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STRUCTURAL AND OPTICAL CHARCTERIZATION OF CHEMICALLY SYNTHESIZED ZnS NANOPARTICLES

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ZnS nanoparticles of different sizes have been synthesized using a simple chemical method. So-prepared ZnS nanoparticles were then characterized using X-ray diffraction and UV-Vis optical absorption spectra. The particle size of the nanoparticles calculated from the XRD patterns has been found in the range 2.2-3.2 nm. Absorption spectras have been obtained using UV-Vis spectrophotometer to find the optical band gap and the obtained values have been found to be in the range 3.8-4.1 eV. It was also found that energy band gap (E_g) increases with the increase in molar concentration of reactant solution.

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1. 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 and have attracted much attention over the past few years because of their novel properties 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. 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)

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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 sizes. 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 without using any capping agent.

2. Experimental details

Samples of different sized nanoparticles have been prepared by chemical method using zinc chloride and thiourea. $ZnCl_2$ was dissolved in distilled water with different molar concentration and so obtained molar solution was stirred continuously for 20 minutes. H_2S produced by heating the thiourea is then passed through the stirred solution. 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.

3. Results and discussion

3.1 Structural Characterization

ZnS nanoparticles were prepared through the reaction of $ZnCl_2$ and H_2S as discussed in the experimental details. Different sizes of nanoparticles has been obtained by changing the molar concentration of the parent solution of $ZnCl_2$. 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 parent solution used in the preparation. In the case of ZnS (A) , ZnS (B), ZnS (C) and ZnS (D), the molar concentrations used is 1.0 M, 0.8 M, 0.6 M and 0.4 M respectively. Fig.1 shows the XRD patterns of ZnS nanoparticles showing reflections from (002), (110) and (200) planes , indicating the formation of ZnS nanoparticles having hexagonal structure with cell parameters a=3.800 and c=6.230. The peak broadening in the XRD patterns clearly indicates the formation of ZnS nanocrystal of very small size.

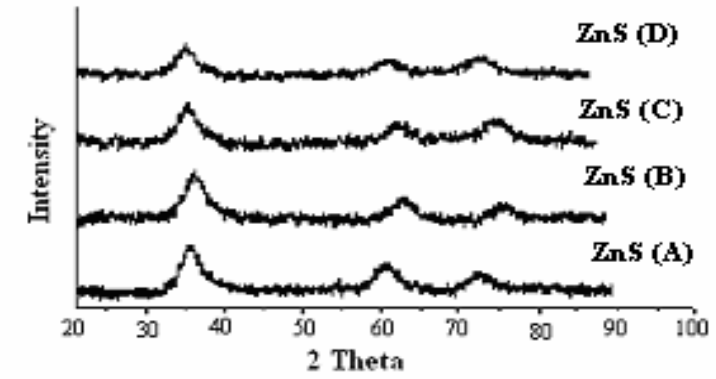


Fig. 1. XRD patterns of ZnS nanoparticles of different sizes.

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 (002) reflection from the XRD pattern. Debye-Scherrer formula for crystallite size determination is given by:

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

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), θ is the Bragg's angle. The values of particle size obtained from XRD for different molar concentrations are listed in **Table 1.**

From Table 1, it is clear that the partcle size decreases with the increase of molar concentration of parent solution $ZnCl_2$.

3.2 Optical Absorption

The optical absorption spectra of the nanocryatallites 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 300 to 600 nm.. Fig. 2 shows the absorption spectra of these samples.

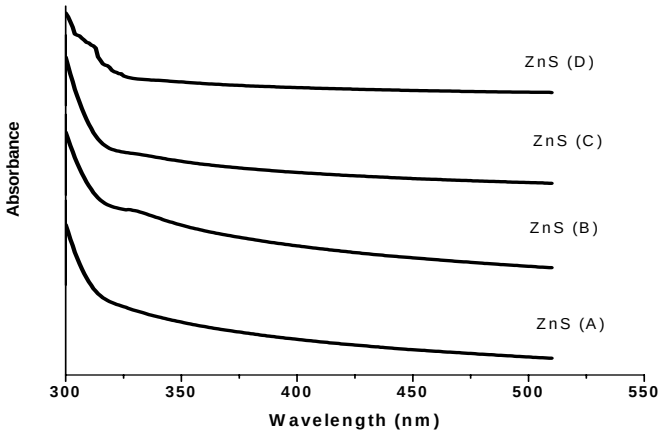


Fig. 2. Absorption spectra of different samples of ZnS nanoparticles.

It is clear from Fig. 2 that all four samples exhibit absorption edges which are blue- shifted with decreasing 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 cofficient (α) and the incident photon energy ($h\nu$) can be written as [15]:

$$(\alpha h\nu) = A\,(h\nu - E_g)^n$$

where, A is a constant, E_g is the band gap of the material and exponent n 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 $(\alpha h\nu)^2$ vs $h\nu$ graph (Fig.3) to $h\nu$ axis . The obtained band gap values for different samples are shown in Table 1.

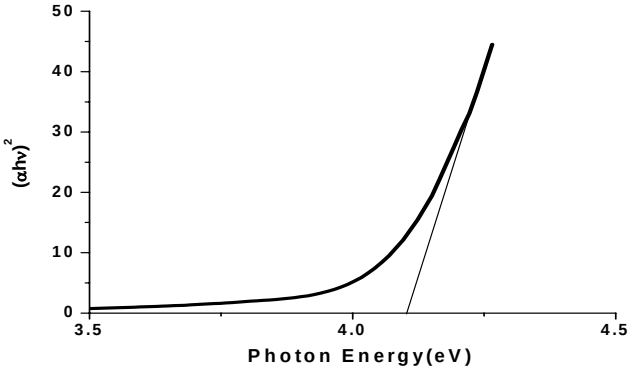


Fig.3. band gap determination of ZnS (A).

Table 1. Particle size and band gap variation with molar concentration.

Sample	**Molar Concentration of reactant solution**	**Radius (r) (nm)**	**Energy Band Gap (E_g) (eV)**
ZnS (A)	1.0	2.2	4.10
ZnS(B)	0.8	2.5	3.98
ZnS (C)	0.6	2.9	3.85
ZnS (D)	0.4	3.2	3.80

From Table 1, it is clear that the values of optical band gap 'E_g' increases with the increase in molar concentration of parent solution $ZnCl_2$. The variation of particle size with the optical band gap is shown in Fig. 4.

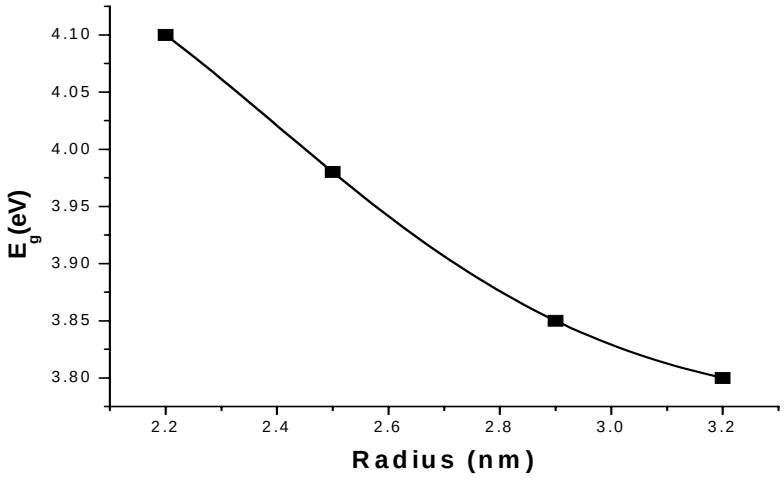


Fig. 4. The variation of particle size with the optical band gap.

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 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 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 favours a 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. 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]. 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 reactants solution varies from 0.4 M to 1.0 M, the reaction rate is highest for 1 M solution and hence the particle size obtained is smallest for 1 M solution as compared to other materials in the series, which is in accordance with the above made argument.

4. Conclusions

It is possible to produce different sized ZnS nanoparticles using a simple chemical method without using a 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 reactant solution. 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 depend upon the molar concentration of reactant solution, a decrease in the size of particle is observed with the increase of molar concentration of reactants.

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References

[1] R. Rossetti, J.L. Ellison, J.M. Gibson, L.E. Brus, J. Chem. Phys. **80,** 4464 (1984).
[2] W. Sang, Yo. Qian, J. Min, Do. Li, L. Wang, W. Shi, Yi. Liu, Solid State Commun. **121**, 475 (2002).
[3] R.R. Prabhu, M. Abdul Khadar, Pramana **5**, 801 (2005).
[4] S. Wageh, Z.S. Ling, X. Xu-Rong, J. Cryst. Growth **255**, 332 (2003).
[5] K. Rajeswar, N R de Tacconi, C R Chenthamarakshan, Chem. Mater. **13**, 2765 (2001).
[6] A. P. Alivisatos Science **271**, 933 (1996).
[7] M. A. Anderson, S. Gorer, R .M. Penner, J. Phys. Chem. B **101**, 5895 (1997).
[8] G. Henshaw, I. P. Parkin , G Shaw, J. Chem. Soc., Chem.Commun. **58,** 1095 (1996)

[9] T. Hirai, Y. Bando, I. Komasawa , J. Phys. Chem. B **106**, 8967 (2002).
[10] Q. Zhai, J. Li, J.S. Lewis, K.A. Waldrip, K. Jones, P.H. Holloway, M. Davidson, N. Evans, Thin Sold Films **414**, 105 (2002).
[11] C. F. Landes, M. Braun, M. A. El-Sayed, J. Phys. Chem. B **105**, 10 554 (2001).
[12] Y. Golan, C. Drummond, M. Homyonfer, Y. Feldman, R. Tenne, J. Israelachvili, Adv. Mater., **11**, 934 (1999).
[13] C. B. Murray, C. R. Kagan, M. G. Bawendi, Annu. Rev. Mater. Sci. **30**, 545 (2000).
[14] A. Guinier, X-ray Diffraction, San Francisco, CA, (1963).
[15] J.Tauc , Amorphous and Liquid semiconductors , J Tauc Edi, New York, Plenum, (1974).
[16] G. P. Joshi, N.S. Saxena, T.P. Sharma V. Dixit and S.C. K Mishra, Ind. J. Pure . Appl. Phys **41**, 462 (2003).
[17] M. de Dios , F. Barroso, C. Tojo, M.C. Blanco, M.A. L´opez-Quintela, Colloids and Surfaces A: Physicochem. Eng. Aspects **270–271** 83 (2005).