International Journal of Mechanical, Industrial and Aerospace Sciences
ISSN: 2517-9950
Vol:6, No:1, 2012

Study of Electro-Optical Properties of ZnS Nanoparticles Prepared by Colloidal Particles Method

A. Rahdar, V. Arbabi, and H. Ghanbari

***Abstract*—**ZnS nanoparticles of different size have been synthesized using a colloidal particles method. Zns nanoparticles prepared with capping agent (mercaptoethanol) then were characterized using X-ray diffraction (XRD) and UV-Vis spectroscopy. The particle size of the nanoparticles calculated from the XRD patterns has been found in the range 1.85-2.44nm. Absorption spectra have been obtained using UV-Vis spectrophotometer to find the optical band gap and the obtained values have been founded to being range 3.83-4.59eV. It was also found that energy band gap increase with the increase in molar capping agent solution.

***Keywords*—**ZnS, Nanoparticle, X-ray.

I. Introduction

DURING the past two decades, the "small-particle" research has become quite popular in various fields of chemistry and physics. The ''small-particles'' now we call nanostructured materials, are very interesting materials both for scientific reason and practical application.

Semiconductor nanocrystals 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 which originating from quantum confinement effect [1–4]. Quantum confinement effect modifies the electronic structure of the nanocrystals when the sizes of the nanoparticles are comparable to that of Bohr excitonic radius of those materials. When the particle radius falls below the excitonic Bohr radius, the band gap energy is widened, leading to a blue shift in the band gap, emission spectra etc. On the other hand, the surface states will play a more important role in the nanoparticles, due to their large surface-to-volume ratio with a decrease in particle size (surface effects). 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.

A. Rahdar, Department of Physics, Faculty of Science, University of Zabol, Zabol, Iran (nano1358@yahoo.com).
V. Arbabi, Departement of Mechanical Engineering, University of Zabol, Zabol, Iran (v.arbabi@gmail.com).
H. Ghanbari, Department of Mechanical Engineering, Firoozkooh Branch, Islamic Azad University, Firoozkooh, Iran (ghanbari@iaufb.ac.ir).

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 [5-9].

Wide band gap II–VI semiconductors are expected to be the novel materials for the optoelectronic devices. ZnS, which is an important member of this family, has been extensively investigated as it has numerous applications to its credit. ZnS has been used widely as an important phosphor 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 finds use as light emitting diode, reflector, dielectric filter and window material [10].

Keeping in view the above discussion, an effort has been made to study the optical properties of ZnS nanoparticles of different molar capping agent solution.

The synthesis of ZnS 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. In the present paper, chemical method has been used to synthesize the ZnS nanoparticles. Till now, many studies on nanoparticles have focused on the synthesis of different nanoparticle assemblies with different capping agents [11–13]. In the present paper, ZnS nanoparticles are synthesized by using mercaptoethanol as capping agent.

II. Experimental Detail

Samples of nanoparticles have been prepared by chemical method using zinc chloride and sodium sulfate as a starting materials and mercaptoethanol as a capping agent. ZnCl2 was dissolved in distilled water with 0.1 molar concentrations and so obtained molar solution was stirred continuously for 20 minutes. Na_2S was dissolved in distilled water with 0.1 molar concentration and so obtained molar solution, too. The white precipitate of the ZnS nanoparticles is formed slowly in the solution. The obtained precipitate was then filtered and dried at room temperature. After sufficient drying, the precipitate was crushed to fine powder with the help of mortar and pestle. The synthesis has done under passing the nitrogen gas.

III. Result and Discussion

A. Structural Characterization

ZnS nanoparticles were prepared through the reaction of ZnCl2 and Na_2S as discussed in the experimental details. Different sample of nanoparticles has been obtained by changing the molar concentration of capping agent. The structures of the so-prepared nanoparticles of different sizes namely ZnS (A), ZnS (B), ZnS (C) and ZnS (D) have been studied at room temperature using the X-ray diffractometer. The samples differ only in the amount of molar concentration of capping agent used in the preparation. In the case of ZnS (A), ZnS (B), ZnS (C) and ZnS (D), capping agent used is 0 M, 0.1 M, 0.3 M and 0.5 M respectively.

Fig. 1 shows the XRD patterns of ZnS nanoparticles showing reflections from (111), (200) and (311) planes, indicating the formation of ZnS nanoparticles having hexagonal structure with cell parameters a=3.800Å and c=6.230Å. The peak broadening in the XRD patterns clearly indicates the formation of ZnS nanocrystal with very small size (1.85-2.44nm).

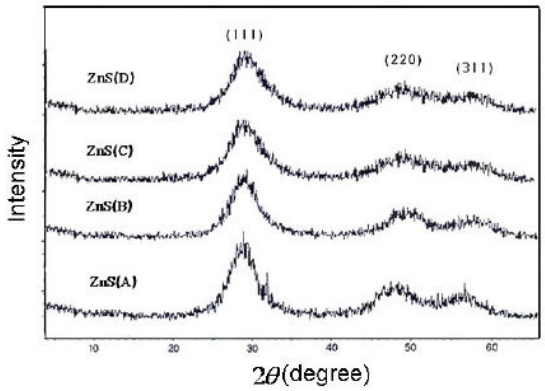

Fig. 1 XRD patterns of ZnS nanoparticles with different capping agent molar

The peak broadening at lower angle is more meaningful for the calculation of particle size, therefore size of nanocrystals has been calculated using Debye-Scherrer formula [14] using (111)reflection from the XRD pattern. Debye-Scherrer formula for crystallite size determination is given by:

$$D = \frac{0.94\lambda}{\beta \cos\theta} \tag{1}$$

Where D is the crystallite size, λ is the wavelength of x-ray, β is the full width at half maximum (FWHM) after correcting the instrument peak broadening (β expressed in radians), and θ is the Bragg's angle. The values of particle size obtained from XRD for different molar agent capping are listed in Table I.From Table I, it is clear that the particle size decreases when increase molar of capping agent.

B. Optical Absorption

The optical absorption spectra of the nanocrystallites were measured using a USB-2000 UV-Vis spectrophotometer. The nanocryatallites powder has 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. Fig. 2 shows the absorption spectra of these samples.

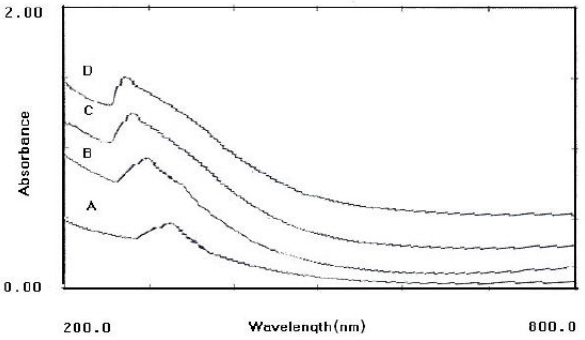

Fig. 2 Absorption spectra of different samples of ZnS nanoparticles

It is clear from Fig. 2 that all four samples exhibit absorption edges decreased with increasing of molar concentration of capping agent that cause to decreased particle size. This blue shift of the absorption edges for different sized nanocrystals arises from quantum confinement effect in the nanoparticles.

The fundamental absorption, which corresponds to electron excitation from the valence band to conduction band, can be used to determine the value of the optical band gap. The relation between the absorption coefficient (α) and the incident photon energy (hν) can be written as [15]:

$$(\alpha h\nu) = A(h\nu - E_g)^n \tag{2}$$

Where, A is a constant, E_g is the band gap of the material and exponent depends on the type of transition [16]. Here, the transitions are direct so we take n=1/2.

The value of optical band gap is calculated by extrapolating the straight line portion of (αhν) 2 vs hν graph (Fig.3) to hν axis. The obtained band gap values for different samples are shown in Table I.

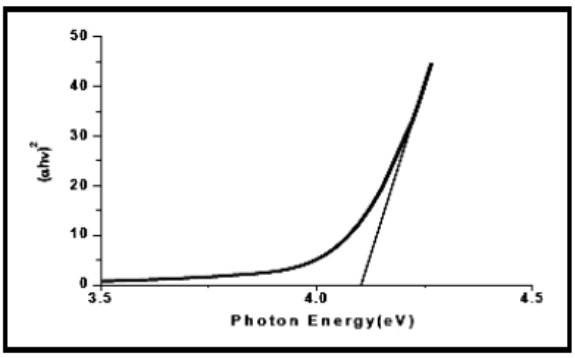

Fig. 3 band gap determination of ZnS (A)

From Table I, it is clear that the values of optical band gap 'E_g' increases with the increase in molar concentration of capping agent and therefore decrease particles size. The

variation of particle size with the optical band gap is shown in Fig. 4.

TABLE I
PARTICLE SIZE AND BAND GAP VARIATION WITH MOLAR CAPPING AGENT

Sample	Molar concentration of Capping agent	Particles size(nm)	Energy band gap E_g (eV)
ZnS(A)	0.0	2.44	3.83
ZnS(B)	0.1	2.38	4.27
ZnS(C)	0.3	2.22	4.49
ZnS(D)	0.5	1.85	4.59

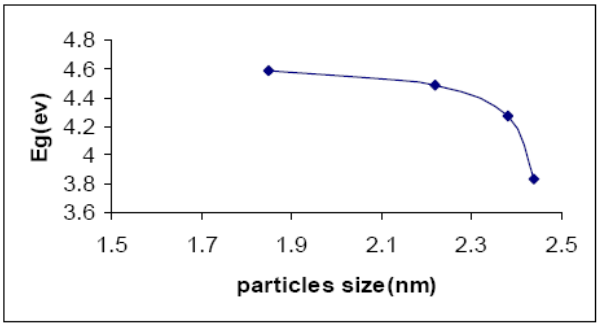

Fig. 4 The variation of particle size with the optical band gap

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 nuclei favor 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 nanoparticle 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 favors 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 [17].

IV. Conclusion

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. Chemical reaction rate affects both nucleation and growth process. It has been shown that nucleation and growth take place simultaneously when the chemical reaction is slow. In addition, the ripening contribution to the growth is larger as the chemical reaction is slower. As the particle size depends upon the molar concentration of capping agent, a decrease in the size of particle is observed with the increase of molar concentration of capping agent.

Acknowledgment

Authors would also like to thank Mr. Aliahmad, Mr. Davarpanah, Ms. Heidari Mokarrar for help in various way.

References

[1] Rossetti.R, Ellison.J.L, Gibson.J.M, Brus.L.E, (1984) J.ChemPhys. 80, 4464.
[2] Sang.W, Qian.Yo, Min.J, Li.Do, Wang.L, Shi.W, Liu.Yi, (2002) "Solid State Commun", 475.
[3] Prabhu.R.R, Abdul Khadar. M, (2005)Pramana 5, 801.
[4] Wageh. S, Ling .Z.S, Xu-Rong. X, (2003) J.Cryst. Growth 255, 332.
[5] Rajeswar.K, Tacconi.N.R.de, Chenthamarakshan.C R, (2001) Chem. Mater. 13, 2765.
[6] Alivisatos.A. P, (1996)Science 271, 933.
[7] Anderson.M.A, Gorer .S, Penner.R.M, (1997) J. Phys. Chem. B 101, 5895.
[8] Henshaw .G, Parkin.I. P, Shaw .G, Chem Soc J, (1996) Chem.Commun. 58, 1095 ,110.
[9] Hirai. T, Bando.Y, Komasawa. I, (2002) J. Phys. Chem. B 106, 8967.