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Synthesis and Characterization of ZnSe/PVA nanocomposites for optical devices

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Abstract

The Paper reports in situ preparation of ZnSe-PVA nanocomposite thin films using ecofriendly, safe, inexpensive, facile and non-organometallic synthetic chemical route, with PVA as the stabilizing agent. The X -ray diffraction (XRD) studies showed the formation of cubic ZnSe nanoparticles in PVA matrix with an average size of ~7 nm. The optical energy band gap (Eg) is determined by absorption edge of UV-VIS absorption spectra, it is revealed increase in band gap with decrease in particle size. The optical properties like Refractive index and Photoluminescence (PL) of ZnSe /PVA with varying concentration of ZnSe are also reported. The blue shift was observed due to reduction in size of ZnSe nanoparticles in PVA matrix.

Keywords— XRD, Absorption, Photoluminescence, Refractive index.

1. Introduction

Semiconductor Quantum dots (QD) having nanometer size range behave very differently as compared to their bulk counter parts owing to the three dimensional confinement. The optical energy band gap of these semiconductor QDs can be controlled by the size of the dot. ZnSe, compounds of II–VI semiconductor material posses wide band gap i.e 2.7 eV. ZnSe have attracted researchers due to its properties like transmittance range (0.5-22μm), higher luminescence efficiency, lower absorption coefficient and its excellent transparency to infrared. It is an important material for preparation of blue diode lasers, light emitting diodes, solar cells and optical device. Researchers there have been many efforts to produce nanosized materials because the electrical and optical properties can be varied via control over size, stoichiometry and inter particle separation. So far, ZnSe nanoparticles are synthesized generally by physical methods [1-4]. There are, however, few reports on the synthesis of ZnSe nanoparticles using wet chemical route. Chemical route offers an effective control on size, stoichimetery and particle-particle separation, in addition to being an economical route for large scale production. Use of polymer like polyvinyl alcohol (PVA) with semiconducting nanoparticles allows the fabrication of thin film light-emitting devices. The CdSe nanocrystals exhibit size dependent tunable photoluminescence; therefore they are potentially useful in a wide range of applications [5]. In the present study ZnSe nanocrystals were synthesized via chemical route using polyvinyl alcohol as a establishing agent and investigate their luminescence and optical characteristics for the development of optical devices.

2. Synthesis

The nanocomposites of ZnSe / PVA are chemically prepared via chemical route. First, the PVA solution is formed using distilled water and then 1 ml of $ZnCl_2$ solution is added. After adjusting the pH to 10, add 1 ml of the prepared Na_2SeSO_3 solution. The mixture is stirred for 90 minutes to obtain a nanocomposite of ZnSe / PVA. PVA is used as a polymer matrix due to water solubility and high viscosity. The solution is placed on a glass substrate which upon evaporation gives nanocomposite films. The variations in crystalline size with change in $ZnCl_2$ concentration were noted. For several samples, the initial $ZnCl_2$ content was changed from 1 ml to 4 ml in 1 ml steps. A large number of samples were prepared with various $ZnCl_2$ contents and details shown in table 1.

Table 1: The weight of various compounds used for preparing ZnSe/PVA composite films (with varying ZnSe content)

S. N	Samples	Weight of PVA in 30 ml distilled water	Vol. of 0.1M $ZnCl_2$ sol^n.	Vol. of 0.1 M Na_2SeSO_3 sol^n.	ZnSe Content (mg/ml)
1	M1	3gm	1ml	1ml	0.66
2	M2	3gm	2ml	1ml	1.25
3	M3	3gm	3ml	1ml	1.80
4	M4	3gm	4ml	1ml	2.31

In the synthesis process, the Sodium selenosulphate is produced by the following reaction.

$$Na_2SO_3 + Se \rightarrow Na_2SeSO_3 \qquad (1)$$

Sodium Sulphite Sodium selenosulphate

During this process selenium passes through a deficiency which results in the oxidation of sodium sulfite in sodium selenesulphate. When sodium selenesulphate is added to the metal ions solution, it gradually leaves the selenide ions after hydrolytic decomposition in the alkaline medium.

$$Na_2SeSO_3 + OH^- \rightarrow Na_2SO_4 + HSe^- \qquad (2)$$

(From ammonia)

$$HSe^- + OH^- \rightarrow H_2O + Se^{2-} \qquad (3)$$

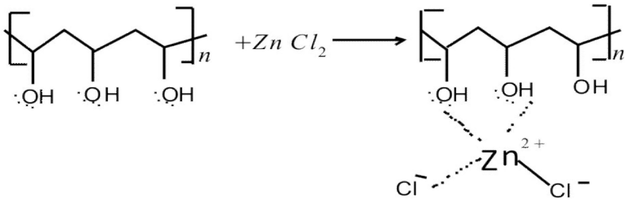
The released selenide ions (se^{2-}) reacted with metal ions to form seed particles.

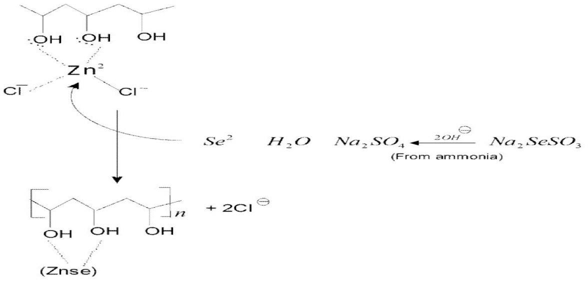
$$m\,Zn^{2+} + mSe^{2-} \rightarrow (ZnSe)_m \qquad (4)$$

The overall process thus occurred is

$$ZnCl_2 + Na_2SeSO_3 + 2OH^- \rightarrow ZnSe + Na_2SO_4 + H_2O + 2Cl^- \qquad (5)$$

Sodium Selenosulfate (Na_2SeSO_3) is relatively stable under slightly basic conditions (pH = 10) and gradually releases selenium ions under hydrolytic decomposition, whereas in the presence of acidic medium, it is necessary to obtain selenium without crystal selenides. In all reaction processes, complex ions have been very important in the preparation of nanocrystalline selenides [6-7]. Under synthetic conditions, these complex ions can gradually omit the free metal ions, which can then be combined with Se^{2-} to form nanoparticles of metal selenide. Otherwise, free metal ions with a high concentration would rapidly combine with Se^{2-}, leading to difficulties in the control of the nucleation and growth of the selenide crystallites and the resultant crystalline grain would growth larger [8]. Polymer matrix limits the size of the crystal and growth of selenides, Vikas Lahariya [9] also reported the preparation of ZnSe/PVA nanocomposite using this technique.





The polymer matrix (PVA) restricted the size of the crystals and growth of selenides (Figure.1).

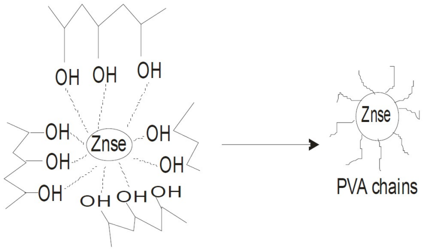


Figure1: PVA Capping around ZnSe nanoparticles.

XRD spectra were recorded with a Rigaku Rotational Anode diffractometer (H-3R) with Cu-Kα radiation (λ = 1.548A). Photoluminescence studies were conducted with F-7000 FL spectrophotometer at MANIT, Bhopal. The particle size is calculated using the Debye Scherrer formula. The refractive index of these films was measured at St. Aloysius Institute Sadar, Jabalpur, India using the Abee's refractometer calibrated for sodium line (589.3nm).

3. Results and Discussions

3.1 X-Ray Diffraction:

Figure 2 represents XRD of four different ZnSe–PVA composite films **(ICSD-II 067791)**. The Bragg diffraction peaks at 2θ = 20º, 27.54º, 45.42º, 53.26º corresponds to the ZnSe network planes (1, 1, 1), (2, 2, 0), (3, 1, 1) for the second, third and fourth peaks, respectively. The first diffraction peak was obtained due to the presence of polymer matrix of PVA. A significant increase in full width at half maximum (FWHM) of XRD peaks is observed indicating finite size of the nanocrystals. The Debye-Scherrer formula was used to calculate the particle size (D) from the FWHM of sample peaks [10].

$$D = \frac{K\lambda}{\beta cos\theta} \qquad (5)$$

Where D is the crystal size, K is the constant, θ is the Bragg angle, λ is the wavelength, β is FWHM.

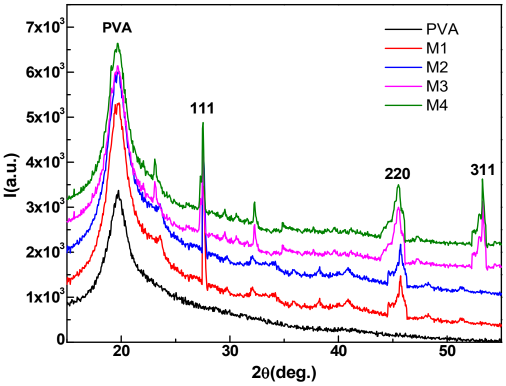


Figure 2: XRD of ZnSe-PVA Nanocomposite films

Table 2: XRD Analysis of ZnSe/PVA Nanocomposites (ICSD-II Card no-067791)

Samples ZnSe/PVA	Vol. of ZnSe content (mg/ml)	Mean 'a' (Å)	FWHM (Degree)	Size D (nm)
M-1	0.66	5.65	0.83	9.86
M-2	1.25	5.65	1.01	8.1
M-3	1.8	5.61	1.5	5.45
M-4	2.31	5.61	1.53	5.35

From the table 2, it is revealed that as ZnSe content is increased from M-1 to M-4, the particle size (D) deceases. The crystallization and size of ZnSe nanoparticles in PVA network depend upon the reaction between Zn and Se ions. PVA networks surround the ZnSe nanoparticles acting as capping agent by limiting the size of particles. The decrease in particle size can be plausibly due to hydrogen bonding. PVA forms an effective packing around $(ZnSe)_m$ particles (figure3), thereby decreasing the value of m resulting smaller particle [6].

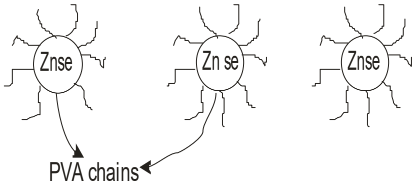


Figure 3: Effective packing of PVA around ZnSe nanoparticles

Decreasing particle size with a higher Zn^{2+} concentration in the polymer matrix can be understood as a higher Zn concentration, most of the Zn atoms remain present for the surface reaction with PVA which in turn causes stabilization of smaller particles. Y. Badr et al. [11] also reported that the reaction between Zn and Se in the PVA medium had a great effect on crystallization as well as the size of the ZnSe nanoparticles. The Zn/Se ratio is increased from 1: 1 to 16: 1, revealing the photon energy gap in the range of 2.58 eV to 3.26 eV due to the lowering of the crystal size of the ZnSe nanoparticles in the PVA matrix.

3.2 Absorption Spectra

Optical absorption was observed in the range of 250 nm to 800 nm using Perkin Elmer Lambda–12 UV-VIS Spectrometer. The optical absorption spectra for ZnSe / PVA~M-1, ZnSe / PVA~M-2, ZnSe / PVA~M-3 and ZnSe / PVA~ M-4 (in Figure 4) is shown with different ZnSe content. In the spectra, almost identical absorption in that visible range was obtained and the sudden absorption increases in the UV region.

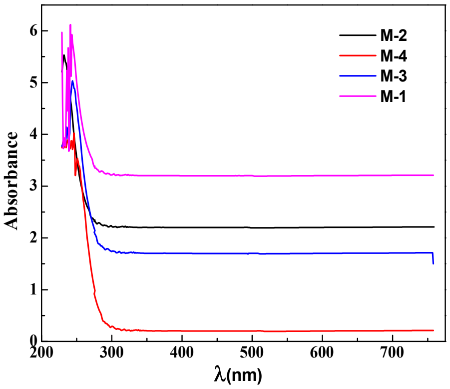


Figure 4: UV/VIS optical absorption spectra of ZnSe/PVA nanocomposites

Absorption spectrum was found to be identical for all samples. The most direct way to calculate optical gap (Eg) is by determining the photon energy at which the absorption increases suddenly. The extent of the optical band of crystalline specimens is calculated by the edge of the absorption using the formula.

$$Eg = \frac{hc}{\lambda} \qquad (6)$$

Where h is Plank's constant, c is the speed of light and λ is the wavelength corresponding to absorption edge.

The estimated band gap (Table no.3) was found to be greater as compared to the ZnSe bulk band gap (2.58eV). Size quantization effect is found to appear in all ZnSe samples. The electron confinement nanocrystal causes the quantization of the energy in the spectrum of conduction band, which shows blue shift in absorption edge with decreasing crystalline size [12, 13]. Hence as compared to bulk material, ZnSe/ PVA nanocomposites exhibit the apparent quantum confinement effect apparently.

Table 3: Absorption spectra/ Photoluminescence analysis of ZnSe/PVA nanocomposites

Samples	ZnSe Content (mg/ml)	absorption edge (nm)	Eg (ev)	PL peak (λ nm)
M-1	0.66	294	4.21	400, 436
M-2	1.25	288	4.3	415
M-3	1.8	274	4.52	410
M-4	2.31	262	4.73	401

3.3 Photoluminescence

The ZnSe / PVA samples with varying Zn^{2+} content were excited by 230 nm UV light and their photoluminescence spectra (PL) are shown in Figure 5. The PL spectrum showed that the PL peak has shifted to a shorter wavelength with increasing the Zn content (Table 3). It has been found that the maximum wavelength of PL emissions decreases as the particle size diminished which could possibly be due to quantum confinement [14, 15]. The effective energy gap of the nanoparticles as obtained from the absorbance spectra corresponds to 250-300 nm. In PL spectra, however, the corresponding peaks were found in the 400-450 nm range, indicating that PL emissions are low energy compared to effective band gap. This emission may be due to the transition of different surface states of nano - ZnSe. The oscillator strength is increased by reducing the nanocrytal size that increases the intensity of PL [16]. The blue shift could possibly be due to the shifting of band edge by reduction in the size of the ZnSe nanoparticles in PVA matrix. Due to adequate passivation of surface, the non-radiative transition is reduced resulting radiative transition (emission) in visible region. The polymer network acts to clutch the nanoparticles, causing size confinement of ZnSe particles in nano-regime. Owing to the PL peak being in the blue region these composite films have potential application in optoelectronic display instruments.

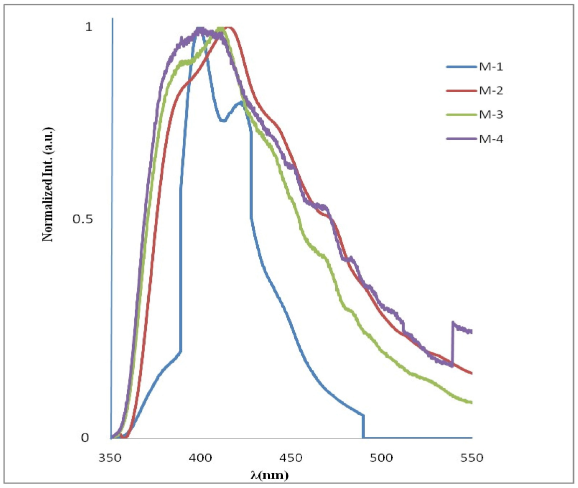


Figure **5:** Photoluminescence spectra of ZnSe/PVA with varying Zn^{2+} content

When PL is excited by 230 nm i.e. photon energy is quite larger than the effective band gap, the electrons transition takes place from valence band (VB) to conduction band (CB). The excited electrons are captured by surface states levels (Es) and the holes produced in VB are captured by Zn^{2+} state. In case of ZnSe varying nanocomposites, electrons are excited from VB to CB and immediately captured by surface state level Es and then some of them radiative decay to valence band giving light emission at about 400 nm; and some recombine with holes trapped at Zn^{2+} levels giving rise to emission at 436 nm. By increasing Zn^{2+} ion content greater proportion of Zn atoms are available which react with PVA giving smaller ZnSe particles and reduces density of Zn^{2+} levels. This causes the two peaks merge together giving abroad PL band and shift in the peak wavelength towards lower values corresponding to emission from surface states to valence band.

Optically transparent ZnSe-PVA nanocomposite film samples having appreciable optical transparency were used for refractive index measurements. The refractive index was measured for yellow light of wavelength (5893Å). The refractometer was first calibrated using distilled water sample and then the measurements were made on the thin film samples. Earlier there have been reports of developing high refractive index nanocomposites by embedding inorganic nanoparticles in compatible polymer [17]. A similar effect was observed on incorporation of ZnSe nanoparticles in PVA matrix, i.e. by increasing the ZnSe content, the refractive index increases in the range of 1.68-1.79, the refractive index profile is shown in figure 6. These nanocomposite materials with such refractive index and transparency and photoluminescence have potential application in anti-reflection coating, optical display devices and photo sensors. High refractive index reduces internal reflection and photoluminescence converts UV light into visible light which enhances efficiency of optical device.

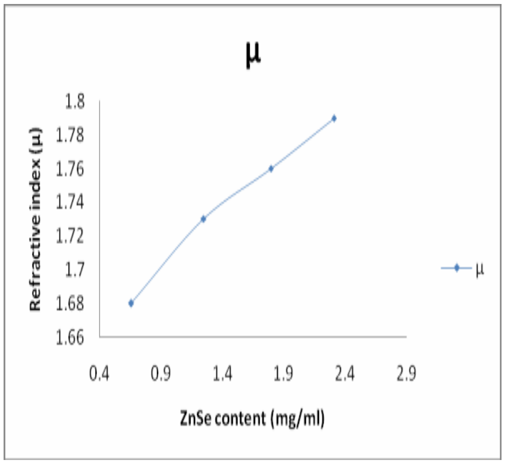


Figure 6: Refractive index profile of ZnSe/PVA with varying Zn^{2+} content

4. Conclusion

Synthesis of ZnSe nanoparticles in the PVA polymer matrix via chemical route is a useful and promising technique for limiting particle size. The PVA polymer plays very important role to restrict the size of ZnSe nanoparticles. The increased band gap estimated through absorption edge opens possibilities of emission wavelength in visible region. The blue shift with reduction in particle size in PL spectra showed quantum confinement effect. All these factors make ZnSe/PVA luminescent films of high refractive index extremely suitable for preparing display devices and various optical applications.

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