

# **UNIVERSITI PUTRA MALAYSIA**

PHYSICAL PROPERTIES OF ZnSe AND CdSe SEMICONDUCTOR NANOPARTICLES SYNTHESIZED BY THERMAL TREATMENT AND GAMMA IRRADIATION ROUTES

**AESHAH NIZAR SALEM** 

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Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirements for the Degree of Doctor of Philosophy

December 2016



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# DEDICATIONS

To my mother and father,

--- and ----

My lovely husband Salman,

My sisters and brothers,

For their great patience and encouragement



Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the Degree of Doctor of Philosophy

## PHYSICAL PROPERTIES OF ZnSe AND CdSe SEMICONDUCTOR NANOPARTICLES SYNTHESIZED BY THERMAL TREATMENT AND GAMMA IRRADIATION ROUTES

By

#### AESHAH NIZAR SALEM

December 2016

Chairman : Professor Elias Saion, PhD Faculty : Science

Several methods have been utilized previously to synthesize metal chalcogenide nanoparticles with enhanced chemical and physical properties. However, most of these methods have used a complicated procedure, longer reaction times, and employed toxic reagents of expensive materials. Current study employed two physical methods, the thermal treatment to synthesis pure ZnSe and CdSe semiconductor nanoparticles and their  $(Cd_{0.5}Zn_{0.5})Se$  nanocomposite under a constant N<sub>2</sub> gas flow. Gamma radiation method was used to prepare pure ZnSe and CdSe semiconductor nanoparticles.

For the first method, an aqueous solutions of metal nitrate at different concentrations were mixed with 2 g of PVP, ethylenediamine(en) as a solvent of Se and deionized water as a solvent were prepared at calcination temperatures of 450-700°C. The samples were characterized by TGA, FTIR, EDX, XRD, TEM, and UV-Vis. FTIR analysis results confirmed the removal of organic matters and the presence of semiconductor nanoparticles at calcination temperatures 450-700°C. The elemental composition of the samples obtained by EDX spectroscopy has further evidence that the formation of ZnSe and CdSe nanoparticles and their nanocomposites. It was found that the phase formations of ZnSe and CdSe nanoparticles were cubic and hexagonal face-centered, respectively. The TEM images confirmed the increment of particle size from 12 to 26 nm for ZnSe and from 6 to 37 nm for CdSe and as well as from 12 to 24 nm for (Cd<sub>0.5</sub>Zn<sub>0.5</sub>)Se nanocomposites due to elevated calcination temperature and material concentration. The particle size of nanocrystals was also determined from XRD spectra. The estimated average sizes in the range 10.5-24 nm for ZnSe, 6-33 nm for CdSe nanoparticles and 10.5-25 nm for (Cd<sub>0.5</sub>Zn<sub>0.5</sub>)Se nanocomposites. While the optical properties were measured using UV-Vis spectrometer and the band gap ranged (3.956-4.158), (2.31-3.69) and (2.24-3.71) eV for ZnSe, CdSe and (Cd<sub>0.5</sub>Zn<sub>0.5</sub>)Se nanostructures, respectively.



ZnSe and CdSe semiconductor nanoparticles were also synthesized using a single-step radiolytic approach in aqueous solution containing metal sulfite were mixed with 2 g of PVP, ethylenediamine(en), deionized water, and IPA alcohol under irradiation with Co-60 gamma rays at dose of 120 kGy. The hydrate electrons created in water are responsible for the formation of CdSe and ZnSe nanoparticles. The final samples were characterized by EDX, XRD, TEM, and UV-Vis. The X-ray powder diffraction patterns reveal successful hexagonal crystal structure for both CdSe and ZnSe nanoparticles, with the average crystallite sizes of 16.3 and 10.7 nm, respectively. The EDX was used to confirm the stoichiometric elemental composition of Zn, Cd and Se in the samples. The TEM micrograph shows that CdSe and ZnSe nanoparticles are spherical in shape, with an average diameter of 17.3 and 11.2 nm, respectively. The optical band gaps determined from UV-Visible absorption spectra are between 2.87 and 3.58 eV for the CdSe and ZnSe nanoparticles, respectively.



Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Doktor Falsafah

# CIRI FIZIKAL NANOPARTIKEL SEMIKONDUKTOR ZnSe DAN CdSe DISINTISIS DENGAN KAEDAH RAWATAN HABA DAN SINARAN GAMA

Oleh

#### **AESHAH NIZAR SALEM**

#### **Disember 2016**

# Pengerusi: Profesor Elias Saion, PhDFakulti: Sains

Beberapa kaedah telah digunakan sebelum ini untuk mensintesis logam nanopartikel chalcogenide yang dipertingkatkan dan ciri-ciri fizikal dan kimianya. Walau bagaimanapun, kebanyakan kaedah-kaedah ini telah menggunakan prosedur yang rumit, masa tindak balas lebih lama, dan menggunakan bahan reagen toksik yang mahal. Kajian ini menggunakan dua kaedah fizikal iaitu rawatan haba untuk sintesis nanopartikel semikonduktor tulin ZnSe dan CdSe serta nanokomposit (Cd0.5Zn0.5)Se di bawah aliran gas N2 yang berterusan. Kaedah sinaran Gamma telah juga digunakan untuk menyediakan nanopartikel semikonduktor tulin ZnSe dan CdSe.

Bagi kaedah pertama, satu larutan akueus nitrat logam pada kepekatan yang berbeza telah bercampur dengan 2 g PVP, ethylenediamine (en) sebagai pelopor Se dan air ternyahion sebagai pelarut dan disediakan pada suhu pengkalsinan 450-700 °C. Sampel telah dicirikan menggunakan TGA, FTIR, EDX, XRD, TEM dan UV-Vis. Keputusan analisis FTIR mengesahkan penyingkiran bahan organik dan kehadiran nanopartikel semikonduktor pada suhu pengkalsinan 450-700 ° C. Komposisi unsur sampel yang diperolehi oleh spektroskopi EDX mempunyai bukti bahawa pembentukan nanopartikel ZnSe dan CdSe dan nanokomposit mereka. Ia telah mendapati bahawa pembentukan fasa nanopartikel ZnSe dan CdSe adalah padu dan heksagon berpusat muka, masing-masing. Imej-imej TEM mengesahkan peningkatan saiz zarah dari 12 kepada 26 nm untuk ZnSe dan dari 6 kepada 37 nm untuk CdSe dan juga dari 12 hingga 24 nm untuk nanokomposit (Cd<sub>0.5</sub>Zn<sub>0.5</sub>) Se disebabkan oleh suhu pengkalsinan yang tinggi dan kepekatan bahan. Saiz zarah nanokristal telah juga ditentukan dari spektrum XRD. Saiz purata dianggarkan dalam nm dalam julat 10.5-24 untuk nanopartikel ZnSe, 6-33 nm untuk nanopartikel CdSe dan 10.5-25 nm untuk nanocomposites (Cd0.5Zn0.5)Se. Walaupun ciri-ciri optik diukur dengan menggunakan spektrometer UV-Vis dan julat jalur adalah di antara (3.956-4.158), (2.31-3.69) dan (2.24-3.71) eV untuk semi konduktur ZnSe, CdSe dan nanokomposit (Cd0.5Zn0.5) Se, masing-masing.



Nanopartikel semikonduktor ZnSe dan CdSe juga disintesis menggunakan pendekatan radiolytic radiasi dalam satu langkah menggunakan larutan akueus yang mengandungi logam sulfit yang telah bercampur dengan 2 g PVP, ethylenediamine (en), air ternyahion, dan alkohol IPA di bawah sinaran gama sumber Co-60 pada dos 120 kGy. Elektron hidrat yang tercipta di dalam air adalah bertanggungjawab untuk pembentukan nanopartikel CdSe dan ZnSe. Sampel akhir telah dicirikan menggunakan EDX, XRD, TEM dan UV-Vis. Corak serbuk pembelauan X-ray mendedahkan struktur kristal heksagon berjaya untuk kedua-dua nanopartikel CdSe dan ZnSe, dengan saiz purata kristal 16.3 dan 10.7 nm, masing-masing. The EDX telah digunakan untuk mengesahkan komposisi unsur stoikiometri Zn, Cd dan Se dalam sampel. Mikrograf TEM menunjukkan bahawa nanopartikel CdSe dan ZnSe adalah berbentuk bulat, dengan diameter purata 17.3 dan 11.2 nm, masing-masing. Jurang jalur optik ditentukan daripada spektrum penyerapan UV-nyata adalah di antara 2.87 dan 3.58 eV bagi nanopartikel CdSe dan ZnSe, masing-masing.

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I certify that a Thesis Examination Committee has met on 22 December 2016 to conduct the final examination of Soheil Roknideilami on his thesis entitled "Solar Tracking System Utilizing Sun Position Sensor with Precision Angle Control" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science.

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# LIST OF ABBREVIATIONS

	K.M	Kubelka-Munk
	DI	Deionized water
	NPs	Nanoparticles
	NCs	Nanocomposites
	SEM	Scanning electron microscopy
	Nm	Nanometre
	eV	Electron volte
	θ	Bragg angle
	h	Hour
	min	Minutes
	Eg	Optical band gap
	°C	Degree Celsius
	λ Wavelength	Wavelength
	D	Diameter
	Т	Transmittance
	Λν	Energy
	В	FWHM
	ZnSe	Zinc selenide
	CdSe	Cadmium selenide
	Å	Lattice parameter
	EDX	Energy dispersive X-Ray
	TEM	Transmission electron microscopy
	FTIR	Fourier transforms infrared spectroscopy
	XRD	X-ray diffraction
	TGA	Thermo gravimetric analysis

#### **CHAPTER 1**

### **INTRODUCTION**

#### 1.1 Introduction

In 1959, the American physics professor and Nobel laureate Richard Feynman proposed a ground-breaking foundation of nanoscience and nanotechnology in his lecture "There is Plenty of Room at the Bottom" (Feynman, 1959). Nowadays, it forms the fundamental of new science and engineering from the basic sciences of physics and chemistry to their applications in materials science, electronics, biology, medicine, pharmaceutical and many engineering fields. There are a variety of definitions of nanoscience and nanotechnology. In general, nanoscience is the study of physical and chemical phenomenon exhibited by nanomaterials, while nanotechnology involves the design, production, characterization, and applications of nanomaterials (Saini et al., 2010). Materials at the nanoscale dimension (1-100 nm) are known as nanomaterials, which are distinctly different from their atom or molecule and bulk counterparts. Nanomaterials possess increased surface-to-volume ratio in such a way that the surface atoms become dominant and so their three-dimensional quantum confinement electrons (Boles et al., 2016). The most studied nanomaterials are metal nanoparticles and semiconductor nanoparticles. The surface electrons regulate the quantum effects that influence the non-linear optical property of semiconductor nanoparticles in electro-optical devices and the chemical property of metal nanoparticles in catalysis.

This thesis encompasses the synthesis and characterization of Group II-IV semiconductor nanoparticles, in particular ZnSe and CdSe nanoparticles. They can be synthesized by a variety of methods including hydrothermal, chemical, sonarchemicals, microwave, micro emulsion, and sol-gel (Aiken and Finke, 1999). The thermal treatment method has been used to prepare several oxide nanomaterials in our laboratory, such as metals ferrite nanoparticles (Nasri *et al.*, 2010), ZnO and CdO nanoparticles (Al-Hada *et al.*, 2016), ZrO<sub>2</sub> nanocrystalline (Keiteb *et al.*, 2016) and thermo luminescence nanomaterials (Erfani *et al.*, 2014). The motivation in the the present study is to synthesis ZnSe and CdSe semiconductor nanoparticles using thermal treatment method by removing oxygen to get the pure material. This technique is relatively simple and environmentally friendly as no toxic material is discharged into the common drainage system.

### 1.2 Nanomaterials

Ancient civilizations used metal nanoparticles for their brilliant colors, and they can be found in the coloured glass windows of the epic times, and yet, they continue to attract considerable attention today (Zhong *et al.*, 2010). Nanoparticles exhibit sizedependent properties such as the tuning of absorption energy with particle size, a blue shift of absorption onset, and an enhancement of photo-catalytic activities with a decrease in particle size (Saion *et al.*, 2013). Semiconductor nanomaterials have elicited renewed interest to researchers due to their capacity to synthesis high quality and large area nanoparticles with extraordinary optical, magnetic, electric and catalytic device applications, along with their improved physical properties like mechanical hardness, thermal stability or chemical passivity (Nalwa 1999; Garibe *et al.*, 2011). Furthermore, studies of such particles provide an opportunity to observe, control and modify the relationship between physical properties (size and shape) for a given chemical compound (Duan *et al.*, 2015).

Bulk material may be classified as a conductor, an insulator, or a semiconductor depending on the energy band structure as a consequence of electronic energy level mixing as many atoms are brought together to form a solid crystal. The valence band is filled with the orbital electrons while the conduction band is empty or partially filled with the conduction electrons. Insulators have a wide band gap so that electrons cannot be promoted from the valence band to the conduction band. On the other hand, semiconductors have a narrow band gap that allows excitation of electrons to the conduction band from the valence band. As the number of atoms are reduced, semiconductor nanomaterials have electronic structure deviated from the continuous electronic structure where their charge carriers are partially confined in their discrete energy levels, a phenomenon known as the quantum confinement effect. Figure 1.1 shows the electronic energy states of band structure of conductor, insulator, semiconductor nanocrystal, and molecule.



**Figure 1.1 : Electronic energy states of band structure of conductor, insulator, semiconductor, semiconductor nanocrystal, and molecule** (Sattler *et al.*, 2011)

Nanomaterials can be in the form of particles or dots, rods or wires, wells or flowers, etc. as long as one of the dimensions is less than 100 nm. The density of states provides information on the electronic states availability at energy level of the particular dimension (Hornyak *et al.*, 2008; Sattler *et al.*, 2011). Figure 1.2 shows the density states of 3D structure of bulk material, and of 2D nanostructure of quantum well, 1D nanostructure of quantum wire, and 0D nanostructure of quantum dot. A high value for the density of states represents a high number for the energetic states ready to be occupied by electrons. If there are no available states for occupation in an energetic level of the nanostructure, the value for the density of states will be zero. The semiconductor nanomaterials that have strong quantum confinement effect are called quantum dots where the band gap increases with decreasing particle size. Consequently, the physical and chemical properties of semiconductor nanomaterials depend on particle size and chemical composition.



Figure 1.2 : Density states of 3D bulk material, 2D nanostructure of quantum well, 1D nanostructure of quantum wire, and 0D nanostructure of quantum dot (Suresh *et al.*, 2013)

### 1.3 Semiconductor Quantum Dots

The semiconductor quantum dots (QDs) may be classified into group III-V and group II-VI nanoparticles, which both have a direct band gap (Sattler *et al.*, 2011). Group III-V consists of the combination of group III metals (B, Al, Ga, In, or Tl) and group V non-metals (N, P, As, Sb or Bi), for examples InP, GaP, GaN, and GaAs QDs. Group II-VI consists of the combination of metals of group II (Zn or Cd) and non-metals of group VI (O, S, Se, or Te). For examples ZnS, ZnSe, CdO, CdS, CdSe, and CdTe are p-type semiconductor QDs and ZnO and ZnTe are n-type semiconductors. They possess tetrahedral bonding geometry of wurtzite or zinc blende structure at room temperature, with their unit cell has both ionic and covalent bonding contributions. Structure of individual quantum dots depend on growth mechanism, pressure, and temperature applied.

Group II–VI semiconductor QDs have attracted considerable attention due to its applications in solar cells, light-emitting diodes, diode lasers emitting blue light, photo-detectors and full color display (Suresh *et al.*,2013). Zinc selenium (ZnSe) QD is an intrinsic semiconductor of n-type. It has wide band gap (bulk band gap 2.7 eV at room temperature) and significantly large binding energy (21 meV) (Zhu *et al.*, 2000). ZnSe structure can possess structure of wurzite (hexagonal) or sphalerite (cubic) at room temperature and is an attractive host for the formation of doped nanocrystals (Norman *et al.*, 2003) On other hand, cadmium selenide (CdSe) ODs possess structure of wurzite (hexagonal), sphalerite (cubic), or rock-salt (cubic) depending on the temperature. The sphalerite CdSe structure is unstable at about 130 °C and converts to the wurtzite at 700 °C. At high pressure rock-salt structure is observed.

### **1.4 Problem Statement**

Semiconductor nanostructures materials can be prepared by various methods like, hydrothermal, electrochemical, combustion, sol-gel, microwaves, micro-emulsions and many other chemical routs. In order to obtain materials of novel physical and chemical properties, the preparation of ZnSe and CdSe nanoparticles through different methods has become an essential focus of the related research and development (Hui et al 2004; Naseri et al 2011). In thermal treatment method the calcination process takes place in air or in a constant oxygen gas flow, is a common feature in the thermal treatment method. Therefore, oxygen in air is the main problem in the synthesis of metal chalcogenides such as ZnSe and CdSe QDs. Nevertheless, in the present fabrication of ZnSe and CdSe semiconductor nanoparticles, our problem was to remove oxygen during calcination process by applying a constant nitrogen gas flow, which otherwise the synthesized ZnSe and CdSe semiconductor nanoparticles will be contaminated with ZnO or CdO nanoparticles. At the same time the single-step radiolytic approach in gamma irradiation route will be tried out where the oxygen is removed by purging nitrogen gas into the reactant solution immediately prior to gamma irradiation.

### 1.5 Significance of study

Metal chalcogenides semiconductor nanoparticles and nanocomposites are attractive subjects of continuous scientific interest and have been deeply investigated in materials sciences, due to their physical-chemical properties that have wide range of applications. In particular, ZnSe and CdSe QDs are commonly used in solar cells, light-emitting diodes, diode lasers emitting blue light, photo-detectors and full color display, catalysis, chemical and biological sensors and many more applications.

In this study, two synthesis methods have been utilized for fabrication ZnSe, CdSe and CdZnSe nanostructures. The first route is thermal-treatment method, where an aqueous solution containing metal nitrates, poly (vinyl pyrrolidone), and deionized water undergone heat treatment to remove organic components. The second route is by gamma irradiation where the formed hydrated electrons become important in chemical reaction to form CdSe and ZnSe nanoparticles in water.



### **1.6** Scope of the Study

Among other metal semiconductor nanoparticles, ZnSe and CdSe nanostructure materials are ideal subjects that have been deeply investigated by researchers due to their impressive physical and chemical properties and their wide range of applications such as sensor, solar cell. The nanomaterial synthesis requires the use of a device or process that fulfills the following conditions: particle size control, size distribution, shape, crystal structure and composition distribution, less impurities, control of agglomeration, higher mass production, and lower costs. In particular, ZnSe and CdSe nanoparticles are commonly used in electronic devices, sensors, light emitting, optics, telecommunication, solar cell, medical and many more applications.

The methodology described above of achieving the synthesis of ZnSe and CdSe nano-particles by using single step radiolytic gamma irradiation and thermal treatment, presents a necessary limitation to the scope of the study. In addition to this, the study takes into consideration the morphological, structural and optical characteristics of the nanomaterials under investigation.

## 1.7 Research Objectives

The main objectives of the study are:

- 1. To produce pure ZnSe and CdSe semiconductor nanoparticles and Zn-CdSe nanocomposites by using thermal-treatment method.
- 2. To study the effect of calcination temperature and metal precursor concentration on the morphology, structural and optical properties of ZnSe and CdSe nanoparticles and Zn-CdSe nanocomposites
- 3. To produce ZnSe and CdSe nanoparticles by gamma-radiolytic route at dose of 120 kGy.
- 4. To study the morphology, structural and optical properties of gamma irradiation synthesized CdSe and ZnSe nanoparticles.

### 1.8 Thesis Layout

This thesis is comprised of five chapters. Chapter 1 briefly elaborate on the background of nanoscience and nanotechnology, semiconductor nanoparticles, problem statements, research objectives and finally the scope of the study.

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Chapter 2 presents an overview of previous works carried out by other researchers including current and past literatures in terms of the background materials and method for the preparation and characterization of semiconductor nanoparticle materials along with their related applications. Chapter 3 considers the theoretical background of the research, looking in details at the material structure, Bragg's Law and optical properties. Chapter 4 discusses the methodology of the research, the utilized materials and sample preparation expressed in significant detail. In addition, this chapter provides the morphological, structural, and optical characterisations of the samples

based on XRD, TEM, SEM, EDX, TGA, DTG, FTIR, UV-Visible spectroscopy and PL analyses. Results and discussion of the study on the obtained ZnSe CdSe and Zn-CdSe semiconductor nanomaterials on the morphological, structural, and optical characterisations are presented in Chapter 5. Finally, Chapter 6 provides the conclusion of the study based the structural and optical properties of the nanomaterials and the recommendations for future research.

Nanoparticles materials



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