International Journal of
Science and Engineering Investigations vol. 1, issue 2, March 2012

Effect of 1-Thioglycerol as Capping Agent on ZnS Nanoparticles: Structural and Optical Characterization

A. Rahdar
Department of Physics, Faculty of Science, University of Zabol, Zabol, Iran
(a.rahdar@uoz.ac.ir)

Abstract— In this work, we report effect of capping agent on structural and optical properties of Nano crystalline ZnS particle, which have been synthesized by co-precipitation method. The structural properties of ZnS nanoparticles have been characterized by X-ray diffraction (XRD) analysis. The XRD patterns show hexagonal structure in nanoparticles. The mean crystallite size calculated from the XRD patterns has been found in the range of 1.85-2.44 nm with the increase in molar concentration of capping agent. Absorption spectra have been obtained using UV-Vis spectrophotometer to find the optical direct band gap. The obtained values have been founded to being range 3.98-4.34 eV. We also found that optical band gap (E_g) increases with the increase in molar concentration of capping agent. This behavior is related to size quantization effect due to the small size of the particles.

Keywords**:** *ZnS nanoparticles, Chemical co-precipitation method, 1-Thioglycerol, Capping agent, Optical band gap.*

I. INTRODUCTION

Semiconductor Nano crystals represent a class of materials that have hybrid molecular and bulk properties. They have attracted much attention over the past few years because of their novel properties originating from quantum confinement effect [13]. In the case of semiconductor nanoparticles, radiative or nonradiative recombination of an exciton at the surface states becomes dominant in its optical properties with a decrease of particle size. Therefore, the decay of an exciton at the surface states will influence the qualities of the material for an optoelectronic device. These size dependent optical properties have many potential applications in the areas of solar energy conversion, light emitting devices, chemical/biological sensors and photocatalysis [5].

Wide band gap II–VI semiconductors are expected to be the novel materials for the optoelectronic devices. In this between, ZnS has been used widely as a promising candidate for photoluminescence (PL), electroluminescence (EL) and cathodoluminescence (CL) devices due to its better chemical stability compared to other chalcogenides such as ZnSe. In optoelectronics, it is used as light emitting diode, reflector, dielectric filter and window material [1].

The synthesis of ZnS nanoparticle remains a topic of interest for researchers, as new synthetic routes are being explored to get single phase material via an economically and technically viable method. Till now, many studies on nanoparticles have focused on the synthesis of different nanoparticle assemblies with different capping agents [7]. Nevertheless the experimental studies on 1-Thioglycerol as capping agent are scare. So in the present paper, we tried to find the structural and optical properties of ZnS nanoparticles with different molar 1-Thioglycerol as capping agent. Our main purpose is to study the effect of capping agent on structural and optical properties of ZnS nanoparticles synthesized by co-precipitation method.

This paper is organized as follows: in experimental procedure section, we give a description of materials and synthesis method of ZnS nanoparticles with different molar concentration of capping agent. The structural and optical properties of synthesized nanoparticles are presented in results and discussion section in details, followed by a conclusion.

II. EXPERIMENTAL PROCEDURE

- *Material*

Zinc chloride ($ZnCl_2$), sodium sulfide (Na_2S) as starting materials, 1-Thioglycerol as a capping agent for control particles size and double-distilled water as dispersing solvent were used to prepare ZnS nanoparticles.

- *Synthesis of ZnS nanoparticles by co-precipitation method*

The ZnS nanoparticles were synthesized by the chemical co-precipitation method as follows. First, $ZnCl_2$ was dissolved in double-distilled water (0.1 M) and then obtained molar

solution was stirred for 20 min at room temperature to achieve complete dissolution. Sodium sulfide (Na_2S) was also dissolved in double-distilled water separately as per molar concentration. Afterwards, first sodium sulfide solution was added drop by drop to the zinc chloride solution and then an appropriate amount of 1-Thioglycerol as a capping agent was added to the reaction medium to control the particle size of ZnS. As a result of this, the white precipitate of the ZnS nanoparticles is formed slowly in the solution. In the final step, the obtained precipitate was filtered and dried at room temperature to remove both water and organic capping and other byproducts formed during the reaction process. After sufficient drying, the precipitate was crushed to fine powder with the help of mortar and pestle. It is mentioned that the synthesis has done under passing the nitrogen gas.

For study of effect of capping agent on structural and optical properties of ZnS nanoparticles, different sample of nanoparticles has been obtained by changing the molar concentration of capping agent namely ZnS(A), ZnS(B), ZnS(C) and ZnS(D) as the amount of molar concentration of capping agent used in the preparation is 0 M, 0.01 M, 0.1 M and 0.2 M respectively.

- *Powders characterization*

The X-ray diffraction (XRD) patterns of ZnS nanoparticles were recorded by Bruker system using Cu K_α radiation (λ=0.154056 nm) with 2θ ranging 5–70°. The optical absorption spectra of nanoparticles were measured using a USB-2000 UV–Vis spectrophotometer. Therefore, obtained nanopowders have been suspended in glycerol using magnetic stirrer and their optical absorption spectra has been recorded at room temperature over the range 200 to 800 nm for determining the optical band gap values.

III. RESULTS AND DISCUSSION

- *Structural Characterization*

The XRD patterns of prepared ZnS nanoparticles with different molar concentration of capping agent 1-Thioglycerol are shown in Fig. 1. All of the crystalline Bragg peaks in the XRD pattern ((111), (200) and (311) planes) are in a good agreement with the diffraction data of hexagonal structure with cell parameters a=3.800 Å and c=6.230 Å from JCPDS card. Furthermore, the peak broadening in the XRD patterns clearly indicates the formation of ZnS Nano crystals with very small size.

The peak broadening at lower angle is more meaningful for the calculation of particle size. The mean crystallite size (D) of nanoparticles was also estimated using the Scherrer formula (Scherrer 1918) using (111) reflection from the XRD pattern as follows:

$$D = \frac{0.9\lambda}{B\cos\theta}, \quad (1)$$

Where λ, B, and θ are the X-ray wavelength of the radiation used (K_α(Cu) = 0.154056 nm), the full width at half maximum (FWHM) of the diffraction peak and the Bragg diffraction angle, respectively.

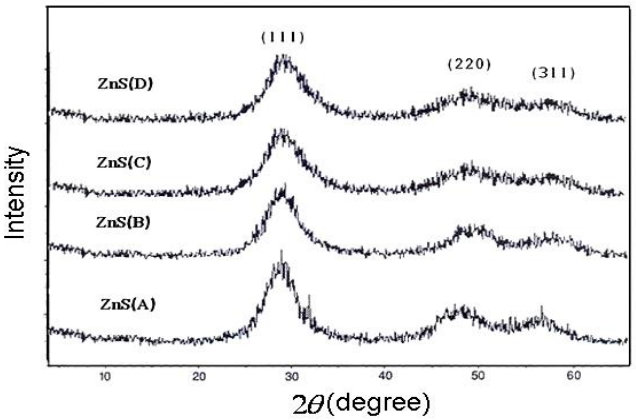

Fig. 1. XRD patterns of ZnS nanoparticles with different of molar (M) capping agent: 0 M (A), 0.01 M (B), 0.1 M (C) and 0.2 M (D).

The values of mean crystallite size obtained from XRD for different molar concentration of capping agent are listed in Table 1. It is clear that the crystallite size decreases (1.85-2.44nm) by increasing the molar of capping agent.

Table 1. Mean crystallite size and optical band gap variation of ZnS nanoparticles with different concentration of capping agent.

Sample	Molar concentration of capping agent	Mean crystallite size (nm)	Optical band gap E_g (eV)
ZnS (A)	0.0	2.43	3.98
ZnS (B)	0.01	2.38	4.06
ZnS (C)	0.1	2.20	4.26
ZnS (D)	0.2	1.84	4.34

- *Optical Characterization*

The absorption spectra of the different samples are shown in Fig. 2. The absorption edge is observed in the range of 324–270 nm, which is blue shifted compared to bulk ZnS. As the molar concentration of capping agent increases, the absorption edge shifts to lower wavelength compared to ZnS(A). This blue shift of the absorption edges for different sized Nano crystals is related to the size decrease of particles and is attributed to the quantum confinement limit reaching of

nanoparticles. The quantum confinement effect is expected for semiconducting nanoparticles, and the absorption edge will be shifted to a higher energy when the particle size decreases [19].

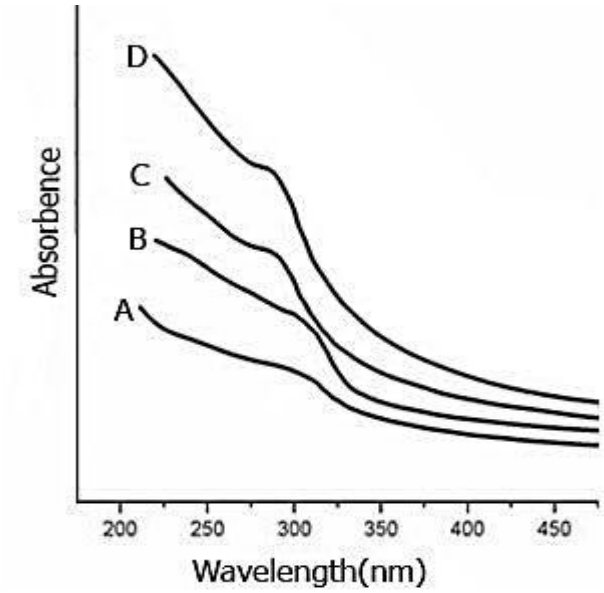

Fig. 2. Absorption spectra of different samples of ZnS nanoparticles: 0 M (A), 0.01 M (B), 0.1 M (C) and 0.2 M (D).

The obtained direct optical band gap values for different samples are shown in Table 1. It is necessary to mention that the optical direct band gap values of the ZnS nanoparticles were determined by Tauc's relation [16]:

$$\alpha h\upsilon = \alpha_0 (h\upsilon - E_g)^{1/2} \quad (2)$$

Where hν, αo and Eg are photon energy, a constant and optical band gap of the nanoparticles, respectively. Absorption coefficient (α) of the powders at different wavelengths can be calculated from the absorption spectra. Finally, the values of E_g were determined by extrapolations of the linear regions of the plot of $(\alpha h\upsilon)^2$ versus $h\upsilon$.

As seen in Table 1, the values of optical band gap 'Eg' increases with the increase in molar concentration capping agent and therefore decrease particles size that as mentioned earlier is due to quantum confinement effect. Also, the variation of optical band gap with particle size is shown in Fig. 3. As illustrated in Fig. 3, the optical band gap values of nanoparticles have changed from 3.98 to 4.34 eV by decreasing the particle sizes. The increase in band gap with increase in molar concentration capping agent is attributed to size quantization effect due to the small size of the particles.

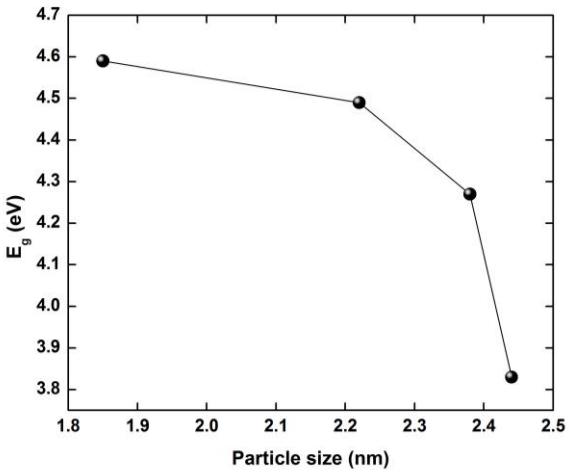

Fig. 3. The variation of optical band gap with particle size.

- *Relation particle size with chemical reaction rate*

Chemical reaction rate directly affects the time evolution of the number of nuclei, which determines both nucleation and growth process. First, the influence on nucleation is obvious: nucleation is faster when the chemical reaction is faster. Second, growth will be strongly influenced by the nuclei number already formed at a given time. A great number of nucleation favours a fast autocatalytic growth, giving rise to a large number of small particles. Chemical reaction controls this kind of growth, being the autocatalytic growth faster as chemical reaction is faster. But in nanoparticles formation, there is another contribution to the growth molecules on the surface of small particle will tend to diffuse through solution and add to the surface of larger particle (growth by ripening). A slow chemical reaction favours continuous nuclei, keeping always a certain number of nuclei in the system. As a result, growth by ripening can take place during the whole process. This fact explains the bigger particle size obtained from a slow reaction. One can conclude that a slow chemical reaction rate is associated with a more important ripening contribution to the growth. A high number of nuclei are still forming at this stage when the reaction is slow at the same time; some particles have already grown to the final value of size. This means that in this case (slow reaction rate), nucleation and growth takes place simultaneously. This overlapping of nucleation and growth processes, which is more pronounced as the chemical reaction is slower, leads to larger nanoparticle sizes [4].

Rate of reaction depends on the molar concentration of reactants solution and increases with the increase in molar concentration of reactants solution. In the present study, the molar concentration of capping agent varies from 0 M to 0.2 M, the reaction rate is highest for 0.2 M solution and hence the

particle size obtained is smallest for 0.2 M solution as compared to other materials in the series, which is in consistent with the above made argument.

IV. CONCLUSIONS

It is possible to produce different size ZnS nanoparticles using a simple chemical method with using different molar concentration of capping agent. XRD and optical band gap data have been obtained to confirm nano-size of these materials. It is also observed that the particle size depends on molar concentration of capping agent. A decrease in formation rate of nanoparticles gives rise to a larger final particle size for all the studied synthesis conditions. As the particle size depends on the molar concentration of doping agent, a decrease in the size of particle is observed with the increase of molar concentration of capping agent. The mean crystallite size range of particles was between 1.84 and 2.43 nm, depending on molar concentration of capping agent. The optical band gap values of ZnS nanoparticles have changed from 3.98 to 4.34 eV by increasing the molar concentration of capping agent. These values exhibit a blue shift in E_g which is related to the size decrease of the particles and to the quantum confinement limit reaching of nanoparticles.

Considering these results, the chemical co-precipitation method using 1-Thioglycerol as a capping agent is very efficient for the preparation of ZnS nanoparticles in order to control the particle size and also for modern optoelectronic technology and other industrial applications.

ACKNOWLEDGEMENT

The authors would like to thank Dr. Aliahmad, Mr. Hossein Rahdar and Mrs. Asoodeh for their support and assistance with this project.

REFERENCES

[1] Alivisatos A P (1996) Semiconductor Clusters, Nanocrystals, and Quantum Dots. *Science* 271, 933-937.

[2] Anderson M A, Gorer S and Penner R M (1997) A Hybrid Electrochemical/Chemical Synthesis of Supported, Luminescent Cadmium Sulfide Nanocrystals, *J. Phys. Chem. B* 101, 5895.

[3] Dios M de, Barroso F, Tojo C, Blanco M C and Lopez-Quintela M A (2005) Effects of the reaction rate on the size control of nanoparticles synthesized in microemulsions. *Colloids and Surfaces A: Physicochem. Eng. Aspects* 83, 270–271.

[4] Godfrey-Alig A R, Akbulut M, Golan Y and Israelachvili J (2006) Forces Between Surfactant Coated ZnS Nanospheres in Dodecane: Effect of Water. *Adv. Funct. Mater.* 16, 2127-2134.

[5] Henshaw G, Parkin I P and Shaw G (1996) Convenient, low-energy synthesis of metal sulfides and selenides; PbE, Ag_2E, ZnE, CdE (E = S, Se). *Chem. Commun.* 10, 1095-1096.

[6] Hirai T, Bando Y and Komasawa I (2002) Immobilization of CdS Nanoparticles Formed in Reverse Micelles onto Alumina Particles and Their Photocatalytic Properties. *J. Phys. Chem. B* 106, 8967-8970.

[7] Landes C F, Braun M, El-Sayed M A (2001) On the Nanoparticle to Molecular Size Transition: Fluorescence Quenching Studies. *J. Phys. Chem. B* 105, 10554–10558.

[8] Liu C M, Zu X T, Wei Q M, Wang L M (2006) Fabrication and characterization of wire-like SnO_2. *J. Phys. D: Appl. Phys*. 39, 2494.

[9] Prabhu RR and Abdul Khadar M (2005) Characterization of chemically synthesized CdS nanoparticles. *Pramana- J. Phys.* 5, 801.

[10] Rahdar A, Asnaasahri Eivari H and Sarhaddi R (2012) Study of structural and optical properties of ZnS:Cr nanoparticles synthesized by co-precipitation method. *Indian Journal of Science and Technology* 5, 1855-1858.

[11] Rajeswar K, Tacconi N R and Chenthamarakshan C R (2001) Semiconductor-Based Composite Materials: Preparation, Properties, and Performance. *Chem. Mater.* 13, 2765.

[12] Rossetti R, Ellison J L, Gibson J M and Brus L E (1984) Size effects in the excited electronic states of small colloidal CdS crystallites *J. Chem Phys*. 80, 4464.

[13] Sang W, Qian Y, Min J, Li D, Wang L, Shi W and Liu Yi (2002) Microstructural and optical properties of ZnS:Cu nanocrystals prepared by an ion complex transformation method. *Solid State Commun.* 121, 475-478.

[14] Scherrer P (1918) Bestimmung der Grösse und der inneren Struktur von Kolloidteilchen mittels Röntgenstrahlen. *Nachr. Ges. Wiss. Göttingen* 26, 98-100.

[15] Tauc J, (1966) Optical Properties of Solids *Academic Press Inc*, New York.

[16] Wageh S, Ling Z S and Xu-Rong Xu (2003) Growth and optical properties of colloidal ZnS nanoparticles. *J. Cryst. Growth* 255, 332-337.

[17] Zhai Q, Li J, Lewis J S, Waldrip K A, Jones K, Holloway P.H, Davidson Ma and Evans. N (2002) Microstructure and electroluminescence of ZnS:Mn doped with KCl. *Thin Solid Films* 414, 105-112.

[18] Zhu H, Yang D, Yu G, Zhang H and Yao K (2006) A simple hydrothermal route for synthesizing SnO_2 quantum dots. *Nanotechnology* 17, 2386.