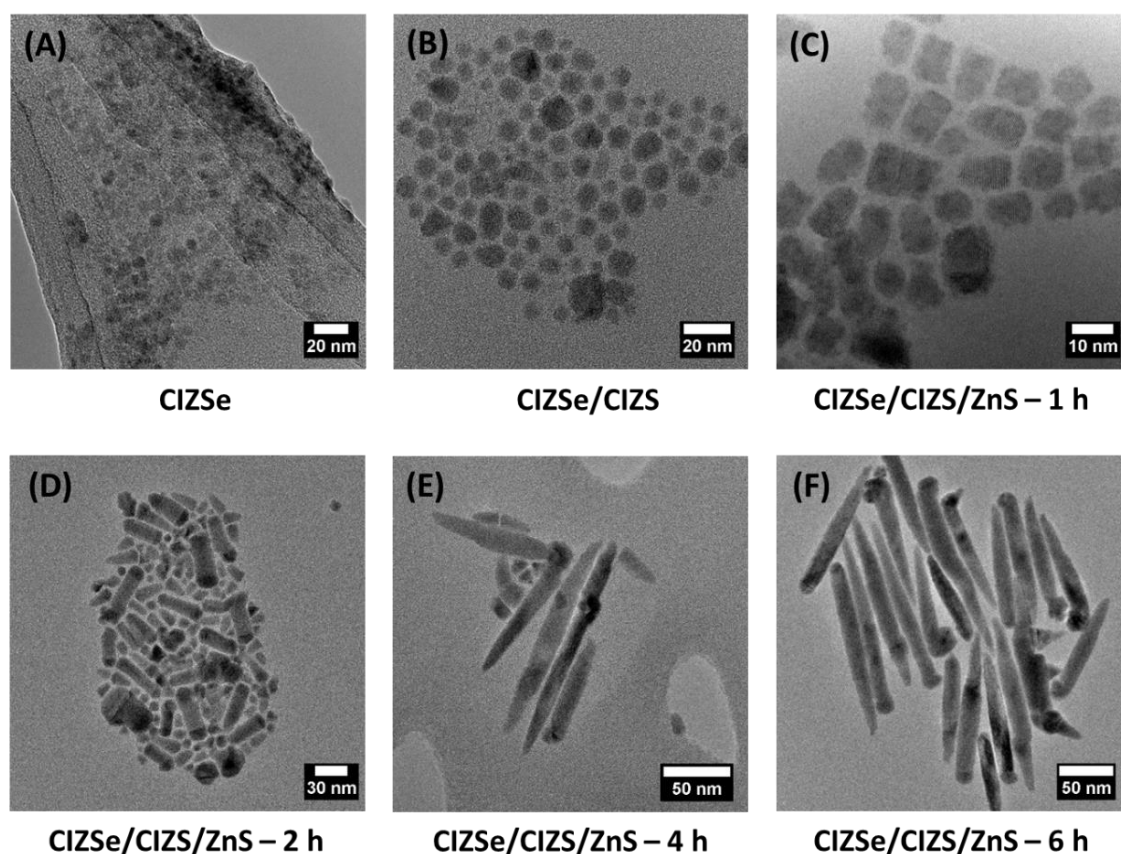


Figure 5. 11 TEM images of (A) CIZSe seeds, (B) CIZSe/CIZS QDs, (C-F) aliquots that taken out from the reaction vessel in the third step at 1 h, 2 h, 4 h and 6 h.

5.7 Synthesis of Au- CIZSe/CIZS/ZnS nanocomposites

A novel metal-semiconductor nanocomposites were prepared *via* the Au deposition onto the surface of CIZSe/CIZS/ZnS HNN. This was carried out by reducing Au (III) using OAm as the reducing agent. As shown in the TEM images of the CIZSe/CIZS/ZnS/Au HNNs (Figure 5.12A-E), small Au NPs with a diameter $\sim 2.3 \pm 0.5$ nm (Figure A13 in Appendix) are distributed on the HNN surface, instead in the form of a shell, consistent with previous reported works⁴⁷⁻⁴⁸. This form of Au deposition is due to the large lattice spacing mismatch between the WZ HNN structure and face-centred cubic Au NPs⁴⁷. The distribution of Au NPs on the surface of CIZSe/CIZS/ZnS HNNs with large absorption coefficient would benefit the efficiency of this nanocomposite for photocatalysis applications⁴⁹ as shown in CdSe/CdS/Au heterostructures. The optical spectroscopy performed on the obtained CIZSe/CIZS/ZnS/Au HNNs is shown in Figure 5.12F, with the UV-Vis spectrum of the sample showing the presence of a strong surface plasmon absorption peak of the CIZSe/CIZS/ZnS/Au HNNs centered at 538 nm. In addition, analysis of the photoluminescence gives the expected result of complete quenching due to the Au growth. This can be explained by fast transfer of photogenerated electrons to the Au followed by non-radiative decay⁵⁰.

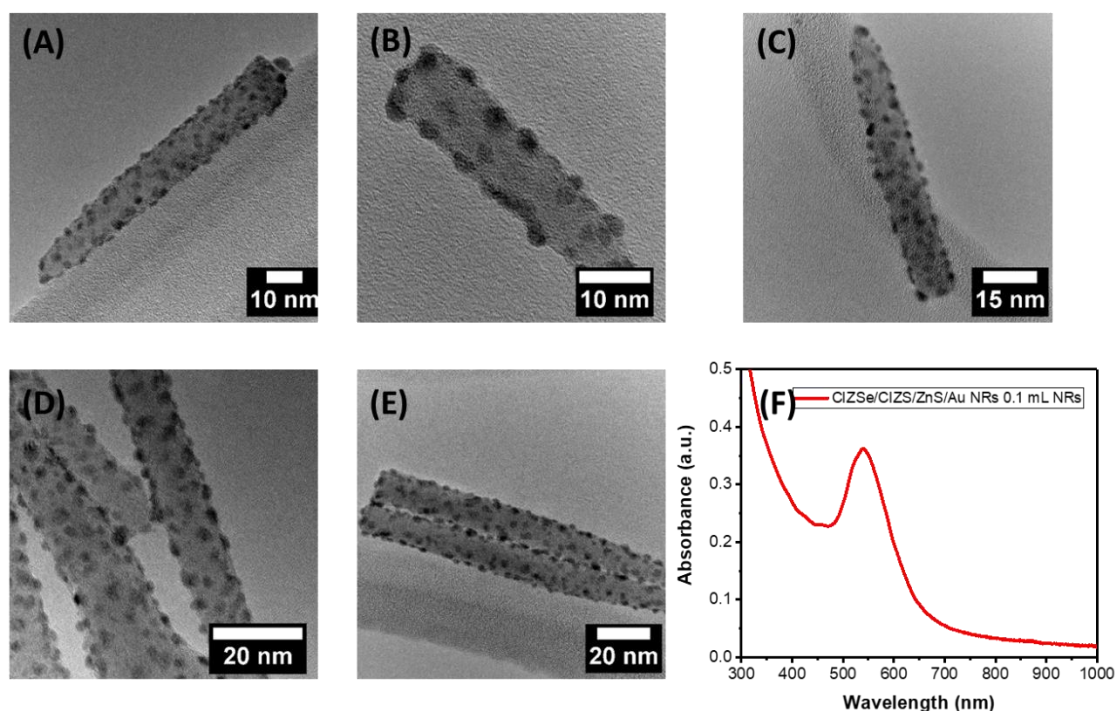


Figure 5. 12 (A-E) TEM images of CIZSe/CIZS/ZnS/Au HNNs. (F) UV-Vis spectrum of CIZSe/CIZS/ZnS/Au HNNs.

Thus, I have developed a multistep protocol to synthesize colloidal CIZSe/CIZS/ZnS HNNs with photoluminescence in the NIR region with the origin of the emission assigned to the CIZSe/CIZS core. I have demonstrated excellent control of the resulting HNN structure either by varying the precursor ratio of Cu, In and Zn used in the second step to produce CIZSe/CIZS core/shell QDs or *via* control of the length of time growing the ZnS shell to produce the final CIZSe/CIZS/ZnS HNNs. The obtained HNNs demonstrate excellent optical properties due to the passivation of the ZnS shell. These findings open up new possibilities in developing techniques for the synthesis of Cu-based multicomponent colloidal asymmetric HNNs. The obtained CIZSe/CIZS/ZnS HNNs with emission in the NIR region are particularly interesting for a range of applications including bioimaging, biosensing, NIR LEDs and photodetectors. In addition, I have explored the incorporation of further modality *via* the controlled growth of Au nanoparticles upon the HNN surface to

produce the Au-CIZSe/CIZS/ZnS nanocomposites. The resulting CIZSe/CIZS/ZnS/Au HNNs are of great interests for photocatalysis applications due to the large absorption coefficient of the CIZSe/CIZS/ZnS HNNs and the overall distribution of Au particles on the surface of the CIZSe/CIZS/ZnS HNNs. In conclusion, huge potential lies in the field of toxic metal free ternary/quaternary quantum confined materials, this work demonstrates the complex structures that can be designed to fully realize the full potential of this still emerging area.

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Chapter 6 Luminescent solar concentrators

6.1 Introduction

Sustainable green solar energy is the natural resource that we can rely on for many generations and significant effort has been focused on this area for decades trying to develop the efficient and cost-effective way to exploit solar energy. It has been proposed that luminescent solar concentrators (LSCs) can be built to lower the cost of exploiting solar energy by concentrating solar radiation to the solar cell that attached to the edge of LSCs¹⁻³. To build LSCs, highly emissive luminophores need to be incorporated into polymer blocks with high refractive index to absorb solar radiation and reemit light in lower energy region, then the emission of the luminophores will be guided onto the attached small area solar cell by total internal reflection⁴⁻⁵.

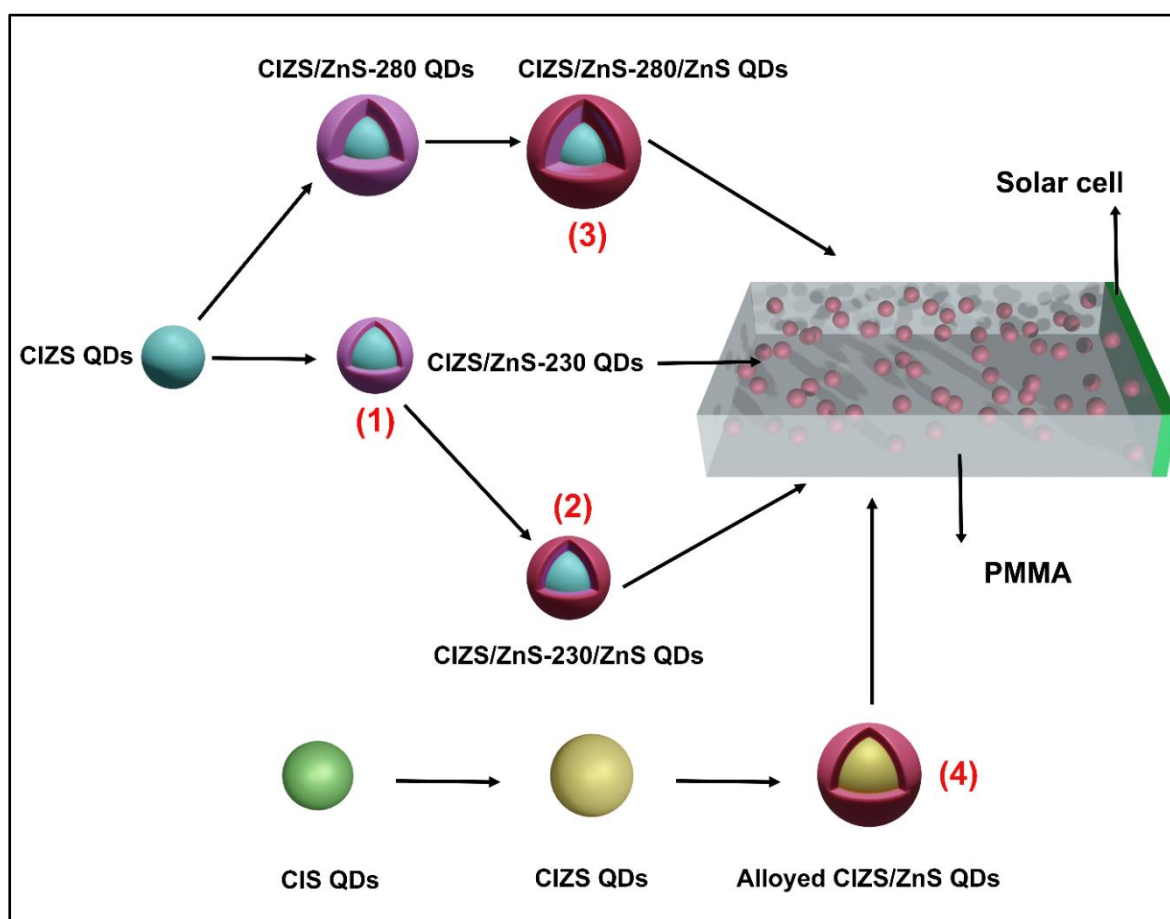
As for the luminophores, inorganic semiconducting nanomaterials - quantum dots (QDs) outperform traditional dye due to their higher photo-stability⁶⁻⁹ and larger absorption cross section¹⁰⁻¹². Group II-VI QDs (Cd- or Pb-based QDs) are no longer the best candidates not only for photovoltaic applications but also many other applications like bioimaging, biomedical and lighting because of the presence of heavily toxic metals (Cd and Pb)^{4, 13}. Due to the fast development of the synthetic techniques for colloidal QDs, Cu-based QDs with not only the most common symmetric spherical shape but also the novel asymmetric nanorod like shape have been obtained¹⁴⁻¹⁹. Compared to Cd- or Pb-based QDs, Cu-based QDs demonstrate some specific properties that are particularly suitable for LSC applications, including higher tunability of absorption and emission range, much prolonged photoluminescence lifetime (PL lifetime) and reduced toxicity²⁰⁻²¹. Especially, the intrinsic large Stokes shift of Cu-based QDs is more suited for LSC applications⁴. Stokes shift refers

to the energy difference between the UV-Vis absorption and the emission peak, which needs to be large enough to avoid the reabsorption issue. In an LSC, if the energy difference is not big enough, then the emission from a certain amount of QDs will be reabsorbed by other present QDs, even with quite high photoluminescence quantum yields (PLQYs) such as 90%, over long optical paths, reduced emitted light is retained and guided to the solar cell that attached to the edge of the LSC. To solve this issue, employing core/shell heterostructured QDs with narrow size distribution, especially type I QDs is the most promising and effective approach. The narrow size distribution insures the decrease of the chance for reabsorption due to disparity of the sizes of QDs (quantum effect). In addition, for type I core/shell heterostructured QDs, the shell dominate the absorption of the solar radiation, while the emission mainly originates from the core, thus the overlap of the UV-Vis absorption spectra and the PL spectra will be minimized to a great level.^{1, 22} Here Cu-based multicomponent type I core/shell heterostructured CIZS/ZnS QDs have been synthesised and used to build the new LSCs, with the ZnS shell dominating the absorption of solar radiation, while the emission mainly originates from the CIZS core. At the same time, the type I core/shell heterostructures helps to protect the excitons in the core away from the surface defects and the external microenvironment (oxygen and moisture), which benefits high PLQYs and good photo stability of the QDs²³⁻²⁵.

The transparency to radiation from ultra violet to near-infrared region, high refractive index (1.49)²⁶⁻²⁷, good mechanical properties²⁸, excellent photo- and chemical stability, and the air and moisture tightness¹³ render PMMA the perfect matrix candidate to embed the luminophores for LSC and guide the light effectively²⁸⁻²⁹. There are several works on the building of LSCs using Cu-based QDs as the luminophore and PMMA as the light guide. However, it has been found that the harsh reaction conditions to perform the polymerization of PMMA block diminish the optical properties of QDs that present in the reaction system.²⁹⁻

³⁰ If this issue can be tackled, then the optical properties of the QDs can be preserved after the polymerization of the PMMA matrix.

I believe that this work on the development of highly efficient LSCs based on Cu-based QDs should give significant insights on the exploring the optimal route to realize the most potential of Cu-based QDs for photovoltaic applications and make it cost-effective for our society to exploit sustainable solar energy to support our daily life and industrial development (Scheme 6.1).



Schematic 6 1. Illustration of the building of LSCs based on Cu-based QDs.

6.2 Building of reaction chamber

In order to conduct the bulk polymerization of PMMA, the first issue to tackle was to build a reaction chamber. As shown in Figure 6.1A, two glass slides (width*length = 2 cm*5 cm),

a PEFT gasket (thickness = 2 mm) and two thin layers of PET polymer films were sealed using silicone glue and clamped together to make the first version of the reaction chamber, which was used to carry out the bulk polymerization of PMMA. However, when the polymerization completed, it was impossible to peel the thin PET polymer films off the obtained PMMA block, which made it challenging to perform the following up characterization of the PMMA blocks that loaded with Cu-based QDs (Figure 6.1B). For the upgraded reaction chamber, the thin PET films were removed from the whole design, with the rest of the components were left to be sealed and clamped together. Using the upgraded reaction chamber, PMMA blocks with low surface optical scattering have been prepared (Figure 6.1C).

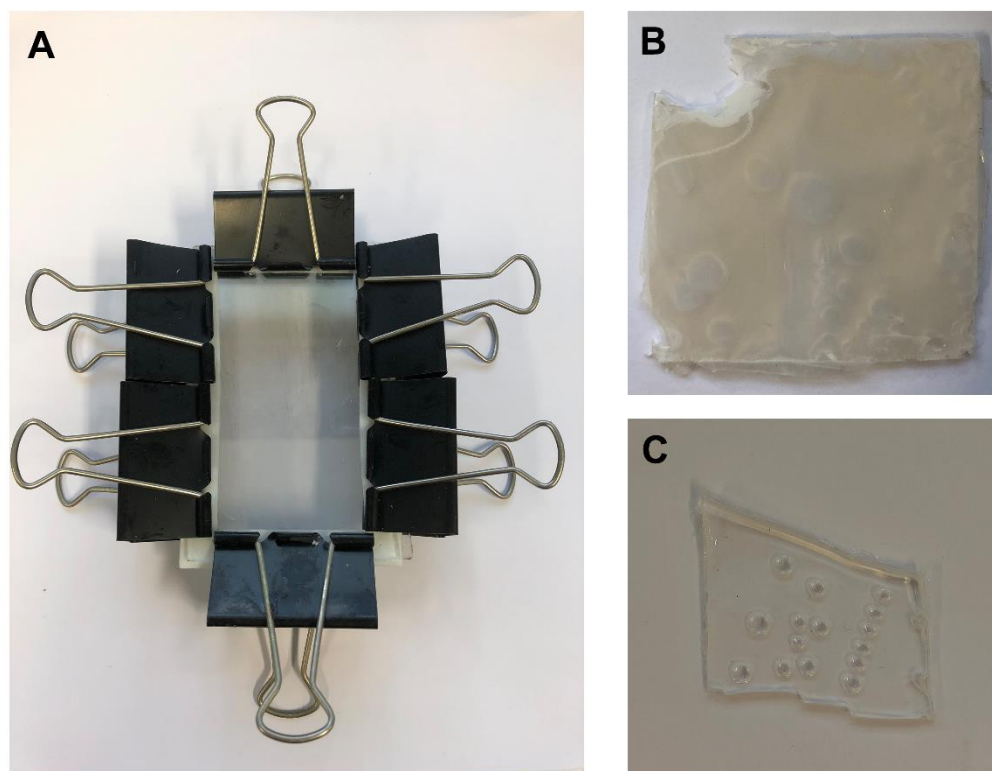


Figure 6. 1. Photograph of the home-made reaction chamber for the bulk polymerization of PMMA.

6.3 Exploring polymerization temperature

There are several developed methods that can be employed to incorporate NPs into PMMA blocks, including solution casting method^{28, 31} and spin coating. The bulk polymerization can be done upon the UV light irradiation³² or heating. Three temperatures have been tried to carry out the bulk polymerization of PMMA to embed the chosen Cu-based QDs in, which were 80 °C, 70 °C and 60 °C. As shown in Figure 6.2A, when 80 °C was used, air bubbles can be observed in the obtained polymer block, which can have a detrimental effect on the optical characterization of the samples and their practical applications. When 70 °C was used, less bubbles can be noticed (Figure 6.2B). There was no air bubbles can be observed in the polymer block that prepared at 60 °C (Figure 6.2C). After the optimal temperature has been found, LSCs based on the above mentioned 3 types of Cu-based heterostructured QDs have been prepared.

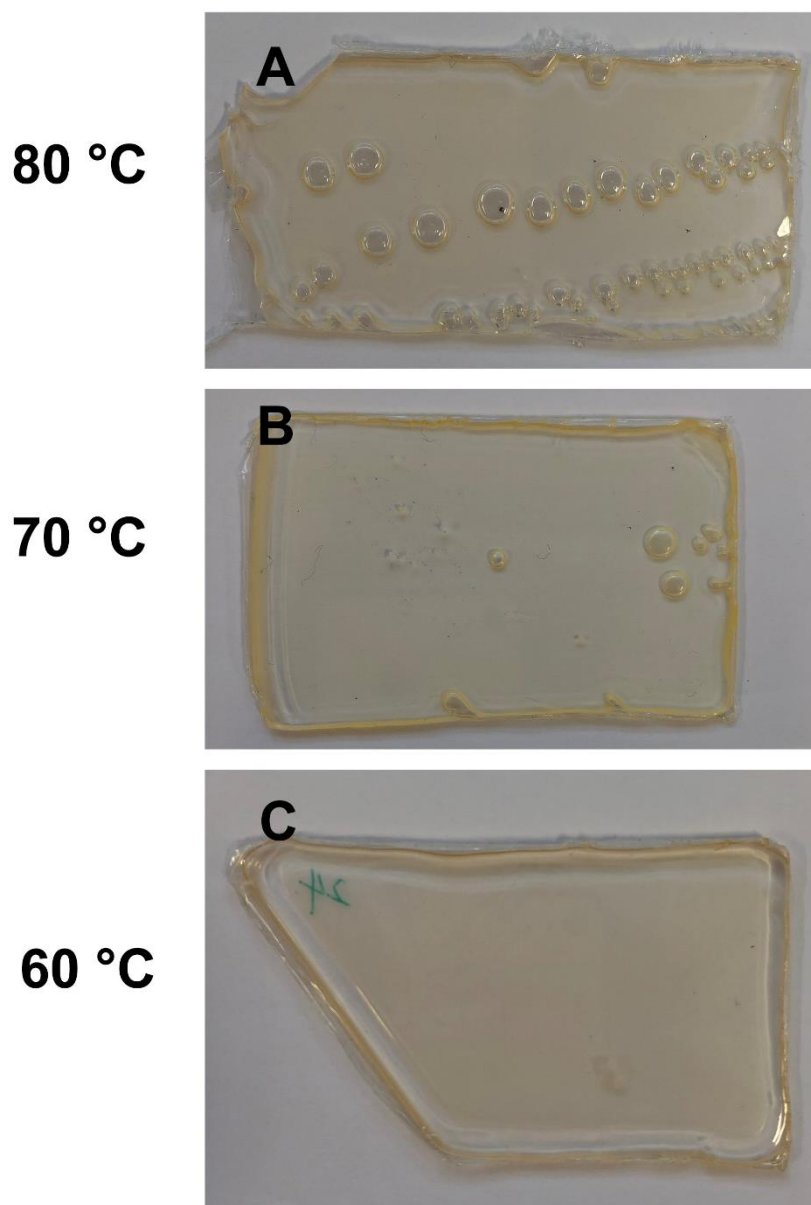


Figure 6. 2. Pictures of PMMA blocks that prepared at (A) 80 °C, (B) 70 °C, and (C) 60 °C, respectively.

6.4 Heterostructured CIZS/ZnS QDs and CIZS/ZnS/ZnS QDs

The first three types of Cu-based heterostructured QDs that embedded into the transparent PMMA blocks are from the synthetic work that presented in Chapter 3.

Figure 6.3 shows the optical properties of the three types of QDs. CIZS/ZnS-230 QDs possess a branched morphology with a 5.1 ± 0.8 nm size and relatively high PLQY $\approx$

28.9±2.9%. After coating a second ZnS shell, CIZS/ZnS-230/ZnS QDs evolved to a more branched shape and have higher PLQY $\approx 41.6\pm4.2\%$. CIZS/ZnS-280/ZnS QDs have the largest size $\approx 12.3\pm1.8$ nm, such thick shell benefits enhanced stability against surrounding micro-environment and solar radiation, though this sample has relatively low PLQY $\approx 12.7\pm1.3\%$.

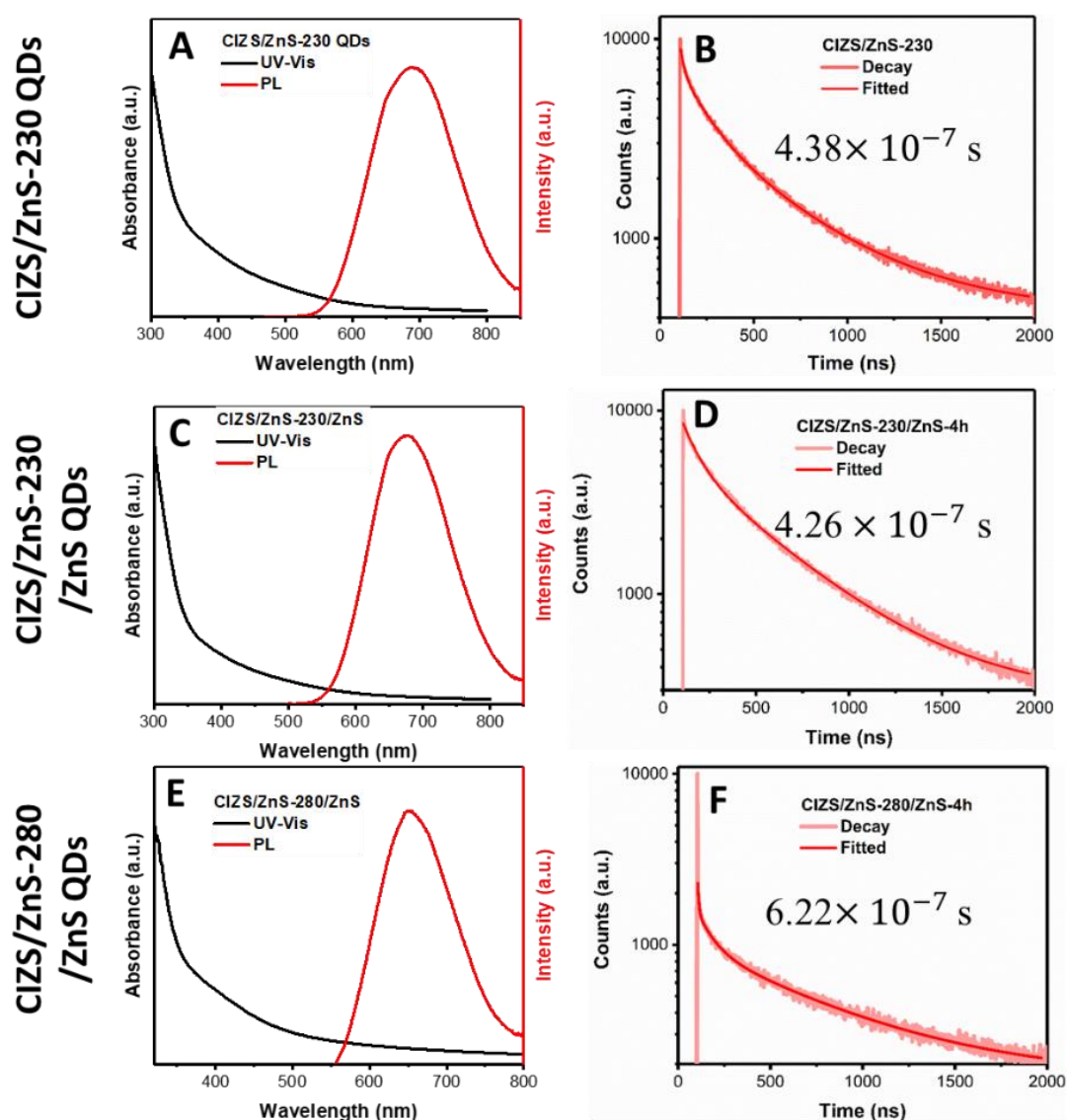


Figure 6. 3. UV-Vis absorption spectra, PL spectra and PL lifetime decay curves of (A-B) CIZS/ZnS-230 QDs, (C-D) CIZS/ZnS-230/ZnS QDs and (E-F) CIZS/ZnS-280/ZnS QDs, respectively.

6.5 LSCs based heterostructured CIZS/ZnS QDs and CIZS/ZnS/ZnS QDs

6.5.1 LSC based on CIZS/ZnS-230 QDs

Sample CIZS/ZnS-230 is the type of heterostructured QDs with relatively thin ZnS shell that prepared at 230 °C. The size was measured to be 5.1 ± 0.8 nm, the emission peak of the QDs is around 690 nm, PLQY was determined to be $28.9 \pm 2.9\%$, and the average PL lifetime was calculated to be 4.38×10^{-7} s. Then this luminophore has been embedded into PMMA block through heat-induced bulk polymerization. As shown in Figure 6.4A, the LSC is transparent under daylight. Under UV lamp (Figure 6.4B), the obtained LSC is fluorescent and the intensity of fluorescence from the edges is higher than that on the top and bottom surfaces. Figure 6.4C shows the UV-Vis spectra of the QD solution and the LSC after the polymerization, no big change has been observed. As demonstrated in Figure 6.4D, a distinct blue shift of 130 nm (from 690 nm of solution to 560 nm of LSC) the PL peak can be noticed. Figure 6.4E shows the PL decay of the obtained LSC, and the average PL lifetime was determined to be 1.27×10^{-7} S (Table A9 in Appendix). No value for PLQY has been obtained using integrating sphere due to the much decreased PL intensity after the polymerization.

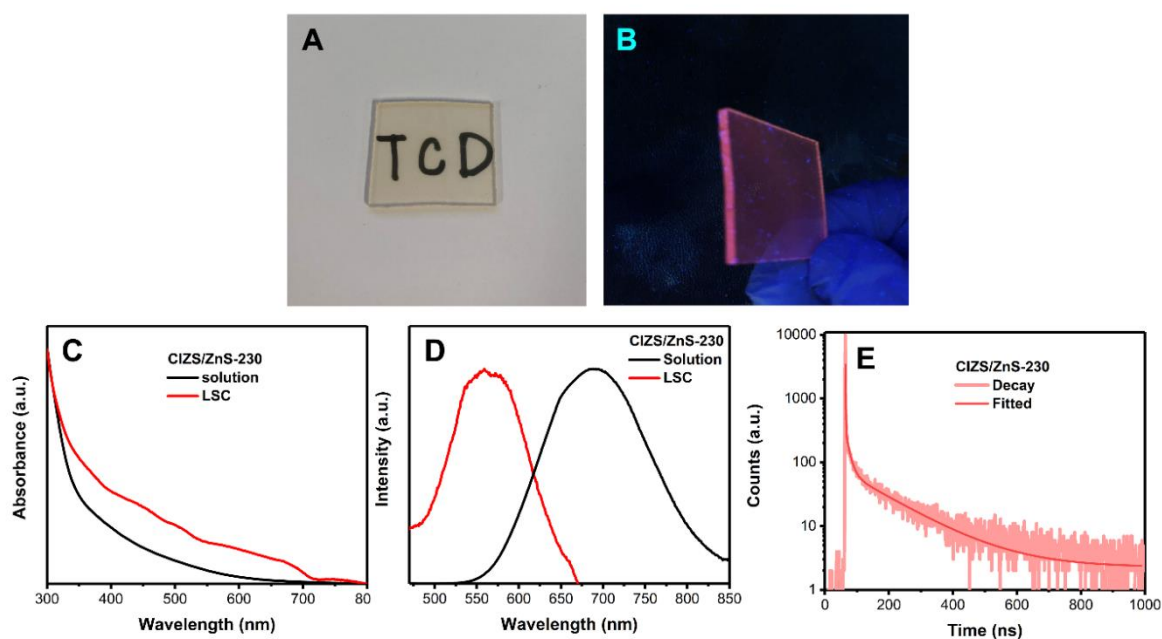


Figure 6. 4. (A-B) Pictures of obtained PMMA block that loaded with luminophor CIZS/ZnS-230 under daylight and UV lamp. (C) UV-Vis spectra, (D) PL spectra and (E) PL decay spectra of the LSCs based on luminophor CIZS/ZnS-230, respectively.

6.5.2 LSC based on CIZS/ZnS-230/ZnS QDs

Sample CIZS/ZnS-230/ZnS is the type with a second ZnS shell. The size was measured to be 6.1 ± 0.9 nm, the emission peak of the QDs is around 675 nm, PLQY was determined to be $41.6 \pm 4.2\%$, and the average PL lifetime was calculated to be 4.26×10^{-7} s. Then this sample has been embedded into PMMA block through heat-induced bulk polymerization. As shown in Figure 6.5A-B, the obtained LSC reveals good transparency and fluorescence performance under daylight and UV light. And the fluorescence intensity of the obtained LSC is higher than that of the LSC that based on luminophore CIZS/ZnS-230 (Figure 6.4B). The UV-Vis spectra have not changed much after the polymerization process (Figure 6.5C). As shown in Figure 6.5D, a large blue shift of 90 nm (from 675 nm to 585 nm of LSC) PL peak can be noticed. Figure 6.5E shows the PL decay curve of the obtained LSC. The average PL lifetime was determined to be 1.11×10^{-7} s (Table A10 in Appendix). The PLQY

of the obtained LSC was calculated to be 3.6% using integrating sphere, which is much lower than the parental QD solution.

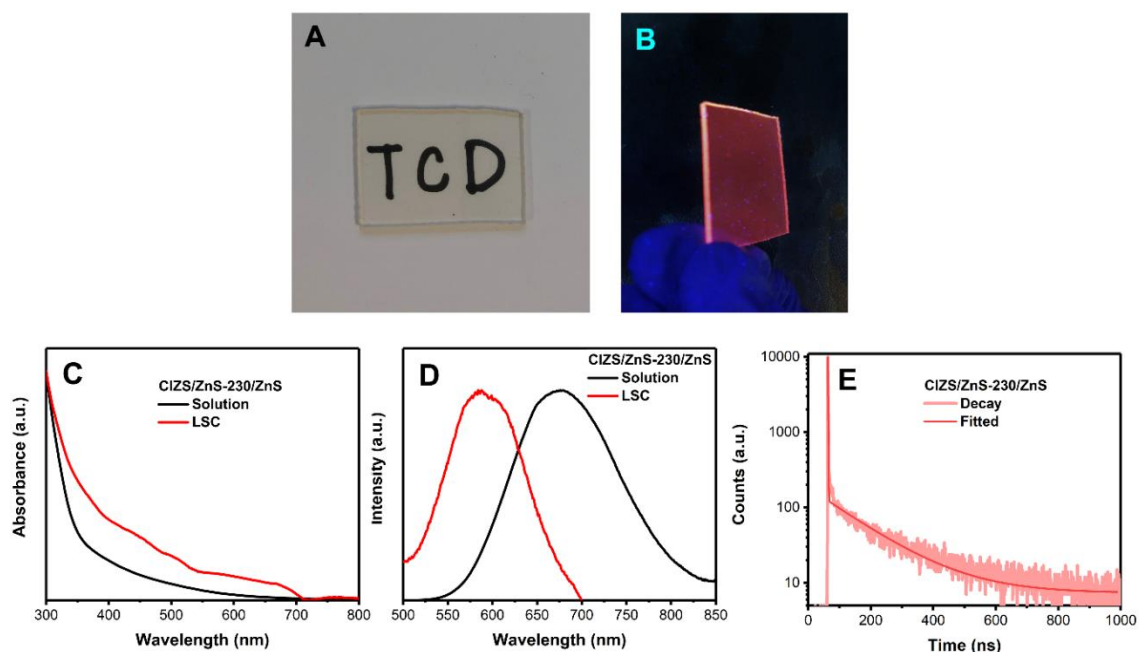


Figure 6. 5. (A-B) Pictures of the obtained LSC under daylight and UV lamp. (C) UV-Vis spectra, (D) PL spectra and (E) PL decay curve of the obtained LSC that based on luminophore CIZS/ZnS-230/ZnS, respectively.

6.5.3 LSC based on CIZS/ZnS-280/ZnS QDs

Sample CIZS/ZnS-280/ZnS is the type with the thickest ZnS shell. The size was measured to be 12.3 ± 1.8 nm, the emission peak of the QDs is around 630 nm, PLQY was determined to be $12.7 \pm 1.3\%$, and the average PL lifetime was calculated to be 6.22×10^{-7} s. Then this sample has been embedded in to PMMA block through heat-induced bulk polymerization. As shown in Figure 6.6A, the obtained LSC reveals great clarity under daylight. It demonstrates luminescence performance under UV lamp (Figure 6.6B). The UV-Vis spectra after the polymerization did not change much as revealed in Figure 6.6C. As shown in Figure

6.6D, a blue shift of 25 nm (from 630 nm of QD solution to 605 nm of the obtained LSC) can be observed. Figure 6.6E shows the PL lifetime decay of the obtained LSC, since the PL intensity is too low, no trustable results has been obtained. No value for PLQY has been obtained using integrating sphere due to the very low PL intensity after polymerization process.

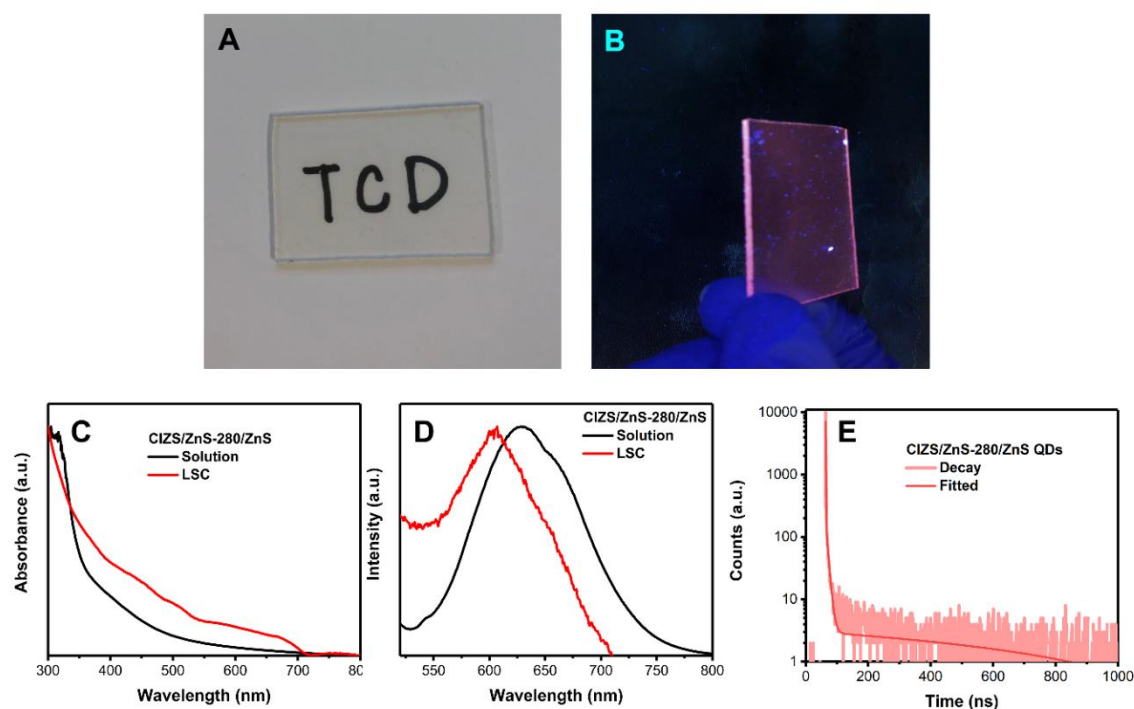


Figure 6. 6. (A-B) Pictures of the obtained LSC under daylight and UV lamp. (C) UV-Vis spectra, (D) PL spectra and (E) PL decay curve of the obtained LSC that based on luminophore CIZS/ZnS-280/ZnS, respectively.

6.6 Synthesis and characterization of alloyed CIZS/ZnS QDs

According to TEM and STEM images shown in Figure 6.7A-B, homogeneous CIZS/ZnS QDs have been obtained with narrow size and shape distributions. These core/shell structures are of pyramidal tetrahedral shape (which is consistent with the reference³³). This sample shows great size uniformity with average size equalling 5.7 nm (with Std equals to 0.8, Figure 6.7C). Observation of the continuous lattice fringes indicates the high

crystallinity of the CIZS/ZnS QDs. STEM images clearly confirmed the nano-pyramidal shape and also the narrow size distribution (Figure 6.7D). EDX has been used to check the chemical composition of the core/shell structure. Elements from the core (Cu, Zn, In, and S) and the elements from the shell (Zn and S) were detected successfully (Figure 6.7E), which is consistent with that in the reference paper.³³ The crystal structure of the obtained CIZS/ZnS QDs was determined to be ZB (zinc blende) using XRD as shown in Figure 6.7F.

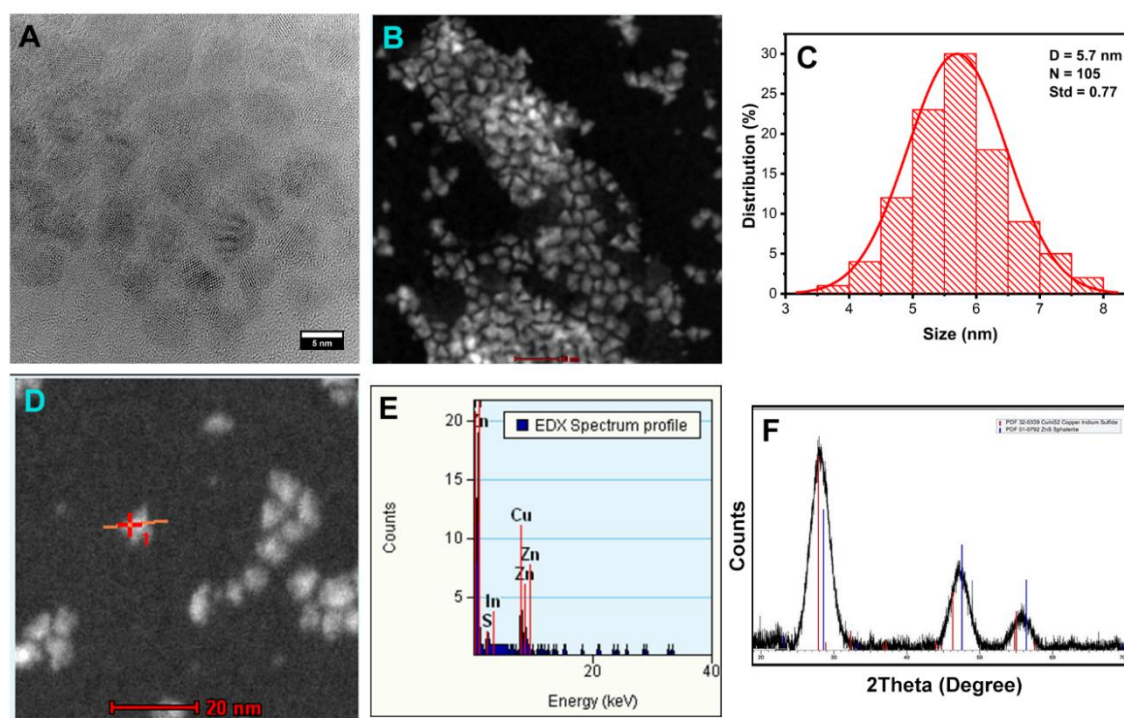


Figure 6. 7. (A) TEM image, (B) STEM image and (C) size distribution histogram of the obtained CIZS/ZnS QDs. (D-E) STEM image and the corresponding EDX spectra of the sample that measured from the position indicated with the red cross in Figure 1D, respectively. (D) XRD pattern of CIZS/ZnS QDs.

CIS seeds (Cu:In:S = 1:2:3) were prepared through heating-up method. The colour change at 160 °C indicated the nucleation of CIS QDs. The colour of the reaction solution proceeded to to darken as temperature increased, which is a sign of the growth of CIS QDs. CIZS QDs (Cu:In:Zn:S = 1:2:3:3) were prepared through the cation exchange method. TOP was used in this step to accelerate the process, which is a soft Lewis base and has higher affinity to

soft Lewis acid Cu^{+1} and therefore the TOP facilitates the incorporation of Zn into CIS QDs³⁴. Because of the penetration of element zinc into the obtained CIS nanostructure, the colour changed from dark red of CIS QDs to orange of CIZS QDs. In the final step, CIZS/ZnS QDs were obtained *via* a seeded-growth method with the injection of zinc and sulphur precursor solutions ($\text{Zn} = 4 \text{ mmol}$). As reaction proceeded, the colour of reaction solution became lighter and lighter and the final sample is in light yellow colour (Figure 6.8A).

UV-Vis and PL spectroscopy were used to characterise the samples from CIS seeds to the final CIZS/ZnS spherical hetero-core/shell structure. As shown in Figure 6.8B, the UV-Vis absorption spectra are featureless, which is typical for Cu-based ternary or quaternary QDs because of the complexity of size distribution, also due to the variation of chemical composition across the QDs. It can be found that after the zinc alloying in the second step, there is a blue shift from CIS to CIZS in the PL spectra (Figure 6.8C). According to Zunger's theoretical model on defects, compared to binary Cd- and Pb-based QDs, Cu-based QDs can bear large stoichiometric tunability³⁵. In this way, changing the composition is another effective way to tune the emission of the NCs in addition to changing the size of the sample. The bandgap of the Cu-based QDs are not only size-dependent but also composition dependent. The same kind of blue shift is also observed in the shell coating process. Further blue shift can hardly be detected after 10 h. The PL spectra was checked for all the samples. It is apparent that the emission peak underwent a blue-shift process because of the zinc alloying, also the intensity of the emission increased. That is because the coating of ZnS shell passivates the surface defects of the CIZS cores and improves the optical properties greatly. The emission peak of the final CIZS/ZnS QDs is approximately 560 nm, which is consistent with reference data.³³ The Stokes shift of the final CIZS/ZnS QDs is as large is 140 nm (the onset of the absorption of the sample is around 420 nm), such large Stokes shift is more than suitable for LSC applications. The PLQY of the final CIZS/ZnS core/shell

structure is as high as 51% (Coumarin 153 was employed as the reference, PLQY = 0.53 in ethanol, excitation = 420 nm, emission range = 440-750 nm, slit = 5). PL lifetime was checked for the final CIZS/ZnS core/shell structure (Figure 6.8D, Table A11 in Appendix). The average lifetime of CIZS/ZnS NCs was calculated as 3.10623E-06 S (CHISQ = 1.2417). Such long PL lifetime is typical for Cu-based multicomponent core/shell structure. This increased lifetime is useful not only for bioimaging³⁶ but also for photovoltaic applications³⁷.

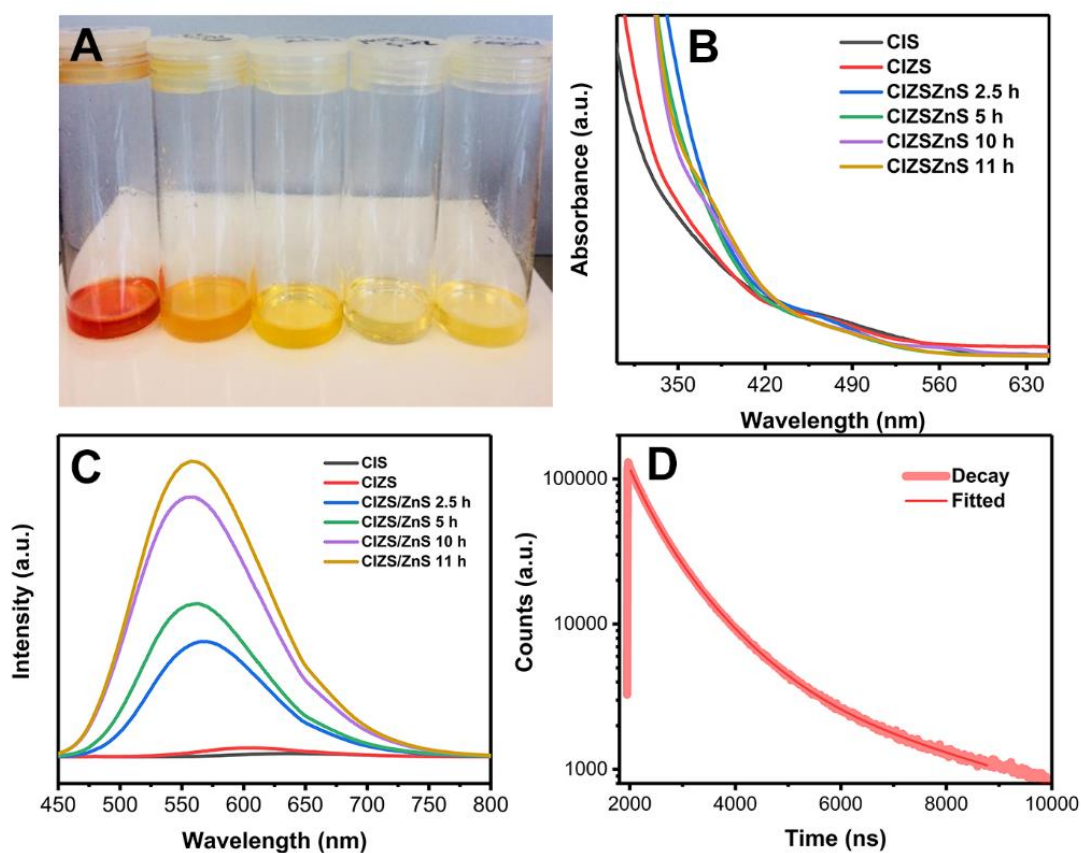


Figure 6. 8. (A) photograph under daylight, (B) UV-Vis absorption spectra, (C) PL spectra of the samples that taken out from the reaction vessel at certain time intervals and (D) PL lifetime curve of the final CIZS/ZnS QDs.

6.7 LSCs based on alloyed CIZS/ZnS QDs

After the highly fluorescent, alloyed CIZS/ZnS QDs have been obtained, the QDs have been introduced into the bulk polymerization reaction system to prepare the LSC using the same

two-step polymerization procedure and the polymerization temperature was set at 60 °C. As shown in Figure 6.9A, the obtained LSC possesses great transparency under daylight. And the LSC reveals quite bright luminescence under UV lamp (Figure 6.9B). There is no big difference of the UV-Vis spectra between the QD solution and the obtained LSC after polymerization (Figure 6.9C). As shown in Figure 6.9D, a relatively small blue shift of 25 nm (from 560 nm of the QD solution to 535 nm of the obtained LSC) can be noticed. Figure 6.9E shows the PL decay of the obtained LSC, the average PL lifetime was determined to be 2.36×10^{-7} S (Table A12 in Appendix). The PLQY of the obtained LSC was calculated to be 9.7% using integrating sphere.

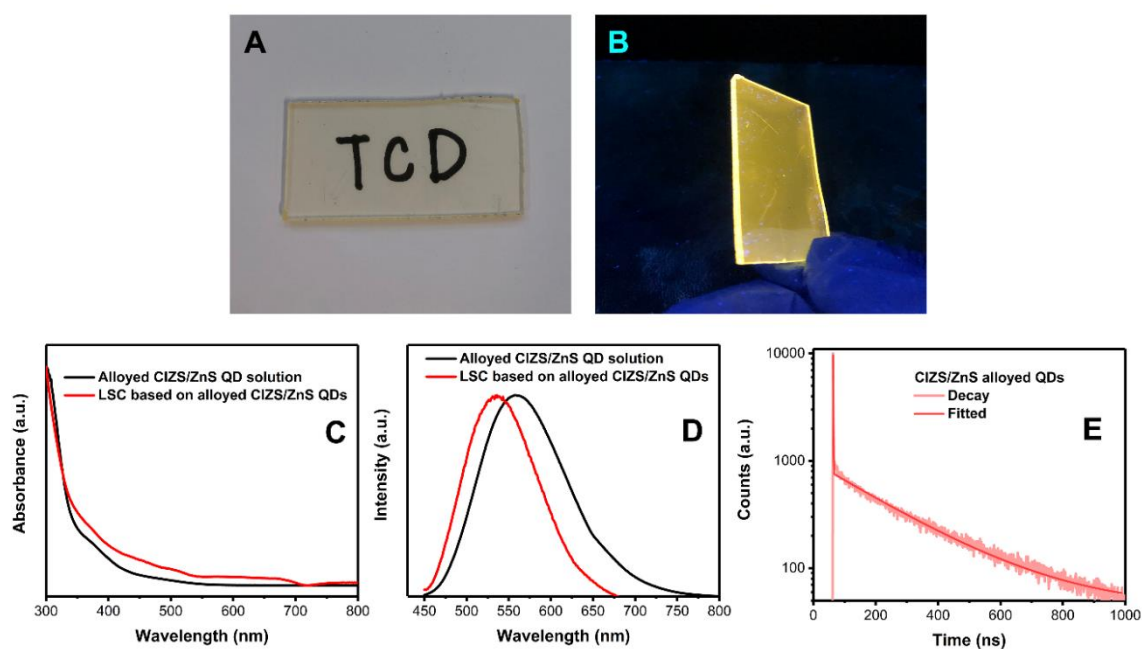


Figure 6. 9. (A-B) Pictures of the obtained LSC under daylight and UV lamp. (C) UV-Vis spectra, (D) PL spectra and (E) PL decay curve of the obtained LSC that based on luminophore alloyed CIZS/ZnS QDs, respectively.

6.8 Discussion

There has been extensive effort to build LSCs using QDs as the luminophores, especially Cu-based heterostructured QDs. In order to realize as high efficiency, several strategies have been proposed regarding the preparation of the QDs that satisfy the requirements^{4, 20, 38-40}, the methods to prepare PMMA blocks^{27, 41} and even some detailed work investigating the effects of the surface ligands on the dispersion of QDs in polymer blocks⁴². In order to get large-area LSC for practical applications, bulk polymerization of MMA monomer with the presence of luminophores is the optimal routine due to the absence of air bubbles and other heterogeneities compared to straightforward solution casting or drop casting methods. The bulk polymerization can be carried out *via* heating –induced process or photo-induced process upon the initiation of corresponding initiators. Such harsh reaction conditions normally give rise to the detrimental influence on the optical properties of the QDs²⁷. Generally, decreased PLQYs along with shorter PL lifetimes can be noticed after the polymerization process. In addition, blue shift of PL peak of the QDs after polymerization process has been reported, and the reason can be attributed to the oxidation effects to the QDs during polymerization²⁹⁻³⁰. Here, I prepared LSCs using 4 different types of QDs (heterostructured QDs with relatively thin ZnS shell – CIZS/ZnS-230 QDs, heterostructured QDs relatively thick ZnS shell - CIZS/ZnS-230/ZnS QDs, heterostructured QDs with much thicker ZnS shell - CIZS/ZnS-280/ZnS QDs and the alloyed CIZS/ZnS QDs) to investigate the effect of chosen polymerization method on the optical properties of the QDs. As expected, decreased PLQYs and shorter PL lifetimes have been observed for all the employed QDs. What is most noticeable is the different levels of blue shift of the PL peaks when make a comparison among the three heterostructured QDs with different ZnS shell thicknesses. The blue shift of LSC based on CIZS/ZnS-230 is as high as 130 nm, which is higher than 90 nm of the LSC based on CIZS/ZnS-230/ZnS. While the blue shift for the LSC

based on CIZS/ZnS-280/ZnS is only 25 nm. This experimental observation indicates that the thick ZnS shell helps to preserve the optical properties of the QDs from the oxidation effects during polymerization. What is interesting is that the blue shift of 25 nm of the LSC based on alloyed CIZS/ZnS QDs is as small as that based on the heterostructured QDs with the thickest ZnS shell. In this case, the heterostructured QDs with quite thick shell and alloyed QDs are suitable for the building for large-area LSCs.

Thus, I have carried out a series of experiments on the building of LSCs starting from the preparation of our home-made reaction cell to the bulk polymerization of PMMA using four different types of “green” Cu-based QDs. It has been found that relatively mild polymerization temperature (60 °C) helps to avoid the formation of air bubbles in the obtained PMMA blocks. The harsh polymerization conditions due to the presence of initiator induced the decreased PLQYs and shortened PL lifetimes of the QDs. The oxidation effects during polymerization gave rise to the blue shift of the PL peaks of the QDs. It has been found that the optical properties of heterostructured QDs with thick shell or the alloyed core/shell QDs have been preserved to the higher level, which makes them potentially suitable to build large-area LSCs.

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7. Conclusions and future work

7.1 Conclusions

In this work, new fluorescent Cu-based multicomponent heterostructured QDs with both symmetric and asymmetric morphologies have been prepared using various synthetic approaches, including hot-injection method, heating-up technique, seeded growth technique, along with well-known post synthetic treatment methods, for example, cation exchange and phase transfer. The overall conclusions from my work are detailed as following.

Initially a series of reactions have been carried out, optimising the synthesis of CIZS/ZnS/ZnS QDs *via* careful control of the ZnS shell deposition. The effects of differing reaction temperatures and growth times on the resulting morphologies and optical properties have been thoroughly examined. It has been found that reaction temperature plays a significant role in the resulting optical properties and morphologies, affecting the deposition dynamics of the shell materials and the onset of severe surface ligand degradation. Based on detailed studies, optimal reaction conditions have been chosen and highly fluorescent CIZS/ZnS/ZnS core/shell/shell heterostructured QDs have been obtained, with PLQYs as high as $41.6 \pm 4.2\%$. “Giant” ZnS shelling (QDs of 13.0 nm) has been achieved for the first time. These results present an important step for CIZS/ZnS/ZnS core/shell/shell heterostructured synthesis enabling optimal optical and morphological properties going forward.

After that, highly fluorescent Cu-In-(Zn)-S/ZnS core/shell heterostructured QDs with asymmetric “ice-cream cone” like shape have been developed. The Cu-In-S core was prepared using a straightforward heating-up method and seeded growth method was

employed to coat the ZnS shell. Aliquots have been taken out from the reaction vessel at certain time intervals for detailed characterization in order to investigate the growth mechanism of this specific asymmetric “ice-cream cone” like morphology. It was found that the growth mechanism involves the transformation of the crystal structure of the sample during the coating of ZnS shell from ZB from the Cu-In-S core to WZ to an aliquot after 60 min of the shell growth time. The obtained asymmetric Cu-based core/shell heterostructures are fluorescent in the visible range of the spectrum with quite high PLQY (27%), which is very promising for various applications.

Then, more complex fluorescent Cu-based CIZSe/CIZS/ZnS core/shell/shell heterostructured QDs with the nail like shape have been developed. In this work, hot injection and seeded growth techniques have been used to synthesize the core and to coat the first and the second shell. ZB CIZSe core was used to coat the CIZS shell to get the CIZSe/CIZS QDs with WZ crystal structure. The selective deposition of the ZnS shell precursors on the WZ CIZSe/CIZS QDs promotes the formation of the asymmetric nanonail like QDs. The obtained CIZSe/CIZS/ZnS HNNs are fluorescent in the NIR region of the spectrum, which is promising for photovoltaics and other applications.

In my work, ZnS has been chosen as the shell material coated onto the preformed seeds producing the core/shell and even core/shell/shell heteronanostructures. Due to the large band gap of ZnS, type I band alignment formed between the core and the shell or between the core/shell and the second ZnS shell. This type I helps to confine the formed excitons in the core away from the micro external environment including oxygen and moisture, which benefits higher photoluminescence quantum yields. In addition, the shell coating also helps to passivate defects that present on the surface of or inside the QDs which can act as nonradiative pathways and thus enhances the optical properties of the QDs. The proposed

emission mechanisms including the DAP and free-to-bound recombination ways are defects related pathways. In our case, the ion radius of Cu, In and Zn are quite similar, which promotes the formation of alloyed nanostructures. In this case, the improved optical properties of Cu-based QDs are mainly due to mitigation of the defects inside the QDs.

Finally, the home-made reaction chamber has been designed to carry out the bulk polymerization of PMMA. Then four types of fluorescent Cu-based QDs including heterostructured CIZS/ZnS-230 QDs with thin ZnS shell, heterostructured CIZS/ZnS-230/ZnS QDs with thicker ZnS shell, heterostructured CIZS/ZnS-280/ZnS QDs with the thickest ZnS shell and the alloyed CIZS/ZnS QDs were chosen to embed into transparent PMMA blocks *via* heating induced bulk polymerization of MMA monomer. Thorough examination has been conducted on the obtained fluorescent LSCs. It has been found that heterostructured Cu-based QDs with quite thick shell and the alloyed Cu-based QDs are more suitable to build high quality LSCs.

I believe that this work has made a valuable contribution to development of Cu-In-Zn-S and Cu-In-Zn-Se based nanostructures, understanding their properties and further advancement of their applications.

7.2 Preliminary studies and future work

7.2.1. Preliminary investigation of QD-loaded sugar glasses

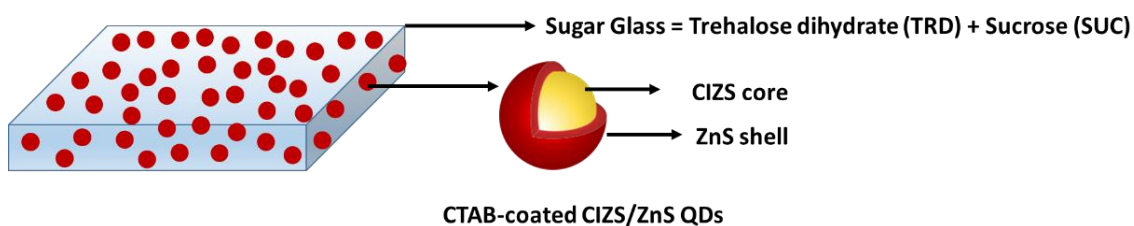
“Green” Cu-based QDs have attracted great attention due to the absence of heavily toxic elements, broad tunability of photoluminescence and excellent stability, especially core/shell structures¹⁻³. Processability of the QDs are limited upon the usage from solution. Incorporating QDs into a matrix is one effective approach to isolate the QDs from the environment and to increase their processability. The most important point of encapsulation

of QDs is preserving initial optical properties of the QDs. The commonly used materials for encapsulation of light emitting entities includes polymers (*e. g.*, PMMA) and inorganic salts (*e. g.*, NaCl). PMMA is most common matrix to incorporate QDs for luminescent solar concentrator (LSC) applications⁴⁻⁶. However, the rigid chemical conditions used in polymerization normally deteriorate the optical properties of QDs to some level⁷⁻⁸. The preparation of QD-NaCl cocrystals was widely explored to obtain light emitting entities for white light emitting diodes (WLEDs)⁹⁻¹¹. However, the crystallization process is quite time-consuming. Comparing to these two common matrix materials, sugars are much less explored. Considering their simplicity, inexpensiveness, and robustness, sugar glasses might be promising matrix materials. Generally, sugar glasses are quite robust, transparent and chemically stable, which are quite suitable for solid-state lighting systems. The absence of ions of sugar solution implies little influence to the optical properties of QDs. Previously, macrodimensional sucrose crystals were used as large-scale robust platform to get plasmonic composite¹². In this work, the thickness of the sucrose macrocrystals needs to be controlled carefully (2-3 mm) to guarantee the optical characterizations of the obtained samples. However, this work shows the great potential of sugar as large-scale robust platforms to embed QDs.

Sucrose is the most common sugar in life, while the T_g^{sucrose} of pure dry sucrose of 60 °C¹³. Sucrose is easy to convert from amorphous to crystalline at rates depend on the relative humidity and temperature¹⁴. Alexandra and Andreas found that $T_g^{\text{trehalose}} > T_g^{\text{sucrose}}$. $T_g^{\text{trehalose}}$ of pure dry trehalose was determined to be 106 °C and the cotton candy made from a 25% trehalose-75% sucrose mixture did not crystallize after 30 days under 33% humidity¹³. Martin and Allender claimed that the interaction between two different sugar molecules (sucrose and trehalose) in solution hindered the formation of individual formations of sugar crystals during dehydration. Here sucrose and trehalose dihydrate were employed to make

sugar glasses based on their work with minor modifications as matrix to incorporate Cu-based core/shell quantum dots¹⁵.

In the preliminary work, sucrose and trehalose dihydrate were employed to prepare sugar glass as the matrix to incorporate Cu-based core/shell QDs (Scheme 7.1). The colloidal CIZS/ZnS QDs can easily be transferred into aqueous phase with CTAB being used. Transparent and emissive QD-sugar glasses were obtained.



Schematic 7 1. Illustration of the incorporation of Cu-based QDs in sugar glass.

Initially the optical properties of the CTAB-CIZA/ZnS QDs after the phase transfer were investigated. As shown in Figure 7.1, the UV-Vis absorption spectrum of the water-soluble sample is very similar to that of the oil soluble sample, without any observable excitonic absorption peak, which is an intrinsic photophysical property of Cu-based multicomponent QDs. It is believed that it is due to the electron transition from the Cu^+ state to the conduction band is allowed, which results in the spectra extending to the lower energy region and gives the featureless UV-Vis absorption spectra¹⁶⁻¹⁷. The PL spectrum of CTAB-CIZS/ZnS QDs was nearly the same as that of the oil soluble CIZS/ZnS QDs, exhibiting a relatively high PLQY of 25% (compared with the original 51% of the oil soluble CIZS/ZnS QDs). The highly preserved PLQY and spectra features (without obvious PL red shift from the

hydrophobic QDs as previously reported¹⁸) benefited from lipophilic CTAB encapsulation on the original CIZA/ZnS QDs without disturbing the originally capping ligands¹⁹.

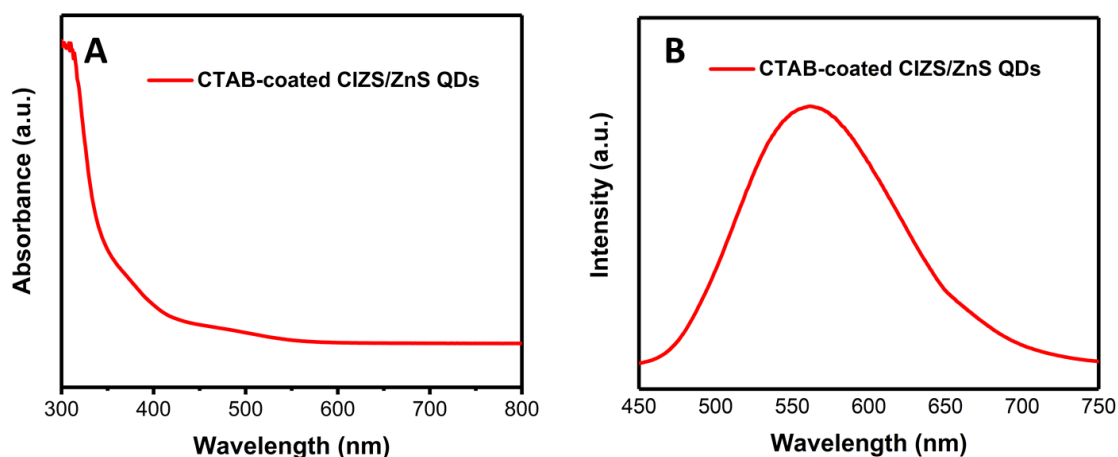
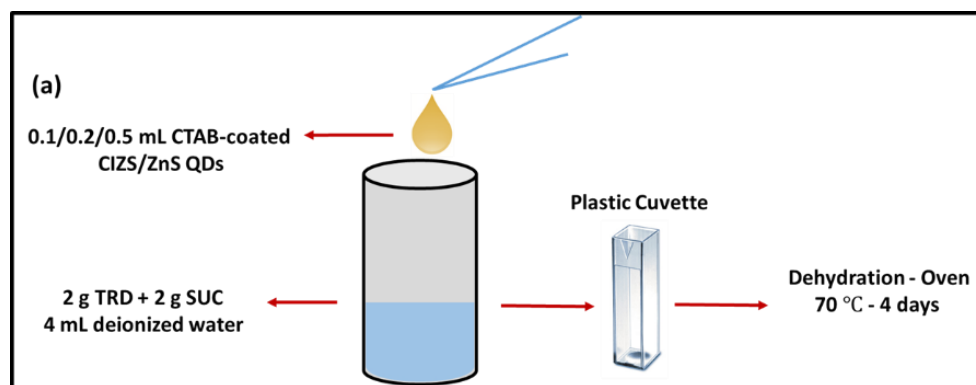


Figure 7. 1 (A) UV-Vis absorption spectra and (B) PL spectra of CTAB-CIZS/ZnS QDs.

The CTAB-CIZS/ZnS QD sugar glasses were obtained *via* dehydration of the mixture of CTAB-coated CIZS/ZnS QD solution and sugar aqueous solution (TRD and SUC) at 70 °C for 96 h as shown in Figure 7.2a. In this work, 9.2 stands for the pure sugar glass without the presence of QDs, 9.2.5, 9.2.6 and 9.2.7 refers to the sugar glass that prepared using 0.1/0.25/0.5 mL of CTAB-CIZS/ZnS QDs, respectively. The picture of the CTAB-CIZS/ZnS QD sugar glasses that took under daylight is shown in Figure 7.2b. The resultant sugar glasses are transparent with light colour due to the presence of CTAB-CIZS/ZnS QDs. The sugar glasses are quite bright under UV lamp (Figure 7.2c). The emission colours are slightly different due to the concentration difference of the CTAB-CIZS/ZnS QDs that incorporated into the sugar glasses.



(b) Daylight

(c) UV lamp

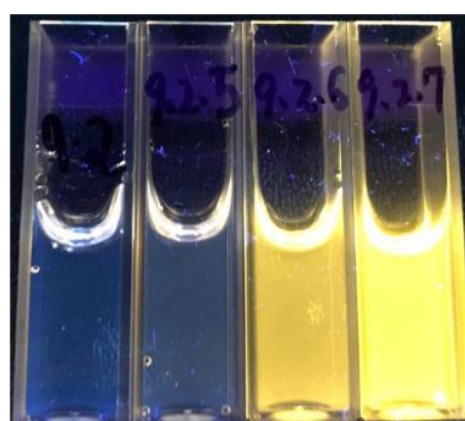
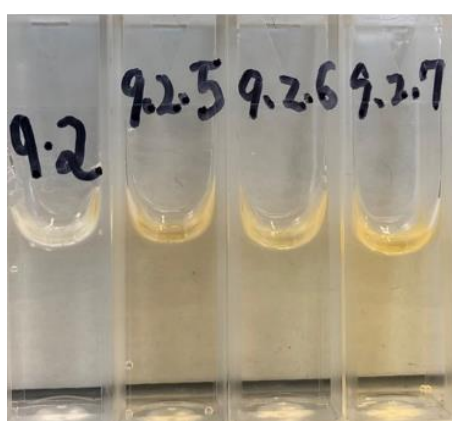


Figure 7. 2 (a) Scheme of the method to prepare sugar glass. Photo pictures of the obtained CTAB-CIZS/ZnS QD sugar glasses under daylight (b) and UV lamp (c).

The UV-Vis spectra of the obtained CTAB-CIZS/ZnS QD sugar glasses were quite similar to that of the CTAB-CIZS/ZnS QD solution (Figure 7.3a). Subsequent to the absorption spectra of the sugar glasses, their fluorescence was measured. Pure sugar matrix is slightly fluorescent in solid state. Figure 7.3b reveals that the emission peak of the pure sugar matrix is around 487 nm (Grey line in Figure 7.3b). After 0.1 mL of CTAB-coated CIZS/ZnS QD solution was added to get the sugar glass 9.2.5, the emission spectrum becomes broader (red line in Figure 7.3b), that can be explained by the overlap of the emission from the sugar matrix (487 nm) and the relatively weak emission from the CTAB-coated CIZS/ZnS QDs (558 nm). When the content of the CTAB-coated CIZS/ZnS QDs increased to 0.25 mL, the intensity of the emission from the QDs is getting high enough that the emission from the

sugar matrix can hardly be observed (blue line in Figure 7.3b). As the amount of QDs used increased to 0.5 mL, the intensity of fluorescence is further increased (green line in Figure 7.3b).

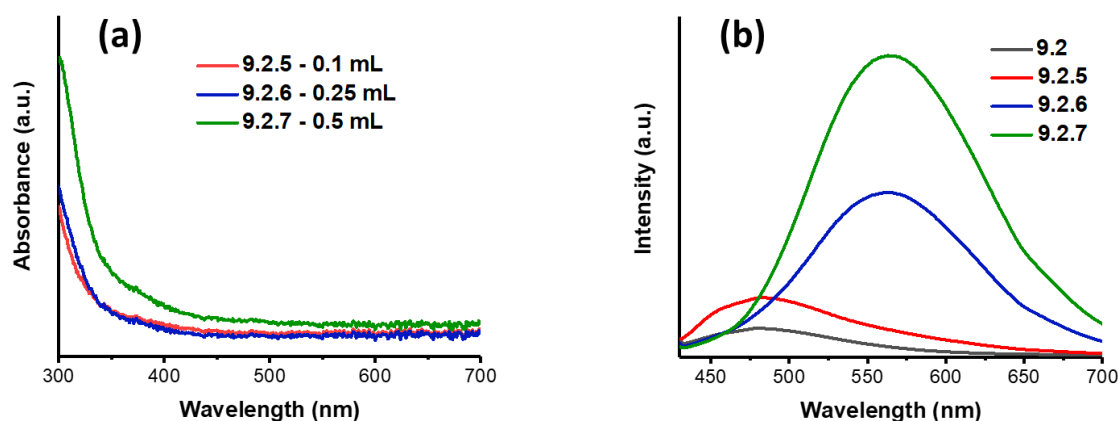


Figure 7. 3 (a) UV-Vis absorption, (b) PL spectra of CTAB-CIZS/ZnS QD sugar glasses (green – 9.2.7, blue – 9.2.6, red – 9.2.5, grey – 9.2).

Thus, a straightforward route to yield fluorescent CTAB-CIZS/ZnS QD sugar glasses has been developed. Colloidal CIZS/ZnS core/shell quantum dots (QDs) were synthesized via a seeded growth technique. The water soluble CTAB-CIZS/ZnS quantum dots were obtained thorough phase transfer. The optical properties were preserved after the phase transfer. Then the resultant water soluble CTAB-CIZS/ZnS quantum dots were dispersed in Trehalose dihydrate (TRD) and sucrose (SUC) aqueous solution, which was followed by a dehydration process of the mixture in the oven to make CTAB-CIZS/ZnS quantum dot sugar glass. The sugar glasses were fluorescent and quite bright under UV lamp. To the best of my knowledge, this is the first work with sugar as the matrix to be embed with “green” Cu-based quantum dots. However, further experimental work and more detailed studies can be done to optimise the preparation of QD-loaded sugar glasses and investigate their optical properties.

7.2.2 Future work

Based on the LSCs results that we have obtained with the highly fluorescent CIZS/ZnS QDs with spherical morphology, we confirmed the promising future of high quality Cu-based QDs for photovoltaic applications. In the future, we will continue our work to produce LSCs with the new developed fluorescent Cu-based nanoheterostructures with “ice-cream cone” like shape. It has been claimed that the anisotropic nanostructures should demonstrate polarized emission. In addition, there are many techniques that can be employed to realize the alignment of the “ice-cream cone” like nanostructures in the matrix, for example, controlled solvent evaporation, applying electric field and so forth. For LSCs, the aligned “ice-cream cone” like nanostructures with polarized emission definitely lowered the chance of emission escape from the waveguide, which translates more light will be guided onto the attached solar cells and higher efficiency can be achieved. We plan to study the new LSCs by various instrumental techniques. Then LSCs will be integrated directly with finished silicon based photovoltaic cells and their performances will be evaluated using standard protocols.²⁰

The encapsulation of QDs in ionic macro salt crystals makes it more than suited for solid-state lighting applications. Otto *et al.* reported the synthesis of CdTe QDs in aqueous system and packaged the obtained QDs into several different ionic matrices (NaCl, KCl, KBr etc.) using traditional slow evaporation method for LEDs¹¹. Normally, the QDs need to be fixed in silicone matrix for the hybridization of the colour converter on the LED platform, which would cause detrimental influence on the optical properties of the QDs. After the QDs have been incorporated in the ionic matrices, no degradation to the PL of the QDs has been observed, which demonstrates the protection from the matrices for the QDs from the environment. Not only Cd-based QDs, recently, researchers have started trying to

incorporate Cu-based QDs into various ionic matrices. CIZS/ZnS core/shell heterostructured QDs were incorporated into 2 different – LiCl and borax matrix using 2 different methods (vacuum assisted and slow evaporation, respectively.)²¹. In their work, as a proof of concept, a colour conversion LED has been fabricated with the QDs-in-LiCl solid composite. Incorporating QDs into air- and moisture-tight ionic macro crystals not only helps to improve processability of QDs, but also protect QDs from external environment and enhance their photostability, thermal-stability and chemical stability, even to enhance the PLQYs of Cd-based QDs. All these factors illustrate the promising future of QDs for solid-state lighting applications. With the fast development of this area, with several methods being proposed to incorporate organic-soluble QDs into ionic matrices without prior ligand exchange or phase transfer, which causes decreased PLQYs of the QDs. For example, the seeded-mediated liquid-liquid diffusion-assisted crystallization (LLDC) method and the cold flow technique. In seed-mediated LLDC approach, the saturated NaCl solution in methanol is added into the dilute QDs solution in chloroform, which results the fast crystallization of NaCl due to its much reduced solubility. Since this process happens too fast, most of the QDs end up attached on the surface of the formed NaCl small crystallites. Then the obtained seeds are used to repeat the LLDC procedure producing much larger salt crystals with QDs sealed inside. In this case, the prior ligand exchange or phase transfer can be avoided. The cold flow approach is based on the sintering behaviour of salts (KCl, KCl, NaCl, CsI, AgI etc.) under high pressure, which translates that the salt powder transform into transparent crystal under high pressure. This technique was developed by Albrecht and his co-workers²². In this method, finely milled salt powder was mixed with the nonpolar solvent (chloroform or hexane) that used to disperse oil-soluble QDs, then the obtained dispersion solution of the salt mixed with the oil-based QDs solution. Then the solvent was evaporated under reduced pressure on a rotary bath, which results the QDs being deposited

on the surface of the salt powders. After that, the dry sample undergoes cold flow under 2.2 GPa pressure for only 5 min, producing transparent salt pellet that loaded with QDs. Using this technique, it takes only several minutes to achieve a much higher loading of oil-soluble QDs, which is a big step forward of this area. Our obtained Cu-based QDs are all organic-soluble, the above two methods are suited to encapsulate the colloidal Cu-based QDs into a broad range of ionic matrices for potential LED applications.

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Chapter 8 Appendix

Table A 1. Details of the PL lifetime of sample CIZS/ZnS-230 (CHISQ = 1.056, 3 exponential fitting).

Components	t_1	t_2	t_3
	1.426485E-07 sec	5.015957E-07 sec	2.104727E-08 sec
Amplitude	B_1	B_2	B_3
	0.2029	0.7791	0.0181

Table A 2. Details of the PL lifetime of sample CIZS/ZnS-260 (CHISQ = 1.094, 3 exponential fitting).

Components	t_1	t_2	t_3
	9.760929E-08 sec	5.032915E-07 sec	8.587953E-09 sec
Amplitude	B_1	B_2	B_3
	0.1445	0.8430	0.0126

Table A 3. Details of the PL lifetime of sample 7.1.5 CIZS/ZnS-280 (CHISQ = 1.084, 3 exponential fitting).

Components	t_1	t_2	t_3
	1.007718E-07 sec	6.081183E-07 sec	1.327636E-08 sec
Amplitude	B_1	B_2	B_3
	0.1341	0.8424	0.0235

Table A 4. Details of the PL lifetime of sample CIZS/ZnS-280/ZnS-2h (CHISQ = 1.072, 3 exponential fitting).

Components	t_1	t_2	t_3
	1.023656E-07 sec	6.595245E-07 sec	1.25553E-08 sec
Amplitude	B_1	B_2	B_3
	0.1156	0.8705	0.0139

Table A 5. Details of the PL lifetime of sample CIZS/ZnS-280/ZnS-4h (CHISQ = 1.042, 3 exponential fitting).

Components	t_1	t_2	t_3
	8.342819E-08 sec	6.770391E-07 sec	6.04293E-09 sec
Amplitude	B1	B2	B3
	0.0839	0.9085	0.076

Table A 6. Details of the PL lifetime of sample CIZS/ZnS-280/ZnS-8h (CHISQ = 1.7096, 3 exponential fitting).

Components	t_1	t_2	t_3
	8.057041E-08 sec	6.622875E-07 sec	5.033062E-09 sec

Amplitude	B ₁	B ₂	B ₃
	0.0848	0.9082	0.007

Table A 7. Details of the PL lifetime of sample CIZS/ZnS-230/ZnS (CHISQ = 1.072, 3 exponential fitting).

Components	t ₁	t ₂
	8.850976E-08 sec	4.710311E-07 sec
Amplitude	B ₁	B ₂
	0.1165	0.8835

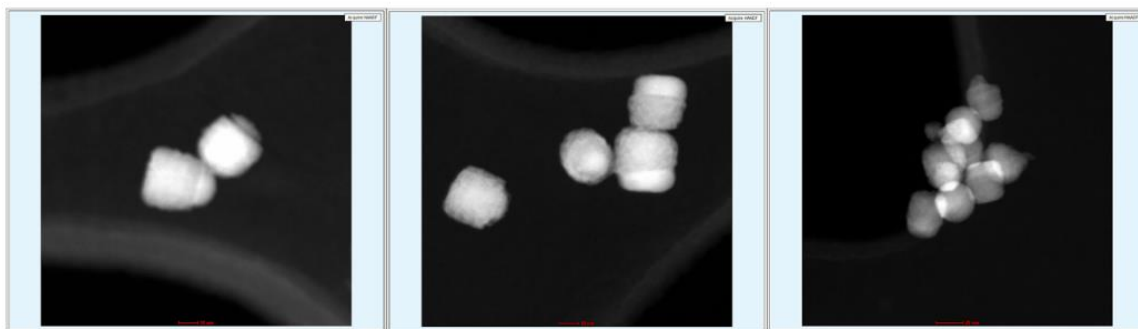


Figure A 1. STEM images of Cu-In-(Zn)-S/ZnS-30.

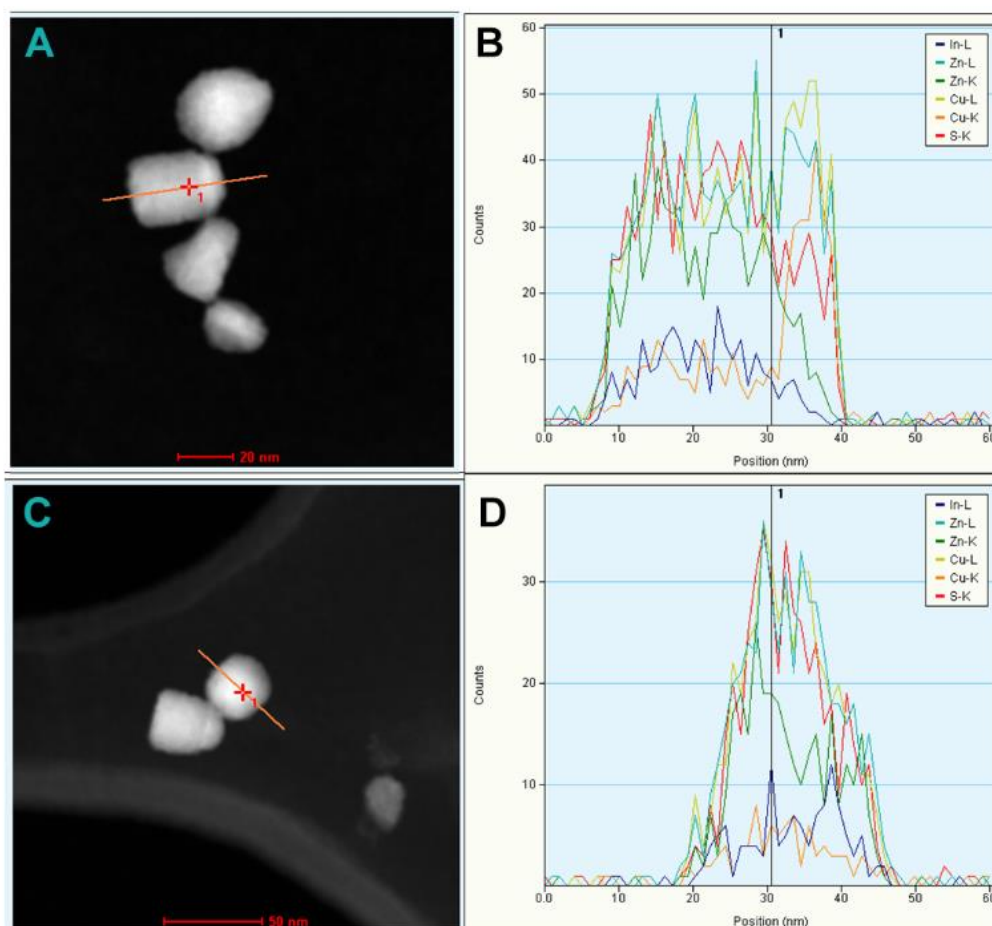


Figure A 2 (A) STEM image of Cu-In-(Zn)-S/ZnS-30 and (B) the corresponding line scanning spectra of the particle in Figure S2A along the direction that indicated with the yellow line (perpendicular to the top and bottom surfaces of the cylindrical structure). (C) STEM image of Cu-In-(Zn)-S/ZnS-30

and (D) the corresponding line scanning spectra of the particle along the direction that indicated with the yellow line in Figure S2C (parallel to the top and bottom surfaces of the cylindrical particle).

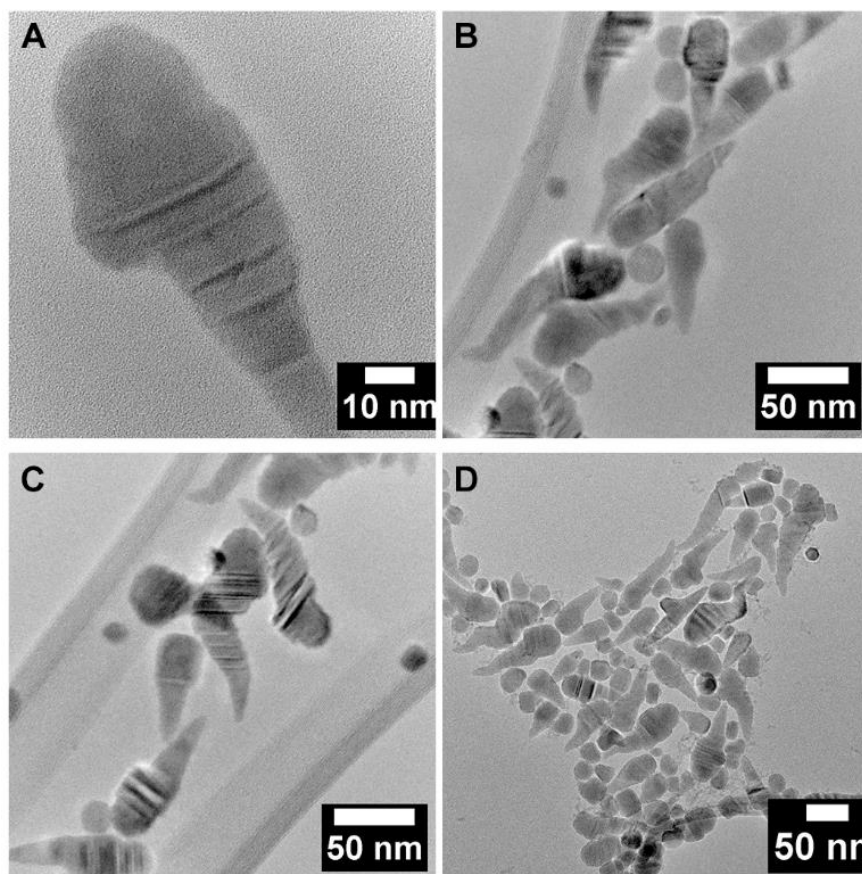


Figure A 3. (A-D) TEM images of the final Cu-In-(Zn)-S/ZnS “ice-cream cone” like nanoheterostructure.

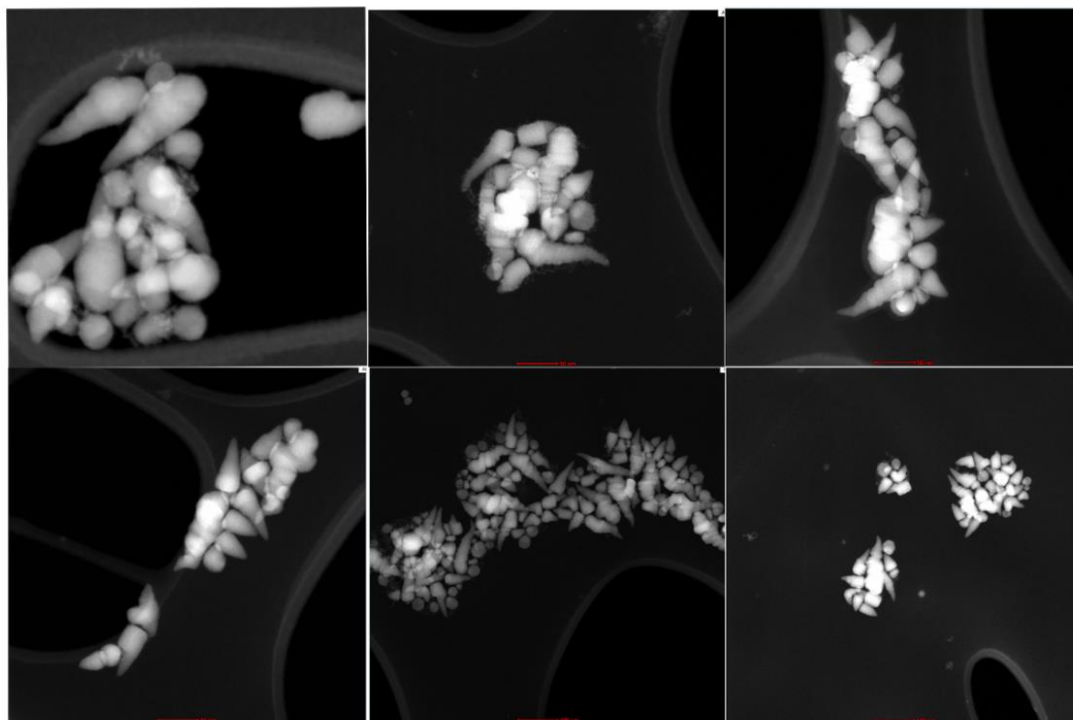


Figure A 4. STEM images of the final Cu-In-(Zn)-S/ZnS “ice-cream cone” like nanoheterostructure.

Table A 8 PL lifetime components for the final Cu-In-(Zn)-S/ZnS “ice-cream” like structure.

Components	t_1 (s)	t_2 (s)
	7.680894E-08	4.285024E-07
Amplitude	B_1	B_2
	0.177	0.823

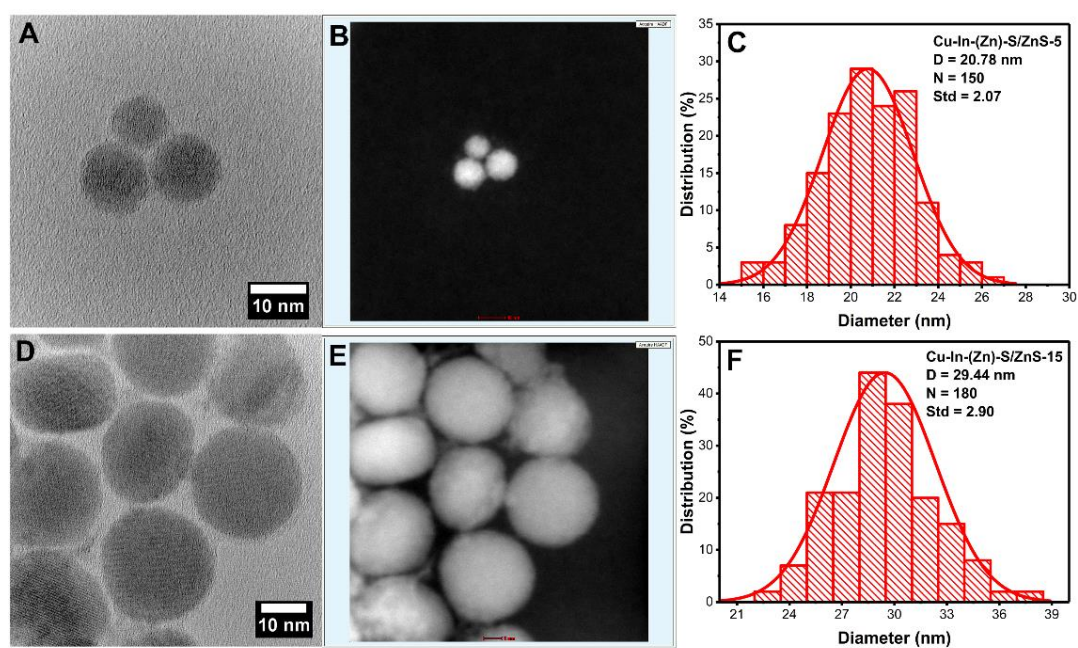


Figure A 5. (A) TEM image, (B) STEM image and (C) Diameter distribution histogram of Cu-In-(Zn)-S/ZnS-5. (D) TEM image, (E) STEM image and (F) Diameter distribution histogram of Cu-In-(Zn)-S/ZnS-15.

Excitation-Emission Matrix

Correction Factor Applied

The correction factor (C_f) considers the absorption at excitation (A_{ex}) and the emission wavelength (A_{em}), using the equation s1 to calculate the correction factor. This can be used to calculate. Using the correction factor, it is possible to correct the initial intensity (I_{obs}) to the corrected intensity (I_c) of emission spectra, using equation s2.

$$C_f = 10^{\frac{(A_{ex}+A_{em})}{2}}$$

Equation A1. Used to calculate the correction factor

$$I_c = I_{obs} \times C_f$$

Equation A2. Used to calculate the corrected intensity from the intensity observed

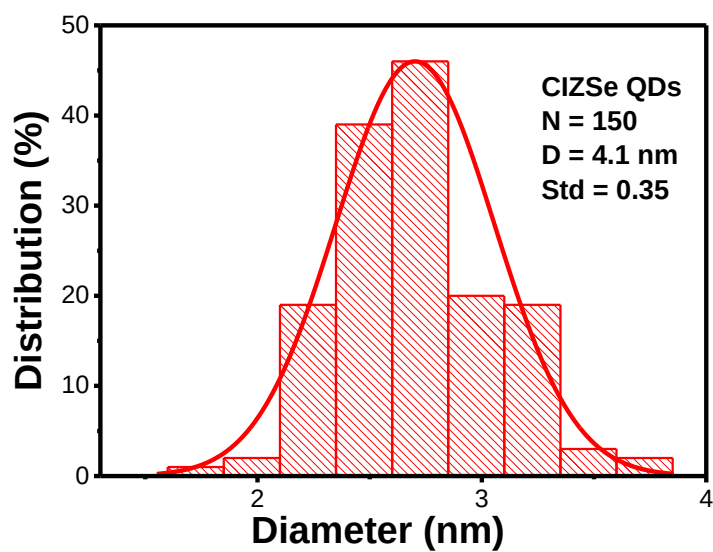


Figure A 6. Size distribution histogram of ClZSe QDs.

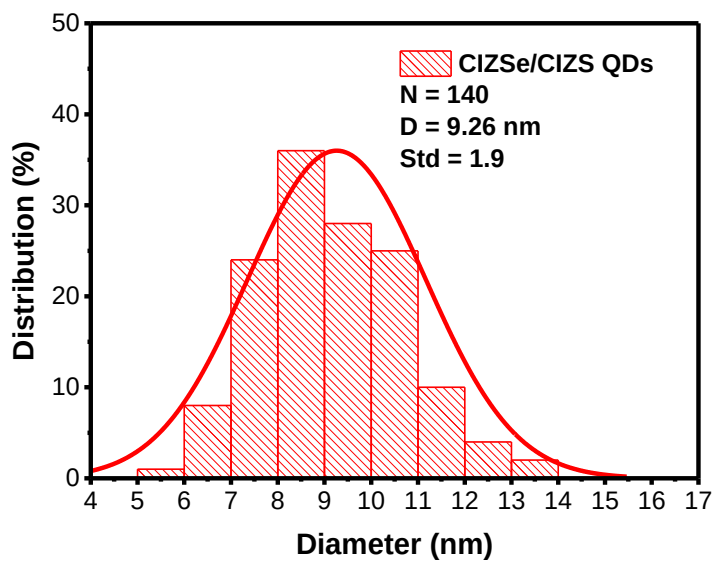


Figure A 7. Size distribution histogram of ClZSe/ClZS QDs.

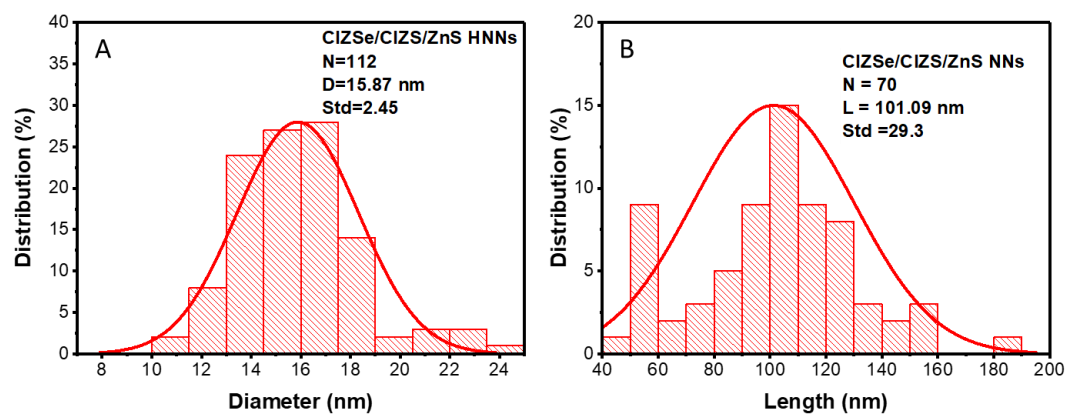


Figure A 8. Diameter (A) and length (B) distribution histogram of the final CIZSe/CIZS/ZnS HNNs.

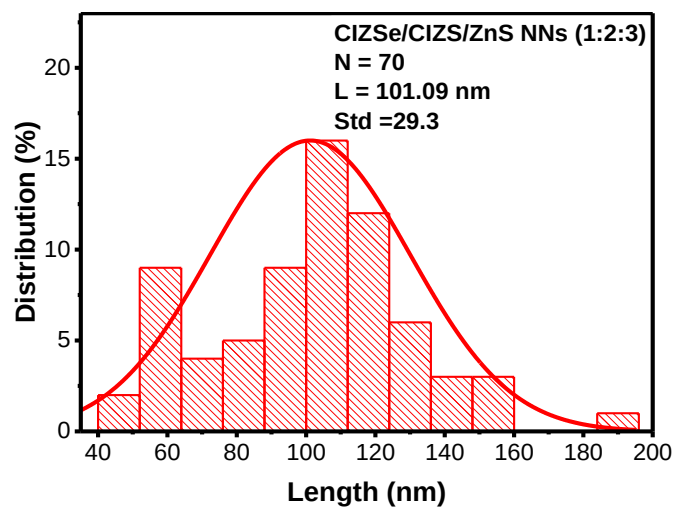


Figure A 9. Length distribution histogram of HNNs (1:2:3)

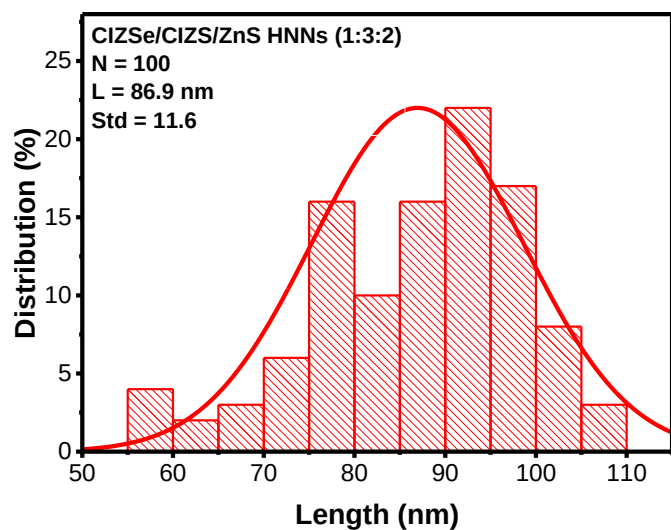


Figure A 10. Length distribution histogram of HNNs (1:3:2)

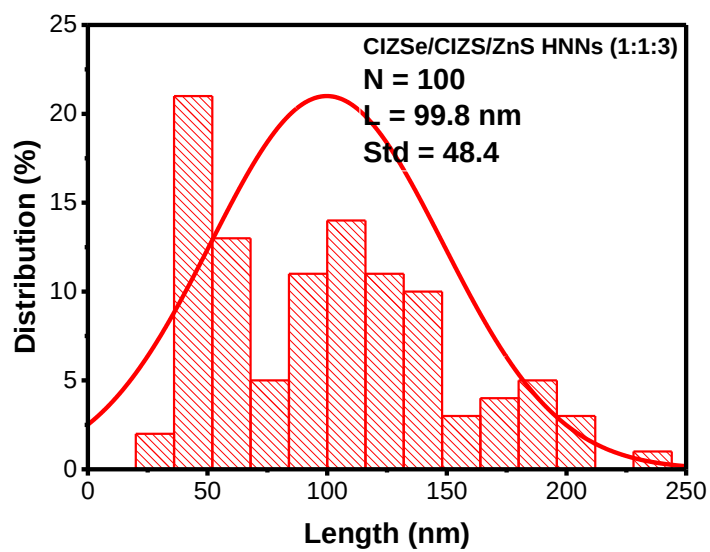


Figure A 11 Length distribution histogram of HNNs (1:1:3)

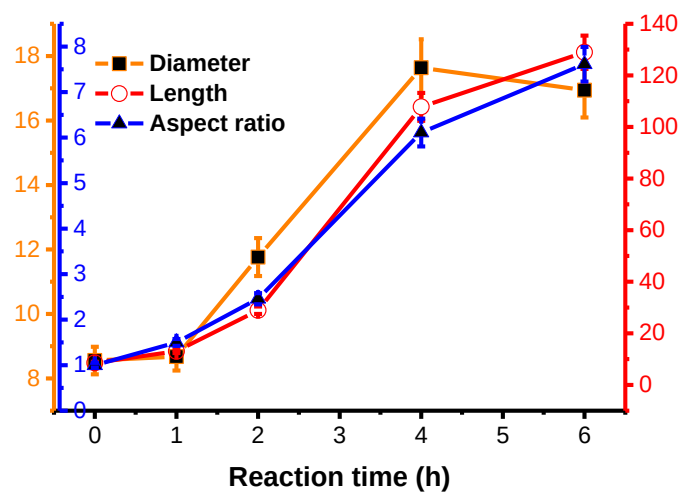


Figure A 12. The change of diameter, length and aspect ratio of the structure as the reaction proceeding.

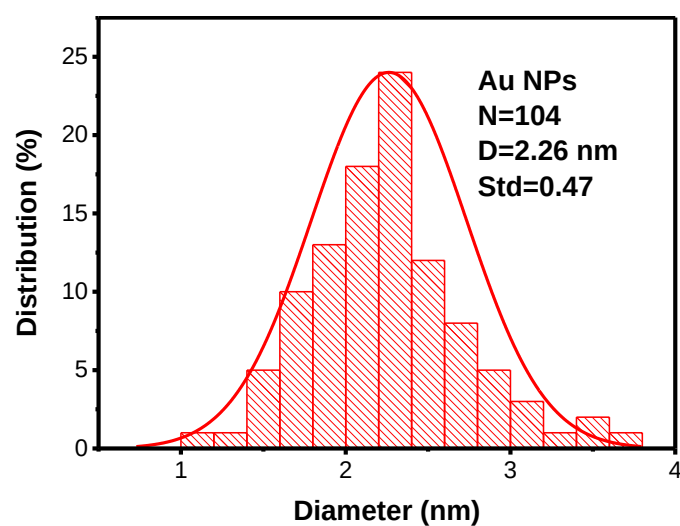


Figure A 13. The size distribution of the Au NPs that deposited on the surface of the obtained HNNs.

Table A 9. Details of PL lifetime of the LSC that based on CIZS/ZnS-230 (CHISQ = 1.195, 3 exponential fitting).

Components (s)	t1	t2	t3
	1.219935E-08	1.448825E-07	5.810816E-10
Amplitude	B1	B2	B3
	0.197	0.6782	0.1247

Table A 10. Details of PL lifetime of the LSC that based on CIZS/ZnS-230/ZnS (CHISQ = 1.845, 2 exponential fitting).

Components (s)	t1	t2
	6.057775E-10	1.484567E-07
Amplitude	B1	B2
	0.2543	0.7457

Table A 11. Details of PL lifetime of the obtained CIZS/ZnS QDs (CHISQ = 1.2417, 3 exponential fitting).

Components	t_1 (s)	t_2 (s)	t_3 (s)
	3.639621E-07	8.917994E-07	4.366451E-06
Amplitude	B_1	B_2	B_3
	0.2157	0.5483	0.2359

Table A 12. Details of PL lifetime of the LSC that based on alloyed CIZS/ZnS QDs (CHISQ = 1.77, 2 exponential fitting).

Components (s)	t1	t2
	6.152362E-10	2.434381E-07
Amplitude	B1	B2

	0.03	0.97
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Table A 13. Excitation wavelengths that used for the PL characterization of all the samples.

Sample	Excitation wavelength (nm)	Dye used for determination of PLQY
CIZS QDs	500	/
CIZS/ZnS-230	450	Rhodamine 6G
CIZS/ZnS-260	450	Rhodamine 6G
CIZS/ZnS-280	450	Rhodamine 6G
CIZS/ZnS-280/ZnS-2/4/8 h	450	Rhodamine 6G
CIZS/ZnS-230/ZnS-2/4/8 h	450	Rhodamine 6G
Cu-In-S QDs	560	HITCI
Cu-In-(Zn)-S/ZnS-60/120	500	Rhodamine 6G

CIZSe QDs	600	/
CIZSe/CIZS QDs	680	/
CIZSe/CIZS/ZnS NRs	600	/
CIZS/ZnS-230 LSC	500	Integrating sphere
CIZS/ZnS-230/ZnS LSC	500	Integrating sphere
CIZS/ZnS-280/ZnS LSC	500	Integrating sphere
Alloyed CIZS/ZnS QDs	430	Coumarin
Alloyed CIZS/ZnS LSC	430	Integrating sphere
CTAB-CIZS/ZnS QDs	400	Coumarin
Sugar glasses loaded with QDs	400	/
9.2/9.2.5/9.2.6/9.2.7		