Effect of pH on the structural and optical properties of ZnS nanoparticles embedded in PVA matrix

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ZnS nanoparticles embedded in polyvinyl alcohol (PVA) matrix have been synthesised with different pH by using wet chemical methods at room temperature. X-ray diffraction (XRD) pattern indicated that prepared nanoparticles with different pH show cubic phase. The average size variation of nanoparticles with pH estimated from the Debye-Scherrer equation and varying optical size by using absorption edge. Also, UV-Vis absorption results show a blue shift by variation of pH. The intensity of PL emission was found to be dependent on the pH of precursors and maximum of intensity related to pH=6. As a conclusion, pH plays vital role in improving PL intensity. It is also observed that particle size depends on the pH and a decrease in the size of particles is observed with the decrease of pH.

1 Introduction

Chalcogenide semiconductor nanoparticles show unique optical properties due to quantum confinement size effect and widely studied because of their potential applications in optoelectronic[1,2.] The effects of quantum confinement are observed when the confined size is of the order of Bohr diameter. In semiconductors, in general, the exciton radius is about the 5-10 nm. ZnS is an important II-IV semiconductor having a wide direct band gap of 3.65 eV in the bulk which became very attractive materials for optical applications especially in crystalline form. ZnS nanostructure in the form of thin film, powder and colloid prepared using various methods such as evaporation[3], sputtering[4], wet chemical[5,6], sol-gel[7,8] and spray pyrolysis[9] were investigated in detail. Polyvinyl alcohol (PVA) has excellent film forming capacity, good transparency and compatibility with additive[10]. Also, significant of PL efficient in nanoparticles has been observed when embedded in polymeric matrices [11]. Ben Nasr *et al*[12]. have reported the effect of pH on the properties of ZnS thin films. Borah *et al*[13]. have reported photoluminescence properties of ZnS/PVA film deposited by chemical route. The synthesis of ZnS still remains a topic of interest for researchers. In the present work, we present a simple, low cost, toxicity and controllable method for preparation of ZnS nanoparticles in an aqueous solution of PVA matrix. The effects of pH on structural, morphological and optical properties of ZnS nanoparticles in PVA matrix have been investigated.

2 Experimental Details

ZnS nanoparticles embedded in a PVA matrix were synthesis by wet chemical methods. All the chemicals were used a received without further purification and obtained from Merck. The typical synthesis procedure is as follows: polymer solution was prepared from polyvinyl alcohol (PVA), 2% in to 20 ml distilled water 0.2 M zinc acetate solution was prepared by dissolving [Zn (CH$_3$OO)$_2$] in distilled water and added to polymeric solution and stirring at 60°C for 3h by applying magnetic stirrer. The solution with different pH in the range 1.5-9 was kept for one day until viscous transparent solutions were obtained. After one day 0.2 M sodium sulphide was prepared by dissolving [Na$_2$S.xH$_2$O] in distilled water then added to Zn/PVA matrix solution and stirred at room temperature for 3 h. Control of temperature provided with oil bath. Finally, the colour of the prepared nanoparticles was milky. Glass slides were used as substrate and kept in nitric acid and distilled water solution for one day, then these glass substrates washed with acetone and distilled water and the milky solution contains ZnS nanoparticles in PVA matrix coated on a glass substrate and kept for one day at room temperature. Typical precursor amount for

preparation of ZnS NPs embedded in a PVA matrix are presented in Table 1.

The X-ray diffraction (XRD) analysis was carried out using a Philips (PW-37-10) and radiation source used was CuK_α with wavelength equal to 1.5418 Å. The morphology of samples was indicated by scanning electron microscopy (SEM), LEO 1430VP instrument operated at an acceleration voltage of 15 and 18 kV. The optical properties of product were characterized by a Varin Carry-100 UV-vis spectrometer. Optical absorption and transmittance measurements were made by placing a PVA coated on glass substrate in reference beam line. Photoluminescence spectra were recorded on a Perkin-Elmer LF5 fluorescence spectrometer.

3 Results and Discussion

ZnS can show two crystallite phases (zinc blend and wurtzite) and both have direct band structure. Fig. 1 shows the X-ray diffraction of ZnS particles in PVA matrix with *p*H=1.5, 3.1 and 8. The diffraction peaks at about 2θ= 27.5°, 48.3° and 57.4° matching with (111), (200) and (311) crystalline planes and correspond to the cubic phase (JCPDS card,

No. 5-0566) of ZnS nanoparticles. Diffraction peak is quite broad, as expected for nanoparticles.

Average crystallite size was estimated from the line width of the most intense peak (111) for the cubic phase by using the Debye-Scherrer formula[14,15]:

$$d = \frac{0.9\lambda}{\beta\cos\theta} \qquad \qquad \ldots(1)$$

where *d* is the coherent length (for spherical crystalline[16], *d*=3/4 *D*, *D* is the diameter of particles), λ is the wavelength of X-ray radiation (1.5418 A), β is the full width at half maximum (FWHM) of the peak and θ is the angle of diffraction. The calculated particle size for different *p*H are presented in Table 2.

Table 1 indicated that with increasing *p*H, the size of ZnS nanoparticles increased. In other word, it is seen that with decreasing *p*H, diffraction peaks became broader and crystallite size decreased. Also, there are few sharp lines in the XRD pattern at *p*H=1.5 which can be raised from other composition or local impurity with very low concentration in the sample and with increasing *p*H disappears.

UV-Vis absorbance spectra as a function of wavelength for the ZnS samples prepared with different *p*H are shown in Fig. 2. In fact, an increase

Table 1 — Typical precursor amount for preparation of ZnS NPs embedded in PVA matrix

Reactant type	Amount of reactant	Distilled water volume (cc)	Stirring time (min)	Concentration
Na_2S	0.312	20	20	0.2 M
$Zn(AC)_2$	0.877	20	15	0.2 M
PVA	0.4		30	2%

Table 2 — Average particle size calculated from the X-ray line width

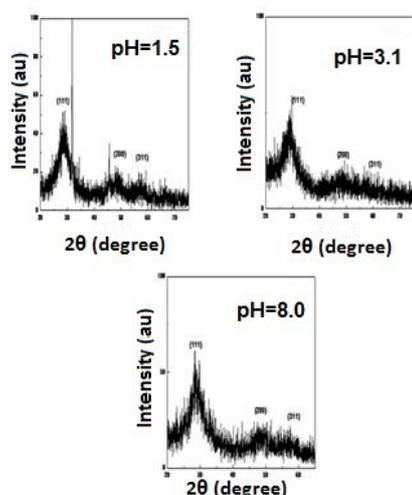| *p*H	Crystallite size (nm)
*p*H=1.5	3.76
*p*H=3. 1	4.15
*p*H= 8	4.80

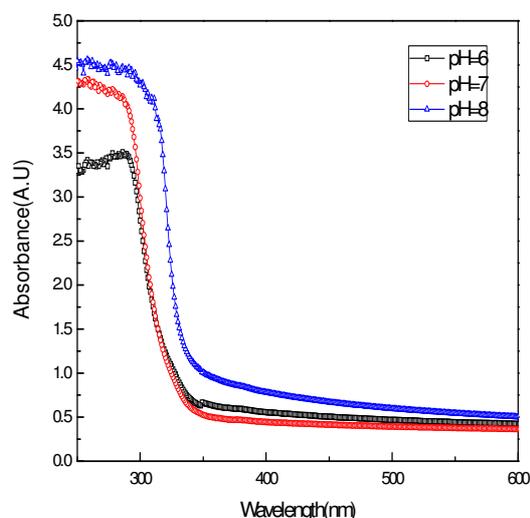Fig. 1 — XRD pattern of ZnS nanoparticles in PVA matrix for *p*H=1.5, 3.1 and 8.0 at room temperature.

Fig. 2 — UV-Vis absorbance as a function of wavelength for ZnS samples with different *p*H

of the pH leads to change growth condition and shift absorption edge to lower wavelength. Therefore, absorption spectra show a blue shift due to quantum confinement effect in the ZnS nanoparticles in the PVA matrix.

The optical band gap values of ZnS NPs were obtained from optical absorption spectra by extrapolating the straight line portion of ($\hbar v \alpha$) plot versus to the energy ($\hbar v$), based on following equation[17,18]:

$$\alpha = A(\hbar v - E_{g^n})   \qquad \dots(2)$$

where α is the absorption coefficient, $\hbar$ is Planck constant, E_g is the absorption band gap, A is constant and n depends on the type of transition. n may have values 1/2 (allowed direct), 2 (allowed indirect), 3/2 (nonradiative direct) and 3 (nonradiative indirect) transition. As shown in Fig. 3, the band gap of ZnS NPs is higher than the band gap of bulk ZnS (3.68 eV) and with increasing pH, the gap energy increased and therefore, the size of particles reduced.

The band gap of NPs is a function of size under tight banding approximation (TBA) as well as an effective mass approximation (EMA). Therefore, the blue shift was caused by the quantum confinement size effect. Brus[19,20] used the effective mass approximation (EMA) to explain the theory of blue shift and energy band gap of NPS (E_g^{np}) as a function of radius of particle (R) is given by Brus equation:

$$E_g^{np} = E_g^{bulk} + \frac{\hbar^2 \pi^2}{2R^2}\left(\frac{1}{m_e^0} + \frac{1}{m_h^0}\right) - \frac{1.8e^2}{4\pi\varepsilon_0\varepsilon_r R} \qquad \dots(3)$$
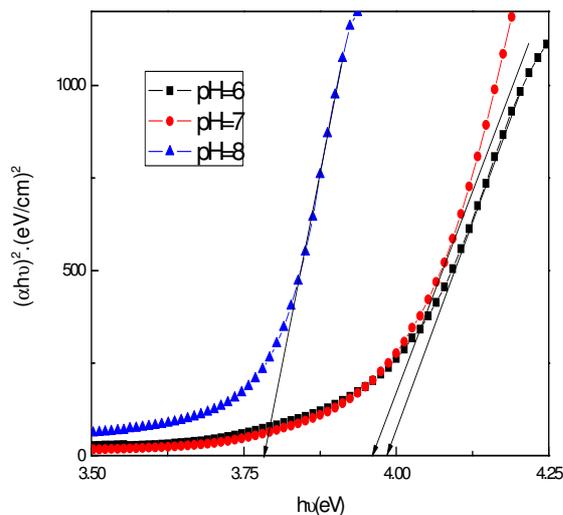
where $\hbar$ is Planck constant, R is the radius of NPs, is the effective mass of electron (m_e^0=0.19m_e), m_h^0 is the effective hole mass (m_h^0 =0.80 m_e), m_e is the mass of the electron, ε_r is the dielectric constant of particles and ε_0 is the permittivity of free space. The terms in Eq. (3) represent an energy gap of the bulk ZnS, the electron-hole pair confinement kinetic energy and last term is the Coulomb interaction energy between the electron and hole. Using Eq. (3), we have estimated the crystallite size of ZnS nanoparticles in PVA matrix prepared with different pH. The obtained band gap and estimated particle size of samples with different pH are presented in Table 3. The quantum effect allows one to tune the emission and excitation wavelengths of nanoparticles by tuning particle size.

ZnS is one of the important luminescence materials and it is transparent in the visible spectral region having exciton binding energy of 40 eV. Induced sub-band gap transitions in ZnS occur at energies in the visible range that allowed the optical detection of traps, radiative recombination centers and surface state. In Fig. 4 photoluminescence emission spectra of samples with different pH=6, 7 and 8 as a function of wavelength are shown. It is observed that there is a strong peak around 420 nm and the other weak peak

Table 3 — Optical band gap and estimated particle size based on EMA (Brus equation)

pH	Optical band gap (eV)	Particle size (nm)
6	3.98	5.13
7	3.95	5.27
8	3.79	5.92

Fig. 3 — Calculated ($\alpha\hbar v$)^2 as a function of $\hbar v$ for direct band gap ZnS nanoparticles with various pH
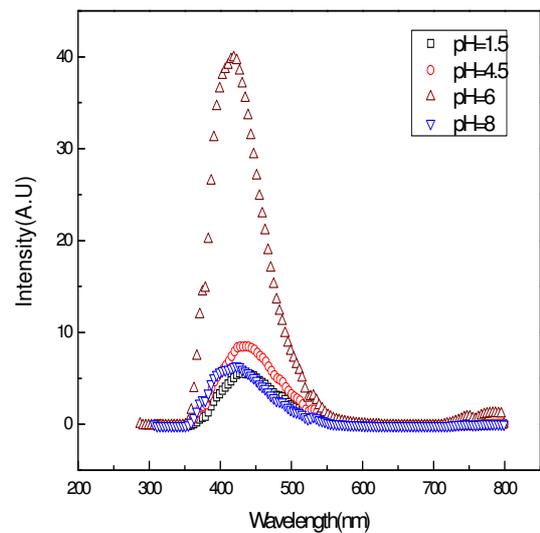

Fig. 4 — Room temperature PL emission spectra of ZnS nanopartcles in PVA matrix with different pH
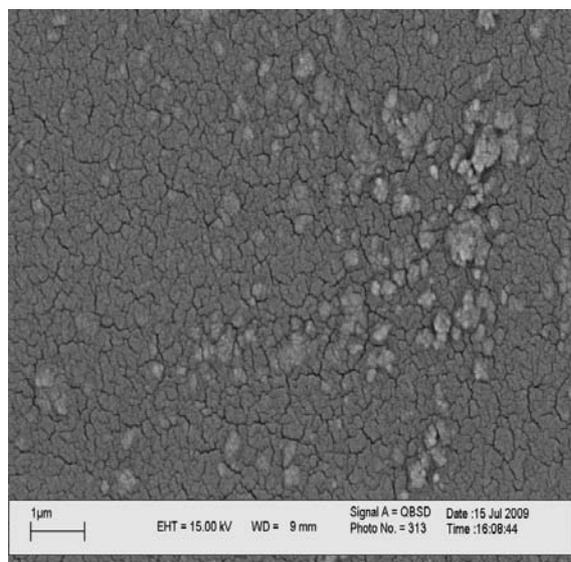
Fig. 5 — SEM photograph of ZnS nanopaticles prepared in 550°C with precursor concentration 0.2 M, PVA=2% and *p*H=6

centered at 525 nm which are attributed to the surface defect, anion vacancy[21] and trap. There is an optimum concentration of vacancy defects that would be responsible for maximizing photoluminescence intensity. In addition, acidic *p*H conditions, show sample with *p*H=1.5 gave the lowest intensity in the given *p*H range. Similarly, in the alkaline region, the sample with *p*H=9 yield lowest PL intensity. Thus, the optimized *p*H=6 yield an enhanced in PL intensity for these ZnS nanoparticles in PVA matrix.

The *p*H dependent of PL intensity in the acidic (alkaline) conditions can be related to creation of donor and acceptor states due to incorporation of some anions (cations) in solution which take part in lattice formation of ZnS nanoparticles as well as surface and trap states. Thus, Na ion can be responsible for quenching the PL emission of the alkaline samples.

SEM brings microscopic information of the surface structure and morphology. The SEM photograph of the ZnS sample with *p*H=6 (Fig. 5) shows the formation of relatively uniform sample with the semispherical particles spread across the matrix.

4 Conclusions

ZnS nanoparticles embedded in a PVA matrix have been synthesised at room temperature by using wet chemical methods. The intensity of PL emission was found to be dependent on the *p*H of precursors and maximum of intensity related to *p*H=6. As a conclusion, *p*H plays vital role in improving PL

intensity. It is also observed that particle size depends on the *p*H and a decrease in the size of particles is observed with the increase of *p*H. The XRD measurement confirmed all prepared ZnS nanoparticles embedded in PVA matrix show cubic phase in all *p*H range. UV-Vis absorption results show a blue shift by variation of *p*H due to quantum confinement effect, while the PVA coating does not affect the microstructure of ZnS nanometerials and the PL spectra of the samples are found to be affected by the PVA concentration as well as the exciting power density. The effect of the polymer coating on the optical properties can be explained by the quantum confinement effect of ZnS nanoparticles in the PVA matrix.

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