

STRUCTURAL AND OPTICAL PROPERTIES OF ZnS NANOPARTICLES

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In this work we report on the growth of ZnS semiconductor nanocrystals embedded in a polymeric matrix (Polyvinyl alcohol) were synthesized by a chemical route. The as-obtained films were characterized by X-ray diffraction (XRD), Transmission electron microscopy (TEM), UV-VIS absorption, and photoluminescence (PL) spectra. X-ray diffraction (XRD) study confirmed the formation of cubic phase of ZnS nanocrystals into the polymer matrix. The particle size variations were achieved by varying the pH in the starting solution. Transmission electron microscopic image as well as XRD studies confirmed the nanometer size particles formation within the polymer matrix. The average particle size was found to lie in the range of 5–7 nm. A UV-VIS optical spectroscopy study was carried out to determine the band gap of the nanocrystalline ZnS thin film and it showed a blue shift with respect to the bulk value. The room temperature photoluminescence spectra of the films showed two peaks centered around 315nm, and 425 nm. We assigned the first peak due to band gap transitions while the latter was due to sulfur vacancy in the films.

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1.Introduction

Nanostructured materials have attracted a great deal of attention in the last few years for their unique characteristics that cannot be obtained from conventional macroscopic materials. Owing to quantum size effects and surface effects, nanoparticles can display novel optical, electronic, magnetic, chemical, and structural properties that might find many important technological applications. An extremely active and prolific field in nanomaterials is finding ways to control size and morphology of the nanoparticles since the properties and applications of the nanoparticles are largely dependent on their size and morphology. The most evident manifestation of properties is the optical light emission in the blue – red spectral region characterized by a blue-shift at smaller crystallite dimensions [1]. Such properties make semiconducting nanostructures suitable for several kinds of applications, from antireflecting coatings [2] to bioelectronics [3] and light emitting devices [4]. In the past decade, II-VI semiconductor nanoparticles attract much attention because of their size-dependent (and thus tunable) photo- and electro- luminescence properties and promising applications in optoelectronics. Among the family of II–VI semiconductors, ZnS [5,6], CdS [7], ZnO [8], CdTe [9], etc. are the foremost candidates because of their favorable electronic and Optical properties for optoelectronic applications. Among those ZnS is a commercially important II–VI semiconductor having a wide optical band gap, rendering it a very attractive material for optical application especially in nanocrystalline form. ZnS can have

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two different crystal structures (zinc blende and wurtzite), both of which have the same band gap energy (3.68 eV) and the direct band structure. ZnS has been used for the cathode ray tube, the field emission display, and the scintillator as one of the most frequently used phosphors [10–12]. In addition, a ZnS crystal laser has been produced using streamer excitation [13], and thin films of ZnS can be used as an active emitting material in such a device, termed the hot electron cold cathode [14]. Optical and luminescent properties of nanocrystalline ZnS prepared in the forms of thin film, powder and colloid using different synthesis techniques such as sputtering [15], co-evaporation [16], wet chemical [17–19], sol-gel [20,21] solid state [22], micro-wave irradiation [23,24], ultrasonic irradiation [25] or synthesis under high-gravity environment [26] were studied in detail. Luminescence measurements were identified as one of the most important techniques to reveal the energy structure and surface states of these particles [17]. Localized trap states inside the band gap were studied [27] in detail to recognize the sub-band gap energy levels. It was found that the defect levels play an important role in determining the luminescence characteristics of the ZnS nanoparticles [28]. In the present work, we report the chemical deposition of ZnS nanoparticles and their characterization by XRD, TEM, SEM, UV-VIS spectrometry and PL spectrometry. The effect of pH on structural, morphological and optical properties of these films is investigated with the objective to optimize the conditions of the deposition process.

2. Experimental

ZnS nanoparticles were synthesized using Polyvinyl alcohol (PVA) as a matrix. PVA being good solute to multiple phase system and it provides uniform gaps that are very close to each other and distributes in the form of array. 5 wt% solution of PVA, ZnCl₂ was added with various concentration (2,3,4 wt%) under a high stirring rate (200rpm) condition using magnetic stirrer. The constant temperature 70°C for 3 hours was maintained during the process of stirring. The sample under preparation was kept for 12 hours for complete dissolution to get a transparent solution. To this solution 2 wt% Na₂S was added till the whole solution appears completely milky. The ZnS nanoparticle containing PVA were casted over glass slides to produce thin film form. The size of the particle is controlled by changing pH value of the whole solution. The chemical reaction occurs as follows



pH controlled the rate of reaction due to the common ion effect. At higher pH the solubility product increases and as a result no formation of ZnS particle is formed.

3. Results and discussion

3.1 XRD measurements

The XRD pattern of prepared sample were taken by Seifert XRD(3003TT) operating at 40KV-30mA. The radiation source used was CuK α ($\lambda=1.542\text{\AA}$) and a Nickel filter was used to block K β radiations. Fig. 1 represent three different spectra of ZnS nanoparticles with variation of pH. The XRD pattern of ZnS₁ contain broad peaks at $2\theta=28.2^\circ$, 46.14° indicating the formation of nanostructure at pH = 1.4 and in ZnS₂ shows broad peaks at $2\theta=28.6^\circ$, 46.3° and ZnS₃ at $2\theta=29^\circ$, 46.7° respectively at pH = 2 and pH = 2.8.

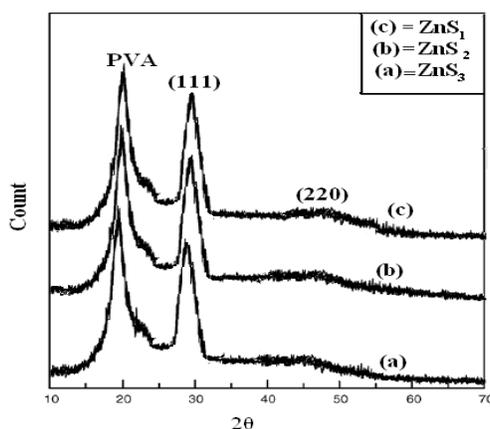


Fig. 1. XRD traces of (a) ZnS_3 (b) ZnS_2 (c) ZnS_1 .

The XRD spectrum of both ZnS_1 , ZnS_2 and ZnS_3 apparently exhibit weak and broad peaks, suggesting small crystallite sizes of Cubic phase (JCPDS card, No. 5-0566). Again it is seen that when pH decreases peaks are more broadened and shifted to higher diffraction angle with decreasing crystal size. The increase in diffraction angle is clearly a result of lattice contraction expected to occur because of higher surface to volume ratio [29]. It is well known that the crystalline PVA has diffraction peak angles at: $2\theta = 19.5^\circ$ and 40.2° [30], while a shallow shoulder was formed corresponding to the amorphous part of the polymer behind the diffraction peak angle at $2\theta = 19.5^\circ$. at all the three samples. The grain size of the crystallite (diameter D) was determined from the full width at half maximum ($\Delta\omega_{2\theta}$) of the (111), (220) and peaks by using the Scherrer formula [31].

$$D = K\lambda / \Delta\omega_{2\theta} \cos\Theta_B \quad (1)$$

Where Θ_B is the Bragg angle and λ is the x-ray wavelength. Here $K=0.89$ for spherical shape (evidence from TEM). For calculation $\Delta\omega_{2\theta}$ is observed by zooming the peak position using origin graphics software. The calculated size is found between 4.9-6.6 nm and also found that when pH increases the crystalline size increases. (Table 1)

Table 1. Particle size calculation from debye sherrer formula

Name of the sample	pH	PVA: $ZnCl_2$	Particle size (nm) (Sherrer formula)
ZnS_1	1.4	5:1	4.9
ZnS_2	2	5:1	5.5
ZnS_3	2.8	5:1	6.6

3.2 Optical measurements

The optical absorption of ZnS_1 , ZnS_2 , and ZnS_3 are shown in Fig. 2. The optical absorbance were recorded at the room temperature using double beam automated spectrophotometers (HITACHI-U3210).

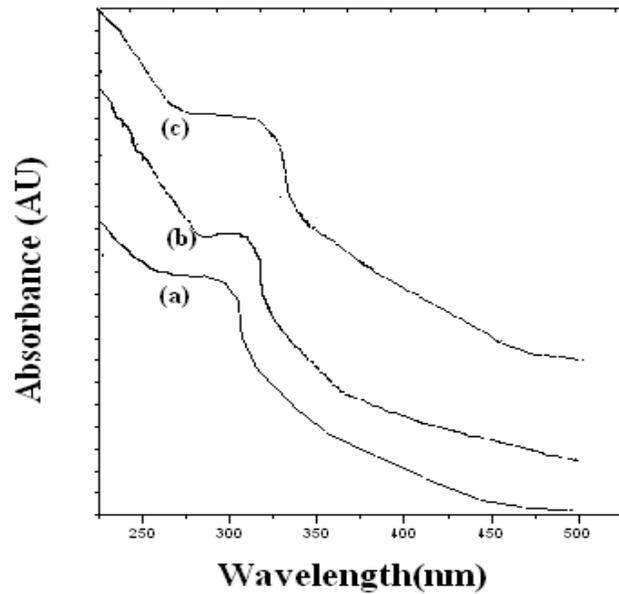


Fig. 2: Absorption Vs wavelength plot of (a) ZnS_1 (b) ZnS_2 (c) ZnS_3 nanoparticles.

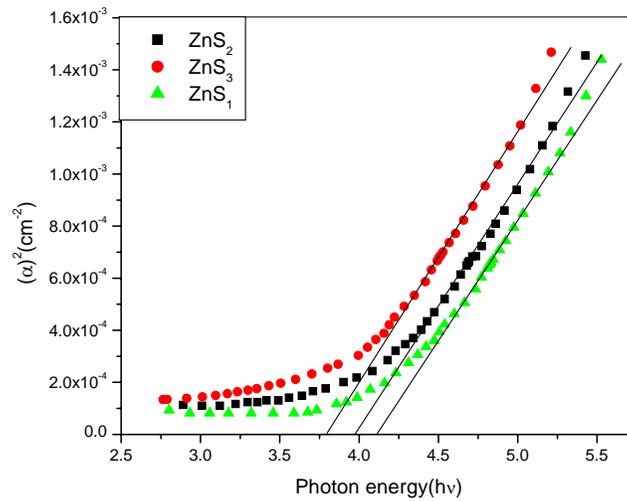


Fig. 3. Plot for the determination of the direct band gap of ZnS/PVA nanocomposite of (a) ZnS_1 (b) ZnS_2 (c) ZnS_3 nanoparticles.

It is evident from the fig.2 that sample exhibit a strong absorption at wavelength 319 nm for ZnS_1 , 311nm for ZnS_2 and 298nm for ZnS_3 suggesting blue shift w.r.t. the bulk arising from quantum confinement effect in the nanoparticles. The band gap of bulk ZnS is 3.68 eV at 300K. The band gap energy of the samples are calculated from the optical absorption experiment. From the absorbance (A) and film thickness (t), the absorption coefficient α (cm^{-1}) is calculated using the equation (2):

$$\alpha = 2.3026 (A/t) \quad (2)$$

Thickness of sample is measured by Gravimetry method using the electronic balanced. According to Gravimetry method the film thickness can be calculated as

$$\text{Thickness}(t)=M/\rho a \quad (3)$$

Where M=mass of the deposited film, ρ =density of ZnS and A=area of film. The band gap energy of the film at wavelength range 200-500 nm has been calculated using the equation (4)

$$\alpha^2 = A(h\nu-E_g) \quad (4)$$

Where A is a constant related to the effective masses associated with the bands, $h\nu$ is the photon energy and E_g is the band gap energy. The band gap energy is measured by a graph of α^2 versus $h\nu$ data using absorption spectra. The extrapolation (Fig.3) of the straight line to $\alpha^2=0$ give the value of band gap energy. Effective mass approximation (EMA) as proposed [32,33] has been used to explain the change of energy gap as a function of particle size. According to EMA the equation derived for radius of particle is given by

$$\Delta E_g = E_g(\text{Film}) - E_g(\text{bulk}) = [\hbar^2/8\mu r^2] - 1.8e^2/\epsilon_0\epsilon_r r \quad (5)$$

Where $1/\mu = 1/m_e^* + 1/m_h^*$ is the reduced mass of electron hole effective mass, $m_e^*=0.34m_0$ and $m_h^*=0.23m_0$ and $\epsilon_r=8.76$ is the permittivity of the sample[34]. The calculated particle size is 6.7 nm for ZnS₁, 5.5nm for ZnS₂ and 4.9 nm for ZnS₃, which is good agreement determined by XRD and TEM observation. A graph is drawn along the band gap vs. particle size from EMA as shown in Fig.4.

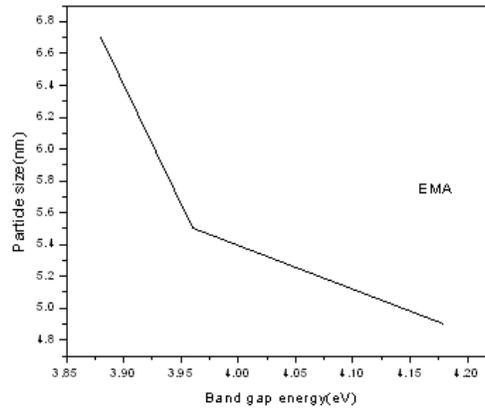


Fig.4 Band gap energy vs particle size

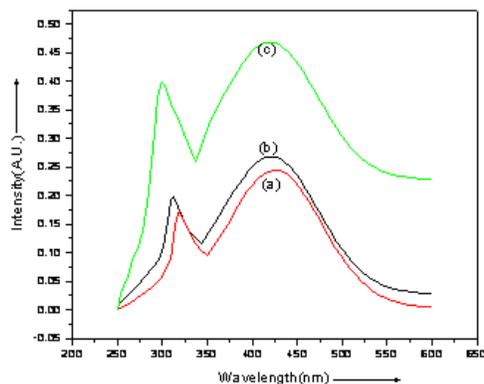


Fig. 5. PL spectrum of ZnS nanoparticles at same excited wavelength 290nm (a)ZnS₃(b) ZnS₂ (c) ZnS₁nanoparticles.

Photoluminescence spectra measured at room temperature (290K) of the nanocrystalline ZnS/PVA thin film deposited on glass surface of sample ZnS₁–ZnS₃ is shown in the fig. 5. These spectra were recorded using (Thermospectronic AMINCO) luminescence spectrometer. All the plots contains two peak centered at 315 nm and 425 nm. The excitation wavelength was 250 nm. Appearance of a broad peaks centered at 425 nm is attributed to the presence of sulphur vacancies in the lattice [35]. This emission results from the recombination of photo generated charge carriers in shallow traps [36, 37]. The other peak centered at 315nm is due to the band to band transition of nanocrystalline ZnS. The absorption edge of UV-VIS spectra appeared at same position, which support the PL result. It is seen that when the size of the nanocrystallites decreases the luminescence has been found to be dominated by the band impurity also, surface passivation by sulphur has resulted in reduced emission intensity of this band indicating involvement of surface defects. The nanostructure observed from TEM (Model JEOL JEM-100cx) shows the size of the nanocrystalline to be spherical in shape and size of the crystal increases with increase of pH, which agrees with the result obtained from XRD observation also.

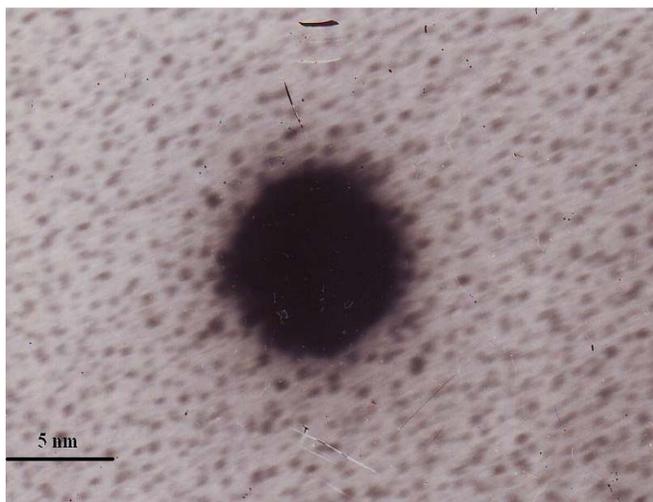


Fig. 6. TEM image of ZnS nanoparticles at pH=2.8.

Table 2: Particle size from TEM.

Name of the sample	pH	PVA:ZnCl ₂	Particle
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			size(nm)(TEM)
ZnS ₁	1.4	5:1	2.8
ZnS ₂	2	5:2	3.6
ZnS ₃	2.8	5:1	3.2

The TEM photograph patterns (Fig.6) were recorded using selected area observation and the particle sizes were determined in higher magnification ($\sim 2 \times 10^5$). The size and shape of the particle size at various conditions are shown in Table2. It is seen that optimum pH value for smaller nanoparticle is found to be 1.4. The PVA:ZnCl₂ ratio also effects the size of the nanoparticles.(not shown)

4. Conclusion

ZnS nanoparticles of different crystalline sizes have been synthesized by chemical route. The particle size is controlled by stirring rate, temperature of the solution, pH and time of stirring. The structural and optical characterization of the samples observed by XRD,TEM,UV-VIS spectrophotometer and PL shows formation of ZnS nanoparticle., having size between 5-7nm. The optimum pH value for minimum size is found to be 1.4 and PVA:ZnCl₂ ratio is found to 5:1 in our observation.

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