

SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING

UNIVERSITI SAINS MALAYSIA

SYNTHESIS OF CADMIUM-FREE QUANTUM DOTS

By

AARON TAN CHENG SHIONG

Supervisor: Dr. Khatijah Aisha bt. Yaacob

Dissertation submitted in partial fulfillment
of the requirements for the degree of Bachelor of Engineering with Honours
(Materials Engineering)

Universiti Sains Malaysia

JUNE 2017

DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled “**Synthesis of Cadmium-Free Quantum Dots**”. I also declare that it has not been previously submitted for the award of any degree or diploma or other similar for any other examining body or university.

Name of Student : Aaron Tan Cheng Shiong Signature:

Date : 22 June 2017

Witness by

Supervisor : Dr. Khatijah Aisha bt. Yaacob Signature:

Date : 22 June 2017

ACKNOWLEDGEMENTS

First of all, I would like to express my utmost gratitude to my supervisor, Dr. Khatijah Aisha bt. Yaacob for patiently guiding and supporting me throughout the completion of the Final Year Project. This project would not be a success without her professional advices and guidance. With her years of experience as a lecturer and researcher, she had imparted the essential experimental skills, techniques and knowledge to me in order for me to complete this project.

This project would not be carried out smoothly without the supports and helps given by the technical staffs of School of Materials and Mineral Resources Engineering. Therefore, I would like to express my gratitude to Mr. Kemuridan, Mr. Abdul Rashid, Mdm. Hasnah, Mdm. Haslina, Mr. Mohd Azam, Mr. Mohd Faizal, Mr. Mohamad Zaini, Mr. Mohd Farid, Mr. Muhammad Khairi, Mr. Mohammad Azrul and Mr. Zulkurnain for their supports and helps throughout the completion of Final Year Project.

Next, I would also like to thank program chairman of Materials Engineering, Assoc. Prof. Dr. Nurulakmal Bt. Mohd. Sharif for facilitating the process of implementing the Final Year Project. I would also like to thank Prof. Dr. Ir. Srimala A/P Sreekantan, Dr. Norlia bt. Baharun and Assoc. Prof. Dr. Zainovia Bt. Lockman for spending their precious time in delivering important briefings.

I would also like to express my gratitude to my coursemates, friends and family for the loves and supports given to me throughout the completion of the project. Last but not least, special thanks to my beloved late father for blessing me all the time.

TABLE OF CONTENTS

Contents	Page
DECLARATION	ii
ACKNOWLEDGEMENTS	iii
TABLE OF CONTENTS	iv
LIST OF TABLES	vii
LIST OF FIGURES	viii
LIST OF ABBREVIATIONS	xi
LIST OF SYMBOLS	xiii
ABSTRAK	xv
ABSTRACT	xvi
CHAPTER 1 INTRODUCTION	1
1.1 Research Background	1
1.1.1 Overview on Nanomaterial	1
1.1.2 Overview on Quantum Dots (QD)	2
1.2 Problem Statement	3
1.3 Objectives	4
1.4 Scope of Research Work	4
CHAPTER 2 LITERATURE REVIEW	6
2.1 Introduction	6
2.1.1 Nanomaterials/Quantum Dots (QD)	6
2.1.2 Quantum Confinement	7
2.2 Quantum Dots (QD)	8
2.3 Cadmium-Based Quantum Dots (Cd-Based QD)	11

2.4	Zinc Selenide Quantum Dots (ZnSe QD)	13
2.5	Synthesis of ZnSe QD	15
2.6	Applications of ZnSe QD	17
CHAPTER 3 MATERIALS & METHODS		19
3.1	Introduction	21
3.2	Materials	21
3.2.1	Zinc acetate (CAS No: 5970-45-6)	21
3.2.2.	Selenium (CAS No: 7782-49-2)	22
3.2.3	Trioctylphosphine (TOP) (CAS No: 4731-53-7)	22
3.2.4	Trioctylphosphine oxide (TOPO) (CAS No: 78-50-2)	23
3.2.5	Hexadecylamine (HDA) (CAS No: 143-27-1)	24
3.2.6	Tetradecylphosphonic acid (TDPA) (CAS No: 4671-75-4)	24
3.2.7	Toluene (CAS No: 108-88-3)	25
3.2.8	Methanol (CAS No: 67-56-1)	26
3.3	Methodology	26
3.3.1	Synthesis of ZnSe QD in mixture of TOPO, HDA and TDPA coordinating solvent	27
3.3.2	Synthesis of ZnSe QD in HDA coordinating solvent	29
3.3.3	Studies of the effects of molar ratio (Zn:Se) and growth time on ZnSe QD	30
3.3.4	Stability study of the ZnSe QD	31
3.4	Characterization	32
3.4.1	Ultraviolet-Visible Spectroscopy (UV-Vis Spectroscopy)	32
3.4.2	Field Emission Scanning Electron Microscopy & Energy Dispersive	33

3.4.2(a) Sample Preparation for FESEM & EDX	34
3.4.3 Fourier Transformed Infrared (FTIR)	35
3.4.4 Zeta Potential Measurement	35
CHAPTER 4 RESULTS & DISCUSSION	37
4.1 Introduction	37
4.2 Synthesis of ZnSe QD in 2 different types of coordinating solvents	37
4.2.1 Synthesis of ZnSe QD in TOPO, HDA and TDPA coordinating solvent	38
4.2.1(a) UV-Vis Spectroscopy	39
4.2.2 Synthesis of ZnSe QD in HDA coordinating solvent	41
4.2.2 (a) UV-Vis Spectroscopy	42
4.3 Effects of molar ratio (Zn:Se) and growth time of the ZnSe QD	46
4.3.1 UV-Vis Spectroscopy	47
4.4 Synthesis of ZnSe QD using the optimum molar ratio (Zn:Se) and growth time	52
4.4.1 FESEM & EDX	53
4.4.2 FTIR	56
4.5 Stability study of ZnSe QD	57
4.5.1 UV-Vis Spectroscopy	59
4.5.2 Zeta Potential Measurement	60
CHAPTER 5 CONCLUSION AND RECOMMENDATIONS	63
5.1 Conclusion	63
5.2 Recommendations for future work	65
REFERENCES	66

LIST OF TABLES

		Page
Table 1.1	Description of each dimensional nanostructure (Pokropivny et al., 2007)	2
Table 3.1	Properties of zinc acetate	21
Table 3.2	Properties of selenium	22
Table 3.3	Properties of TOP	23
Table 3.4	Properties of TOPO	23
Table 3.5	Properties of HDA	24
Table 3.6	Properties of TDPA	25
Table 3.7	Properties of toluene	25
Table 3.8	Properties of methanol	26
Table 4.1	Combination of molar ratio (Zn:Se) and growth time	47

LIST OF FIGURES

	Page
Figure 2.1	7
Classification of nanomaterials: (a) three-dimensional (3D) structures, (b) two-dimensional (2D) structure, (c) one-dimensional (1D) structure and (d) zero-dimensional structures (Pokropivny et al., 2007)	
Figure 2.2	10
Schematic diagram showing band gaps for nanoparticles and bulk materials (Chukwuocha et al., 2012)	
Figure 2.3	14
Models showing the difference between (a) zinc-blende and (b) wurtzite crystal structures (Zhang et al., 2016).	
Figure 2.4	17
Oleic acid structure (Ferreira et al., 2015)	
Figure 3.1	20
General overview of the project	
Figure 3.2	28
Set-up of the experiment	
Figure 3.3	28
Close-up view at the three neck flask	
Figure 3.4	34
Electron trajectory simulation of an electron beam interaction with sample (Leng, 2009)	
Figure 4.1	39
ZnSe QD synthesized in TOPO, HDA and TDPA coordinating solvent	
Figure 4.2	40
UV-Vis absorbance spectra for ZnSe QD synthesized in TOPO, HDA and TDPA coordinating solvent with different growth time	

Figure 4.3	ZnSe QD synthesized in HDA coordinating agent	42
Figure 4.4	UV-Vis absorbance spectra for ZnSe QD synthesized in HDA coordinating solvent with different growth time	43
Figure 4.5	UV-Vis absorbance spectra for ZnSe QD synthesized in HDA using molar ratio (Zn:Se) of 1:1 at different growth time	48
Figure 4.6	UV-Vis absorbance spectra for ZnSe QD synthesized in HDA using molar ratio (Zn:Se) of 1:2 at different growth time	48
Figure 4.7	UV-Vis absorbance spectra for ZnSe QD synthesized in HDA using molar ratio (Zn:Se) of 1:3 at different growth time	49
Figure 4.8	UV-Vis absorbance spectra for ZnSe QD synthesized in HDA using molar ratio (Zn:Se) of 2:1 at different growth time	49
Figure 4.9	(a) SEM image of ZnSe QD synthesized in HDA using molar ratio (Zn:Se) of 1:2 with growth time of 15 minutes. (b) Diameter distribution of ZnSe QD based on SEM image in (a) calculated using ImageJ software	54
Figure 4.10	EDX elemental analysis of ZnSe QD synthesized in HDA using molar ratio (Zn:Se) of 1:2 with growth time of 15 minutes	54
Figure 4.11	Figure 4.11: (a) FTIR spectrum of HDA, (b) FTIR spectrum of ZnSe QD	57
Figure 4.12	(a) ZnSe QD at initial. (b) ZnSe QD at 4th week	58
Figure 4.13	UV-Vis absorbance spectra of ZnSe QD over period of time	59

LIST OF ABBREVIATIONS

0D	Zero-Dimensional
1D	One-Dimensional
2D	Two-Dimensional
3D	Three-Dimensional
EDX	Energy Dispersive X-Ray
FESEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transform Infrared Spectroscopy
HDA	Hexadecylamine
TDPA	Tetradecylphosphonic Acid
TOP	Trioctylphosphine
TOPO	Trioctylphosphine Oxide
TOPSe	Selenium Precursor in Trioctylphosphine
TOPZn	Zinc Presuresor in Trioctylphosphine
UV-Vis Spectroscopy	Ultraviolet-Visible Spectroscopy
ZnSe QD	Zinc Selenide Quantum Dots
CdTe	Cadmium Telluride
CdSe	Cadmium Selenide
CdS	Cadmium Sulfide

ZnS	Zinc Sulfide
ZnTe	Zinc Telluride
PbSe	Lead Selenide
PbS	Lead Sulfide
PbTe	Lead Telluride
InP	Indium Phosphide
InAs	Indium Arsenide
CuInS ₂	Copper Indium Sulfide
AgInS ₂	Silver Indium Sulfide
Si	Silicon
Ge	Germanium
Eu	Europium

LIST OF SYMBOLS

a_B	Exciton Bohr Radius
\hbar^2	Reduced Planck Constant
ε	Dielectric Constant
m_e	Effective Mass of an Electron
m_h	Effective Mass of a Hole
<	Less than
g	Gram
ml	Millilitre
°C	Degree Celsius
%	Percentage
At%	Atomic Percent
Wt%	Weight Percent
E	Band Gap Energy
ΔE_g	Difference between band gaps of nanoparticles and bulk
r	Radius of the quantum dots
h	Planck Constant
c	Speed of Light

λ

Wavelength

SINTESIS TITIK KUANTUM KADMIUM-BEBAS

ABSTRAK

Disebabkan oleh keracunan titik kuantum berasaskan kadmium, penggantian dengan titik kuantum tanpa cadmium harus diberi tumpuan. Dalam projek ini, sintesis titik kuantum zink selenide (ZnSe QD) akan dilakukan dengan kaedah suntikan panas. Berdasarkan penyelidikan hari ini, diethylzink digunakan sebagai pelopor. Walau bagaimanapun, diethylzink mempunyai isu keselamatan di mana ia bertindak ganas dengan air and mudah menyala jika terdedah dengan udara. Oleh itu, bahan baru (asetat zink) telah dicadangkan dalam projek ini. Pelopor-pelopor telah disediakan dengan melarutkan asetat zink dan selenium di dalam *trioctylphosphine* (TOP). Pelopor-pelopor ini telah disuntikkan ke dalam dua jenis pelarut penyelarar, iaitu campuran oksida *trioctylphosphine* (TOPO), *hexadecylamina* (HDA) dan asid *tetradecylphosphonik* (TDPA), dan hanya *hexadecylamina* (HDA) untuk pertumbuhan titik kuantum zink selenide. Sintesis ZnSe QD dalam pelarut penyelarar HDA didapati berjaya. Nisbah molar (Zn:Se) dan masa pertumbuhan telah diubah untuk parameter optimum. Parameter optimum untuk mensintesis ZnSe QD adalah menggunakan nisbah molar (Zn:Se) 1:2 dengan 15 minit masa pertumbuhan. Daripada spektrum penyerapan UV-Vis, jejariya didapati 3.61 nm, dikira dengan menggunakan anggaran jisim efektif. Jejari ini lebih kecil daripada exciton pukal Bohr ZnSe (5.7 nm). Kajian kestabilan ZnSe QD sepanjang sebulan telah dijalankan. Puncak spectrum kekal di 431nm sepanjang bulan itu, maksudnya, tidak ada berlakunya saiz perubahan. Menurut bacaan potensi zeta, mulamulanya titik kuantum zink selenide didapati bahawa ia menggumpal (tidak stabil) mulamulanya (11.5 mV) dan menjadi lebih stabil sepanjang tempoh masa (-21.1 mV). Kesimpulannya, kaedah sintesis ZnSe QD dengan zinc asetat dan HDA adalah berjaya.

SYNTHESIS OF CADMIUM-FREE QUANTUM DOTS

ABSTRACT

Due to the toxicity issues of cadmium-based quantum dots, there is a need to replace it with cadmium-free quantum dots. In this project, synthesis of zinc selenide quantum dots (ZnSe QD) using hot injection method will be studied. In today's researches, diethylzinc is used as the zinc precursor. However, diethylzinc possess safety issues in which it reacts violently with water and easily ignites upon contact with air. Therefore, a new material (zinc acetate) was proposed in this project. The precursors were prepared by dissolving zinc acetate and selenium into trioctylphosphine (TOP). They were then injected into two different types of coordinating solvents, that were mixture of trioctylphosphine oxide (TOPO), hexadecylamine (HDA) and tetradecylphosphonic acid (TDPA), and hexadecylamine (HDA) only. Synthesis of ZnSe QD in HDA coordinating solvent was found to be successful. Growth time and molar ratio (Zn:Se) were manipulated to determine the optimum parameters. The optimum parameters to synthesize ZnSe QD were at molar ratio (Zn:Se) of 1:2 and growth time of 15 minutes. Based on the UV-Vis absorbance spectra, the radius of ZnSe QD was calculated by using effective mass approximation and was found to be 3.61 nm in which, it is smaller than the bulk exciton Bohr radius of ZnSe (5.7 nm). Stability study on ZnSe QD showed that the ZnSe QD was stable and did not agglomerate much throughout one month period. The UV-Vis absorption spectra remained at 431 nm throughout the month, indicating that there were no changes in the particle size. Based on zeta potential measurement, ZnSe QD were found to agglomerate (unstable) at first (11.5 mV) and became stable over period of time (-21.1 mV). In conclusion, synthesis of ZnSe QD using zinc acetate as Zn precursor with HDA coordinating solvent was successful.

CHAPTER 1

INTRODUCTION

1.1 Research Background

1.1.1 Overview on Nanomaterial

Nanomaterial is a material where some controllable relevant dimension is in the order of 100 nm or less. It can also be characterized by at least one dimension in the nanometer range. The processing, structure and properties of materials with grain size in the tens to several hundreds of nanometer range are research areas of considerable interest over the past years. On nanoscale, some physical and chemical properties can differ significantly from those of the bulk structured materials of the same composition. For nanomaterial, the number of surface atoms or ions becomes a significant fraction of the total number of atoms or ions and the surface energy also plays a significant role in the thermal stability. High surface-to-volume ratio of nanomaterial often has a prominent effect on material's performance (Pokropivny et al., 2007).

The reduction in the dimension of nanomaterial leads to confinement of particles in a particular crystallographic direction within a structure. This leads to changes in physical properties of the system in that direction. Hence, nanomaterial can be classified by number of dimensions which lie within the nanometer range, i.e. zero-dimensional nanostructure (0D), one-dimensional nanostructure (1D), two-dimensional nanostructure (2D) and three-dimensional nanostructure (3D) (Pokropivny et al., 2007). The description of each dimensional nanostructure is listed in Table 1.1.

Table 1.1: Description of each dimensional nanostructure (Pokropivny et al., 2007).

Dimensions	Description	Examples
Zero-dimensional nanostructure (0D)	The nanostructure has all dimensions in the nanometer range.	Nanoparticles, quantum dots, nanodots
One-dimensional nanostructure (1D)	One dimension of the nanostructure is outside of the nanometer range.	Nanowires, nanorods, nanotubes, nanofibers
Two-dimensional nanostructure (2D)	Two dimensions of the nanostructure are outside of the nanometer range.	Nanolayers, nanodisks, thin film
Three-dimensional nanostructure (3D)	Three dimensions of the nanostructure are outside of the nanometer range.	Bulk

1.1.2 Overview on Quantum Dots (QD)

Quantum dots (QD) are semiconductor nanocrystals (typically 2-10 nm in diameter) that exhibit quantum mechanical properties possess outstanding optical properties which include bright luminescence, a broad excitation profile, narrow emission peaks and remarkable photostability (Landry et al., 2014; Xu et al., 2016). QD possess size-dependent optical properties due to quantum confinement effect. The quantum confinement effect is contributed by the fact that the physical dimensions of QD nanocrystals are smaller than the exciton Bohr radius (Altıntas et al., 2016). Therefore, the photoluminescence (PL) of the QD can be finely tuned by simply controlling the particle size. The variable PL emitted from QD of different sizes can be simultaneously excited with a single excitation light source (Wang et al., 2009). Due to the outstanding optical properties and the uniqueness of QD, QD have attracted a lot of attention in the past few decades, especially in biological and medical imaging applications as they

possess an enhanced photoluminescence stability as compared to typical dyes (Mirnajafizadeh et al., 2016).

1.2 Problem Statement

The combination of TOP from the precursors (TOPSe and TOPZn) and TOPO from the coordinating solvents (TOPO, HDA and TDPA) that were used to synthesis ZnSe QD has been proven to be unsuccessful by some researchers (Hines and Guyot-Sionnest, 1998; Song and Lee, 2001; Cozzoli et al., 2005). The researchers explained that this was due to TOPO binding too strong and TOP binding too weak to Zn which decreases the QD surface passivation and monodispersity of QD nanocrystals. It can also be explained that the dispersed nanocrystals are too small and cannot be isolated by standard solvent/nonsolvent precipitation techniques (Hines and Guyot-Sionnest, 1998; Shu et al., 2013; Green, 2014).

There has not been a study that uses zinc acetate to produce Zn precursor to synthesize ZnSe QD. All of these researches on synthesis of ZnSe QD were done using diethylzinc (Et_2Zn) as the Zn precursor (Hines and Guyot-Sionnest, 1998; Song and Lee, 2001; Cozzoli et al., 2005). Therefore, in order to synthesize ZnSe QD using zinc acetate as the Zn precursor, several parameters were manipulated and studied. Hence, studies on effects of coordinating solvent, growth time and molar ratio of Zn precursor to Se precursor and stability of ZnSe QD that uses zinc acetate as Zn precursor were proposed in this project.

1.3 Objectives

There were three objectives as follows:

- i) To synthesize ZnSe QD using hot injection method which uses zinc acetate as the Zn precursor and selenium as the Se precursor.
- ii) To compare ZnSe QD synthesized in 2 different types of coordinating solvents (HDA only and combination of TOPO, HDA and TDPA).
- iii) To study the effects of growth time, molar ratio (Zn:Se) and stability of the ZnSe QD.

1.4 Scope of Research Work

In this project, synthesis of ZnSe QD using hot injection method was studied. Zn precursor and Se precursor were prepared and dissolved in TOP in the glovebox. The coordinating solvents (HDA only and combination of TOPO, HDA and TDPA) were dried, degassed under vacuum and refluxed in fume cupboard. This set-up was connected to the Schlenk line. After period of time and at certain temperature, the precursors were injected into the coordinating solvent via syringe. Once the desired nanoparticle size was achieved, the reaction mixture was quenched in toluene at room temperature.

The synthesized ZnSe QD was characterized using Ultraviolet-Visible Spectroscopy (UV-Vis Spectrometer), Zeta Potential Measurement, X-Ray Diffraction (XRD), Field Emission Scanning Electron Microscope & Energy Dispersive X-Ray Spectroscopy (FESEM & EDX), Atomic Force Microscope (AFM) and Fourier Transformed Infrared (FTIR).

Several parameters were changed in the synthesis stage. This includes changing of coordinating solvent, growth time and molar ratio of Zn to Se. The effects of these changes were measured and investigated using UV-Vis Spectrometer. The stability of the synthesized ZnSe QD was also studied using UV-Vis Spectrometer and Zeta Potential Measurement.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

2.1.1 Nanomaterials/Quantum Dots

Semiconductor nanomaterials are widely used in various nanoscale electronic and optoelectronic devices such as nanowire lasers, single-electron transistors and single-molecule sensors (Deng et al., 2010). Nanomaterials always show behavior which is intermediate between the bulk materials and that of an atomic or molecular system. The properties of a material in nanoscale would be totally different from its own bulk materials. This is attributed to the nature of nanomaterials where the number of atoms or ions on its surface is a significant fraction of the total number of atom or ions and hence, this significantly influences the properties of a material in nanoscale. Nanomaterials are capable to possess properties which do not belong to the realm of their bulk counterparts (Parak et al., 2010). In this project, quantum dots (QD) are the nanomaterials that are going to be discussed. The properties of the QD can be explained by the laws of quantum confinement.

As discussed earlier, nanomaterials can be classified into three-dimensional (3D) structures, two-dimensional (2D) structure, one-dimensional (1D) structure and zero-dimensional structures. The schematic diagrams of these classification can be shown in Figure 2.1.

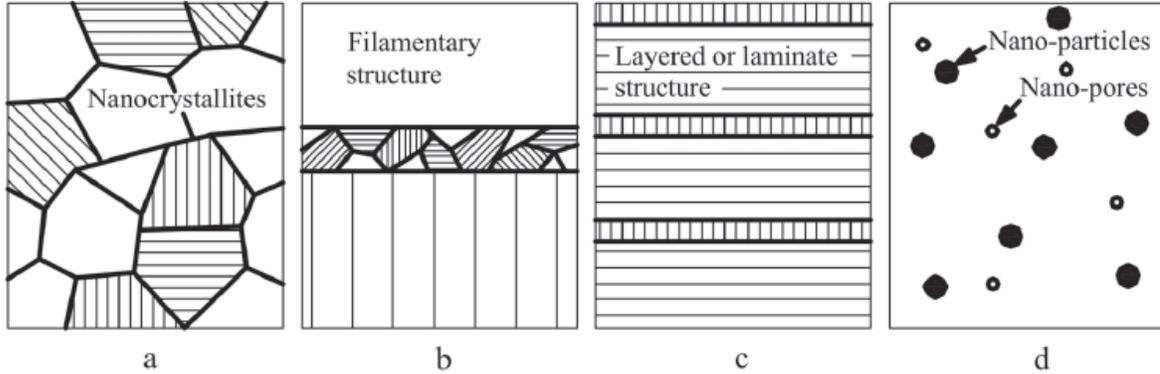


Figure 2.1: Classification of nanomaterials: (a) three-dimensional (3D) structures, (b) two-dimensional (2D) structure, (c) one-dimensional (1D) structure and (d) zero-dimensional structures (Pokropivny et al., 2007).

2.1.2 Quantum Confinement

Quantum mechanics is introduced by de Broglie and the fundamental aspect of this quantum mechanics is the particle-wave duality. According to quantum mechanics which states that, any particle can be associated with a matter wave whose wavelength is inversely proportional to the particle's linear momentum. This quantum confinement effect basically describes the phenomenon of semiconductor nanomaterials result from electrons and holes being squeezed into a dimension that approaches a critical quantum measurement (Deng et al., 2010). As the size of a physical system becomes comparable to the wavelength of the particles, quantum mechanics can be used to explain the behavior of the particles. Quantum mechanics is not used to explain the behavior of the particles in a bulk material. This is because the size of the physical system is much larger than the wavelength associated with the bulk material and therefore, it can be explained by using principles of classical mechanics (Parak et al., 2010).

In a bulk semiconductor, the carriers (electrons and holes) are free to move throughout the crystal when energy is provided. An electron-hole pair is typically bound within a characteristic length, known as exciton Bohr radius (Deng et al., 2010). An exciton is the bound state of an electron and an imaginary particle called an electron hole in the semiconductor and it is a Coulomb-correlated electron-hole pair. The motion of the carriers can be explained by linear combination of plane waves of the carriers. As the size of the semiconductor is reduced and becomes comparable to the wavelength of the carriers, the carriers are said to be confined in the structure and behave as a particle in a potential box. This is known as quantum confined (Parak et al., 2010). This quantum confinement effect influences the electronic structure of a semiconductor.

2.2 Quantum Dots (QD)

Quantum dots (QD) have attracted interest over the years due to the differences of their properties as compared to the bulk semiconductors and can be tuned by controlling the particle composition, size and surface. Apart from that, their surface chemistry can be readily manipulated which allows for easy solution processing and surface functionalization. QD possess quantum confinement effect in which the physical dimensions of the QD nanocrystals, in all three dimensions, are smaller than the exciton Bohr radius. This allows QD semiconductor to possess size-dependent optical properties (Altintas et al., 2016; Xu et al., 2016).

As discussed in Chapter 1, QD are semiconductor nanocrystals where they are typically 2-10 nm in diameter and exhibit mechanical properties that possess outstanding

optical properties which include bright luminescence, a broad excitation profile, narrow emission peaks and remarkable photostability (Landry et al., 2014; Xu et al., 2016). Due to their outstanding properties, QD had turned into promising materials for various applications such as lasers, light-emitting diodes, photodetectors, photovoltaic materials and biological imaging (de Mello Donegá et al., 2003; Eilers et al., 2014).

The exciton Bohr radius (a_B) is the average separation of the excited electron and hole that make up an exciton in a bulk semiconductor (Xu et al., 2016). In analogy to the Bohr model of the hydrogen atom, it can be explained in the Equation 2.1 as follows:

$$a_B = \frac{\hbar^2 \varepsilon}{e^2} \left(\frac{1}{m_e} + \frac{1}{m_h} \right) \quad (\text{Equation 2.1})$$

where \hbar is the reduced Planck constant, ε is the dielectric constant of the semiconductor, e is the charge of an electron, m_e is the effective mass of an electron and m_h is the effective mass of a hole.

Both dielectric constant and effective masses of the electron and hole are material-dependent and therefore, the exciton Bohr radii for different semiconductor vary substantially (e.g. 4.1 nm for CuInS₂, 2.3 nm for ZnO, 46 nm for PbSe and 18 nm for PbS). As the radius of a semiconductor nanocrystal approaches the exciton Bohr radius, the movement of electron and hole are confined. Therefore, the electronic structure and optical properties of QD differ from their bulk due to quantum confinement effect (Xu et al., 2016).

In a semiconductor, the energy bands for free electrons and holes are separated by energy gap, E_g . In a bulk semiconductor, the states are quasi-continuous and any point in the energy bands represents an individual state (Parak et al., 2010). In QD semiconductor, this

quasi-continuous states (energy bands) develop into discrete levels in which, it corresponds to hybridization of a finite number of atomic orbitals. The energy gap, E_g between the conduction band and valence band in QD increases as the QD size decreases. The increase of E_g is associated with recombination/exciton generation process where this process produces a blue shift of both absorbance and photoluminescence (PL) spectra with decreasing size of the QD (Xu et al., 2016).

Based on the diagram in Figure 2.2, it can be clearly seen that the ΔE_{nano} (band gap energy for nanoparticles) is greater than ΔE_{bulk} (band gap energy for bulk materials). This is because of the increase of confinement energy in the nanoparticles (quantum dots). This confinement energy can affect the optical and electronic properties of the semiconductor materials (Deng et al., 2010).

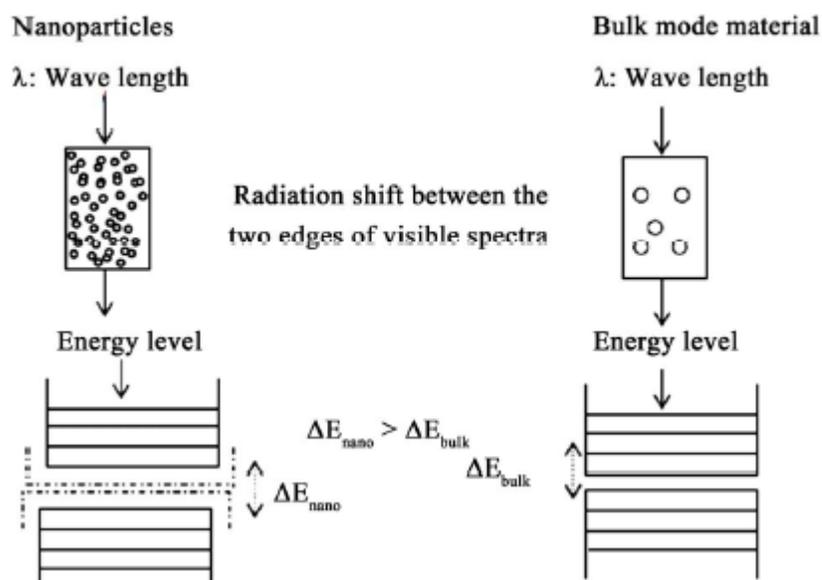


Figure 2.2: Schematic diagram showing band gaps for nanoparticles and bulk materials (Chukwuocha et al., 2012).

In quantum confinement regime, the growth of QD can be generally explained with progressively smaller particles sizes of nucleation, size-focusing and Ostwald ripening. Nucleation takes place within milliseconds to seconds, right after the monomer concentrations reach supersaturation, which forms small nuclei. In the size-focusing stage, QD grow from the nuclei at the expense of remaining monomers. The faster the growth rate of the small particles, the narrow the size distribution. Lastly, as the monomers depleted, Ostwald ripening stage begins, in which the larger particles grow at the expense of the smaller particles (Jiang and Muscat, 2012).

Typically, a single QD contains hundreds to thousands of atoms of group II-VI elements (e.g. CdTe, CdSe, CdS, ZnS, ZnSe or ZnTe), group IV-VI elements (e.g. PbSe, PbS or PbTe), group III-V elements (e.g. InP or InAs), group I-III-VI₂ elements (e.g. CuInS₂ or AgInS₂) or group IV elements (e.g. Si or Ge) (Xu et al., 2016).

2.3 Cadmium-Based Quantum Dots (Cd-Based QD)

Cadmium-based quantum dots (Cd-based QD) are widely employed in biological, medical and solar cell applications due to their ease of synthesis, readily available precursors and straightforward synthesis method. Some of the examples of Cd-based QD that are used in these applications include CdSe, CdS, CdTe and CdTe/CdSe core/shell QD. Especially for biolabeling applications, this type of QD has received many interest due to their optical advantages over the commonly used organic fluorophores. Apart from their tunable optical properties, cadmium chalcogenide also has a low photodegradation rates (Andrade et al.,

2009; Xu et al., 2016). They can be synthesized by using readily available precursors and straightforward solution phase synthesis methods (Yaacob et al., 2013; Xu et al., 2016).

One of the examples of Cd-based QD is cadmium selenide (CdSe). CdSe QD can be regarded as the typical QD material due to its tunable emission across the visible range of the electromagnetic spectrum. This allows CdSe QD to be used in various applications, typically, in optoelectronic applications (Green, 2014). A research done by de Mello Donegá et al. (2003), stated the importance of reaction temperature and molar ratio of cadmium to selenium precursor. These parameters determine the size polydispersity, band-edge photoluminescence quantum yields and exciton lifetimes of colloidal CdSe nanocrystals (de Mello Donegá et al., 2003).

Another example of Cd-based QD is cadmium sulfide (CdS). It is one of the earliest materials to be discovered and studied due to its ease of preparation. As compared to CdSe QD, CdS QD shows a small change in the optical properties when prepared on the nano scale. This can be explained by the difference in Bohr radius of the exciton (CdSe, $\alpha_B = 32 \text{ \AA}$; CdS, $\alpha_B = 19 \text{ \AA}$). This implies that CdS particles have to be significantly smaller than CdSe to exhibit QD properties, which is size quantization effects. Therefore, CdS QD display a smaller shift in the band edge (Green, 2014).

However, Soenen et al. (2014) and Xu et al. (2016) had reported that Cd-based QD possess potential toxicity, especially detrimental to biological and medical applications. This is because Cd-based QD can degrade in a biological environment and potentially releasing highly cytotoxic Cd^{2+} ions. Cadmium is classified as heavy metals whereby it is harmful to human and many Cd-based QD for consumer-goods applications are banned in many regions of the world today (Soenen et al., 2014; Xu et al., 2016).

Regarding this toxicity issue of Cd-based QD, there is a need of seeking for materials to substitute cadmium ions. At present, there are two approaches to address these concerns. The first approach is to use biocompatible and long-lasting polymeric layers to encapsulate the Cd-based QD. This prevents Cd-based QD from breaking down in vivo. The second approach is to use Cd-free QD (Xu et al., 2016). In this project, the second approach will be studied.

2.4 Zinc Selenide Quantum Dots (ZnSe QD)

Zinc selenide (ZnSe) is one of the important II-VI semiconductor whereby it is one of the first semiconductors discovered and is one of the most important electronic and optoelectronic materials. It has various prominent applications in nonlinear optical devices, flat panel displays, light emitting diodes (LEDs), logic gates, transistors and so on. ZnSe nanostructures have gained a lot of interest recently due to the valuable and impactful potentials for both fundamental physical researches and applications in constructing nanoscale electronic and optoelectronic devices (Zhang et al., 2016).

As one of the binaryoctet semiconductors, ZnSe has two commonly available allotropes: cubic zinc-blende and hexagonal wurtzite structure. It can be illustrated in Figure 2.3. The differences lie in the relative handedness of the fourth interatomic bond and their dihedral conformations. Zinc-blende ZnSe structure consists of zinc coordinated in a tetrahedral and selenium atoms are stacked in the ABCABC pattern. As for wurtzite ZnSe structure, the same building blocks are stacked in the ABABAB pattern. The lattice parameters of zinc-blende ZnSe structure are $a = b = c = 5.68 \text{ \AA}$ whereas for wurtzite ZnSe

structure are $a = b = 3.98 \text{ \AA}$, $c = 6.53 \text{ \AA}$. Due to the relatively low difference in the total energy between the zinc-blende ZnSe structure and wurtzite ZnSe structure ($5.3 \text{ meV atom}^{-1}$), ZnSe can exhibit wurtzite-cubic zinc-blende polytypism. Cubic ZnSe has a bulk band gap of 2.7 eV (460 nm) at room temperature (Zhang et al., 2016).

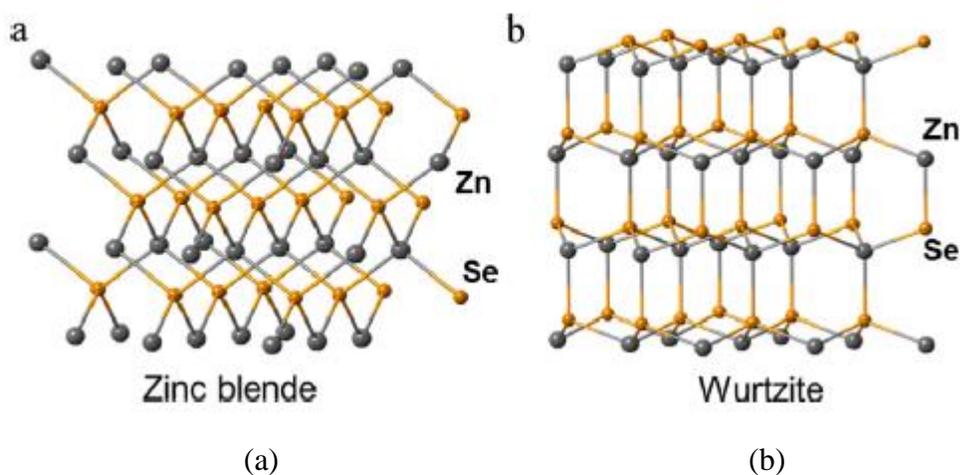


Figure 2.3: Models showing the difference between (a) zinc-blende and (b) wurtzite crystal structures (Zhang et al., 2016).

With the development of cellular molecule image based on QD, low cytotoxicity QD had gained much interest and attention. In this context, it refers to Cd-free QD since Cd-based QD possess cytotoxicity issues. There are many Cd-free QD available to substitute Cd-based QD. In this project, zinc selenide (ZnSe) was chosen to substitute Cd-based QD. As compared to CdSe QD and CdS QD, ZnSe QD exhibit blue-ultraviolet (UV) luminescence, high photoluminescence quantum yields and better stability. Practically, cadmium-based QD like CdSe QD and CdS QD are impossible to obtain UV range, for which the toxicity of cadmium imposes an added disadvantage (Reiss et al., 2004; Lan et al., 2007).

ZnSe QD possess great band gaps ranging from 2.8-3.4 eV (bulk ZnSe having band gap of 2.7 eV). Due to this properties, ZnSe QD have attracted attention as interesting materials over a region from UV to blue and became the choice of materials for fabrication of blue diode lasers and LED. This wide band gaps properties also makes ZnSe QD ideal for inorganic passivation of variety of QD to form core-shell QD, such as CdSe-ZnSe and InAs-ZnSe QD (Lan et al., 2007).

2.5 Synthesis of ZnSe QD

Several methods of synthesizing ZnSe QD had been reported for the past decades. The common synthesis method for CdSe QD, i.e. hot injection method, as reported by Yaacob et al. (2013), which uses trioctylphosphine (TOP) in the precursors of TOPCd and TOPSe, and trioctylphosphine oxide (TOPO) in the coordinating solvent, cannot be directly employed to synthesize ZnSe QD. It can be explained that the combination of TOP and TOPO was successful for the synthesis of CdSe QD, where TOP binds preferentially to Se and TOPO binds to Cd. However, this combination of TOP and TOPO was not successful for the synthesis of ZnSe QD. This can be explained as TOPO binding too strong to Se and TOP binding too weak to Zn (Hines and Guyot-Sionnest, 1998).

Hence, synthesis of ZnSe QD in hot coordinating solvent of hexadecylamine (HDA) was employed and studied (Hines and Guyot-Sionnest, 1998; Song and Lee, 2001). In this method, the precursors were prepared by dissolving diethylzinc (Et_2Zn) and selenium powder (Se) into TOP to produce TOPZn and TOPSe precursors. The coordinating solvent was prepared by degassing HDA under vacuum and heated under N_2 flow. After certain

temperature was reached, the precursors (TOPZn and TOPSe) were then injected into the coordinating solvent for the growth of QD. The growth of QD could be indicated by the change of colour of the solution in which, the solution turns yellow. The synthesized QD were then characterized by using Ultraviolet-Visible Spectroscopy (UV-Vis Spectrometer), X-Ray Diffraction (XRD), and Transmission Electron Microscopy (TEM) (Hines and Guyot-Sionnest, 1998; Song and Lee, 2001; Cozzoli et al., 2005). By using HDA as the coordinating solvent, the emission from ZnSe QD was found to be band edge with quantum yields of 20-50% due to the high growth temperatures and efficient capping of amine and phosphine (Hines and Guyot-Sionnest, 1998). The size of ZnSe QD synthesized from this method is in the range of 3-5 nm which could be obtained within the reaction time of 4-5 hours (Cozzoli et al., 2005). ZnSe QD synthesized by this method were well passivated by the HDA.

Another synthesis method, i.e. one-pot synthesis, as reported by Srinivas Rao et al. (2007) and Syed and Chawla (2015), was also employed to synthesize ZnSe QD. It was claimed that this method is much simpler, involves lower reaction temperature, less expensive reagents and it is a non-toxic process which uses oleic acid, a naturally occurring hydrocarbon instead of toxic external reducing agents like phosphine (Srinivas Rao et al., 2007; Syed and Chawla, 2015). In this method, the precursors were prepared by dissolving zinc acetate and selenium powder in oleic acid and stirred. The mixture was then evacuated, undergone nitrogen bubbling and heated at certain temperature in an inert atmosphere. Same goes to the previous method, the growth of QD could be indicated by the change of colour of the solution in which, the solution turns yellow (Syed and Chawla, 2015). Based on the ZnSe QD synthesized from this method, the size of ZnSe QD is in between 3-5 nm (Srinivas

Rao et al., 2007; Syed and Chawla, 2015). The ZnSe QD synthesized from this method is monodisperse and monophasic due to the high thermal stability of oleic acid that allows for solvation of reagents. Besides that, oleic acid has long carbon chain and possesses a central double bond (Figure 2.4) in which, this provides optimal capping of the small formed particles from external influence (Beri et al., 2010; Syed and Chawla, 2015).

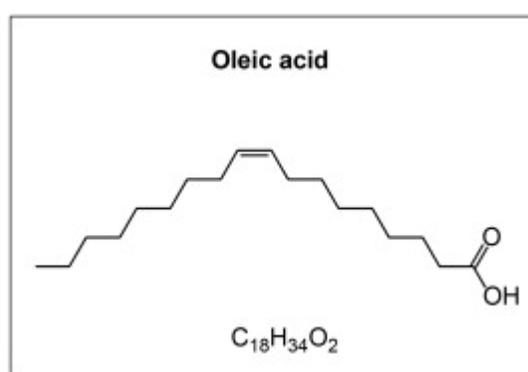


Figure 2.4: Oleic acid structure (Ferreira et al., 2015).

2.6 Applications of ZnSe QD

Wide band gap nanostructures such as nanodots (quantum dots), nanorods and nanowires are promising for the achievement of low defects with potential applications in short wavelength optoelectronic device applications. As one of the important wide bandgap semiconductor materials, ZnSe has wide potential applications in the UV spectrum of blue (460 nm) with wide bandgap energy of 2.7 eV. As discussed earlier, ZnSe QD has inferior properties as compared to Cd-based QD, therefore, in order to improve the ZnSe QD, doping has been done to provide powerful and effective way to change the intrinsic properties of

ZnSe QD by creating new electronic states that facilitate the transition of electrons from one level for a more energetic and less energetic level (Zhang et al., 2016).

ZnSe QD is an important member of II-VI semiconductor QD as it has been used in wide applications. It has been used in optoelectronics such as diode laser structures, green-blue light emission and solar cells. Apart from that, ZnSe QD has also been used as a material for windows, lenses, output couplers, beam expanders and optically controlled switching. These applications are possible due to its low absorptivity at infrared wavelength, visible transmission and giant photoresistivity (Beri et al., 2010).

Solid-state lighting devices such as light-emitting diodes (LEDs) are a promising alternative to incandescent bulbs and fluorescent lamps. This is because they offer higher efficiency, longer lifetime, lower power consumption and a faster response time. ZnSe QD are usually doped to improve the intrinsic properties and used for this application. One of the researches presented a colour-tunable emitter comprising of Eu complex-capped ZnSe organic-inorganic hybrid QD and were used in LEDs application (Kwon et al., 2011). In that research, the ZnSe QD were synthesized by hot injection method with the addition of Eu precursor. Apart from that, white-light emission also receive huge interest, especially for the purpose of generation of photometrically high quality white light while maintaining the energy efficiency for solid state lighting. Single component white-light emitters with an improved colour stability. This reduces the complexity of the device. For this single component white light emitters, research has been done showing that Mn-doped ZnSe QD can be a potential candidate to generate phosphors and avoid the issues of toxicity and self-absorption (Sharma et al., 2014).

CHAPTER 3

MATERIALS & METHODS

3.1 Introduction

In this chapter, the details and description of materials, equipment, methodology and characterization techniques used to synthesize ZnSe QD will be discussed. The material used and the methodology employed were different from current researches.

In this project, the zinc acetate was used to produce Zn precursor instead of diethylzinc (Et_2Zn), which was used in current researches (Hines and Guyot-Sionnest, 1998; Shu et al., 2013; Green, 2014). Since the material used in this project was different from current researches, therefore, the methodology would be slightly different from current researches, typically, in terms of the concentration of the precursors and growth time. The general overview of the project can be illustrated in Figure 3.1.

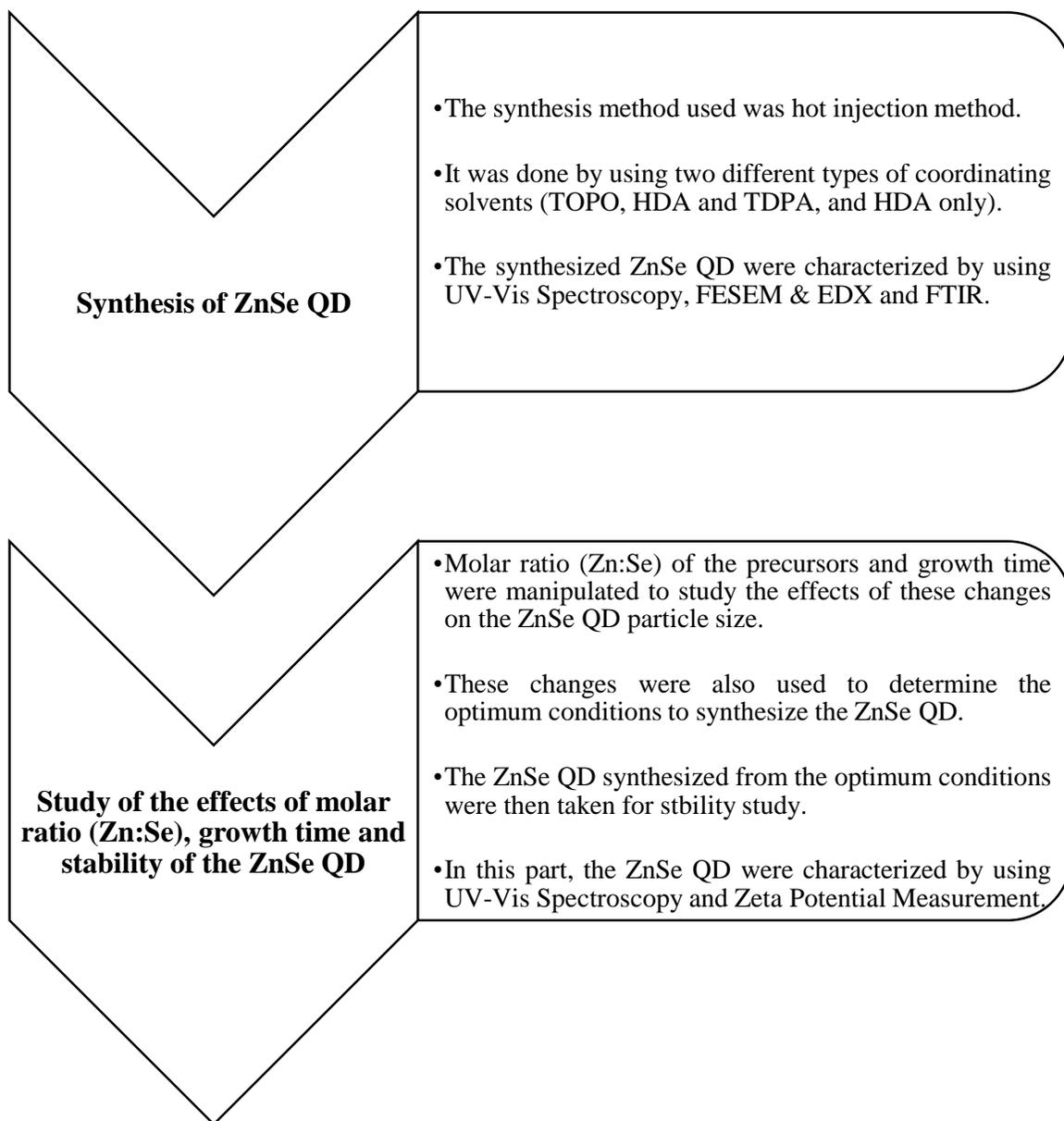


Figure 3.1: General overview of the project.

3.2 Materials

In this project, the materials were used without further purification to prevent the materials from any contamination due to the purification process. The materials used were as follows:

3.2.1 Zinc acetate (CAS No: 5970-45-6)

Zinc acetate was used to produce Zn precursor instead of diethylzinc (Et_2Zn). This is because based on the Materials Safety Data Sheets (MSDS), diethylzinc (Et_2Zn) possesses higher hazards due to its nature of easily flammable. Besides that, one of the most common QD, i.e. CdSe QD, were typically synthesized using cadmium acetate as the Cd precursor. Since both cadmium and zinc are from the same group in periodic table (Group 12), therefore, it was believed that zinc acetate would behave like cadmium acetate. The properties of zinc acetate were listed in Table 3.1.

Table 3.1: Properties of zinc acetate

Molecular Formula	$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$
Molecular Weight	219.51 g/mol
Melting Point	83 – 85 °C
Form	Solid Powder
Supplier	Merck

3.2.2 Selenium (CAS No: 7782-49-2)

Selenium was used to produce Se precursor. Typically, based on the molar ratio (Zn:Se), Se rich is preferred. This is because selenium enriched surface attracts Zn^{2+} ions more effectively (Andrade et al., 2009). The properties of selenium were listed in Table 3.2.

Table 3.2: Properties of selenium

Molecular Formula	Se
Molecular Weight	78.96 g/mol
Melting Point	220.8 °C
Form	Solid Powder
Supplier	Sigma-Aldrich

3.2.3 Trioctylphosphine (TOP) (CAS No: 4731-53-7)

Trioctylphosphine (TOP) was used as solubilizing agent for Zn and Se precursors (Reiss, 2007). Once the Zn and Se precursors were completely dissolved in TOP, they were then ready to be injected into the reaction solution for the growth of ZnSe QD. The properties of TOP were listed in Table 3.3.

Table 3.3: Properties of TOP

Molecular Formula	$(\text{CH}_3(\text{CH}_2)_7)_3\text{P}$
Molecular Weight	370.64 g/mol
Boiling Point	284 – 291 °C
Form	Liquid
Supplier	Sigma-Aldrich

3.2.4 Trioctylphosphine oxide (TOPO) (CAS No: 78-50-2)

Trioctylphosphine oxide (TOPO) was used as coordinating solvent and stabilizing ligand for the growth of ZnSe QD (Reiss, 2007). However, it is typically used in synthesizing CdSe because the combination of TOPO coordinating solvent and TOP solubilizing agent from the precursors worked well in passivating the surface of the CdSe QD. In this project, TOPO will be tested out to synthesize ZnSe QD. The properties of TOPO were listed in Table 3.4.

Table 3.4: Properties of TOPO

Molecular Formula	$(\text{CH}_3(\text{CH}_2)_7)_3\text{PO}$
Molecular Weight	386.63 g/mol
Melting Point	50 – 52 °C
Form	Solid Powder
Supplier	Sigma-Aldrich

3.2.5 Hexadecylamine (HDA) (CAS No: 143-27-1)

Hexadecylamine (HDA) was an amine that passivate the surface of the QD. HDA is widely used in synthesis of ZnSe QD due to its great passivation ability and promote the growth of ZnSe QD (Reiss, 2007). The properties of HDA were listed in Table 3.5.

Table 3.5: Properties of HDA

Molecular Formula	CH ₃ (CH ₂) ₁₅ NH ₂
Molecular Weight	241.46 g/mol
Melting Point	43 – 45 °C
Form	Solid Powder
Supplier	Sigma-Aldrich

3.2.6 Tetradecylphosphonic acid (TDPA) (CAS No: 4671-75-4)

Tetradecylphosphonic acid (TDPA) was used together with trioctylphosphine oxide (TOPO) and hexadecylamine (HDA) as coordinating solvent and stabilizing ligand for the growth of ZnSe QD (Reiss, 2007). The properties of TDPA were listed in Table 3.6.