Investigation of synthesis of doped, and core/shell nanocrystals

Master of Science thesis for master program, Materials and Nanotechnology

Submitted by

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Göteborg, Sweden, 2010

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This work is performed in Bayer Technology Service, Leverkusen, Germany, under supervision of Dr. Huachang Lu
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<tr>
<td>DA</td>
<td>Decanoic acid</td>
</tr>
<tr>
<td>D-NCs</td>
<td>Doped semiconductor Nanocrystals</td>
</tr>
<tr>
<td>LED</td>
<td>Light emitting diodes</td>
</tr>
<tr>
<td>NC</td>
<td>Nanocrystal</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>OA</td>
<td>Oleic acid</td>
</tr>
<tr>
<td>ODA</td>
<td>Octadecylamine</td>
</tr>
<tr>
<td>ODE</td>
<td>1-Octadecene</td>
</tr>
<tr>
<td>OLA</td>
<td>Oleylamine</td>
</tr>
<tr>
<td>PL</td>
<td>Photoluminescence</td>
</tr>
<tr>
<td>PLE</td>
<td>Photoluminescence excitation</td>
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<tr>
<td>QY</td>
<td>Quantum yield</td>
</tr>
<tr>
<td>SILAR</td>
<td>Successive Ion Layer Adsorption and Reaction</td>
</tr>
<tr>
<td>TBP</td>
<td>Tri-n-butylphosphine</td>
</tr>
<tr>
<td>TOP</td>
<td>Trioctylphosphine</td>
</tr>
<tr>
<td>TOPO</td>
<td>Triocetylphosphine oxide</td>
</tr>
<tr>
<td>XAS</td>
<td>X-ray absorption spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray powder diffraction</td>
</tr>
<tr>
<td>ZDC</td>
<td>Diethyldithiocarbamic acid zinc salt, $[(C_2H_5)_2NCSS]_2Zn$</td>
</tr>
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</table>
Abstract

Nanocrystals (NCs) exhibit very interesting size-dependent electrical, optical, magnetic, and chemical properties that cannot be achieved by their bulk counterparts. A quantum dot (QD) is a semiconductor NC which exhibits size dependent photoluminescence property because of quantum confinement effect. Generally, within the quantum confinement region, the larger the QD is, the redder its fluorescence spectrum will be. Doped semiconductor NCs (D-NCs) can not only retain nearly all advantages of intrinsic QDs, but also eliminate their self-quenching due to reabsorption/energy transfer and the use of harmful elements (Class A elements Cd, Hg, and Pb). Zinc based systems are good candidates with zinc compounds as cheap and nontoxic precursors. Doped and undoped zinc based NCs can cover a broad range of visible spectra, from 400nm to 600nm.

In this work, doped and undoped ZnSe NCs are synthesized without the use of phosphine containing coordinating solvents, such as TOP, TBP and TOPO which are not only highly toxic and pyrophoric, but also rather expensive. Instead we use Se-ODE which is a good candidate as Se precursor and very reactive if prepared properly. We achieved phosphine free synthesis of ZnSe and MnSe/ZnSe ZnSe NCs, and enhanced their photostability by overcoating ZnS shells using successive ion layer absorption and reaction, or single molecular source ZDC, respectively. For synthesis of Cu:ZnSe doped NCs, surfaced doped NCs was obtained, however ZnSe shell overcoating process was not successful, which still needs further investigation.
CHAPTER 1 Introduction

1.1 Quantum Dots (QDs) - Semiconductor Nanocrystals (NCs)

NCs exhibit very interesting size-dependent electrical, optical, magnetic, and chemical properties that cannot be achieved by their bulk counterparts. A QD is a semiconductor NC whose excitons are confined in all three spatial dimensions. As a result, they have properties that are between those of bulk semiconductors and those of discrete molecules. QDs are semiconductors whose conducting characteristics are closely related to the size and shape of the individual crystals. The reason why QDs exhibit size dependent properties is the quantum confinement effect. The quantum confinement effect can be observed once the diameter of the particle is of the same magnitude as the wavelength of the electron wave function, typically in nanoscale. When the particle is this small, the energy spectrum becomes discrete; as a result, the difference between energy states and band gap become size dependent.

![Diagram showing quantum confinement effect](image)

Figure 1-1 Quantum confinement effect [Ref. 1]

When the size of the NC comes to its quantum confinement region, the smaller the size of the crystal is, the larger the band gap is, the greater the difference in energy between the highest
valence band and the lowest conduction band becomes, therefore more energy is needed to excite the dot, and concurrently, more energy is released when the crystal returns to its resting state. The red shift of absorption and photoluminescence (PL) of QD with size is also a consequence of quantum confinement effect. Quantum confinement effect does not just exist in QDs, but also quantum wires which exhibit confinement effect in two dimensions, and quantum wells which exhibit confinement effect in one dimension.

1.1.1 Photoluminescence (PL)

High PL is one of the reasons that QDs attract so much attention. When a dot absorbs a photon and comes to the exited state, it needs to release energy to return back to its resting state, and one way is to release another photon, and this is why QDs are photoluminescent. As mentioned above, because of quantum confinement effect, QDs exhibit size dependent photoluminescent ability. Generally, within the quantum confinement region, the larger the QD is, the smaller the difference in energy between the highest valence band and the lowest conduction band becomes, the lower the energy of the photon the QD absorbs, and subsequently, the lower the energy of the photon the QD emits when it returns to its resting state. If the energy level of the photon it emits is within the region of visible light, the QD becomes fluorescent, and the larger the QD is, the redder its PL spectrum will be.

![Figure 1-2](image)

Figure 1-2 (Left) Correlation between the size of ZnSe NCs and their band gap [Ref. 2] (Right) Schematic drawing representing the changes on optical behavior of nanoparticles associated with their size due to quantum confinement effect [Ref. 3]
1.1.2 Application

Semiconductor NCs have been used in many different technological areas, including biological labeling and diagnostics \[^{4,5}\], chemical sensing \[^{6}\], light emitting diodes (LED) \[^{7,8}\], electroluminescent devices, photovoltaic devices, lasers, and single-electron transistors. The traditional high quality semiconductor NCs always contain cadmium, which is carcinogenic, therefore, more and more research are now focusing on cadmium free systems. Not only the nontoxicity, but also the photo and thermal stability are required when they are brought to real application.

1.1.3 Different types of Semiconductor NCs

Typically, there are three main groups of semiconductor NCs under investigation for their PL abilities. \(\text{II}-\text{VI}\) is the most investigated group, with CdSe, CdS as pioneers, until now greener candidates, such as ZnSe and ZnTe, are favored. The most important \(\text{II}-\text{V}\) semiconductor NC is InP, with a bulk band gap of 1.27eV, because of the possibility of its PL covering a wide range of visible spectrum with increasing NC size. \(\text{IV}-\text{VI}\) semiconductor NCs, such as PbSe and PbS mainly exhibit near-infrared emission.

1.2 Core/Shell Semiconductor NCs

The nanoscale crystal size results in a very high surface-to-volume ratio. A significant fraction of these core NCs typically exhibit surface-related trap states acting as fast non-radiative de-excitation channels for photogenerated charge carriers, thereby reducing the fluorescence quantum yield (QY). In order to improve NCs’ surface passivation, a method overgrowth of a second semiconductor on the core is developed. In this way, the fluorescence efficiency and stability against photo-oxidation of various types of semiconductor NCs have been significantly improved. Furthermore, by the appropriate choice of the core and shell materials, it is possible to tune the emission wavelength in a larger spectral window than with both materials alone. According to the band gaps and the relative position of electronic energy levels of the involved semiconductors, the QS NCs are classified into three types. Here just a brief introduction is presented, and detailed information can be referred to a review \[^{9}\]. Figure 1-3 gives an overview of the band alignment of the bulk materials, which are mostly used in NC synthesis.
Figure 1-3 Electronic energy levels of selected III-V and II-VI semiconductors using the valence-band offsets from Reference [10] (VB: valence band, CB: conduction band) [Ref. 9]

Figure 1-4 Schematic representation of the energy-level alignment in different Core/Shell systems. The upper and lower edges of the rectangles correspond to the positions of the conduction and valence band edges of the core (center) and shell materials, respectively. [Ref. 9]

1.2.1 Type - I Core/Shell NCs

In type - I Core/Shell NCs, the shell materials have larger band gaps with the conduction band energy being higher than that of core materials and valence band energy being lower than that of the core, for example, ZnSe/ZnS Core/Shell Core/Shell NCs.

The shell of the NC physically separates the surface of the optically active core from its surrounding medium, so that the sensitivity of the optical properties to changes in the local environment, like the presence of oxygen or water molecules, is reduced. The main consequence of type - I capping is that the exciton generated in the core is hindered from spreading over the entire particle and by this it is forced to recombine while being spatially confined to the core and in most cases this is accompanied by enhanced luminescence. At the same time, type - I capping reduces the number of surface dangling bonds, which can act as trap states for photogenerated charge carriers. As shown in Figure 1-3, the band gap of ZnS bulk material is larger than most III-V and II-VI semiconductors. ZnS has been used as the shell material for many cores to improve PL quality and stability.
If Zn precursor or S precursor is in excess, direct injection of S precursor or Zn precursor can lead to growth of ZnS shell \cite{11}. S precursor can also be added during the growth stage of the cores, so that the shell layer contains both anions of the core material and S \cite{12, 13}. In specific cases, S precursor is added at the very first step with all other cationic and anionic precursors if the reactivity of precursors varies with reaction progress. It is achieved in a single-step synthesis of QDs with chemical composition gradients \cite{14}. Successive Ion Layer Adsorption and Reaction (SILAR) technology was used to grow CdS shell on CdSe core \cite{15}. One monolayer was grown at a time by alternating injections of cationic and anionic precursors into the reaction mixture with core NCs. Later on, SILAR technology was also extended to ZnS shell growth on a variety of cores, such as ZnSe \cite{16, 17}. A single-molecular source of ZnS - diethyldithiocarbamic acid zinc salt, \((\text{C}_2\text{H}_5)_2\text{NCSS}_2\text{Zn}\) (ZDC) was used to overcoat ZnS shell on CdSe NC core in a microfluidic reactor. Microfluidic technology was used to control reaction temperature and time precisely, so that to achieve a better control over shell thicknesses \cite{18}.

1.2.2 Type - Ⅱ Core/Shell NCs

In type - Ⅱ Core/Shell systems, the band gaps of core and shell materials are staggered, such as ZnTe/ZnSe and Cu$_2$S/CdS Core/Shell NCs \cite{19, 20}.

The staggered band alignment gives rise to a spatially indirect transition that occurs at lower energies than both band gap energies of the two materials used. Hence, this type of QDs can be emitters at wavelengths that cannot be achieved with either of the two materials alone. Furthermore, the luminescence lifetime is strongly increased. An overgrowth of an appropriate material can be used in the same way as in type - Ⅰ systems to improve the fluorescence QY and photostability.

1.2.3 Reverse Type - Ⅰ Core/Shell NCs

In this type of Core/Shell NCs, either the valence band edge or the conduction band edge of the shell material is located in the band gap of the core, such as ZnS/ZnSe NCs. Efficient energy transfer was achieved from ZnS core to ZnSe shell when exciting the NC with wavelength absorbed by ZnS core \cite{17}.
Charge carriers are at least partially delocalized in the shell and the emission wavelength can be tuned by the shell’s thickness. Generally, a significant red-shift of the band gap with the shell thickness is observed. The resistance against photo bleaching and the fluorescence QY of these systems can also be improved by the growth of a second shell of a larger band gap on it.

1.2.4 Core/Shell/Shell structures

The early reports of Core/Shell/Shell structures were CdSe/ZnSe/ZnS \[^{[21]}\] and CdSe/CdS/ZnS \[^{[22]}\] structures. In either one, the outermost ZnS shell is to avoid charge carrier penetration towards the surface of the particles and ZnS is a good candidate for this because of its large bandgap (3.7eV). In Core/Shell systems, one problem may be encountered that the lattice mismatch can be large, so an intermediate shell, like here, the ZnSe or CdS shell can act as a “lattice adapter”. Another benefit of Core/Shell/Shell structures is their greatly increased photostability. Other attempt to include an alloyed layer of Zn\(_{0.5}\)Cd\(_{0.5}\)S in the structure was also reported \[^{[23]}\].

Another interesting Core/Shell/Shell structure was reported by Peng’s group \[^{[24]}\] which is a reverse quantum-dot-quantum-well system with a large band gap material ZnS between two small band gap CdSe. When the ZnS layer is thick enough, no shift of emission signal can be observed and instead a second emission signal occurs at higher energies, which is explained as the phenomenon of “coupled and decoupled quantum systems in one semiconductor nanocrystal”.

1.3 Doped Semiconductor NCs

1.3.1 Why doped semiconductor NCs come upon the stage

Impurities, or dopants, can strongly modify electronic, optical, and magnetic properties of bulk semiconductors \[^{[25]}\]. Doped semiconductor NCs can not only retain nearly all advantages of intrinsic QDs, but also eliminate their self-quenching due to reabsorption/energy transfer. The energy from absorbed photons can be efficiently transferred to impurities, suppressing undesirable reactions on the NC surface or reabsorption by the band gap because of the small stokes shift between absorption and emission wavelengths. The energy transfer to impurities
greatly enhances their thermal and chemical stability. In addition, D-NCs can be made from less harmful elements than those currently used (Class A elements Cd, Hg, and Pb). The emission wavelength of doped semiconductor NCs can also be tuned. The interesting system, Mn and Cu doped ZnSe semiconductor were demonstrated as efficient emitters covering the blue to orange color window.

Figure 1-5 (Left) PL spectra of ZnSe based doped semiconductor emitters (Right) PL from doped NCs at above 200 °C [Ref. 26]

1.3.2 Synthesis and doping routes

Generally, physical and chemical methods are used to synthesize NCs. The advantage of physical methods is the production of a large quantity of NCs whereas uniform-sized NCs and their size control are difficult to achieve. In contrast, colloidal chemical synthetic methods can synthesize uniform NCs with controlled size, but large scale production is still a challenge.

Organic-phase synthetic methods have been widely used to synthesize NCs because of their many advantages, such as their versatility, reproducibility, high crystallinity and monodispersity of the synthesized nanoparticles and their high dispersion ability in organic solvents. The synthesis routes studied here are all based on organic-phase synthesis methods.

Hot injection method is used widely in synthesis of colloidal NCs. It separates the stages of nucleation and growth into burst of nucleation, quenching of nucleation and growth, and growth of the NCs. This consists with the theory of Hyeon [27] and Vanmaekelbergh [28] that synthetic techniques for the separation of nucleation and growth are very important to obtain monodispersed NCs. In the former, a comprehensive mechanism of formation of monodispersed NCs is given.
Doping a few ions into a NC is thermodynamically unfavorable, especially when the dopant ions do not have a matched bonding geometry with the counterions in the lattice. Fundamentals need to be understood in order to create synthetic routes which can dope impurities into host lattice successfully.

As first reported by Peng [26], the method decoupling doping from nucleation and/or growth was used for doping Mn and Cu into ZnSe host, and it resulted in two different strategies, nucleation-doping and growth-doping, respectively. According to Norris [29], the binding energies of Mn adsorbing on (001) facet of zinc-blende structure is much bigger than on the other two zinc-blende orientations or any facet of crystals with the wurtzite or rock-salt structures. The unique difference of this facet is the various arrangements of anion dimmers, which provide very stable binding sites that absent from the (110) and (111) surfaces of zinc-blende crystals, and all surfaces of wurtzite and rock-salt crystals. Mn incorporation rises with increasing Se:Zn ratio, but falls rapidly to zero for NCs smaller than 20 Å, suggesting that a central core resists doping. Till now, most successful doping reported for Mn in ZnSe or ZnS host is nucleation doping [16, 26, 30, 31], and in contrast, most successful doping reported for Cu in ZnSe or ZnS host is growth doping [13, 16, 26]. Mn doped ZnSe or ZnS has been studied relatively thoroughly comparing to Cu doped ones. Besides the usual way of doping Mn into ZnSe using nucleation doping, some other attempts had also been tried. For example, highly luminescent Ultra-narrow Mn doped ZnSe nanowires had been synthesized using single source clusters \( \text{Li}_4[Zn_{10}\text{Se}_4(\text{SPh})_{16}] \) and manganese stearate, and the QY reached 40% after passivating the crystals with a CdSe shell [32]. A different attempt, doping Mn into shell, had also been reported. And application as ratiometric chemical sensing agents had been realized as functionalizing this kind of NC with organic dye [6].

As illustrated in the figure above, for growth-doping strategy, the small ZnSe or ZnS host NCs are synthesized first, and are quenched by lowering the reaction temperature, at which
active dopant precursors are introduced and doping occurs without the growth of the host. Nucleation doping is realized by a mixed dopant and host precursors during the nucleation. After nucleation, the reaction conditions are tuned to be sufficiently mild to make the dopant precursors inactive, and the growth of the host becomes the only process, which overcoats the dopants. The concentration of the dopants in the nuclei can be tuned by varying the precursor ratio. In an extreme case, the nuclei could be formed with pure dopant cations, which is usually the case for recent Mn doped ZnSe or ZnS NCs.

1.3.3 Temperature dependence of “Elementary process” in doping semiconductor NCs

There are four “elementary processes” that can explain doping process. “Surface adsorption” and “lattice incorporation” are especially of help to explain growth doping. At the beginning of growth doping process, the dopant ion is adsorbed on the surface of the host. A loosely adsorbed dopant ion can act as a surface trap that quenches the host PL. Then it incorporates into the host lattice and is isolated from the solution environment before it can act as an electron-hole recombination center that gives rise to dopant PL. These particular dopant centers were incorporated only in the lattice near the NC surface. “Lattice diffusion” and “lattice ejection” explain the processes of nucleation doping and also shell overcoating process in growth doping. When overcoating host shell in both growth doping and nucleation doping, the dopant center might move toward the surface, which is called lattice diffusion. Lattice diffusion is necessary in nucleation doping (when a pure dopant core is used), because dopant ions need to diffuse into the host shell and form a doped interface where energy transfer and dopant emission occur. But lattice diffusion should be controlled because if it is so intense that the dopant ions are driven to mean free path (the depth of the direct “lattice ejection” zone), it will be ejected from the NCs, which is called “lattice ejection”. Therefore, temperature and time are two important parameters of a successful doping synthesis. More details please refer to the reference [33].

1.3.4 PL of Mn and Cu doped ZnSe NCs

PL of Mn and Cu doped ZnSe or ZnS NCs are different from those of traditional intrinsic ones. Their PL property depends on the band gap of the host and/or the dopants. For dopant ions like Mn$^{2+}$ and Pb$^{2+}$, as the particle size decreases, the wavelength for excitation of the
dopant emission shifts to higher energies while the emission color is unaffected. The insensitivity of the dopant emission energy to the particle size is due to the fact that these electronic transitions involve wave functions localized on the dopant cations and the neighboring ligand anions. The localized wave functions are not influenced by quantum size effects. For other dopant ions like Cu$^{2+}$, emission may involve recombination of a delocalized charge carrier and the dopant. The emission from Cu$^{2+}$ centers in ZnS and ZnSe is assigned to recombination of a delocalized electron with Cu$^{2+}$ \cite{34}, as illustrated in figure 1-7 below.

![Figure 1-7 Schematic representation of electron-hole recombination in Mn$^{2+}$ and Cu$^{2+}$ doped ZnSe NCs](image)

In both of them, energy is absorbed by host ZnSe, and efficiently transferred to dopants where PL exhibits. In Mn$^{2+}$ doped ZnSe, a nonradiative transition first occurs from conduction band of ZnSe host to the upper dopant hole, followed by a radiative transition ($^{4}T_{1} - ^{6}A_{1}$) between Mn$^{2+}$ d states. In Cu$^{2+}$ doped ZnSe, PL occurs between conduction band of host and the hole of dopants, and that’s why Cu doped ZnSe shows quantum confinement effect when tuning the host size, typically from 470nm to 550nm. It is surprising that the PL from Mn doped ZnSe NCs could also be tuned slightly, from about 575nm to 595nm when ZnSe shell grows thicker. Pradhan et al. suggested that as the ZnSe outer-shell grew thicker, the crystal field for each dopant ion became more symmetric in long range. Consequently, the crystal field splitting of the d-orbitals became smaller, which resulted in a PL red shift. They further demonstrated their interpretation in a later publication by changing the neutral ligands to a charged one, observing a significant red-shift of PL spectra to 610nm \cite{30}. PL of Cu$^{2+}$ and Mn$^{2+}$ doped ZnS have a similar electron-hole recombination to ZnSe ones.
1.4 Aim and Scope of this work

As Cd based high quality colloidal NCs had been thoroughly studied, focus was starting being transferred to other systems, especially the ones without Class A metals to avoid intrinsic toxicity. Zinc based systems are good candidates with zinc compounds as cheap and nontoxic precursors. Doped and undoped zinc based NCs can cover a broad range of visible spectrum, from 400nm to 600nm. In previous synthetic routes, coordination solvents containing phosphine, such as TOP, TBP and TOPO were used as solvents and for preparation of anionic precursors \[4, 12, 14, 17, 25, 26, 30\]. These solvents are not only highly toxic and pyrophoric, but also rather expensive. Recently some other kinds of anionic precursors are used. The newly used selenourea as an alternative selenium source broke the restrict that spherical ZnSe NCs can only grow below 5nm size using TBP, and allowed the size to grow up to 10-12 nm \[35\]. The one attracting more and more attention is directly dissolving elemental anion precursors to non-coordination solvent, i.e. 1-octadecene (ODE) to form an anion complex \[16, 31, 36\]. Heating temperature and heating time influence the reactivity of the Se-ODE precursor very much, especially under high temperatures, i.e., more than 200 °C. Photoluminescence excitation (PLE) measurements, X-ray absorption spectroscopy (XAS), Nuclear magnetic resonance (NMR), and EI mass spectra were used to study the structure characteristic of active and inactive Se-ODE samples \[37\]. The aim of this work is to study the methods synthesizing doped and undoped ZnSe NCs using phosphine free solvents, to optimize the synthetic routes from preparation of precursors, parameters of reactions, to details of operations to find out robust and reproducible protocols. Nucleation, growth, shell overcoating, and purification are to be studied step by step to try to find all-sided methods from beginning of reactions to the end where NCs are ready for use.
2.1 Materials and Instruments

Zinc oxide (ZnO) (99.99 %, metals basis), cadmium oxide (CdO) (≥99.99 %, metals basis), zinc diethylidithiocarbamate (ZDC, 98 %), octadecylamine (ODA) (≥ 99 %), Oleic acid (OA) (tech. 90 %), tri-n-butylphosphine (TBP) (97 %), trioctylphosphine (TOP) (tech. 90%), n-hexane (anhydrous, 95 %), toluene (anhydrous, 99.8 %), cyclohexane (99.5 %), and methanol (anhydrous, 99 %) were purchased from Sigma-Aldrich. 1-Octadecene (ODE) (tech. 90 %), selenium powder (- 200 mesh; 99.999 %, metals basis), and sodium stearate (NaSt) were purchased from ABCR GmbH & Co. KG. Zinc stearate (ZnSt$_2$) (pure) was purchased from Applichem. Zinc acetate (Zn(OAc)$_2$) (pure, 99 %), decanoic acid (DA)(99 %) and oleylamine (OLA) (80-90 %) were purchased from ACROS. Copper (II) chloride dihydrate (CuCl$_2$·2 H$_2$O) was purchased from Fisher Scientific. Sulfur powder (S) was purchased from Riedel-de Haen. Mangan (II) - chlorid tetrahydrat 99-100% and paraffin viscous were purchased from Merck. Diphyl THT was purchased from Kurt obermeier GmbH & Co. KG.

UV-VIS absorption was measured using Lambda 25 UV/VIS Spectrometer from Perkin Elmer. Photoluminescence and photoluminescence excitation were measured using LS 55 Fluorescence Spectrometer from Perkin Elmer. The vacuum oven used was VT 6060P – BL from Kendro. Centrifugation was done by Centrifuge 5804 from Eppendorf.

2.2 Reaction setup

All reactions were conducted in a three neck flask, with the left neck connected to a temperature controller, the right neck connected to nitrogen flow and the middle neck connected to a condenser.

![Figure 2-1 Reaction setup for QDs synthesis](image-url)
2.3 Reactions

2.3.1 Synthesis of ZnSe and ZnSe/ZnS QDs

The synthetic method was modified from the one reported [16].

**Preparation of stock solution:**

Zn precursor I: A mixture of 2 mmol ZnO, 8 mmol DA, and 18.5 ml paraffin oil were loaded in a 50 ml three neck flask and heated to 300 °C under nitrogen flow to obtain a colorless clear solution.

Zn precursor II: A mixture of 2 mmol ZnO, 8 mmol OA, and 17.5 ml paraffin oil were loaded in a 50 ml three neck flask and heated to 300 °C under nitrogen flow to obtain a colorless clear solution.

Zn precursor for shell growth: A mixture of 2 mmol ZnO, 16 mmol OA, and 13.7 ml paraffin oil were loaded in a 50 ml three neck flask and heated to 310 °C under nitrogen flow to obtain a colorless clear solution.

Se-ODE precursor: It was prepared by dissolving 2 mmol Se powder in 20 ml ODE at 220 °C, samples were taken at 1.5 and 4 hours. During this period, the color of the mixture changed from transparent to orange and red, and finally turned yellow.

S-ODE precursor: It was prepared by dissolving 2 mmol S powder in 20 ml ODE at 130 °C for 5 minutes. The solution was colorless.

ZDC-OLA precursor stock solution for shell growth: It was prepared by dissolving 1 mmol of ZDC powder in 10 ml OLA under ultrasonic.

**Procedure of synthesis of ZnSe QDs:**

**Se-ODE injection method:**

1) 1 ml Zn precursor I and 4 g paraffin oil were loaded into a three neck flask, heated up to 330 °C under nitrogen flow.

2) At this temperature, 2 ml Se-ODE stock solution (prepared at 220 °C for 1.5 or 4 hours) was injected swiftly, and the temperature was allowed to cool to 300 °C for crystal growth.
CHAPTER 2 Experimental

3) The reaction was stopped by removing the heater after 5 min of growth.

**Zn injection method (inverse injection method) using prepared Se-ODE stock solution:**

1) 4 ml Se-ODE stock solution (prepared at 220°C for 1.5 hour) and 8 g paraffin oil were loaded into a three neck flask, heated up to 310°C under nitrogen flow.
2) At this temperature, 4 ml heated Zn precursor II was injected swiftly, and the temperature was allowed to cool to 300°C for crystal growth. Aliquots were taken at different time intervals.
3) The reaction was stopped by removing the heater after 30 minutes of growth.

**Zn injection method directly heating Se, ODE and paraffin mixture to 310°C**

1) 0.4 mmol Se powder, 4 ml ODE and 8 g paraffin oil were loaded into a three neck flask, heated to 100°C for 20 minutes to remove air and moisture, and subsequently heated to 310°C for nanocrystal growth.
2) At this temperature, 4 ml heated Zn precursor II was injected swiftly, and the temperature was allowed to cool to 300°C for crystal growth.
3) The reaction was stopped by removing the heater after 30 minutes of growth.

**Procedure of synthesis of ZnSe/ZnS QDs:**

**Purification of ZnSe QDs:**

The ZnSe QDs synthesized was purified by adding acetone into the mixture, heating the mixture until it started to boil. The organic solvents dissolved in hot acetone and ZnSe QDs precipitated on the wall of the flask. The QDs obtained can be redispersed in toluene, chloroform or hexane.

The other way of purification was to dissolve the solution into about two times as much toluene, eliminating the unreacted reagents by centrifugation if necessary, and then methanol was added slowly until no precipitates appeared. The precipitated QDs can be collected by centrifugation again. The QDs obtained can be redispersed in toluene, chloroform or hexane.
Shell growth procedures using “successive ion layer adsorption and reaction” (SILAR) method:

1) The purified ZnSe QDs in hexane (approximately 5.3 nm in diameter, $8.76 \times 10^{-8}$ mol (calculated amount), synthesized by Zn injection method directly heated Se, ODE and paraffin to 310 °C and allowed ZnSe QDs to grow for 3 minutes), certain amounts of ODA and ODE were loaded into a three neck flask and heated to 100 °C for 30 minutes to remove the hexanes and other undesired materials of low vapor pressure.

2) Increase the temperature to 240 °C, a designed amount of Zn precursor for shell growth was injected followed by the same amount of S stock solution after 10 minutes.

3) After 10 minutes, another designed amount of Zn precursor for the second shell growth was injected, followed by the same amount of S stock solution after 10 minutes. The third shell was grown the same way. Aliquots were taken after each shell growth.

Shell growth procedures using single precursor $[(C_2H_5)_2NCSS]_2Zn$ (ZDC):

1) The purified ZnSe QDs in hexane (approximately 5.3 nm in diameter, $8.76 \times 10^{-8}$ mol (calculated value), synthesized by Zn injection method directly heated Se, ODE and paraffin to 310 °C and allowed ZnSe QDs to grow for 3 minutes), certain amounts of ODA and ODE were loaded into a three neck flask and heated to 100 °C for 30 minutes to remove the hexanes and other undesired materials of low vapor pressure.

2) The mixture was heated to 150 °C, and designed amount (1 ml) of ZDC-OLA stock solution was injected into the flask. The temperature was maintained for 30 minutes. Aliquots were taken at different time intervals.

2.3.2 Synthesis of Cu doped ZnSe QDs

The synthetic method was modified from the one reported [16].

Preparation of copper stearate (CuSt2):

Sodium stearate (NaSt) (20 mmol) was dissolved in 80 g of methanol and heated to 50-60 °C until it became a clear solution. CuCl$_2$ solution of 10 mmol in 10 g methanol was added dropwise with vigorous stirring and precipitation of CuSt$_2$ slowly flocculated. The precipitates were separated by centrifugation and washed repeatedly with methanol three times and then
dried under vacuum around 80 °C overnight.

**Preparation of stock solutions:**

Zn precursor I: A mixture of 2 mmol ZnO, 8 mmol DA, and 18.5 ml paraffin oil were loaded in a 50 ml three neck flask and heated to 300 °C under nitrogen flow to obtain a colorless clear solution.

Zn precursor II: A mixture of 2 mmol ZnO, 8 mmol OA, and 17.5 ml paraffin oil was loaded in a 50 ml three neck flask and heated to 300 °C under nitrogen flow to obtain a colorless clear solution.

Se-ODE precursor: It was prepared by dissolving 2 mmol Se powder in 20 ml ODE at 220 °C for 3 hours. During this period, the color of the mixture changed from transparent to orange and red, and finally turned yellow.

Cu precursor: It was prepared by dissolving 0.002 g CuSt$_2$ in 3 ml OLA (0.001 M) between 80 to 120 °C and kept at room temperature under protection of nitrogen. It’s better to use newly prepared Cu precursor every time.

**Procedure:**

1) 2 ml Se-ODE stock solution (prepared at 220 °C for 3 hour) and 4 g paraffin oil were loaded into a three neck flask, heated up to 310 °C under nitrogen flow.

2) As soon as the temperature reached 310 °C, 2 ml heated Zn precursor II was injected swiftly. The heater was removed right away after injection, and sample was taken to check if there were ZnSe nuclei formed and where the PL peak position was.

3) After formation of host nuclei, the reaction mixture was cooled to 60 °C, and 5 ml Se precursor was added and the temperature was increased to 160 °C.

4) 0.5 ml Cu precursor was added dropwise under this temperature. Temperature was increased to 240 °C slowly and annealed for 20 minutes (in this experiment, about 3 °C / min).

5) 2 ml Zn precursor I was injected dropwise at 240 °C and annealed for 30 minutes. Another 3 ml was injected and annealed for another 30 minutes.

6) The reaction was stopped by removing the heater and cooled down to room temperature.
2.3.3 Synthesis of Mn doped ZnSe QDs

The synthetic method was modified from the one reported \cite{31}.

**Preparation of manganese stearate (MnSt$_2$):**

Sodium stearate (NaSt) (20 mmol) was dissolved in 80 g of methanol and heated to 50-60 °C until it became a clear solution. MnCl$_2$ solution of 10 mmol in 10 g methanol was added dropwise with vigorous stirring and precipitation of MnSt$_2$ slowly flocculated. The precipitates were separated by centrifugation and washed repeatedly with methanol three times and then dried under vacuum around 80 °C overnight.

**Preparation of stock solutions:**

The manganese precursor solution were prepared by dissolving 0.025 g MnSt$_2$ in 2.5 g of ODE and heated to 100 °C under nitrogen flow.

The Zn precursor was prepared by dissolving 0.48 g ZnSt$_2$, and 0.0533 g HSt in 4 ml ODE at around 150 °C under nitrogen flow.

The Se-ODE stock solution for multiple injections were prepared by dissolving 0.0474 g of Se powder into 18 g of ODE and 0.1 g of OLA at 220 °C for 3 hours (The time kept under this condition has not been optimized. It was possible that the Se-ODE stock solution prepared in this way is not active, so better results could be expected).

ZDC-TOP precursor stock solution for shell growth: It was prepared by dissolving 1 mmol of ZDC powder in 10 ml TOP under ultrasonic.

**Procedure:**

1) 0.0474 g Se powder, 0.1 g OLA, and 9 g ODE were loaded into a three neck flask and degassed at 110 °C for 15 min under nitrogen flow, and then heated to 280 °C until Se powder was completely dissolved and the temperature was stable.

2) At this temperature, 2 ml manganese precursor solution was injected swiftly, and the temperature was allowed to decrease to 260 °C for NC growth.

3) After 4 min of growth of MnSe nanoclusters, the temperature was cooled to designed
temperature quickly (such as 240 °C), and 1 ml Zn precursor was injected dropwise, followed by 0.2 ml OLA.

4) After a time the PL area didn’t increase any more (such as 50 minutes for 240 °C), the temperature was set at the second overcoating temperature, and another 2 ml Zn precursor was injected dropwise, followed by 0.4 ml OLA.

5) If thicker shell is needed, lower the temperature to 180 °C after the PL area didn’t increase any more, and designed amount of Se precursor was injected. Heat back the temperature to the third overcoating temperature till it was stable, then extra amount of Zn precursor was injected dropwise, followed by designed amount of OLA.

6) Aliquots were taken after formation of each shell. The reaction was stopped by cooling the reaction mixture to room temperature.

The temperatures chosen for overcoating ZnSe shell were 220 °C, 240 °C and 260 °C. Typically, if the ZnSe shell was coated at 260 °C, the time kept under this temperature was 10 minutes. If the temperature for overcoating was 240 °C, the time kept under this temperature was 50 minutes. And the time for overcoating at 220 °C was 100 minutes.

In order to find out the most important parameter to get Mn doped ZnSe QDs with good quality, series of experiments were made. It will be introduced in detail in Chapter 3.

**Purification of MnSe/ZnSe QDs:**

MnSe/ZnSe QDs were purified by dissolving the solution into about two times as much toluene, eliminating the unreacted reagents by centrifugation if necessary, and then methanol was added slowly until no precipitate appeared. The precipitated QDs can be collected by centrifugation again. The QDs obtained can be redispersed in toluene, chloroform or hexane.

**ZnS shell growth to increase photostability:**

In a typical experiment, 3 ml MnSe/ZnSe crude solution was loaded into a three neck flask, degassed, and heated to 150 °C until stable. Then a designed amount of ZDC-TOP solution was injected dropwise at this temperature. After 15 to 20 minutes, the reaction was stopped by cooling down the reaction mixture to room temperature.
Continuous experiment:
One experiment was tried to see the possibility of synthesizing doped NCs by continuous reaction.

1) First, MnSe core was synthesized in a three neck flask using exactly the same way as batch experiment.
2) The crude MnSe core solution and 1 ml Zn stock solution were mixed together and kept warm in a 90 °C water bath under protection of nitrogen.
3) The flow rate was set at 0.5 ml / min, and sample was collected using a vial under protection of nitrogen.
The collected crude solution and 2 ml Zn stock solution were mixed together and reacted the same way as step 3).

2.4 Characterization

2.4.1 UV – Vis absorption spectra
The solvent used for absorption measurement is toluene. Typically, spectra were measured from 350 nm to 800 nm with the scan speed of 960 nm / min.

2.4.2 Photoluminescence (PL) spectra
The solvent used for PL measurement is toluene. Typically, spectra were measured from 385 nm to 700 nm, with the excitation wavelength of 365 nm and scan speed of 480 nm / min. The excitation slit and emission slit were both set at 10 nm or 5 nm.

2.4.3 Photoluminescence excitation spectra (PLE)
The solvent used for PLE measurement is cyclohexane, because it doesn’t absorb UV light along the region where measurements was took. Typically, spectra were measured from 270 nm to 430 nm with the emission wavelength of 450 nm and scan speed of 480 nm / min. The excitation slit and emission slit were both set at 10 nm or 5 nm.

2.4.4 Transmission electron microscopy (TEM)
TEM measurements are done by PT-MT-MCT Surfaces Characterization
CHAPTER 3 Results and Discussion

3.1 ZnS and ZnSe/ZnS Core/Shell QDs

3.1.1 ZnSe QDs

Till then, a lot of methods have been studied to synthesize ZnSe QDs, most of which use coordinating solvents, such as TOP, TBP or TOPO in reaction mixture or preparation of Se precursors. These phosphine containing solvents are not only expensive, but also toxic, pyrophoric, and unstable, which usually require operations in glove boxes \(^{[12, 17, 38, 39]}\). An excellent review summarizes the synthesis, shape control, core/shell, alloy and doped systems of ZnSe based colloidal NCs, but almost focused on above mentioned coordinating solvents \(^{[2]}\). Several lately used methods with phosphine-free Se precursors were reported \(^{[16, 35]}\), opening a brighter window for synthesis of NCs with group VI elements. In this work, the emphasis is on economic and environmental friendly synthetic routes using phosphine-free reagents.

3.1.1.1 Se precursor by dissolving element Se in ODE

In this synthetic route, Se dissolving in ODE is used as anionic precursor. Element Se dissolving in ODE has been used in preparing CdSe \(^{[40]}\), ZnSe \(^{[16]}\), and also doped ZnSe NCs \(^{[31]}\). This precursor is much more reactive than previously used TOPSe or TBPSe if it is properly prepared. A thorough account of preparation and properties of this precursor had been reported \(^{[37]}\), but the particular Se-ODE studied was prepared at moderate temperatures (i.e. from 180 °C to 220 °C). When “inverse injection” methods (cationic precursor injection) were used, which were found generating better NCs, Se-ODE precursors were heated at high temperatures for injection, during which its reactivity could change a lot. It is hard to propose a precise period of time of hours or minutes that the Se-ODE solution should be kept at high temperature because of different heating rates and abilities of maintaining a temperature of different temperature controllers.

It has to be mentioned that two kinds of temperature controllers “J” and “E” were used in this work. “J” can heat up solutions quickly, but it only switches off heating after the temperature reaches the set value and switches on again when the temperature cools down to the set value.
In this way, the temperature of the solution cannot be controlled precisely, and always fluctuates around the set value, at least within 10 degrees, sometimes even 30 to 50 degrees if the volume of solution is small. “E” can control the temperature much better than “J” because it switches off heating before the temperature reaches the set value and switches on prior to it falls down to the set value again, which means it takes overheating and overcooling into consideration and tries to minimize the influence. One thing is that “E” can only heat solutions up to 302 °C. In summary, when a fast heating rate is needed and/or a higher temperature than 302 °C is required, “J” temperature controller is chosen to control the temperature. When the temperature should be controlled precisely below 302 °C, “E” temperature controller should be chosen. There are also variations between batches even the same temperature controller is used because of differences in operations. In this way, it is recommended that experience could be concluded in some way regarding a specific temperature controller by a certain operator.

It had been demonstrated that PLE is a good indicator of Se-ODE precursor efficiency, independent of the temperature of preparation. Detailed information of Se-ODE precursor used will be shown in the following discussion.

### 3.1.1.2 Results of Se precursor injection

In an earlier study, it was reported that a homogeneous yellow solution was prepared by heating a mixture of Se in ODE at 200 °C for 2 hours. Prolonged heating at 200 °C produced a solution that was found to no longer nucleate with cadmium oleate at temperatures near 300 °C \[41\]. The change of PLE spectrum of Se-ODE prepared at 200 °C can be referred to from Ref. 37. Se-ODE precursors prepared at 220 °C for 1.5 and 4 hours were used for ZnSe synthesis to see if Se-ODE prepared for prolonged heating would also fail to nucleate under this condition.

Figure 3-1 Change of PLE spectrum of Se-ODE prepared at 200 °C [37]
Surprisingly, both of the Se-ODE precursors succeeded to nucleate with zinc oleate under this condition, and the PL peak position of ZnSe prepared were more or less the same. The PL peak position of ZnSe prepared from prolonged heated Se-ODE even exhibited a 4 nm red shift comparing with the other one.

The reason the Se-ODE with prolonged heating also nucleated with Zn could attribute to the high temperature of nucleation (330 °C) and the excess amount of Se comparing with Zn. Although the PL peak position of ZnSe prepared from the prolonged heated Se-ODE red shifted about 4 nm comparing with the other one, we cannot say that prolonged heated Se-ODE was more reactive under this condition. It is possible that by using the Se-ODE heated for 1.5 hour, more Se precursor was consumed at the nucleation stage and resulted in a slower growth rate. The nucleation and growth process need to be monitored to get a conclusion.

![Figure 3-2](image)

Figure 3-2 (Left) 0.1 M PLE of Se-ODE solution prepared at 220 °C for 1.5 h and 4 h, respectively ($\lambda_{\text{em}} = 450$ nm, slit width = 5 nm) (Right) PL spectra of ZnSe synthesized using different Se-ODE precursors prepared at 220 °C for 1.5h and 4 h, respectively, by Se injection (the growth time were both 5 minutes)

### 3.1.1.3 Results of Zn precursor injection

In the earlier study using Se-ODE as anionic precursor and paraffin as solvents to synthesize CdSe NCs \[^{40}\], it was found that, when reaction was too fast, the quality of the NC surfaces would be destroyed, therefore the photogenerated excitons would relax through nonirradiation surface defects and the band-gap emission could not be detected any more. It was also possible that no emissions appeared even though absorption spectra were relatively good. Typically, ZnSe NCs grew very fast using Se precursor injection methods, however the QY
reported was relatively lower than using “inverse injection” methods. The less perfect surface resulted from too fast growth rate could be one of the reasons for the lower QY. From this point of view, only high reactivity doesn’t promise a NC with high quality. The balance between nucleation and growth is needed to obtain NCs with good controlled shape and less surface defects.

As discussed above, the reactivity of Se-ODE heated at high temperature changes a lot within a short time, and it is also closely related to the temperature controller used and the operations by a specific operator. In our experiment using Se-ODE stock solution prepared at 220 °C for 1.5 hour as Se precursor, 310 °C and 300 °C as the injection and growth temperatures, no ZnSe nucleation was observed even 30 seconds after injection. ZnSe band gap absorbance was observed after 1 minute of injection. The growth rate was really fast after nucleation comparing with the results reported \cite{16}, especially from 1 minute to 3 minutes period, which should be resulted from less consumption of monomers during nucleation stage. The PL peak positions are shown in the following schematics.

![Figure 3-3 Growth kinetics of ZnSe NCs using Se-ODE precursor prepared at 220 °C for 1.5 h by Zn injection method. (Injection / growth temperature are 310 °C/300 °C, respectively)](image)

There was also a very interesting observation that when Se-ODE solution was heated at high temperatures for a relatively longer time or at moderate temperatures for a prolonged heating, it started to generate blue PL under UV light. The reason of this phenomenon is not yet clear and needs further investigation. When using Zn injection method to synthesize ZnSe QDs, Se-ODE solution in paraffin needed to be heated to 310 °C before injection. During this period, the reactivity of Se-ODE could have changed a lot and blue PL started to be observed under UV light. Especially, after some time at 310 °C, the color of the solution could exhibit a
change from yellow to orange red and then to yellow again. After this transition, the solution showed very bright blue PL under UV light, and the Se-ODE had probably turned to inactive at that time. Using this kind of Se precursor, it was not possible for ZnSe to nucleate, which can be demonstrated by UV/VIS and PL results. Absorbance and PL spectra of pure 0.03 M Se-ODE solution prepared at 220 °C for 3 hours is also shown as comparison.

![PL of 0.03 M Se-ODE 220 °C 3h](image)

Figure 3-4 (Left) PL of 0.03 M Se-ODE solution prepared at 220 °C for 3 hours. (Right) Results of optical measurements after 60 minutes of injection of Zn precursor into inactive Se-ODE solution (Se-ODE was heated at 310 °C until transition of color was observed, no ZnSe QDs was formed under this condition)

From the spectra above, it is clear that no ZnSe was generated under this condition although bright blue PL was observed which should come from the precursor itself. In the earlier study [37], one possible structure (C\textsubscript{18}-Se-Se-C\textsubscript{18}) was suggested by Bullen et al. how Se dissolves in ODE from the comparison of X-ray absorption data between samples prepared at 180 °C, Se powder and calculated spectrum of C\textsubscript{18}-Se-Se-C\textsubscript{18} structure. They also demonstrated an isomerization process of the alkene from 1-2 to 2-3 position occurred after Se dissolved. They criticized the proposed structure of Se-ODE found by Shen [16] for their samples heated at 220 °C for 3 hours that, rather than the heterocyclic addition product proposed, the species may have a terminal SeH moiety. From the absence of ODE+2Se, and 2ODE+2Se signals in EI mass spectra of the inactive Se-ODE comparing with the active one, they concluded that prolonged heating leads to a reduction in Se-Se bridging. This conclusion consisted with the finding by Shen et al. and further demonstrated the terminal SeH structure of the sample prepared under that condition. It was reported by Deng [42], and Yordanov [43] that, H\textsubscript{2}S and H\textsubscript{2}Se are generated through a hydrocarbon dehydrogenation reaction at elevated temperatures.
when S-ODE and Se-ODE are heated in a range of organic solvents, including ODE. We also found that pungent gas was being generated when Se-ODE was heated under high temperature. It could be possible that the dehydrogenation reaction induced more double bonds or conjugated double bond in hydrocarbon chains, accounting for the phenomenon of increasing blue PL under UV light. Further experiments, such as NMR, need to be carried out to clarify this phenomenon. In conclusion, from the earlier study and our findings, the dissolution process of Se power in ODE could be explained as first dissolution of long-range Se-Se into short chain Se species and formation of C\textsubscript{18}-Se-Se-C\textsubscript{18} structure, and then reduction of Se-Se bridging, leading the structure turning to terminal SeH one, being accompanied by isomerization of the alkene from the 1-2 to the 2-3 position, and finally loss of Se because of formation of H\textsubscript{2}Se through hydrocarbon dehydrogenation reaction, inducing more double bonds or conjugated double bonds, which caused increasing blue PL under UV light. The different processes happen at the same time, so the active and inactive structures are generating simultaneously for the dissolved and undissolved Se species. Therefore both temperature and time should be adjusted to get optimized active Se-ODE precursor.

As Se precursor has to be heated to high temperature for injection anyway, it is recommended that Se powder in ODE could be directly heated to injection temperature for some time to prevent strong deactivation from overheating. One experiment was conducted under this condition and the PL peak position after 3 minutes of growth reached 423 nm, relatively slower than using pre-prepared Se-ODE solution as Se precursor. The smaller growth rate may come from fewer monomers for growth after consumption of large amount during nucleation. Interestingly, another experiment keeping other parameters the same, just injecting Zn precursor once the temperature reached 310 °C showed a different result. The ZnSe band gap absorbance was not observed until 3 minutes after injection, but after that no emissions appeared even though absorption spectra were relatively good. In this experiment, Zn precursor was injected as soon as the Se precursor reached 310 °C although there is still some Se powder remained undissolved. From the discussion about Se-ODE solution, it can be presumed that, when the temperature first reached 310 °C, there is still some Se powder undissolved, and Se had not yet formed active structure as proposed above (C\textsubscript{18}-Se-Se-C\textsubscript{18}). In this way, it took some time before Se was active enough to nucleate with Zn. The ZnSe
obtained this way had an imperfect surface structure and excitons relaxed through nonirradiation surface defects, therefore no emissions were observed although there were band gap absorbencies.

### 3.1.2 ZnSe/ZnS Core/Shell QDs

ZnSe/ZnS is a type of Core/Shell structure, which means the ZnS shell can passivate the surface states of ZnSe core, preventing excitons from relaxing through the nonirradiation way, and at the same time, increase photo and thermal stability of the NCs.

The purified sample synthesized using Zn precursor injection method by heating Se powder, ODE and paraffin directly to 310 °C, with a growth time of 3 minutes was used as the core for shell growth. The sample was purified in hot acetone twice, and redispersed in hexane.

Aliquots were taken before the injection of the first shell precursor, and after formation of each shell. PL was measured without purification, and this is why there are big shoulders at the right side of the peaks. These shoulders are background noise, which probably come from impurities of precursor solutions.

It was observed that PL spectrum of ZnSe core after purification blue shifted comparing with the unpurified one. The PL peak position shifted from 423 nm to 415 nm. The reason can be that, after purification, a lot of ligands bonded on the QD surface or the atoms which did not corporate sufficiently into the crystal lattice were washed off, subsequently the size of the NC decreased. The purified ZnSe core solution was placed under room temperature for several days, and during this period the PL quenched a lot as shown in figure 3-5. One of the important reasons is excitons generated relaxed from the surface states of ZnSe QDs more easily because of lack of surface passivating ligands. It makes it necessary to overcoat ZnSe with higher band gap material, ZnS in this case, if practical application is required.

When ZnS shells were overcoated on ZnSe core using SILAR method, red shift of PL was observed which corresponds with the increment of NC size. The PL intensity increased with the increasing shell thickness as the passivation effect became better, but it started to decrease when a certain thickness of shell had been reached, the third shell in this case (spectrum isn’t
show in the figure).

Figure 3-5 (Left) PL spectra of ZnSe QDs and ZnSe/ZnS Core/Shell QDs prepared by SILAR method (Samples were not purified, real time measurements). The inset is the PL peak positions before and after formation of each shell. (Right) Comparison of PL spectra of newly prepared ZnSe (without purification), ZnSe before SILAR shell coating and ZnSe/ZnS final product after purification. (All the spectra are normalized to the same absorbance at the excitation wavelength)

Figure 3-6 TEM image of ZnSe/ZnS Core/Shell QDs synthesized using SILAR method. The inset is the size distribution of QDs.
An example of calculation of amount of precursors needed for each shell is given below:

In this experiment, the ZnSe cores for shell growth were about 5.3 nm in diameter (judging from the PL peak position). The amount of Zn and Se precursors used were 0.4 mmol.

Figure 3-7 Unit cell structure of zinc-blende ZnSe and ZnS crystal [44]. The lattice parameter is 566.8 pm for ZnSe, and 596 pm for ZnS.

As shown in above cell structure of ZnSe crystal, in one cell there are 4 Zn atoms and 4 Se atoms, respectively, and the volume of one cell of ZnSe is $0.5668^3$ nm$^3$, of ZnS is $0.596^3$ nm$^3$.

Therefore, in one ZnSe crystal with a diameter of 5.3 nm, the amount of Zn and/or Se atom is:

$$\frac{4}{3}\pi \times 2.65^3 \times 4 = 1.7124 \times 10^3$$

In this case, the mole amount of ZnSe crystals synthesized is (assume all reactants have been consumed):

$$\frac{4 \times 10^{-4} \text{mol}}{1.7124 \times 10^3} = 2.3359 \times 10^{-7} \text{mol}$$

Usually, the thickness of one monolayer of ZnS is about 0.31 nm. The number of Zn and/or S atoms needed for one ZnSe crystal to grow the first shell is:

$$\frac{4}{3}\pi [(2.65 + 0.31)^3 - 2.65^3] \times 4 = 5.7970 \times 10^2$$

The mole amount of Zn and/or Se precursors needed for the growth of first shell on as prepared ZnSe QDs is:

$$2.3359 \times 10^{-7} \text{mol} \times 5.7970 \times 10^2 = 1.3541 \times 10^{-4} \text{mol} = 0.135 \text{mmol}$$
The mole amount of Zn and/or Se precursor needed for the growth of second or third shell on ZnSe QDs or other QDs were calculated using the same method as conducted above. No more calculation details will be presented below.

It should be pointed out again that the assumption using this method to calculate the amount of shell precursors needed is that all the precursors are consumed for core growth (In this experiment, we assumed 25% lost). Actually, there are still precursors unreacted in many cases, so that the calculated values are higher than needed. Only approximate amount of precursors needed is obtained using this method. The relationship of optical density as a function of QDs concentration is needed if more precise value is required.

It had also been tried to overcoat ZnS shell on ZnSe using single molecular source ZDC (ZnSe cores used were the same purified sample as that used in SILAR method), but unfortunately, it was not successful. The reason of failure could be the preparation and amount of ZDC precursor used, the overcoating temperature or else which needs further investigation.

3.1.3 Future work for ZnSe and ZnSe/ZnS Core/Shell NCs

3.1.3.1 Synthesis with better control over nucleation and growth

As discussed above, balance between nucleation and growth is important to synthesize monodispersed, high quality ZnSe QDs with minimized surface defects. The reactivity of precursors should be high enough for nucleation of NCs, but at the same time, also low enough to lead a relatively slower and more homogenous growth of NCs with monodispersed size distribution and less surface defects. The complexity of operation should also be taken into consideration to create a robust and reproducible synthetic route.

It is recommended that Se precursor can be heated directly up to injection temperature without pre-steps. One reason is that Se-ODE can be deactivated under high temperature very fast, and the other is that it takes much less time than preparing Se-ODE stock solution at 220 °C for hours. Se can also be dissolved in paraffin directly at 220 °C without use of ODE. In this way, the time of this solution kept at high temperature should be optimized using
more precise temperature controller. Generally, time chosen should between the total dissolution of Se powder and total deactivation of Se-ODE at high temperature.

The ratio of Zn and Se precursors in Zn injection method was kept at 1:1. Usually, ratio between precursors has influence on nucleation and growth of QDs. In the future, the ratio between Zn and Se can be varied and optimized to get better QDs. Fatty acid and amine can be added in Se precursor as surfactants to control nucleation and growth \(^\text{[40]}\). More fatty acid restricts the nucleation of NCs because of stronger complexation with cationic species. The more residual monomers accelerate the growth of QDs. Amine activates cationic precursors, therefore more nuclei are formed in the nucleation stage, and less residual monomers slow down the growth rate. Amine is better to be added with Se precursor as it seems to attack the carbonyl group to release the cation bonded to the carboxylate group. If no selenium is added, the reaction between amines and zinc fatty acid salts results in zinc oxide NCs \(^\text{[39]}\).

As discussed above, the temperature controllers used have some restricts depending on specific experiment condition. Only “J” temperature controller can be used if 310 °C is chosen as injection temperature. The temperature after injection can not be controlled precisely because of the intrinsic characteristic of the temperature controller. The turbulence of temperature would probably result in inhomogeneous growth rate, which is not good for the formation of monodispersed, well shaped, and defect-free QDs. Under this condition, injection at 300 °C using “E” temperature controller can be tried, so that the growth rate will be controlled better after injection. QDs with better quality are expected, but further experiments are needed.

### 3.1.3.2 Possibility of synthesizing ZnSe QDs in continuous system

Systematic experiments of continuous reaction to synthesize ZnSe NCs have not been tried yet, but the possibility of it has been approved by accident.

Once continuous experiment was tried for Mn doped ZnSe NCs to grow ZnSe shell on MnSe core, but it failed. Surprisingly, ZnSe itself formed instead of ZnSe shell on MnSe. This can be approved by the band gap absorbance peak and emission after reaction (see figure 3-8) as absorbance spectrum of MnSe/ZnSe usually doesn’t have this peak except that ZnSe shell
grows into branched structure after long and high temperature heating \cite{31}. Although the Zn precursor used was ZnSt\textsubscript{2} but not ZnO/OA/Paraffin mixture, the formation of ZnSe QDs in continuous reactor at a temperature as low as 240 °C implies a promising possibility of synthesizing ZnSe QDs using continuous reactor.

![Continuous sample](image)

Figure 3-8 UV/VIS spectrum of sample prepared using continuous reactor (mixture of MnSe core, Se-ODE, ZnSt\textsubscript{2} go through continuous reactor at 240 °C)

One problem could be encountered using continuous reactor to synthesize ZnSe QDs is that Zn precursor solutions become suspension or emulsion when temperature goes down. Suspension or emulsion is not good for nucleation because homogenous atmosphere is required for monodispersed nuclei to form. Suspension or emulsion is also not good for continuous reactor as it will stick the tube of reactor (It happened when we tried this experiment). In order to prevent this problem, both temperature and concentration of Zn precursor should be optimized. Zn and Se precursors can be mixed as stock solution for continuous reaction. The temperature of the stock solution can be maintained in oil bath or using temperature controller. Placing a set up used for batch reaction upstream and keeping the stock solution in three neck flask at a certain temperature using temperature controller is recommended because heating is more homogeneous and efficient this way.

### 3.1.3.3 Possibility of overcoating ZnS shell in continuous system

It is not easy to overcoat shells in continuous reactor because a condition active enough to overcoat shells on core, whereas inactive enough for nucleation of shell precursors themselves should be found. SILAR method is used in batch reaction to grow shells but it is not suitable for continuous reaction because cation and anion need to be adsorbed and reacted with core
separately. Two runs are needed for overcoat each layer of shell. Usually, two or three layers of shells need to be coated, which means four to six runs of continuous reactions need to be carried out. Furthermore, purification of core is needed to facilitate shell growth. SILAR method is too complex to be used in continuous reaction. For shell overcoating, using single molecular source ZDC as the shell precursor is a promising way. Generally, microreactor technology has beneficial for producing nanoparticles with well controlled size, because the temperature and reaction time can be controlled precisely. It also has beneficial for controlling shell thickness homogeneously \[18\]. Both the amount of ZDC and residence time can be optimized to control the shell thickness. Although batch experiment for overcoating ZnS shell was not successful, experience and earlier study both indicate continuous reaction in microreactor for shell growth is worth trying.

3.2 Doped ZnSe NCs

Doping a few ions into a NC is thermodynamically unfavorable. To meet this challenge, decouple the doping process from nucleation and / or growth is necessary. As introduced in Chapter 1, most successful doping routes for Mn doped ZnSe NCs were nucleation doping, and in contrast, for Cu doped ZnSe NCs were growth doping.

Although several different approaches had been tried to synthesize doped ZnSe NCs, few worked out. It should not because of the problem of approach itself, but mastery of control over each elemental step during the whole doping process. To synthesize doped NCs, temperature, time, amounts of precursors and condition of solutions need to be controlled precisely to succeed. No matter for doped NCs prepared by growth doping or nucleation doping, both energy transfer and emission processes should occur at the interface of the nuclei with the dopant ions as the emission centers and the pure host overcoating layer as the absorption zone \cite{30}. Details will be discussed further below.

3.2.1 Cu doped ZnSe NCs

Synthesis of Cu dope ZnSe NCs using growth doping method has a strict requisite for reaction condition. It should be made sure that the reaction atmosphere is moisture and air free. The procedure used in this work is not the optimized protocol of this synthetic route,
therefore there are ways to promote it according to earlier study and experience which will be discussed below.

3.2.1.1 Size of host nuclei

It was found that the size of ZnSe nuclei decided the difficulty of doping process \(^{[16]}\). If the size of ZnSe NC is very small, it is very easy to adsorb Cu\(^{2+}\) onto its surface, and then is also easy to overcoat ZnSe shells. When ZnSe NC is too big, it is difficult to adsorb Cu\(^{2+}\) ions on the surface. Most of our unsuccessful Cu doping experiments should come from the failure of synthesizing small-sized ZnSe cores.

There was no Fluorescence spectrometer in the lab earlier, so there was no possibility to monitor ZnSe size before Cu doping. When retrospecting the PL spectra of ZnSe cores from unsuccessful Cu doing experiments, it was found that there were either no ZnSe formed or too big ZnSe were formed. When using ZnO/OA/Paraffin as Zn precursor, Se-ODE as Se precursor to synthesize ZnSe cores (the method described in experimental section), if a significant color change of Se-ODE precursor from yellow to orange red then back to yellow was observed, there were always no ZnSe cores formed. This is because Se-ODE precursor turned to inactive after this transition as discussed before. However, interestingly, the absorbencies of the final product (after Cu doping and ZnSe shell coating) always had ZnSe band gap absorption. It indicated that ZnO/DA/paraffin (Zn precursor for ZnSe shell growth) was able to nucleate with this “inactive” Se precursor. Based on this fact, the overcoating temperature could be even lower down using this more active Zn precursor. Steven \(^{[29]}\) found that dopant incorporation falls rapidly to zero for NCs smaller than 20 Å, suggesting a central core resists doping. Combining these facts, conclusion can be made that ZnSe core with a size between 2 to 3 nm is ready to accept dopant incorporation.

Integrating all these findings, protocol for Cu doping was modified (see experimental). Se-ODE prepared at 220 °C for 3 hours with paraffin was heated and Zn precursor injection took place as soon as it reached 310 °C. Heater was removed right after injection and the reaction mixture was allowed to cool to 60 °C. Sample was taken to check the UV/VIS absorbance and PL. After making sure that small ZnSe nuclei did formed, we carried on the
doping process.

### 3.2.1.2 Temperature of shell growth

After Cu precursor was injected, temperature was increased to 240 °C, and aliquots were taken to monitor the reaction. It was found that the band gap emission was red shifting during this period, indicating the growth of ZnSe host. The growth of host is not good for dopant adsorption, therefore, lower overcoating temperature should be used to prevent it. As discussed above, Zn/DA/Paraffin precursor can even react with “inactive” Se-ODE precursor at 240 °C, which also proves the possibility of lowering the overcoating temperature. There is another reason why lower overcoating temperature is better. In the excellent study of temperature dependence of “elementary processes” in doping semiconductor NCs \[^{33}\], it was found that doped cores that were overcoated at any temperature above 220 °C had significantly lower copper dopant PL intensity when compared to cores that were overcoated at 210 °C or under. In addition, doped cores with outer shell layers grown at temperatures beyond 220 °C, even when the ZnSe outer layers were thicker, consistently had lower dopant PL QY compared with doped cores with thinner shells that were overcoated at 210 °C or below. These results suggest that the doped centers might have moved toward the surface via “lattice diffusion” and/or ejected from the NCs via “lattice ejection” during the overcoating of the pure ZnSe shell at temperatures higher than 220 °C. According to this fact, temperature between 200 °C to 220 °C should be chosen as the overcoating temperature (also depend on the reactivity of precursor at these temperatures), and this temperature range also consists with the finding of promising Cu\(^{2+}\) doping results when the temperature was set between 200 °C to 240 °C.

### 3.2.1.3 Quenching of Cu dopant PL

Cu dopant emission suffers from a serious photostability problem because of photooxidation in the presence of air and light \[^{26}\]. Hence the emission resulting from Cu doped ZnSe degrades on exposure of a few seconds in air, making even the usual spectroscopic measurements difficult. This is the reason why we always can’t observe the dopant emission using the usual way, especially for surface doped NCs. A thicker shell or thiol ligands on the surface of doped NCs only improve the emission stability to a few hours. Quenching problem
was also observed during the experiment. Although dopant emission could be seen under nitrogen protection, it quenched as soon as it exposed to air. The figure below shows the color change of the solution.

Figure 3-9 Color change of Cu doped ZnSe NCs. (Left) Crude product after synthesis under nitrogen protection (Right above) Crude product transferred to vial under air within a few seconds (under nitrogen protection in vial) (Right below) The residual crude product at the bottom of the three neck flask exposed to air (All the photos were taken at room temperature.)

It’s also because of quenching that PL spectra we measured during experiment only show band gap emission of ZnSe. Air free techniques are needed to monitor Cu doping experiments in the future.

The PL from as prepared Cu doped ZnSe was not rather green but cyan, because ZnSe shell was thin in this sample. Judging from the TEM result, the size was only less than 6 nm in diameter (Figure 3-10). In literature, a 9.2 nm host ZnSe resulted in a 515 nm Cu dopant emission, therefore the sample prepared in this experiment was actually between blue and cyan region. The thin shell was also the reason it quenched as soon as it exposed to air, although there was still nitrogen protection after transferring it to the vial (figure 3-9, right above). However, there is another explanation for this cyan PL which we believe is more proper under this condition that, there were possibly both Cu doped ZnSe and intrinsic ZnSe NCs together in the solution. ZnO/DA/Paraffin precursor is very reactive and it possibility nucleated with Se-ODE to form ZnSe QDs itself rather than formed shells on surface doped ZnSe. Subsequently, Cu dopant ions stayed near surface without protection of ZnSe shells, so that dopant emission quenched as soon as it was exposed to air, leaving blue emission of ZnSe itself. It further approves that overcoating temperature should be lowered to facilitate shell growth rather than nucleation.
3.2.1.4 Future work for Cu doped ZnSe NCs

3.2.1.4.1 Optimizing Se and Zn precursors

The method used to synthesize ZnSe nuclei for Cu doping was the same one used to synthesize ZnSe QDs, therefore some optimization methods of synthesizing ZnSe and ZnSe/ZnS QDs are applicable for Cu doped ZnSe QDs too. For example, Se precursor can be directly heated to reaction temperature to simplify the operation and prevent Se-ODE deactivation at high temperature. Amine and fatty acid can be used to tune the reaction rate. Ratio of Se and Zn precursor can be adjusted to control nucleation of ZnSe and reaction rate after. The (001) surfaces of zinc-blende crystals, which typically consist of various arrangements of anion dimmers provide very stable binding sites that are absent from the (110) and (111) surfaces of zinc-blende crystals, and from all surfaces of wurtzite and rock-salt crystals. The (001) facet fraction of the whole surface is higher under Se rich condition, and falls to zero under Zn rich condition [29]. It suggests that a higher ratio of Se to Zn should be
used to synthesize ZnSe cores to facilitate dopant adsorption.

### 3.2.1.4.2 Multiple injection of shell growth

Overcoating shell at a high temperature (> 210 °C) for a long time will drive Cu dopant centers toward the surface via “lattice diffusion”, and the longer it is kept at high temperature, the more dopants will be driven to the surface and ejected from the lattice via “lattice ejection”, resulting in low QY. However enough time is needed for shell to grow to a certain thickness if higher emission wavelength and better photostability are required. Therefore, it is better to grow shell with multiple injection of shell precursor. The time needed after each injection can be optimized by monitoring the PL area. The reason for multiple injection of shell precursor for Cu doped ZnSe NCs is almost the same as Mn doped ZnSe NCs, and it will be discussed more in the result section of Mn doped ZnSe NCs.

### 3.2.1.4.3 Prevention of photooxidation

As shown in the above pictures, Cu doped ZnSe NCs suffer from the serious photooxidation problem. To prevent it, a material with larger band gap, such as ZnS, can be coated. Recently a promising way of growing a Se/S alloyed outermost shell had proved photostability can be enhanced efficiently minimizing the surface exposed Se atoms \[13\]. Towards the end of the growth a calculated amount of S precursor was injected together with Zn precursor. In this way, no purification step and/or additional step to grow ZnS shell is needed, whereas the passivation effect is efficient. The amount of S precursor to be injected can be optimized.

### 3.2.2 Mn doped ZnSe NCs

Mn\(^{2+}\) is a harder lewis acid compared with Zn\(^{2+}\). Therefore, the Mn\(^{2+}\) precursor should be significantly less reactive than Zn\(^{2+}\) if they both have the same carboxylate ligand. The X-ray powder diffraction (XRD) and electron diffraction patterns reported before had both confirmed the doped NCs had a zinc-blende structure similar to ZnSe, and the lattice constants of zinc-blende ZnSe and MnSe were almost identical (about 4% lattice difference) \[26\]. The operation details of the synthesis method have been studied step by step, in order to find out an optimized robust condition for synthesis.
3.2.2.1 Condition of precursors

The conditions of precursors specially mean the conditions of precursors right before injection or reaction. To synthesize MnSe nuclei, both Se injection\cite{31} or Mn injection\cite{46} method were reported. When Se injection method is used, MnSt$_2$ precursor in ODE is better to be heated to 100 °C for some time to remove moisture and air, and then heated to injection temperature quickly. MnSt$_2$ in ODE is stable till 300 °C, and self decomposes to MnO at above this temperature\cite{47}. MnO NCs can be synthesized by thermal decomposition of manganese acetate in the presence of either OA or OLA\cite{27}, therefore these surfactants are better to be added with Se precursor to prevent potential formation of MnO NCs.

The property of Se-ODE precursor has already been discussed a lot above. Optimization of Se-ODE precursor is a general question remained in all these synthesis. Typically, when synthesizing Mn doped ZnSe NCs, Se-ODE was directly heated to 280 °C until all Se powder was dissolved and ready for injection of Mn precursor. “E” temperature controller was used to heat up Se-ODE solution. Because of its characteristic of controlling the heating rate and increasing temperature to set value steadily, it usually took about 16 minutes to heat up the Se-ODE solution from 110 °C to 280 °C (much longer than using “J” temperature controller), and till then Se powder was already completely dissolved. PLE spectra of Se-ODE solution heated at 280 °C for different period of time are shown in Figure 3-11. From the spectra, we can see that the deactivation process proceeds really fast at such high temperature. When the solution had just reached 280 °C, peaks at 306 nm and 320 nm were still obvious, indicating that Se-ODE precursor was during active stage. After 5 minutes at 280 °C, the peak at 306 nm had decreased, and the intensity of the region higher than 320 nm had increased, relating to the deactivation process. Further heating caused the peak at 306 nm disappear totally and the red shift of spectra. Based on this fact, using “E” temperature controller to heat up Se-ODE solution to 280 °C, there is no need to keep the solution at 280 °C for a longer time. Usually Se powder was already dissolved until the temperature reached and was stable at 280 °C, and Se-ODE was ready for reaction at that time, therefore Mn precursor can be injected as soon as 280 °C is reached, or at least within 5 minutes.
3.2.2.2 Control of the size of MnSe core

Formation of MnSe nanoclusters plays a critical role in determining the properties of the resulting Mn doped ZnSe NCs. MnSe nanoclusters grew very fast at 260 °C. The dopant PL intensity increased as the formation time of MnSe nanoclusters increased at 260 °C, reached a maximum at about 4 minutes [31]. It is quite different from the case when TBPSe is used as Se precursor. Typically, about one hour is needed for formation of MnSe nanoclusters if TBPSe is used [30]. The lattice parameter of the unit cell of zinc-blende MnSe should be in 0.5-0.6 nm range. The optimal size of MnSe nanoclusters is 1.8 nm, which is around the length of three unit cells. A too big MnSe nanocluster is not good for formation of good interface between MnSe core and ZnSe shell, which is where dopant emission generates. Moreover, a too big MnSe core would place the dopant ions nearer to the NC surface, which means less uniform environment of the dopant ions, and higher possibility to be influenced by surface trap states.

In order to control the size of MnSe within optimal range, not only time for MnSe growth, but also the reactivity of Se-ODE precursor needs to be controlled. Three experiments were conducted to study this relationship. The control experiment was conducted by injecting Mn
precursor at 280 °C and allowing MnSe to grow for 5 minutes at 240 °C, then overcoating ZnSe shell at 240 °C for 30 minutes. Another one kept the other parameters the same except that Se-ODE was heated at 280 °C for 20 minutes before Mn injection. The last one was conducted by injecting Mn precursor at 280 °C and allowing MnSe to grow for 4 minutes at 260 °C, then overcoating ZnSe shell at 240 °C for 30 minutes. The time between Mn precursor injection and shell precursor injection was 5 minutes and a half. The D-NCs prepared with Se-ODE with prolonged heating at 280 °C should have the smallest MnSe cores. From the PLE spectrum above we already know Se-ODE under this condition should be very unreactive, resulting in a much lower growth rate of MnSe. The small MnSe cores can be proved by the low QY and relative redder PL peak position (579.5 nm). The MnSe cores grew at 240 °C for 5 minutes should have a size in between (PL peak position at 578.5 nm), whereas the D-NCs prepared had the highest QY. Under this condition, the MnSe cores should have a relative optimal size, supporting by its best PL performance. The MnSe grew at 260 °C had the biggest MnSe cores and should have exceeded the optimal size. Therefore the QY of D-NCs prepared with these MnSe cores was lower than the former one. Its big core size is also supported by its lowest PL peak position (576.5 nm).

![Figure 3-12 (Left) PL spectra of MnSe/ZnSe NCs (1 ZnSe shell) under different conditions (normalized to the same absorbance at excitation wavelength). (Blue) Se-ODE was heated at 280 °C for 20 minutes before Mn precursor injection. MnSe grew at 240 °C for 5 minutes, and then was overcoated with ZnSe at 240 °C for 30 minutes. (Red) Mn precursor was injected as soon as Se-ODE reached and was stable at 280 °C. MnSe grew at 240 °C for 5 minutes, and then was overcoated with ZnSe at 240 °C for 30 minutes. (Green) PL Intensity (a.u.)](image-url)
Mn precursor was injected as soon as Se-ODE reached and was stable at 280 °C. MnSe grew at 260 °C for 4 minutes, and then temperature was lowered to 240 °C, and MnSe was overcoated with ZnSe shell for 30 minutes. MnSe totally grew for 5 minutes and a half. (Right) The relationship of PL intensity of Mn doped ZnSe NCs verses the reaction time of the MnSe at 260 °C [31].

3.2.2.3 Control of ZnSe shell growth

3.2.2.3.1 Control of temperature and time for overcoating

The temperature chosen for ZnSe overcoating must facilitate diffusion of dopant ions into host layer. A too low overcoating temperature restricts dopant ions within the interior lattice of D-NCs, even results in another emission center at about 640 nm, which is the emission center with a Mn ion next to the Mn emission center (Mn-Mn centers). A too high overcoating temperature results in a too fast diffusion rate, and at the same time facilitates “lattice ejection”. High temperature chemical reaction would provide sufficient thermal energy to anneal out defects in the NCs, however, since any embedded impurity atom would always be within a few lattice constants of the surface of the NC, the same thermal energy can also anneal out the Mn “defects” [48]. A temperature helps gentle diffusion of the dopant ions into the host layer would result in isolated dopant centers within the host lattice, which should thus yield high performance D-NCs.

The overcoating temperatures chosen in this system is between 220 °C to 260 °C. The growth rate of ZnSe sets the lower limit and the growth temperature of MnSe nanoclusters sets the higher limit. If ZnSe shell was overcoated at 240 °C or 260 °C, an increase followed by a decrease of PL intensity was observed. Lattice diffusion of Mn doped ions was the reason of PL increase, but as time went on, Mn ions diffused to the direct “lattice ejection” zone. Direct “lattice ejection” happened to the dopants located at a distance (from the NC surface) not greater than their mean free path (the depth of the direct “lattice ejection” zone) of diffusion in the host lattice. When Mn dopants diffused to this zone, it would be ejected from NC lattice quickly, which was the reason of PL decrease after the maximum. With an increase in temperature, the mean free path increased, and thus resulted in a quicker and earlier PL decrease. If ZnSe shell was overcoated at 220 °C, PL intensity was increasing steadily all the
time. It indicates that Mn dopant ions didn’t diffuse to the mean free path at this temperature. Therefore, different period of time was needed for overcoating ZnSe shells at different temperatures, and it has already been documented in the earlier study (see figure 3-13).

Figure 3-13 Temporal evolution of PL intensity of MnSe/ZnSe NCs at different ZnSe overcoating temperatures. [31]

3.2.2.3.2 Multiple injection of Shell precursor

“Lattice ejection” which happens after Mn dopant ions diffusing to the mean free path causes PL intensity to decrease after its maximum, but it can be prevented by multiple injection of shell precursor. There is another possible reason for the decrease of PL intensity. The emission properties of Mn\(^{2+}\) ions are closely related to the distribution of Mn\(^{2+}\) ions in the D-NCs and the structure of the D-NCs [36]. Intraparticle ripening, in which material is redistributed on the same NC due to evolution of the particle shape, happens until the Zn and/or Se precursors are depleted in the reaction solution, decreases the average number of Mn impurities per NC as the reaction proceeds, however, it can also be avoided if the reactant concentration is maintained by addition of more reactants [49]. The evolution of particle shape was demonstrated by the absorption peak after PL reached its maximum at 260 °C. This absorption peak corresponded to branch-shaped MnSe/ZnSe D-NCs, and branched D-NCs were found to show a relatively low PL QY [50]. In order to avoid losing Mn dopant ions per NC, additional shell precursor was added before PL intensity came to decrease stage. One or more injections can be done according to the requirement of shell thickness. Figure 3-14 shows the Mn dopant PL after 30 and 50 minutes of each shell precursor injection at 240 °C. The PL peak position shifted from 578.5 nm (first shell coating after 30 minutes) to 581 nm (second shell coating after 50 minutes), indicating the continuous shell growth.
In order to find out the best temperature combination for multiple shell overcoating, a series of experiments overcoating ZnSe shells at different combinations of temperatures were conducted. The results are shown in Figure 3-15, from which we can see that overcoating of two ZnSe shells both at 240 °C for 50 minutes yielded the highest PL intensity in the end. The critical diffusion temperature for Mn doped ZnSe was reported to be around 240 °C \[^{[33]}\], and the results in figure 3-15 further confirms that overcoating ZnSe shells around critical diffusion temperatures results in more efficient isolated dopant centers.
Figure 3-15 Comparison of PL intensity of MnSe/ZnSe NCs (2 ZnSe shells) overcoated two ZnSe shells at different combinations of temperatures.

### 3.2.2.4 ZnS overcoating to enhance photostability

It was found that as prepared MnSe/ZnSe NCs with two ZnSe shells still face the quenching problem. It is recommended that the NCs are better to be purified right after reaction. If they are not purified, the solution will turn into emulsion after a while and thus the dopant emission decreases. However purification step or directly dissolving the unpurified samples in toluene both resulted in quenching of dopant emission. To enhance the photostability, thicker ZnSe shells need to be coated, or in another way, a ZnS shell can be coated to protect the MnSe/ZnSe NCs.

In this work, single molecular source ZDC was tried to grow an outermost ZnS shell on MnSe/ZnSe NCs. The photostability was enhanced successfully, proved by comparison of dopant emissions before and after growth of ZnS shell (Figure 3-16). However whether or not growing a ZnS shell increased the dopant emission by passivating the surface trap state had not been proved yet. That’s because samples were not purified right after reaction, thus either emulsification or solidification happened to the crude products and quenched the dopant
emission, no matter ZnS were coated or not. The comparison of purified and unpurified samples shows purified sample has a higher photostability (Figure 3-17). Theoretically, the PL intensity should be increased if an outermost ZnS shell with a suitable thickness is coated. Further investigation is needed to find out the optimal amount shell precursor.

Figure 3-16 Comparison of PL of MnSe/ZnSe (left vial in both pictures) and MnSe/ZnSe/ZnS (right vial in both pictures). (They are of the same concentration.) (Left picture) PL of both samples after diluting them into toluene after reaction. (Right picture) PL of both samples after a month of diluting them into toluene and exposition to air on purpose. (Only several days were needed for MnSe/ZnSe sample to quench completely without exposition to air.)

Figure 3-17 Comparison of PL of MnSe/ZnSe (left), MnSe/ZnSe/ZnS without purification (middle), and MnSe/ZnSe/ZnS after purification (right) in toluene after one month. (They are of the same concentration.)
3.2.2.5 Future work for Mn doped ZnSe QDs

3.2.2.5.1 Adjusting the MnSe growth temperature

Although the growth temperature of MnSe nanoclusters used was 260 °C, it had already been demonstrated that 240 °C was also sufficient for MnSe growth, as only MnSe nanoclusters with very small size was needed. In this case, the growth temperature for MnSe could be set at 240 °C at the beginning. The reason for this change is that, overcoating of two ZnSe shells at 240 °C for 50 minutes gave the best PL QY (Figure 3-15). If the temperature is set originally at 240 °C, there will be no need to change the temperature before ZnSe shell growth, so that eliminating potential uncertainty between batches, and at the same time, the growth time of MnSe can be controlled precisely. Therefore growth time for MnSe nanoclusters at 240 °C can be optimized.
CHAPTER 3 Results and Discussion

3.2.2.5.2 Adjusting the amount of Se precursor and thicker ZnSe shells

The amount of Se precursor used was a constant. If the third ZnSe shell is needed, additional Se-ODE precursor is also needed. Based on the fact that MnSe/ZnSe with two shells would always quench in toluene, a thicker ZnSe shell is necessary to enhance photostability. A larger amount of Se could be used to avoid additional Se-ODE precursor preparation for multiple Se injection, which would always take hours. Increasing the amount of Se in the reaction will change the MnSe growth rate, therefore the time for MnSe growth needs to be optimized again under this condition.

3.2.2.5.3 The overcoating temperature for the last ZnSe shell growth

It has been discussed before that when ZnSe was coated at 220 °C, no decrease of dopant PL intensity was observed because the dopants didn’t diffuse to its mean free path at this temperature. Overcoating ZnSe shells at higher temperature would always result in a decrease following an increase of dopant PL. Therefore it is recommended that no matter at which temperature the previous ZnSe shells are overcoated, the last ZnSe shell is better to be overcoated at 220 °C. The idea is to prevent dopants from diffusing to the mean free path, so that to place the dopants relatively far away from the surface trap states, and also help the dopants avoid the potential of being ejected under extreme environment. For Cu doped ZnSe, this temperature limit is 210 °C.

3.2.2.5.4 ZnS shell growth to prevent photooxidation

ZnS had already been overcoated onto MnSe/ZnSe to enhance its photostability in batch experiment, but as written above, further experiments need to be done to study their PL QY before and after ZnS shell growth. Purification and measurements of PL spectra should be done during or right after reactions. ZnS shell growth also needs to be done as soon as MnSe/ZnSe is prepared. The amount of ZnS precursor needed needs to be optimized because thin ZnS shell is not enough to passivate the surface trap states while too thick ZnS shell will instead weaken dopant emission. In the section of ZnSe/ZnS core/shell QDs, the advantage of overcoating ZnS shell with a single molecular source ZDC in continuous microreactor was discussed, and this idea is also applicable here. Both the amount of ZDC and residence time in reactor can be optimized to control the shell thickness.
3.2.2.5.5 Another way of synthesizing doped ZnSe NCs by mixing cation and anion precursors together

Recently, an interesting approach of synthesizing Mn doped ZnS NCs was published $^{[zz]}$. In this approach, MnSt$_2$, ZnSt$_2$, and S powder were mixed together in ODE to synthesize Mn doped ZnS core first, and then additional Zn precursor was injected to grow ZnSe shell, after which the QY increased a lot. Controlled nucleation with proper amount of Mn precursor and the ratio of initial Zn and S precursors were the two most critical quantities responsible for such an efficient emission. In the light of this approach, synthesizing Mn and Cu doped ZnSe NCs by first synthesizing doped cores mixing all precursors together and then overcoating ZnSe shells can be tried. One difference is that Se powder cannot dissolve in ODE at mild temperature like S (below 100 °C). Usually temperatures higher than 200 °C are needed and it will take a period for Se to dissolve completely. The slow dissolving rate is not good for nucleation of doped cores, thus pre-dissolution of Se powder is needed for this approach.
Summary

In conclusion, in this work, we achieved phosphine free synthesis of doped and undoped ZnSe NCs. Instead of using pyrophoric and expensive coordinating solvents such as TBP, TOP and TOPO, we used noncoordinating solvent ODE, and directly diluting Se into ODE to form the Se-ODE complex as the Se precursor. ZnSe QDs are successfully synthesized and overcoating two ZnS shells using successive ion layer absorption and reaction method gives the highest quantum yield efficiency. MnSe/ZnSe NCs are also successfully synthesized, and the temperature and time for nucleation and ZnSe shell growth have been optimized. Furthermore, the photostability is enhanced by overcoating ZnS shell using single molecular source ZDC. For Cu$^{2+}$ doping experiment, surface doped ZnSe NCs are obtained, but ZnSe shell overcoating process is not successful. The temperature for coating should be lower to facilitate shell coating rather than nucleation again, and it needs further investigation.
Acknowledge

I would like to express my sincere gratitude to everyone who helped and supported me during this thesis work. First of all, I really appreciate this opportunity Bayer Technology Service offered me to conduct and complete my thesis work here.

Foremost I would like to thank my supervisor Dr. Huachang Lu, for his patience, great suggestions and supervision, and also care and help for my life here in Germany. In addition, I would like to express my appreciation to Ms. Liedtke and all the co-works in the laboratory for their technical support.

Special thanks to Prof. Dr. Krister Holmberg, my examiner, for his support and encourage, and to Pia Hepsever, who is ready to give me any help during my career here.

I have to thank you all who work in Lab 250, and all the interns and diploma workers, for being nice mates and the friendly atmosphere provided.

Finally, I want to thank my parents who are always supporting me for no matter what I want and no matter what I want to do, for your unconditional faith in me.
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