

Faculty of Science Chemistry Department

Preparation and Characterization of Semiconductor Nanoparticles

Thesis Submitted in Partial Fulfillment for the Requirements of M.Sc. Degree

In

Inorganic Chemistry

Presented by

Hanaa Selim Ali Selim

B. Sc. in Physics-Chemistry (2007)

Supervised by

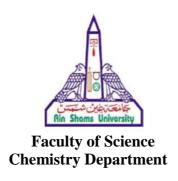
Prof. Dr. Mostafa M.H. Khalil

Professor of Inorganic and Analytical Chemistry, Faculty of Science Ain Shams University Prof. Dr.Sc. Mohamed F. Kotkata

Professor of Materials Science Physics Department, Faculty of Science Ain Shams University

Dr. Hatem H. Amer

Assist. Professor, Solid State Department
National Centre for Radiation Research and Technology (NCRT)
Atomic Energy Authority (AEA)



Preparation and Characterization of Semiconductors Nanoparticles

A Thesis Submitted by

Hanaa Selim Ali Selim

For the Degree of M.Sc. of Science in Inorganic Chemistry

To

Department of Chemistry Faculty of Science Ain Shams University



Approval Sheet

Name of candidate: **Hanaa Selim Ali Selim** Degree: M.Sc. Degree in Chemistry

Thesis Title: Preparation and Characterization of Semiconductor Nanoparticles

This Thesis has been approved by:

- 1- Prof. Dr. Mostafa M.H. Khalil
- 2- Prof. Dr.Sc. Mohamed F. Kotkata
- 3- Dr. Hatem H. Amer

Approval

Chairman of Chemistry Department

Prof. Dr. Maged Shafik Antonious Nakhla



I do appreciate my god for giving me wonderfully parents who are enlightening and always supporting me in all my Life.

I also thank my brother and sisters for listening and for always being there through everything.

I also many thanks to my Prof. Dr. M. S.

Al-Koth for continuous encouragement and help.





First and last thanks to **Allah** who give me the power to go forward in a way illuminated with his merciful guidance.

I would like to express my thanks to **Prof. Dr.**Sc. M. F. Kotkata, Professor of Material Science,
Physics Department, Faculty of Science, Ain Shams
University, for giving me the chance to be one of his
students and for his generous advices, valuable
discussions, which helped me greatly, and the good
proof reading of this thesis. He did not only guide this
work and find time to discuss with me but also gave
me the confidence to express my ideas freely. I will
always remember how his ideas and suggestions
always work and how he could simply pick the small
mistakes. Actually he was more than a supervisor, he
was a teacher who inspired me and pushed me
forward.

I would like to express my thanks to **Prof. Dr.**Mostafa M. H. Khalil, Professor of Inorganic and Analytical Chemistry, Faculty of Science, Ain Shams University, for giving me the chance to be one of his students. He was always kind enough to suggest the topics of research and follow up the progress of the work with keen interest, guidance and valuable criticism and whose efforts made this humble work as possible, for helping and revising the whole manuscript.

I am so grateful to **Dr. H. H. Amer**, Solid State Department, National Center for Radiation and Technology in Atomic Energy Authority, for his continuous help, encouragements, the good proof reading and facilities offered by his throughout the work.

Special thanks to Dr. M. S. Al-Kotb. Semiconductors *Technology* Lab. **Physics** Department, Faculty of Science, Ain Shams his encouragements, University, for warm supervising the practical work, continuous assistance, guidance, valuable advice during this research work and without which fulfillment of this work would be impossible, for helping and revising the whole manuscript.

I would also like to thank my Colleagues in the Chemistry Department and Physics Department, Faculty of Science, Ain Shams University for their help.

I am thankful to all staff members and colleagues, Solid State Department, National Center for Radiation and Technology, Atomic Energy Authority for their support and appreciated help.

This work has been supported and financed by Academy of Scientific Research Technology (ASRT), grant reference no: **ASRT/TRG/B/2010-5.**

Contents

List of Tables and Scheme	Page No
List of Figures	ii
Abstract	vi
Chapter 1: Introduction	
1.1. Nanoparticles and Nanotechnology	1
1.2. Classes of Nanomaterials	5
1.3. Semiconductor Nanomaterials	6
1.4. Classification of Semiconductors	9
1.5. Chalcogenide Semiconductors Nanoparticles	10
1.6. Methods for Semiconductors Preparation	12
1.7. Size Effects	13
1.8. Surface Reactivity	20
1.9. Photoluminescence Property	20
1.10. Literature Survey on ZnS	23
1.11. Aim of the Present Work	29
Chapter II: Samples Preparation and Experimental Techniques	
2.1. Materials	31
2.2. Synthesis of SDS–Capped ZnS Nanoparticles	
via Simple Non-toxic Colloidal Method	31
2.3. Synthesis of ZnS Nanoparticles via Solid State	
Chemical Method	35
2.4. Structural measurements	36
2.4.1. X-Ray Analysis	37

2.4.2. Transmission Electron Microscope Technique (TEM)	40
2.4.3. Scanning Electron Microscope Technique (SEM)	40
2.4.4. Thermal Gravimetric Analyzer (TGA)	41
2.4.5. Fourier Transform Infrared Spectroscopy (FT-IR)	42
2.4.6. UV-Vis Absorption Spectrometry	43
2.4.7. Photoluminescence (PL)	45
Results & Discussion	
Chapter III: Structural Characterization of ZnS Qu Dots Prepared by Aqueous Chemical Met	
3.1. Reaction Mechanism	45
3.2. Structural Characterizations	48
3.2.1 Energy Dispersive X-ray Analysis (EDX)	48
3.2.2 X-Ray Diffraction Analysis (XRD)	51
3.2.3. X-Ray Diffraction of Powder Samples	52
3.2.4. Transmission Electron Microscope (TEM)	55
3.2.5. Thermal Analysis	57
3.2.6. Fourier Transform-Infrared (FT-IR)	58
3.2.7. Optical Analysis	59
Chapter IV: Structural Characterization of ZnS Qu	antum
Dots Prepared by Solid-State Method	
4.1 Structural Characterizations	63
4.1.1 Energy Dispersive X-ray Analysis (EDX)	63
4.1.2. X-Ray Diffraction Analysis (XRD)	64
4.1.3. Scanning Electron Microscope (SEM)	67
4.1.4. Transmission Electron Microscope (TEM)	69
4.2. FT-IR Studies of the As-prepared ZnS QDs	71

4.3. Thermal Characterization of The as-prepared	ZnS
QDs	73
4.4. Optical Characterization	84
4.4.1. Quantum Confinement Effect	84
4.4.2. Photoluminescence Spectra	89
Summary and Conclusion	92
References	96
Published Articles from the Present Thesis	107
Arabic Summary	,

List of Tables and Scheme

<i>Table (4.1)</i>	Average Particle Size Calculation
	Average Particle Size Calculation from Williamson-Hull's Formula.
<i>Table (4.2)</i>	Particle Size and Band Gap
	Variation with Molar Concentration.
Scheme (4.1)	The thermal Decomposition Steps of
	ZnS QDs.

List of figures

Fig.(1.1)	Schematic Changes in the Band Structure on going from a Bulk Crystal to a Nanocrystal to Molecule.
Fig.(1.2)	Schematics Representation of the Three General Types of Semiconductor Structures, Amorphous (a), Poly- crystalline (b) and Single Crystal (c).
Fig.(1.3)	Excitations in Semiconductors.
Fig.(1.4)	Photo Excitation in Semiconductors.
Fig.(2.1)	Structure of Sodium Dodecyl Sulphate (SDS).
Fig.(2.2)	Design flow for Preparation of SDS— Capped ZnS Nanoparticles via Chemical Method.
Fig.(2.3)	Design flow for Preparation of ZnS Nanoparticles via Solid-State Reaction Method.
Fig.(3.1)	A schematic Diagram showing the Formation of SDS-Capped ZnS NP.
Fig.(3.2)	EDX Analysis of the As-product ZnS QDs. The inset shows a Typical SEM Image.

Fig.(3.3)	XRD Pattern of As-product QDs showing preferred orientation of ZnS Cubic Phase.
Fig.(3.4)	Williamson-Hull's Plot (β cos θ versus 4sin θ) to determine the Particles Size D according to Eq. (3.5).
Fig.(3.5)	TEM Image of ZnS Nanoparticles
Fig.(3.6)	Diameter Distribution Histogram obtained from Counting 200 Particles.
Fig.(3.7)	TGA Curves of As-product ZnS QDs as recorded at a Constant Heating Rate of 10^{0} C/min.
Fig.(3.8)	FT-IR Spectra of both ZnS QDs and SDS.
Fig.(3.9)	UV-visible absorption spectrum of the ZnS nanoparticles.
Fig.(3.10)	Energy Band Gap Determination of ZnS Nanoparticles.
Fig.(4.1)	EDX Qualitative Analysis for ZnS (Sample 1).
Fig.(4.2)	XRD Patterns of ZnS Nanoparticles Milled for 1, 2, 3 and 4 hours, respectively.
Fig.(4.3)	SEM Photograph of ZnS QDs Milled for 1, 2, 3 and 4 hours, respectively.
Fig.(4.4)	TEM Image of ZnS QDs Milled for 1, 2, 3 and 4 hours, respectively.

	<u> </u>
Fig. (4.5)	Magnified TEM of a Single ZnS Nano-rod (Sample 3).
Fig. (4.6)	FT-IR Spectra of ZnS QDs Milled for First hour (A), Second hours (B), Three hours (C) and four hours (B).
Fig. (4.7)	TGA of ZnS QDs Milled for 1, 2, 3 and 4 hours, respectively, at Heating Rate 5°C/min.
Fig. (4.8)	TGA of ZnS QDs Milled for 1, 2, 3 and 4 hours, respectively, at Heating Rate 10° C/min.
Fig. (4.9)	TGA of ZnS QDs Milled for 1, 2, 3 and 4 hours, respectively, at Heating Rate 15°C/min.
Fig. (4.10)	TGA of ZnS QDs Milled for 1, 2, 3 and 4 hours, respectively, at Heating Rate 20°C/min.
Fig. (4.11)	XRD Patterns of ZnS QDs Milled for 1, 2, 3 and 4 hours, respectively. Under Investigation of TGA at Different Rates at 800°C.
Fig. (4.12)	FT-IR Spectra of Both ZnS QDs Milled for one hour (A), Second hours (B), Three hours(C), and Four hours (D). Under Investigation of TGA at Heating rate 10 °C/ min at temp.800 °C.

-	
Fig. (4.13)	TGA of ZnS QDs at Heating Rate 100 C/min 490 °C.
Fig. (4.14)	XRD of ZnS Nanoparticles Milled for one hour under Investigation of TGA at Heating Rate 10 °C/ min at temp. 490°C.
Fig. (4.15)	FT-IR Spectra of Both ZnS QDs under Investigation of TGA at Heating Rate 10° C/min at temp.490°C.
Fig. (4.16)	Absorption Spectra of ZnS Nanoparticles Milled for one, two, three and four hours.
Fig. (4.17)	Energy Band Gap Determination of ZnS Nanoparticles Milled for one, two, three and four hours.
Fig. (4.18)	The Variation of Particle Size with the Optical Band Gap.
Fig.(4.19)	Photoluminescence Spectrum of ZnS QD's Milled for 1, 2, 3 and 4 hours at λ_{ex} =320 nm.
Fig. (4.20)	Photoluminescence Spectrum of ZnS QDs Milled for 1, 2, 3 and 4 hours at λ_{ex} =260 nm.