



UNIVERSITI PUTRA MALAYSIA

**SYNTHESIS AND OPTICAL PROPERTIES OF PbS/MnS CORE SHELL
QUANTUM DOTS**

MUHAMMAD SAFWAN BIN ZAINI

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By

MUHAMMAD SAFWAN BIN ZAINI

**Thesis Submitted to the School of Graduate Studies, Universiti Putra
Malaysia, in Fulfilment of the Requirements for the Degree of Master of
Science**

September 2019

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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Master of Science

SYNTHESIS AND OPTICAL PROPERTIES OF PbS/MnS CORE SHELL QUANTUM DOTS

By

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September 2019

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Faculty : Science

Optical characteristics of colloidal quantum dots (QDs) are influenced by the dot size, composition and the capping molecules. This thesis focuses on the study of PbS/MnS core shell (CS) QDs where PbS serves as the core and MnS is the shell. The colloidal chemistry method was used to synthesise PbS QDs at room temperature. The growth of MnS shell by a simple ions substitution called cation exchange was successfully applied to fabricate the PbS/MnS core shell QDs in this research. This is a unique chemistry reaction which only can be occurred in chalcogenide material.

This research also focuses on structural and optical properties of the PbS QDs and PbS/MnS core shell QDs. The structural properties were characterised by using High Resolution Transmission Electron Microscopy (HRTEM) and Energy Dispersive X-ray (EDX). The HRTEM results show that the average size of the PbS QDs was 6.00 ± 1.00 nm with spherical in shape. For PbS/MnS core shell QDs, its average size was enlarged to 7.00 ± 0.50 nm and 7.40 ± 0.60 nm for PbS/MnS CS 0.3 and PbS/MnS CS 0.6, respectively. The size was increased due to the growth of MnS shell after the cation exchange. Besides that, the analysis of elemental composition via EDX has confirmed the presence of MnS composition. From the spectrum, an EDX peak associated with Mn was observed at 5.9 keV.

The optical properties and the behaviour of the charge carriers inside the PbS and PbS/MnS QDs were investigated by photoluminescence (PL) at different temperature (10-300 K), power excitation (10-200 mW) and exposure time (3-40 minutes). At room temperature, the PL peak energies of PbS/MnS core shell QDs were blue shifted upon the increasing shell thickness due to strong confinement effect induced by the shell.

Temperature dependent PL shows the effect on the PL peak energy, full width half maximum (FWHM) and PL intensity. In general, the PL peak energy and FWHM were monotonically increased as the temperature increased which related to the interaction of charge carriers with phonons. In contrast, the PL peak intensities were quenched as the temperature increased which associated with the excitation of carriers out of the QDs into non-radiative recombination centres. Photoenhancement phenomenon was studied by exposed the samples under illumination up to 40 minutes and we found that the PL intensity was increased over period of time due to the presence of oxygen. In power dependent PL, the integrated PL intensity (IPL) was increased with the increasing power density. From the graph of IPL as a function of power density, generally gradient of the graph was close to unity where the radiative recombination is dominant. The development of PbS/MnS core shell QDs would be useful in the future especially in the application of photovoltaic devices.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Master Sains

SINTESIS DAN SIFAT OPTIK TITIK KUANTUM TERAS DALAMAN LUARAN PbS/MnS

Oleh

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Sifat optik titik kuantum koloid dipengaruhi oleh saiz titik, komposisi dan molekul penutup. Tesis ini memberikan tumpuan kepada pembelajaran ke atas teras dalaman-luaran titik kuantum PbS/MnS di mana PbS bertindak sebagai teras dan MnS ialah petala. Kaedah kimia berkoloid telah digunakan sebagai teknik untuk sintesis titik kuantum PbS pada suhu bilik. Pertumbuhan petala MnS oleh penggantian ion mudah yang dipanggil pertukaran kation telah berjaya dilaksanakan untuk menghasilkan teras dalaman-luaran titik kuantum PbS/MnS di dalam penyelidikan ini. Ini adalah satu tindak balas kimia yang unik di mana ia hanya boleh dilakukan di dalam bahan kalkogen.

Penyelidikan ini juga memberikan tumpuan kepada sifat struktur dan sifat optik titik kuantum PbS dan juga titik kuantum teras dalaman-luaran PbS/MnS. Sifat struktur dicirikan menggunakan mikroskop elektron transmisi tinggi (HRTEM) dan serakan tenaga X-ray (EDX). Keputusan HRTEM menunjukkan bahawa saiz titik kuantum PbS ialah 6.00 ± 1.00 nm serta berbentuk sfera. Untuk titik kuantum teras dalaman-luaran PbS/MnS, purata saiznya membesar kepada 7.00 ± 0.50 nm dan 7.40 ± 0.60 nm masing-masing untuk PbS/MnS CS 0.3 dan PbS/MnS CS 0.6. Pembrebaran saiz titik kuantum itu disebabkan oleh pertumbuhan petala MnS selepas pertukaran kation. Selain itu, analisis komposisi bahan oleh EDX telah mengesahkan kehadiran komposisi MnS. Daripada spektrum, puncak EDX yang bersekutu dengan Mn telah jelas diperhatikan pada 5.9 keV.

Sifat optik dan kelakuan pembawa cas di dalam titik kuantum pula diasas menggunakan spektroskopi fotoluminesens (PL) pada suhu yang berbeza (10-300 K), kuasa pengujaan (10-200 mW), dan masa pendedahan (3-40 minit). Pada suhu bilik, kuasa puncak PL titik kuantum teras dalaman-luaran PbS/MnS

terjadi anjakan biru setelah peningkatan ketebalan petala yang disebabkan kesan pengurangan kuat daripada petala.

Kesandaran suhu PL menunjukkan kesan ke atas kuasa puncak PL, lebar separuh ketinggian maksimum (FWHM) dan keamatan PL. Secara umumnya, kuasa puncak PL dan (FWHM) menaik secara berkala apabila suhu dinaikkan yang berkaitan dengan tindak balas pembawa cas dengan fonon. Sebaliknya, puncak keamatan PL menurun apabila suhu dinaikkan yang disebabkan oleh pengujaan pembawa yang keluar daripada titik kuantum kepada pusat penggabungan semula tidak menyinar. Fenomena foto-peningkatan telah dikaji dengan mendedahkan sampel selama 40 minit penyinaran yang berlarutan dan kami mendapati bahawa keamatan PL telah meningkat terhadap masa yang disebabkan oleh kehadiran oksigen. Dalam kesandaran kuasa PL, keamatan PL bersepadu (IPL) telah meningkat dengan peningkatan kuasa ketumpatan. Daripada graf IPL sebagai fungsi ketumpatan kuasa, secara umumnya kecerunan graf telah menghampiri keunitan di mana penggabungan semula menyinar ialah dominan. Pembangunan titik kuantum teras dalam luaran PbS/MnS akan berguna pada masa akan datang terutamanya dalam aplikasi peranti fotovolta.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

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LIST OF ABBREVIATIONS

QDs	Quantum Dots
HRTEM	High Resolution Transmission Electron Microscopy
EDX	Energy Dispersive X-ray
TEM	Transmission Electron Microscopy
ZnS	Zinc sulphide
CS	Core shell
TGL	Thioglycerol
DTG	Di-thioglycerol
DOS	Density of states
eV	Electron volt
mW	Milliwatt
InGaAs	Indium gallium arsenide
CCD	Charge couple device
rpm	Revolution per minute
E_g	Energy band gap
PbS	Lead sulphide
MnS	Manganese sulphide
Si	Silicon
PL	Photoluminescence
λ	Wavelength
α	Temperature coefficient
T	Temperature
Mn	Manganese
Pb	Lead
CdSe	Cadmium selenide
CdS	Cadmium sulphide
m	Gradient
P	Power
E_v	Valence band
E_c	Conduction band
$h\nu$	Photon
ML	Monolayer
DPSS	Diode-pumped solid state
FWHM	Full width half maximum
Cu	Copper
PbSe	Lead selenide
ZnSe	Zinc selenide
ODE	Octadene

CHAPTER 1

INTRODUCTION

Study of materials at nano-scale has gained a great deal of interest as it fills the gap between bulk and molecules or atoms, thus improving our understanding of fundamental properties and providing new physical effects. Quantum dots (QDs), also can be called as semiconductor nanocrystals are particles that have physical dimension smaller than exciton Bohr radius and categorised in zero-dimensional system (0-D). The advantage of QDs is the confinement of charge carriers in three dimensions, where the electrons and/or holes are fully localised. Studying the physics of QDs from optical spectroscopy enables us to understand quantum confinement due to their extremely small size.

In the last few decades, this semiconductor nanocrystals have played vital roles in both theoretical and experimental physics. Research related to the QDs also has been expanding due to rapid advancements in growing and fabrication techniques as well as their numerous possible applications such as photovoltaic application (Xu & Heo, 2014; Reilly *et al.*, 2014; Alam *et al.*, 2015). The band gap of the QDs is tunable, therefore the QDs are desirable for photovoltaic devices. Frequencies in the near infrared are difficult to achieve with conventional solar cells. However, it can be obtained by using colloidal lead sulphide (PbS) QDs and PbS/MnS core shell QDs. This thesis begins with the fundamental of low dimensional system where it could give us understanding related to the QDs.

1.1 Fundamental of low dimensional system

Nanomaterials are defined as a set of materials where at least one dimension approximately smaller than 100 nm (Tiwari *et al.*, 2012). Nanomaterials can be classified into three-dimensional (3-D), two-dimensional (2-D), one-dimensional (1-D) and zero-dimensional (0-D) systems.

Low dimensional systems are usually classified based on the number of reduced dimensions they have. As size of bulk materials reduced to nanoscale, the overall behaviour of bulk crystalline materials will change, and quantum effect will occur (Jitendra *et al.*, 2012). Precisely, dimensionality is referred to the number of degrees of freedom in the particle momentum. The confinement of charge carriers (electron and hole) to a low dimensional system leads to dramatic change in their behaviour and properties. The classification depending on the dimensionality as shown in Figure 1.1.

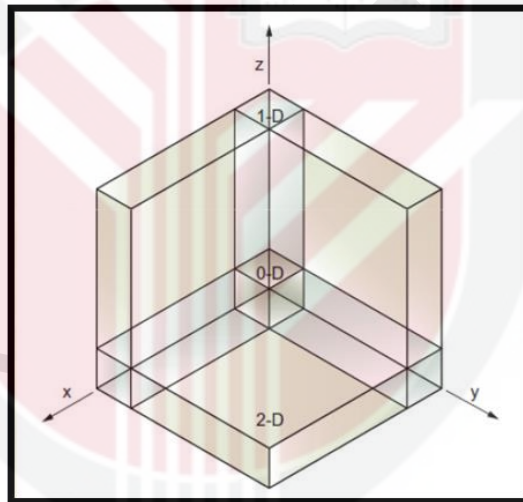


Figure 1.1: Three-dimensional system of nanomaterials (Jitendra *et al.*, 2012).

3-D system or bulk is material that are not confined to nanoscale in any dimension. Thus, this material is characterized by having three arbitrarily dimensions above 100 nm. The electrons are fully delocalised which means they are freely to move in three dimensions.

For 2-D system, two of the dimensions are not confined to nanoscale and only one of the dimensions is in nanoscale range. This factor leads the 2-D nanomaterials exhibit plate-like shape such as quantum well; where the electrons are free to move in two directions. In this case, the conduction electrons will be confined across the thickness and delocalised in the plane of the sheet.

In 1-D system, there is only one dimension that is outside nanoscale and this leads to tube-like shape nanomaterials such as nanotubes, nanorods and nanowires. In this system, electron confinement occurs in two dimensions, whereas delocalisation takes place along the axis of the nanowire, nanorod or nanotube.

For 0-D system, all of the dimensions are reduced within nanoscale. Electrons are confined in three dimensions space. The most common representation of 0-D system are nanoparticles such as QDs. If any of the structural dimensions is reduced and squeezed to be comparable to the de Broglie wavelength of the charge carrier or the exciton Bohr radius, the motion of carriers become constrained in the corresponding direction. This leads to the quantum confinement effect where the energy carrier levels and DOS are strongly dependent to the structural size, and entirely different from the bulk form (Jitendra *et al.*, 2012).

In QDs, the charge carriers are confined in all three dimensions which the electrons exhibit a discrete energy spectrum, and will be described in subtopic 2.1.2 related to the quantum confinement effect in the QDs. This research will focus on PbS and PbS/MnS core shell QDs in colloidal form.

1.2 Introduction of quantum dots

QDs are one type of semiconductor nanocrystals and can be defined as particles with physical dimensions smaller than the exciton Bohr radius. QDs also have special characteristic, which is the band gap of QDs is influenced by its size. Small size QDs emit higher energy light compared to larger QDs, making the wavelength of light emitted can be tuned by changing the size of the QDs (Guyot-Sionnest, 2008).

In 1980, Russian solid state physicist, Alexey I. Ekimov discovered QDs in a glass matrix and first colloidal QDs was discovered in AT&T Bell Lab Laboratories by Louis Brus back in 1982 (Angell, 2011). Following the successful discoveries, systematic advancement in the science of QDs was started after 1982 when Alexander Efros derived a relation between size and energy gap for semiconductor nanoparticles by applying a particle in a sphere model approximation to the wave function for bulk

semiconductors (Kaya *et al.*, 2014). However, it took nearly ten years to successful synthesis of colloidal cadmium chalcogenide CdY (Y= S, Se, Te) QDs with size-tunable band-edge absorption and emission, which was synthesised by Murray *et al.*, (Murray *et al.*, 1993). Their excellent optical and electrochemical properties make CdY widely investigated QDs.

QDs have contributed a lot from their kinds to the various application areas. Traditional nanocrystals are composed of elements from groups III-V, II-VI and IV-VI of the periodic table such as GaAs, CdSe and PbS, respectively (Schöll *et al.*, 2019; Landry *et al.*, 2014; Zhao *et al.*, 2005). QDs have many advantages such as producing excellent fluorescence properties and have been widely used in industry. One of the applications of these QDs is used in optoelectronic devices (Talpin *et al.*, 2010; Angell, 2011).

In the study of QDs, the interesting phenomena associated with it is the exciton (electron-hole) pair which are created through external energy. Upon the absorption of light, the electron will get excited if the energy absorbed is equal or more than the band gap. Vacancy it left behind is called a hole, that carries positive charge. The electron-hole pair is called an exciton and the separation distance between electron and hole is an exciton Bohr radius (Fang *et al.*, 2012).

Generally, there are two methods to fabricate QDs. The first method is top-down approach in which the dimension of the bulk is reduced to a smallest dimension particle. Other method is bottom-up approach in which QDs are grown via chemical synthesis or epitaxial growth to produce large dimension particle (Mousa, 2011). These methods have been able to produce QDs with diameters of a few nanometres, whose sizes are small enough to display quantum mechanical properties.

1.3 Properties of bulk materials

It is important to introduce the main semiconductor materials used in this research which are lead sulphide (PbS) and manganese sulphide (MnS). An overview of the properties of these bulk materials is presented in the following subtopic.

1.3.1 Bulk lead sulphide

Lead chalcogenides such as lead selenide (PbSe), lead telluride (PbTe) and lead sulphide (PbS) are materials that play a major role for infrared optoelectronics devices. They have large dielectric constants, narrow band gaps and share similar band structures (Smith *et al.*, 2011).

PbS is categorised in the group of IV-VI semiconductor with a direct narrow band gap of $E_g = 0.259$ eV at 4 K and 0.41 eV at room temperature (Dalven, 1969). It has a rock salt structure with a lattice constant, $a = 5.963$ Å. The electronic band structure of PbS is shown in Figure 1.2 where the position of the conduction band and valence band was highlighted with the red arrow. The conduction and valence bands extrema are at the L-point of the first Brillouin zone, which make PbS a direct band gap semiconductor (Smith *et al.*, 2011).

The reduction in E_g as the temperature decreases means the temperature coefficient, dE_g/dT of bulk PbS is positive, where $dE_g/dT = +0.52$ meV/K (Dalven, 1969). This means that the energy band gap of the PbS is temperature dependent. It can be seen in Figure 1.2 that the band gap of bulk PbS is 0.41 eV at room temperature. This unique property also can be observed in other lead chalcogenides. Furthermore, PbS has an exciton Bohr radius of 18 nm arising from effective electrons and holes masses, which are almost equal and relatively small: $m_e^* \approx m_h^* \approx 0.08m_0$, where m_0 is the electron mass in vacuum. This Bohr radius is considered large compared to other semiconductor materials such as CdSe (5.4 nm). These make the PbS QDs is easily to synthesise and leads to the strong confinement of charge carriers in nanocrystals when the radius of QDs is less than the exciton Bohr radius.

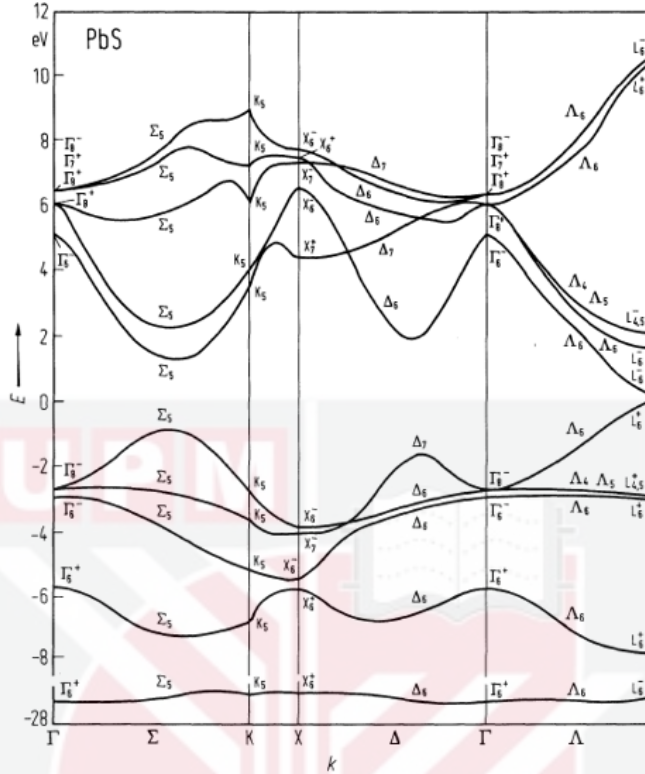


Figure 1.2: Electronic band structure of bulk PbS (Bergman & McHale, 2012).

Due to these factor, PbS QDs are essential semiconductor material for various potential applications, such as optoelectronic devices and photovoltaic solar cells (Tessler *et al.*, 2002; Phuruangrat *et al.*, 2009). In photovoltaic application, PbS can be an interesting material for semiconductor nanocrystals because PbS can tune the band gap with QDs size to make solar light absorption more efficient.

1.3.2 Bulk manganese sulphide

Manganese sulphide (MnS) is a direct wide band gap semiconductor with a band gap of $E_g = 3.2$ eV, lattice constant of 5.2 Å and temperature coefficient $dE_g/dT = -2$ meV/K (Nishitani *et al*, 1991). Both of PbS and MnS have similar rock-salt crystal structure. However, their band gap energies and dE_g/dT are different. Table 1.1 shows a comparison of important properties of bulk PbS and MnS.

Table 1.1: Properties of bulk PbS and bulk MnS.

	PbS	MnS
Lattice Constant, α (Å)	5.9	5.2
Energy band gap, E_g (at 300 K) (eV)	0.41	3.2
dE_g/dT (meV/K)	+0.52	-2

1.4 Motivation and problem statements

In recent years, many researchers have been working on the synthesis of colloidal QDs that can improve efficiency and produce excellent optical properties. However, QDs nanoparticles capped with organic ligands have low fluorescence quantum yield due to surface defects and surface trap state. This problem can be solved by growing a semiconductor shell layer around QDs core, forming core shell QDs. The shell will passivate the surface of the core from oxidation and provide stability to enhance the luminescence properties. This is due to smoothening of core-surface defects results in saturation of defect states and dangling bond that can cause non-radiative recombination of electron-hole pair.

There are numerous methods had been used to synthesise core shell QDs such as organometallic and electrochemical synthesis (Reilly *et al.*, 2014; Gu *et al.*, 2009). However, these methods produced low quality structure and used long synthetic procedure. Among mentioned methods, organometallic method commonly used to synthesise core shell QDs where high temperature and long procedure are needed. Unfortunately, it is also produced higher defect density introduced by high temperature synthesis which restricted by boiling point of solvents.

Electrochemical synthesis has been used due to their advantages such as usage of aqueous solvent, room temperature deposition and low cost. Unfortunately, due to difficulty of preparing electrically addressable arrays of nanoparticles, the use of electrochemical technique to produce core shell QDs was difficult. This motivates us to synthesise core shell QDs by another technique which is simple yet effective; cation exchange method.

In cation exchange method, only the precursor of cationic component of the shell material is introduced and the formation of the shell proceeds through the cationic replacement of the core material. Also, the exchange between cations within the core and cations in the surrounding solution may produce defect-free heterostructure. In this work, cation exchange was used to synthesise the core shell QDs in aqueous solution following the method described by Levina *et al.*, (Levina *et al.*, 2005).

This method uses low cost of production as water is used as a solvent. The cation exchange method also suitable for lead chalcogenide. In this case, PbS core QDs was synthesised as a control sample. By introducing Mn^{2+} precursor, the exchange between between Mn^{2+} and Pb^{2+} will form MnS shell. Hence, a great attention to synthesise the core shell QDs by making MnS ($E_g= 3.2$ eV) shell over the PbS ($E_g= 0.41$ eV) core to further study on the effects of the MnS shell towards the structural and optical properties.

As mentioned before, the cation exchange method was used to fabricate the PbS/MnS core shell QDs, and MnS shell is expected to grow on the PbS core QDs. In order to confirm the growth of the shell, HRTEM and EDX were used to identify the particle size and the elemental composition can then be analysed.

Temperature and power dependence of PL emission of PbS QDs and PbS/MnS core shell QDs were studied in order to examine the effect of temperature and power excitation on the QDs. Since all of electronic devices mostly perform at room temperature, the ability of the devices to working well at any temperature is still on-going improvement. Varying the temperature and the power excitation, dominant carrier recombination in the PbS QDs and PbS/MnS core shell QDs can be examined. In addition, performing PL measurements at low temperature can yield information about low energy states of the QDs that would otherwise be hidden by thermal effects at room temperature (Fomin *et al.*, 1998).

Despite many works have been conducted on the PL enhancement of semiconductor nanocrystals, the mechanism of this process is not yet fully understood. This is because the parameters factor such as water, oxygen and stabilising agents can influence the QDs during photoenhancement process (Llopis *et al.*, 2011). This motivates us to study on the photoenhancement phenomenon of the PbS QDs and PbS/MnS core shell QDs.

1.5 Research objectives

The objectives of this research are:

- i. To synthesise colloidal PbS QDs and PbS/MnS core shell QDs with different shell thicknesses by cation exchange method.
- ii. To examine the structural properties of PbS QDs and PbS/MnS core shell QDs with the variation of shell thicknesses.
- iii. To investigate the behaviour of the charge carriers (carrier transport) in the PbS QDs and PbS/MnS core shell QDs with the variation of temperature, power excitation and time exposure of photoluminescence measurements.

1.6 Thesis outlines

This thesis starts with **Chapter 1** where the introduction of the low dimensional system and the properties of bulk lead sulphide (PbS) and manganese sulphide (MnS) are presented. In **Chapter 2**, a brief explanation of the background theory of fundamental semiconductor properties and quantum dots are described. A description of a cation exchange method, core shell band alignments and the photoluminescence (PL) peak shift will be reviewed to give more information related to this research. Next, in **Chapter 3**, the methodology of this research including calculations and materials used to synthesise PbS core and PbS/MnS core shell QDs samples will be explained. Then, in **Chapter 4**, the characterisation will be analysed and elaborated comprehensively. The results include the effects of MnS shell thickness towards the structural and optical properties. The photoenhancement of photoluminescence (PL) of the PbS core QDs and PbS/MnS core shell sample is described in **Chapter 5**. A mechanism and recombination of charge carriers inside the QDs based on the PL analysis also will be explained in this chapter. Finally, the last chapter will conclude the research and suggestions for any future works will be discussed in **Chapter 6**.

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BIODATA OF STUDENT

Muhammad Safwan Zaini was born on the 2nd of July 1994 in Lumut, Perak. He began his early education in MINDEF kindergarten, Kuala Lumpur and Pulai primary school in Melaka. Then, he had his lower and upper secondary in SMK Seri Mahkota, Melaka. In 2012, he enrolled into Melaka Matriculation College and a year later pursued his higher education in Universiti Putra Malaysia. He obtained his degree in Bachelor of Science with Honours Major in Physics from Universiti Putra Malaysia (UPM) in the year 2017. After graduating he pursued his study at the Faculty of Science, Universiti Putra Malaysia (UPM) in the field of Nanotechnology.

During his first degree, he was awarded two awards; which are “*Gemilang Putra Fizik 2017*” and “*Hadiah Terbaik Kokurikulum*” sponsored by professor in his faculty. His interest in physics research grew in his third year as an undergraduate, where he was selected to represent Malaysia at the European Organisation for Nuclear Research (CERN) Summer Student Programme 2016 which held in Geneva, Switzerland. His interest in research will keep on until he achieved his dreams to pursue doctorate study in the future.

LIST OF PUBLICATIONS

Zaini, M. S., Kamarudin, M. A. Chyi, J. L. Y., Mohmad A. R. (2019). Temperature and Power Dependence of Photoluminescence in PbS Quantum Dots Nanoparticles. *Sains Malaysiana*, 48 (6), 1281-1288.

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Conferences And Poster Presentations

Zaini, M. S., Kamarudin, M. A. Chyi, J. L. Y., Mohmad A. R., “Discovering Temperature Dependent Behaviour of the PbS Quantum Dots Charge Carriers for Potential Photovoltaic Application”, Materials Technology Challenges 2019, Malaysian Solid State Science & Technology, Selangor, Malaysia, 23 March 2019.

Zaini, M. S., Kamarudin, M. A. Chyi, J. L. Y., Mohmad A. R., “Effect of MnS Shell Thickness Towards Photoluminescence of PbS/MnS Core Shell Quantum Dots”, 34th International Conference on the Physics of Semiconductor (ICPS2018), Montpellier, France, 29 July-3 August 2018.

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