

Effect of Capping Agent Concentration on Photophysical Properties of Zinc Sulfide Nanocrystals

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Abstract: Zinc Sulfide (ZnS) nanoparticles with varying concentration of capping agent were prepared using chemical technique. These particles were characterized using scanning electron microscope (SEM), atomic force microscope (AFM) and x-ray diffraction (XRD). It is observed that particle size decreases with increasing capping agent concentration. Optical absorption studies show that the absorption edge shifts towards blue region as the capping agent concentration is increased indicating that effective band gap energy increases with decreasing the particle size. Using the effective mass approximation model the particle size of nanoparticles has been estimated from the increased band gap, which is practically the same as obtained by XRD. Photoluminescence (PL) investigations show that ZnS samples give single peak with stoke shift. PL emission peak is obtained at 460 nm for uncapped nanoparticles. The PL spectra of ZnS nanoparticles with different capping agent concentration reveals that the emission becomes more intensive and shifts towards blue as the size of the particles is reduced.

INTRODUCTION

Semiconductor nanocrystals have attracted growing interest during the last four decades [1,2]. This class of new materials has not only provided many unique opportunities but also exhibited novel optical and transport properties, which are potentially useful for technological applications [3] like indicators, analysis of water pollution, environmental studies, pathological investigations etc. Blue shift in the optical absorption spectrum, size dependent luminescence, enhance oscillator strength, non-linear optical effects, geometrical structure, chemical bonds, ionization potential, mechanical strength, melting point etc. are all affected by particle size. The change in the properties of nanoparticles is driven mainly by two factors, namely the increase in the surface to volume ratio and change in the electronic structure of the material due to quantum confinement effects.

Zinc sulfide is well-studied material due to its luminescence characteristics among other interesting properties. With a good surface modification, one can obtain zinc sulfide nanoparticles, which have enhanced luminescence properties. In this work zinc sulfide nanocrystals are prepared by chemical precipitation technique and mercaptoethanol has been used for capping, which modifies surface of nanoparticles and prevents the growth of the particles to larger size. The effect of concentration of mercaptoethanol on the particle size, optical absorption and PL spectrum has been investigated.

MATERIALS AND METHODOLOGY

(a) Synthesis of ZnS nanoparticles

The free standing ZnS nanoparticles were synthesized using chemical precipitation technique described by Herron *et al.* [4]. For synthesis, the 0.01M aqueous solution of $ZnCl_2$ and 0.01M aqueous solution of Na_2S were mixed in the presence of various concentration of mercaptoethanol solution while stirring the solution continuously. The obtained precipitate was washed three times in double distilled water and then separated by centrifuge at 3500 rpm, and finally air-dried. Five different samples ZnS-I, ZnS-II, ZnS-III, ZnS-IV and ZnS-V were prepared by changing the capping agent concentration 0 M, .005 M, .01M, .015 M and .02 M respectively.

(b) Characterizations

All the samples were characterized at Inter University Consortium (IUC) Indore by Scanning Electron Microscope (SEM), Atomic Force Microscope (AFM) and X-ray Diffraction (XRD). JSM – 5600 LV was used for SEM and DIAFM-4 for AFM studies. X-ray diffraction patterns have been obtained by Rigaku Rotating Anode (H-3R) diffractometer with irradiation from K_{α} line of copper ($\lambda=1.5418 \text{ \AA}$). The particle size was calculated using the Debye-Scherrer formula.

(c) Photophysical Properties

Absorption and photoluminescence of the samples prepared with various concentrations of capping agent were studied. Perkin Elimer λ -12 spectrometer was used to obtain the absorption spectra of ZnS nanoparticles. The luminescence was excited by 250 nm radiation using a UV lamp and

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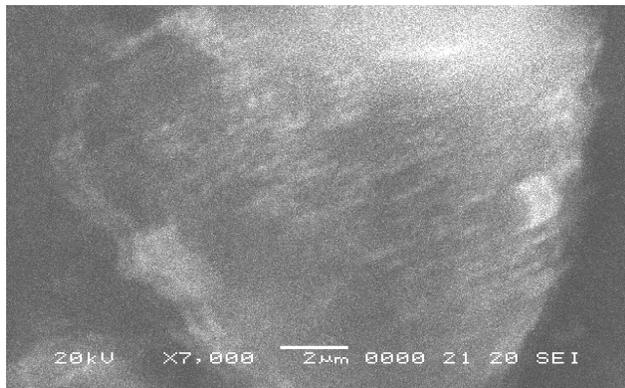


Fig. (1). SEM image of ZnS nanoparticles.

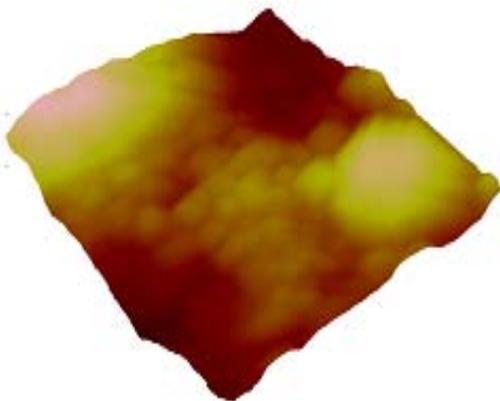


Fig. (2). AFM image of ZnS nanoparticles.

filter. The intensity of emitted light at different wevelengths was measured using monochromator (HM-104) and photomultiplier tube (RCA-931). A model is proposed to explain the size dependence of the PL of these nanocrystals.

RESULTS AND DISCUSSION

A typical SEM image of ZnS nanoparticles is shown in Fig. (1). The particle sizes obtained from SEM images are found to be in the range of 13 nm to 54 nm and these are given in column 5 of Table I. It is observed that small particles are obtained as the capping agent concentration is increased. Similar results are observed by AFM also. Fig. (2) shows a typical AFM image and the particles sizes obtained by AFM are given in column 6 of Table I. By AFM the particle sizes are obtained in the range of 27 nm to 50 nm.

The XRD patterns for the samples are shown in Fig. (3). Three different peaks are obtained at 2θ values of 29.5°, 49° and 57.8°. This shows that the samples have zinc blende structure and the peaks correspond to diffraction at (111), (220) and (311) planes respectively [8]. The lattice parameter has been computed as 5.34 Å, which is very close to the standard value (5.42 Å). From the Fig. (3) it is also seen that peaks are broadened for higher concentration of capping agent. The broadening of peaks indicates nanocrystalline behavior of the particles. The size of the particles has been computed from the width of first peak using Debye Scherrer formula [5].

$$D = \frac{K\lambda}{\beta \cos\theta} \dots(1)$$

where K is constant, λ is the wavelength of X-rays, β is the full width at half maximum and θ is Bragg angle. The particle sizes obtained from XRD are of the order of 2-3 nm and given in column 7 of the Table I. From the Table I, it is clearly seen that the particle size is decreasing with increasing capping agent concentration. The size obtained by SEM and AFM are of the order of few tens of nm whereas by XRD these are only of a few nm order. The discrepancy associated with size of ZnS nanoparticles may be because of the fact that SEM and AFM shows the lateral dimension of the particles whereas XRD gives the regularity in the atomic arrangement. Perhaps the lateral dimension (including the

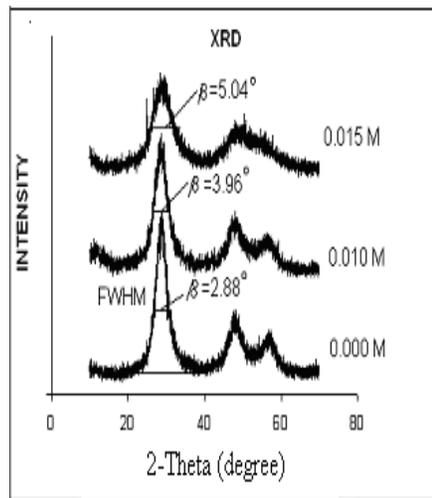


Fig. (3). XRD pattern of ZnS nanoparticles.

Table I. Size of ZnS Nanocrystals by Various Techniques

S.N.	Sample	Capping Agent Conc. (in Mol.)	Effective Band Gap (in eV)	Size by (in nm)			
				SEM	AFM	XRD	EMA
1.	ZnS-I	0.000	4.76	54	50	2.87	2.4
2.	ZnS-II	0.005	4.96	-	44	-	2.2
3.	ZnS-II	0.001	5.16	-	37	-	2.08
4.	ZnS-IV	0.015	5.39	36	35	2.08	1.9
5.	ZnS-V	0.02	5.63	13	27	1.63	1.78

capping agent also may be agglomeration of the nanoparticles) is of the order of a few tens of nm, but the individual nanoparticle with regular atomic lattice extends only up to a few nm. In nanomaterials, binding energy per atom decreases with decreasing particle size, which would result in non-spherical geometry of the particles, which may cause the difference in the particle size determined by different methods.

The study of optical absorption is important to understand the behavior of semiconductor nanocrystals. A fundamental property of semiconductors is the band gap—the energy separation between the filled valence band and the empty conduction band. Optical excitation of electrons across the band gap is strongly allowed, producing an abrupt increase in absorption at the wavelength corresponding to the band gap energy. This feature in the optical spectrum is known as the optical absorption edge. Fig. (4) shows the optical absorption spectra of ZnS nanoparticles in the range of 800 nm–200 nm. It can be seen that the spectra are featureless and no absorption occur in visible region (800 nm–390 nm). Absorption edge was obtained at shorter wavelength in UV region at 260 nm, 250 nm, 240 nm, 230 nm and 220 nm for ZnS-I, ZnS-II, ZnS-III, ZnS-IV and ZnS-V samples respectively. This clearly shows that the absorption edge shift towards shorter wavelengths as the capping agent concentration is increased. The observed blue shift in the absorption edge is reflection of the band gap increase owing to quantum confinement effect. In the bulk material the band gap can be found from the graph between $(\alpha h\nu)^2$ vs $h\nu$, whereas in the nanomaterials the band gap is obtained from

$$\Delta E = \frac{\hbar^2 \pi^2}{2r^2} \left[\frac{1}{m_e^*} + \frac{1}{m_h^*} \right] - \frac{1.786 e^2}{\epsilon r} - \frac{0.124 e^4}{\hbar^2 \epsilon^2} \left[\frac{1}{m_e^*} + \frac{1}{m_h^*} \right]^{-1} \quad \dots(2)$$

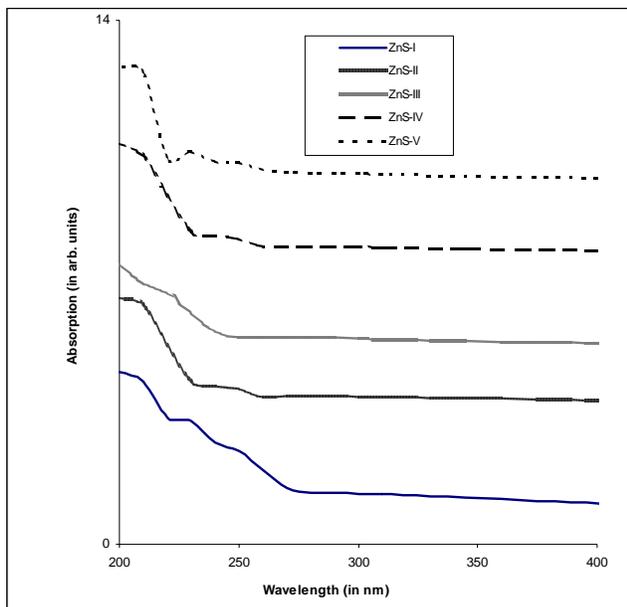


Fig. (4). Absorption Spectra of ZnS nanoparticles.

nanomaterials the band gap is obtained from the absorption maxima. In our samples absorption peak was not obtained. The absorption edge was found at shorter wavelength. The band gap energy of the samples corresponding to the absorption edge is found to 4.76 eV, 4.96 eV, 5.16eV, 5.39 eV and 5.63 eV, respectively with increasing the capping agent concentration. It is observed that no optical absorption occurs at surface states and therefore these do not affect to the absorption spectra. Only the widening of the band gap is indicated. Similar results are reported by Kumbhojkar *et al.* [6] on mercaptoethanol capped ZnS nano-particles. They have obtained a broad featureless and small absorption peak at 280 nm (4.4eV) Martinez *et al.* [7] have studied absorption spectra of CdS nanoparticles. They have not obtained any peak. Band gap computed from absorption edge has been reported as 2.57 eV. Mahamuni *et al.* [8] have obtained absorption peak at 238 nm (5.2eV) and 258 nm (4.8eV) for ZnS nanoparticles of size 7Å and 23Å respectively, but no peak was observed for a particle size of 23 Å. This result is in agreement with our results.

Some theoretical models have been proposed [9,10], relating the effective band gap of material with the particle size. The simple model predicting the variation of exciton energy with particle size is based on the effective mass approximation (EMA). The lowest excited state of the crystallite is assumed to be the ground state of an electron hole pair. The ground state energy of exciton or the increase in effective band gap as a function of crystalline size is estimated as [9].

Where m_e^* and m_h^* are the effective mass of the electrons and holes respectively, r is the radius of the particles and ϵ is the dielectric constant of the semiconductor. In this equation first term is the kinetic energy of the electrons and holes, the second is their Coulomb attraction and the last term corresponds to the correlation between the two particles. The second and third terms are much smaller than the first term therefore they can be neglected. Thus equation may be expressed as

$$\Delta E = \frac{\hbar^2 \pi^2}{2r^2} \left[\frac{1}{m_e^*} + \frac{1}{m_h^*} \right] \quad \dots(3)$$

The value of effective mass of electrons and holes for ZnS are $0.41m_e$ and $0.61m_e$ [11]. The particle size from this model is given column 8 in Table 1. It is seen that particle size estimated from absorption edge is of the same order as that obtained from broadening of XRD peaks. Increase in band gap corresponds to the smallest dimension of the nanocrystals, whereas XRD corresponds to average size. Nearly same values of particle size by effective band gap and XRD reveal that nanoparticles are spherical in nature. The

variation of particle size with capping agent concentration is shown in Fig. (5).

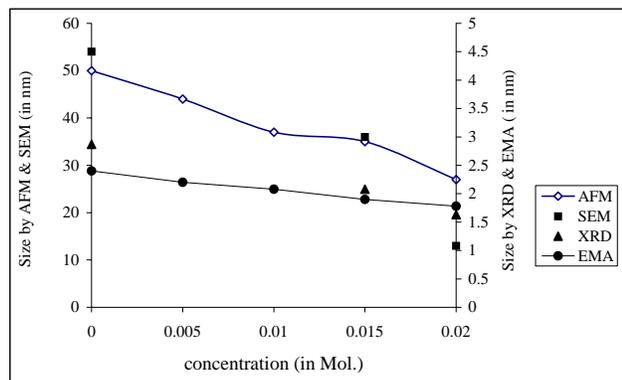


Fig. (5). Graph between capping agent concentration and Particle size.

Luminescence studies provide information regarding defect states, which take part in radiative de-excitation of the sample. In nanocrystals, the defect states may shift or the density may increase which is revealed by PL studies. Fig. (6) shows the luminescence spectra of ZnS-I, ZnS-II, ZnS-III, ZnS-IV and ZnS-V samples in the range 800 nm-200 nm prepared with various capping agent concentrations. It can be seen from the figure that only one Stoke-shifted PL peak is obtained at 460 nm, 440 nm, 430 nm, 420 nm and 390 nm for ZnS-I, ZnS-II, ZnS-III, ZnS-IV and ZnS-V samples respectively. The PL emission is at longer wavelength as compared to the excitation wavelength (250 nm). This indicates involvement of impurity or surface states in the PL phenomenon. The PL spectra of ZnS nanoparticles with different capping agent concentration reveals that the emission becomes more intensive and shifts towards smaller wavelength as the size of the particles is reduced. PL emission peak is obtained at 460 nm for uncapped nanoparticles. The peak shifts towards shorter wavelength as the capping agent concentration is increased. Fig. (7) shows the variation of PL intensity and wavelength of PL peaks with the capping agent concentration.

The luminescence mechanism can be understood from the energy level diagram shown in Fig. (8). The energy states within the band gap in the nanocrystals are produced due to surface states or Zn^{2+} or S^{2-} ions. Photons of higher energy (4.9eV) excites the electrons from the valance band (VB) or Zn^{2+} levels, which reaches the conduction band (CB). The excited electrons decay non-radiatively to surface-states and then decay radiatively to valance band and emit a photon of lower energy. When the particle size decreases, the valance band edge shifts downwards. Therefore, the emitted photon has comparatively higher energy giving photoluminescence peak at shorter wavelength.

In ZnS nanoparticles, a large fraction of total number of atoms resides on the surface. The SH group of mercaptoethenol dissociates and organic group gets attached to Zn ions. Thus, the organic legends are instrumental in removing Zn dangling orbitals from the gap. The sp^3 hybridized orbital of surface S atoms dangle out of the crystal surface. More unsaturated S dangling bonds will be present on the surface.

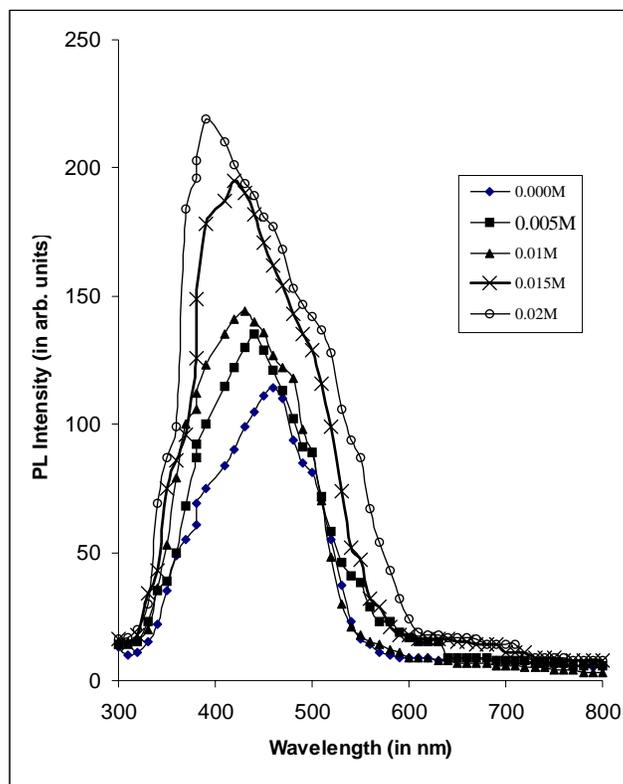


Fig. (6). PL spectra of ZnS nanoparticles.

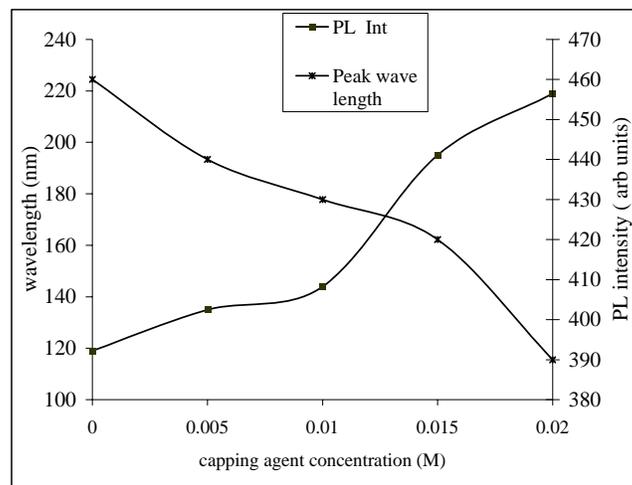


Fig. (7). Graph between PL peak intensity and their corresponding wavelength for various concentration of capping agent concentration.

Hence, the legend-terminated surfaces often show deep hole traps. Therefore, at excitation energy as high as 4.7 eV will preferentially luminescence. These observations indicate that the PL peak obtained at shorter wavelength with reducing the particle size is due to hole traps, originating from unsaturated sp^3 orbital of surface S atoms. It is to be noted that PL peak is obtained in uncapped particles, which indicates intrinsic nature of the peak. Similar results are obtained by

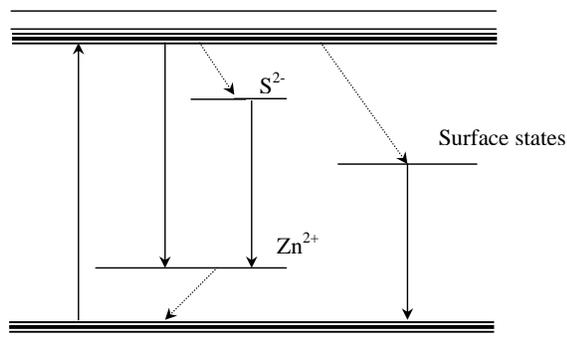


Fig. (8). Band gap diagram of nanoparticles.

Biswas *et al.* [12] and Chen *et al.* [13] Biswas *et al.* have found PL peak at 400 nm. Chen *et al.* have compared the results with that of bulk. They obtained PL emission at 400 nm for ZnS nanoparticles where as 450 nm for bulk ZnS. We have also obtained the PL peak at 460 nm for uncapped ZnS nanoparticles, which has shifted up to 370 nm as capping concentration is increased. Similar results are obtained by Yang *et al.* [14]. They have observed blue emission centered at 440 nm-450 nm for undoped ZnS nanocrystals. Though the many workers have studied the PL of capped as well as uncapped ZnS nanoparticles, but none has reported the effect of capping agent concentration. Our study of PL of ZnS nanoparticles at different capping agent concentrations has shown that blue shift in PL peak is linear up to 0.01 M mercaptoethanol concentration, but above 0.015M concentration, there is fast decrease in PL peak wavelength and particle size. The PL intensity increase rapidly as mercaptoethanol concentration is increases from 0.01 to 0.015M.

CONCLUSION

The studies have revealed that capping agent restricts the growth of crystals and by increasing its concentration, smaller crystals can be obtained. Nanoparticles with a narrow size distribution can be obtained by controlling the capping agent concentration. The size of crystals decreases almost linearly with the capping agent concentration. It is found that SEM and AFM see the agglomeration of nanocrystals and therefore larger size is observed whereas XRD give the extent to which regular arrangement of atoms exists and hence gives the average crystal size. Absorption spectra

is related to the effective band gap of crystals and therefore corresponds to the smallest dimension of the crystals. Nearly equal size of nanocrystals from XRD and absorption spectra show that the crystals are spherical. The results may be improved by crushing the samples before taking the SEM or AFM micrographs in order to avoid agglomeration. SEM with higher resolution is required for better results. In ideal case, all the techniques should give approximately the same particle size. Photoluminescence indicate Stoke-shifted emission with increased intensity and blue shift in the PL spectra by decreasing the particle size. This can be attributed to radiative recombination of excited electrons from surface states to holes in valence band. Density of surface states increases by decreasing the size, thus increasing the intensity and blue shift in PL peak is due to downward shifting of valence band edge. Further studies are needed to optimize the capping agent concentration for best performance. Such highly luminescent nanophosphors with tailorable spectrum and fast decay may find applications in various devices.

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