UNIVERSITI PUTRA MALAYSIA

CHARACTERIZATION OF ZnXCd1-XS TERNARY SEMICONDUCTOR NANOPARTICLES SYNTHESIZED BY MICROWAVE-ASSISTED HYDROTHERMAL TECHNIQUE

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By

MINA ASKARI VERNOSFADERANI

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

July 2014

DEDICATION

I lovingly dedicate this thesis to my husband, Mahdi, who supported me each step of the way and remains willing to engage with the struggle,

My dear family, for being so supportive,

and my sweetheart daughter Gisu

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

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Chairman: Professor Elias Saion, PhD

Faculty: Science

In this work, the microwave-assisted hydrothermal method was used to synthesize $Zn_xCd_{1-x}S$ ternary quantum dots. In order to study the effect of different stoichiometries on $Zn_xCd_{1-x}S$ properties, the molar ratio of Zn/Cd was chosen as 0.1/0.9, 0.3/0.7, 0.5/0.5, 0.7/0.3, and 0.9/0.1, and to use semiconductor quantumdots in technology, the stability of these materials is very important and can achieve by capping the particles with either organic or inorganic materials like polymers. Zinc chloride ($ZnCl_2$), cadmium chloride ($CdCl_2$), and sodium sulfide (Na_2S) were used as Zn, Cd, and S sources respectively, and polyvinylpyrrolidone (PVP) and thioglycolic acid (TGA) were used as capping agent and stabilizer to control particle's growth and distill water as a solvent. The solution was heated in a microwave oven with 100% power for 4 minutes and the resulting precipitation was centriguged, washed, and dried at 100 ºC for 24 hours. By increasing the value of x from 0.1 to x=0.9, the powder color changed from dark yellow to white as verified by X-ray diffraction (XRD). The average particle sizes of Zn_xCd_1-xS nanoparticles as deduced from Sherrer's equation by XRD peaks and from the images of transmission electron microscopy (TEM) were found to vary within range 3-5 nm with x values. The optical band gap energy in the range of 2.3 to 2.93 ev was calculated by Tauc plot of the UV-visible spectra. The band gap has increased with increasing the value of x due to a decrease in particle size.

The synthesized $Zn_{0.9}Cd_{0.1}S$ quantum dots capped by TGA and PVP have band gaps between 2.93 to 3.43, and 2.91 to 2.98 respectively. PL spectra for $Zn_xCd_{1-x}S$ have three emission peaks related to sulfur, zinc, and cadmium vacancies respectively. The emission peaks II that are belong to zinc vacancies are observed at 484, 483, 483, 481, and 478 that are shifted to the lower wavelengths by increasing the value of x, and correspond to 2.56, 2.57, 2.57, 2.58, and 2.6 (eV). This significant continuous shift is an evidence for the formation of the ternary $Zn_xCd_{1-x}S$ quantum dot, rather than forming separate CdS, ZnS, or core-shell nanoparticle structure.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
Sebagai memenuhi keperluan untuk ijazah Master Sains

PENCIRIAN $Zn_xCd_{1-x}S$ TERNARY SEMIKONDUKTOR NANOPARTIKEL DISINTESIS OLEH MIKROWAVE-DIBANTU HIDROTERMA TEKNIK

Oleh

MINA ASKARI VERNOSFADERANI

Julai 2014

Pengerusi: Professor Elias Saion, PhD

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Dalam karya ini, kaedah hidroterma dibantu ketuhar gelombang mikro telah digunakan untuk mensintesis titik kuantum, nanopatikel ternary ZnxCd1-xS, (x = 0.1, 0.3, 0.5, 0.7 dan 0.9). Zink klorida ($ZnCl_2$), kadmium klorida ($CdCl_2$) dan natrium sulfida (Na2S) telah digunakan sebagai sumber, Zn, Cd dan S masing-masing dan polyvinylpyrrolidone (PVP) dan asid thioglycolic (TGA) digunakan sebagai ejen menutup dan penstabil kepada pertumbuhan nanopartikel secara terkawal dan air suling sebagai pelarut. Larutan dipanaskan di dalam ketuhar gelombang mikro dengan kuasa 100% selama 4 minit dan mendakan yang terhasil mengalami emparan, dibasuh dan dikeringkan pada 100 ° c selama 24 jam. Dengan meningkatkan nilai x daripada 0.1 untuk x = 0.9, warna serbuk bertukar daripada kuning gelap kepada putih dan keristiliti zarah ditukar daripada struktur hexagon kepada struktur kubus seperti yang disahkan oleh belauan sinar-x (XRD). Saiz purata nanopartikel $Zn_xCd_{1-x}S$ seperti yang ditentukan dari persamaan Sherrer oleh puncak XRD dan imej-imej transmisi elektron microscopy (Julai) didapati berada dalam julat 3-5 nm dengan pertambahan nilai x. Jurang jalur tenaga optik telah dikira dengan plot Tauc untuk cahaya UV-tampak . Jurang tenaga telah meningkat dengan peningkatan nilai x antara 2.75 dan 3.02 (eV). Sintensis $Zn_xCd_{1-x}S$ dengan TGA dan PVP mendapati jurang tenaga antara 2.98 hingga 3.04 eV dan 2.90 hingga 3.21 masing-masing. Spektrum PL untuk ZnxCd1-xS mempunyai tiga puncak penyinaran yang berkaitan dengan sulfur, zink dan kadmium masing-masing. Puncak penyinaran II dipunyai untuk zink yang dapat dilihat di 484, 483, 483, 481, dan 478 yang akan berpindah ke gelombang lebih rendah dengan meningkatkan nilai x, dan sesuai dengan nilai 2.56, 2.57, 2.57, 2.58 dan 2.6 (eV) masing-masing.

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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This is to confirm that:

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LIST OF ABBREVIATIONS

$CdCl_2$	Cadmium chloride
LED	Light-emitting diode
Na_2S	Sodium sulfide
PL	Photoluminescence
PVP	Polyvinilpyrollidine
QD	Quantum dot
TEM	transmission electron microscope
TGA	Thioglycolic acid
UV-Vis	Ultraviolet-Visible light spectroscopy
XRD	X-ray diffraction
$ZnCl_2$	Zinc chloride

LIST OF SYMBOLS

A	Absorbance
C_P	Specific heat capacity
C_s	Saturated concentration of the ions in the solution
C_{ss}	Supersaturated concentration of the ions in the solution
E_a	Activation energy
E_c	Energy of conduction band
E_g	Energy of band gap
E_v	Energy of valence band
E^2_{rms}	Root mean square of the internal electric field
Ƒ	Frequency
$G_{l \to s}$	Free energy change per unit volume when new nuclei are formed from a liquid
I_0	Incident light
I(z)	Flux density
J	Current density
K	Rate constant of chemical reaction
M	Rest mass of electron
M^*	Mass of the particle
R	Gas constant
T	Absolute temperature
T_b	Bulk temperature
T_i	Instantaneous temperature
Z	Distance
α_0	Bohr's radius of hydrogen atom

$\alpha(z)$	Absorbtion coefficient
β	Line boardening at half maximum intensity
γ	Specific surface energy of the nucleus
ε	Dielectric constant
ε_0	Dielectric permittivity of free space
$\breve{\varepsilon}_{eff}$	Effective relative dielectric loss factor
θ	Bragg angle
κ	Boltzman's constant
λ_0	Wavelength of microwave
ν_s	Volume per molecule in the solid
ρ	Density
σ	Electrical conductivity
Φ	Work function

CHAPTER 1

INTRODUCTION

1.1 Background of study

Nanoscience is a wide study area pertaining to diverse methods of synthesis and characterization of nanomaterials such as metal nanoparticles and semiconductor quantum dots- which is a type of nanocrystal made of semiconductor materials that are small enough to exhibit quantum mechanical properties- leading to their high potential applications in medicine, cancer therapy, optical devices, catalysis, and solar cell. Because of their particle size varies in range 1- 100 nm, their electronic parameters are size dependent such that they are promising candidates for optical devices. These types of materials have different electronic and optical properties compared to their bulk material counterparts. Their expanded surface leads to a new atomic arrangement which has an effect on optical properties of nanoparticles. The high surface to volume ratio can cause an increase in surface specific active sites for chemical reactions and photon absorption to enhance reaction and absorption efficiency, and an increase in the surface states, which changes the activity of electrons and holes and affects the chemical reaction dynamics. By decreasing the size of particles, the confinement charge carriers and the quantum size effect can occur, both conduction and valence band can split into discrete electronic states, and the band gap and optical and electronic properties become size dependence.

Ternary chalcogenide-based semiconductor quantum dots have unique size-tunable, optical, and electronic properties. These semiconducting materials have a broad range of applications in photovoltaic devices and solar cells. The Zinc Cadmium Sulfide (ZnCdS) ternary quantum dot is promising candidate as blue emitter and wide bandgap window material in photoconductive devices and heterojunction solar cells.

Among the expand range of nanomaterials, the $Zn_xCd_{1-x}S$ semiconductor quantum dots (QDs) are the best wide band gap window materials due to its tunable size, shape, and emitting color. To control the shape and size of corresponding QDs many different synthesis methods are presented such as gas-phase process, microwave-assisted hydrothermal method, co-precipitation method, chemical bath deposition, and solvothermal method. The hydrothermal method is useful for the growth of crystals with the ability of good control of their composition. Methods of synthesis the nanoparticles are expected to modify the nanoparticle's surface and properties and form them with narrow size distribution.

1.2 Problem statement

Semiconductor nanoparticles have an important role in new world due to their wide range of applications such as optical devices. In order to use them in technology, their particle size, size distribution, morphology, and optical properties are necessary to be controlled. Recent studies improve the way of synthesis nanoparticles and introduce some solution to control their properties during the formation process. The optical properties of semiconductor quantum dots are affected by their size distribution and surface that should be controlled to achieve desired optical characters. Some of the synthesis methods cause the large size and unstable particles or require longer hours to complete. Furthermore the products may result in amorphous phase, poor dispersion and with impurities. The microwave-assisted method and capping the nanoparticles with some materials as stabilizer can overcome these problems and give the semiconductor quantum dots with desired properties. In order to use semiconductor nanoparticles in technology, the stability of these materials is very important and can achieve by capping the particles with either organic or inorganic materials like polymers. The utilization of capping agents in nanoparticles synthesis is a way to provide chemical passivation, and improve the surface state that has a significant effect on the optical and electronic properties of nanoparticles. They prevent agglomeration of the nanoparticles and boost their optical properties and stability.

1.3 Study objective

In the terms of knowledge creation, this work includes fundamental research of semiconductor QDs synthesis process, effect of precursor's concentration, and also capping agents on physical and optical properties of nanoparticles. In details, in this project the high quality $Zn_xCd_{1-x}S$ semiconductor ternary QDs were synthesized via microwave irradiation with x values of 0.1, 0.3, 0.5, 0.7, and 0.9, and two types of capping agents with concentration from 1% to 5% and characterized to find their properties. To activate successful achievement of these, the thesis research is divided into the following particular objectives:

1- To synthesize high purity and quality ZnCdS semiconductor ternary QDs by hydrothermal microwave-assisted synthesis process in deionized water as solvent.

2- To study the effect of variation of x (x= 0.1 to 0.9) of $Zn_xCd_{1-x}S$ quantum dot in particle size, size distribution, morphology, and optical properties.

3- To investigate the influence of capping agents on synthesis and the growth process of $Zn_{0.9}Cd_{0.1}S$ semiconductor nanoparticles, and their physical and optical properties.

1.4 Scope of study

This work will deal with the important understanding of the synthetic conditions and the surface modification process relation of chalcogenide-based semiconductors. In particular, this thesis prepares and characterizes the $Zn_xCd_{1-x}S$ semiconductor QDs to examine their interesting properties and potential for extensive research. The microwave-assisted synthesis method is used to make the semiconductor QDs. Microwave irradiation of precursors decreases the time of reaction from days to minutes and produces smaller particles with a narrow particle size distribution and high purity. With a knowledge of nucleation and growth process, the tunning the size and controlling the shape, structure, and optical properties can be studied. The production of the best quality materials is carried out through selectively isolating the materials that actively contribute to the most nucleation events followed by efficient growth of the nanoparticles through the use of microwave irradiation. The experimental condition such as concentration of precursors, and the type and concentration of capping agents has also influence in quality of nanoparticles. This thesis is divided into two sections. In the first section the $Zn_xCd_{1-x}S$ with different values of x (0.1, 0.3, 0.5, 0.7, and 0.9) was synthesized through the reaction of zinc chloride, cadmium chloride, and sodium sulfide in deionized water as solvent with the aid of microwave radiation as a heating source in order to study the effect of concentration of precursors on the size distribution, optical properties, and morphology of nanoparticles. Second section provides a synthesis process of PVP and TGA capped $Zn_{0.9}Cd_{0.1}S$ with different concentration of stabilizer from 1% to 5% to monitor the effect of capping agents on the synthesis process, particle size, and size distribution of semiconductor QDs.

1.5 Thesis outline

This thesis presents a microwave-assisted hydrothermal synthesis rout and characterization of ZnCdS semiconductor ternary QDs with variable concentrations of Zn as one of the precursors,and PVP, and TGA as capping agents. The outline of this thesis comes as follow:

Chapter 1 presents an introduction of this research, including the background of study , problem statement, scope, and objective of the study. Chapter 2 deals with a history of Nanoscience, quantum dot, and chalcogenide $Zn_xCd_{1-x}S$ semiconductor nanoparticles and related literature in view of the synthesis process of nanoparticles. Chapter 3 is focused on a theory of electronic states of semiconductors and QDs, growth and nucleation process in the synthesis of nanoparticles, and microwave irradiation and its effect on materials. Chapter 4 provides the methodology of this work containing materials, experiment section, and characterization of semiconductor nanoparticles and the related methodes. The major part of this thesis has come in Chapter 5 which describes the experimental results and related analysis. The summery and suggestions for future work has presented in last chapter (Chapter 6).

REFERENCES

A. Rahdar, V.A., and H. Ghanbari Study of Electro-Optical Properties of ZnS Nanoparticles Prepared by Colloidal Particles Method. International Journal of Chemical and Biological Engineering.

Al-Gaashani, R., Radiman, S., Tabet, N., Daud, A.R. 2011. Effect of microwave power on the morphology and optical property of zinc oxide nano-structures prepared via a microwave-assisted aqueous solution method. Materials Chemistry and Physics, 125, 846-852.

Bawendi, M., Wilson, W., Rothberg, L., Carroll, P., Jedju, T.M., Steigerwald, M., Brus, L. 1990. Electronic structure and photoexcited-carrier dynamics in nanometer-size CdSe clusters. Physical review letters, 65, 1623.

Bruckman, G. (1933). Preparation and properties of thin lead sulfide films with special reference to their detector action: Kolloid.

Cheon, J., M. Guile, et al. (1999). "Gas phase photoproduction of diatomic metal nitrides during metal nitride laser chemical vapor deposition." Inorganic chemistry 38(9): 2238-2239.

El-Shall, M., Edelstein, A., Cammarata, R. 1996. Nanomaterials: synthesis, properties and applications. Institute of Physics Publishing, Bristol and Philadelphia, PA13-54.

Enderlein, R., Horing, N.J.M. 1997. Fundamentals of Semiconductor Physics and Devices: World Scientific.

Faraday, M. 1857. The Bakerian lecture: experimental relations of gold (and other metals) to light. Philosophical Transactions of the Royal Society of London, 147, 145-181.

Giesche, H. 1994. Synthesis of monodispersed silica powders II. Controlled growth reaction and continuous production process. Journal of the European Ceramic Society, 14, 205-214.

Horikoshi, S., Serpone, N. 2013. Microwaves in Nanoparticle Synthesis: Fundamentals and Applications: Wiley.

Hou, L., C. Wang, et al. (2010). "pH-Controlled interfacial assembly and disassembly of highly luminescent blue emitting $Zn_xCd_{1-x}S$/dodecylamine complexes." Journal of colloid and interface science 349(2): 626-631.

Iijima, S. 1991. Helical microtubules of graphitic carbon. nature, 354, 56-58.

Kittel, C. 2004. Introduction to Solid State Physics: Wiley.

Komarneni, S., Katsuki, H. 2002. Nanophase materials by a novel microwave-hydrothermal process. Pure and Applied Chemistry, 74, 1537-1543.

Kulkarni, S., Winkler, U., Deshmukh, N., Borse, P., Fink, R., Umbach, E. 2001. Investigations on chemically capped CdS, ZnS and ZnCdS nanoparticles. Applied surface science, 169, 438-446.

Leonelli, C., Mason, T.J. 2010. Microwave and ultrasonic processing: now a realistic option for industry. Chemical Engineering and Processing: Process Intensification, 49, 885-900.

Li, Y., Ye, M., Yang, C., Li, X., Li, Y. 2005. Composition-and Shape-Controlled Synthesis and Optical Properties of $Zn_xCd_{1-x}S$ Alloyed Nanocrystals. Advanced Functional Materials, 15, 433-441.

Lu, K. 2012. Nanoparticulate Materials: Synthesis, Characterization, and Processing: Wiley.

Mahdi, M., Hassan, J., Hassan, Z., Ng, S. 2012. Growth and characterization of $Zn_xCd_{1-x}S$ nanoflowers by microwave-assisted chemical bath deposition. Journal of alloys and compounds, 541, 227-233.

Murray, C., Norris, D., Bawendi, M.G. 1993. Synthesis and characterization of nearly monodisperse CdE (E= sulfur, selenium, tellurium) semiconductor nanocrystallites. Journal of the American Chemical Society, 115, 8706-8715.

Nagarajan, R., Hatton, T.A., Colloid, A.C.S.D.o., Chemistry, S., Meeting, A.C.S. 2008. Nanoparticles: synthesis, stabilization, passivation, and functionalization: American Chemical Society.

Oghbaei, M., Mirzaee, O. 2010. Microwave versus conventional sintering: A review of fundamentals, advantages and applications. Journal of alloys and compounds, 494, 175-189.

Ouyang, J., Ripmeester, J.A., Wu, X., Kingston, D., Yu, K., Joly, A.G., Chen, W. 2007. Upconversion luminescence of colloidal CdS and ZnCdS semiconductor quantum dots. The Journal of Physical Chemistry C, 111, 16261-16266.

Peled, A. 1997. State of the art in liquid phase photodeposition processes and applications (LPPD)-Review. Lasers in Engineering, 6, 41-&.

Peter, A.J., Lee, C.W. 2012. Electronic and optical properties of CdS/CdZnS nanocrystals. Chinese Physics B, 21, 087302.

Sakly, A., Safta, N., Mejri, A., Mejri, H., Lamine, A.B. 2010. The excited electronic states calculated for Cd 1-x Zn x S quantum dots grown by the sol-gel technique. Journal of Nanomaterials, 2010, 37.

Salem, A. 2002. Structure, refractive-index dispersion and the optical absorption edge of chemically deposited ZnxCd (1-x) S thin films. Applied Physics A, 74, 205-211.

Schmid, G. 2011. Nanoparticles: From Theory to Application: Wiley.

Seoudi, R., Shabaka, A., Eisa, W., Anies, B., Farage, N. 2010. Effect of the prepared temperature on the size of CdS and ZnS nanoparticle. Physica B: Condensed Matter, 405, 919-924.

Shao, J., Yan, W., Microwave assisted inorganic syntheses. Modern inorganic synthetic chemistry. (2011).

Soltani, N., Gharibshahi, E., Saion, E. 2012a. Band gap of cubic and cubic CdS quantum dots- experimental and theoretical studies. Chalcogenide Letters, 9, 321-328.

Stöber, W., Fink, A., Bohn, E. 1968. Controlled growth of monodisperse silica spheres in the micron size range. Journal of colloid and interface science, 26, 62-69.

Toumey, C.P. 2009. Reading Feynman into nanotechnology. Techné: Research in Philosophy and Technology, 12, 133-168.

Wu, J.-C., Zheng, J., Zacherl, C.L., Wu, P., Liu, Z.-K., Xu, R. 2011. Hybrid Functionals Study of Band Bowing, Band Edges and Electronic Structures of Cd1–x Zn x S Solid Solution. The Journal of Physical Chemistry C, 115, 19741-19748.

Xu, X., Lu, R., Zhao, X., Zhu, Y., Xu, S., Zhang, F. 2012. Novel mesoporous $Zn_xCd_{1-x}S$ nanoparticles as highly efficient photocatalysts. Applied Catalysis B: Environmental, 125, 11-20.

Yu, W.W., Peng, X. 2002. Formation of High-Quality CdS and Other II–VI Semiconductor Nanocrystals in Noncoordinating Solvents: Tunable Reactivity of Monomers. Angewandte Chemie International Edition, 41, 2368-2371.

Zhao, J., Yan, W. (2011). Chapter 8 - Microwave-assisted Inorganic Syntheses. In R. Xu, W. PangQ. Huo (Eds.), Modern Inorganic Synthetic Chemistry (pp. 173-195). Amsterdam: Elsevier.

Zhigang Chena, Qiwei Tiana, Yuelin Songa, Jianmao Yangb, Junqing Hua,∗ 2010. One-pot synthesis of ZnxCd1−xS nanocrystals with tunable optical properties from molecular precursors. Journal of Alloys and Compounds, 506, 804–810.

Zhong, X., Feng, Y., Knoll, W., Han, M. 2003. Alloyed Zn x Cd1-x S Nanocrystals with Highly Narrow Luminescence Spectral Width. Journal of the American Chemical Society, 125, 13559-13563.