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Synthesis and optical properties of ZnS nanoparticles in PVA matrix

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We have synthesized ZnS nanocrystials embedded in a polyvinyl alcohol (PVA) as a matrix by chemical route. The formation of ZnS has been characterized by X-ray diffraction (XRD), Transmission Electron Microscopy (TEM), UV-VIS absorption and Photoluminescence (PL) spectra. The TEM images as well as XRD studies confirm the nanometer size particles formation within the the polymer matrix. The average particle size is found to lie in the range of 3-6 nm. The band gap of the nanocrystalline material is determined from UV spectrograph. The absorption edge is shifted towards the lower wavelength side whicw shows a blueshift with respect to the bulk value. This is also supported by spectral response curves. An increase of molarity decrease the grain size which in turn increases the band gap.

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1. Introduction

There has been increasing interest in the development of reliable luminescent materials for application of flat panel displays. Most research efforts in this area have been directed towards film deposition techniques and different types of materials which are used as active components in electroluminescent device [1]. ZnS is a direct-transition semiconductor with the widest energy band gap (3.68 eV) among the group II-VI compound materials. The most striking feature of ZnS nanocrystallites are that their chemical and physical properties differ dramatically from those of the bulk solids [2, 3]. Semiconductor nanoparticles have attracted much attention because of their novel electric and optical properties originating from surface and quantum confinement effects [4-6]. It is observed as a result of blueshift in absorption spectra with decrease of particle size [7-9]. As the size is reduced to approach Bohr excitation radius, there are some drastic changes in the electronic structure and physical properties, for example a shift to higher energy [10-12]. These nanoparticles may find applications in solar cells, thin film coating in optical and microelectronic industries [13]. Optical and luminescent properties of ZnS prepared in the form of thin film, powder and colloids using different synthesis techniques such as sputtering [14], thermal evaporation [15], sol-gel [16], microwave irradiation [17], pulse laser deposition [18], ion beam deposition [19] and chemical bath deposition technique [20] have been studied in detail. The chemical deposition method is a simple and inexpensive, an alternative to more complex chemical vapour deposition (CVD) and physical technique. On the other hand chemical deposition technique offers a simple means to synthesize such particle with good control of shape and size distribution [21, 22]. In the present investigation, we have prepared ZnS nanocrystals embedded in PVA matrix which are characterized by XRD, HRTEM, UV-VIS and PL spectrometry. The size of the particles is controlled by changing molarities of the solution.

2. Experimental

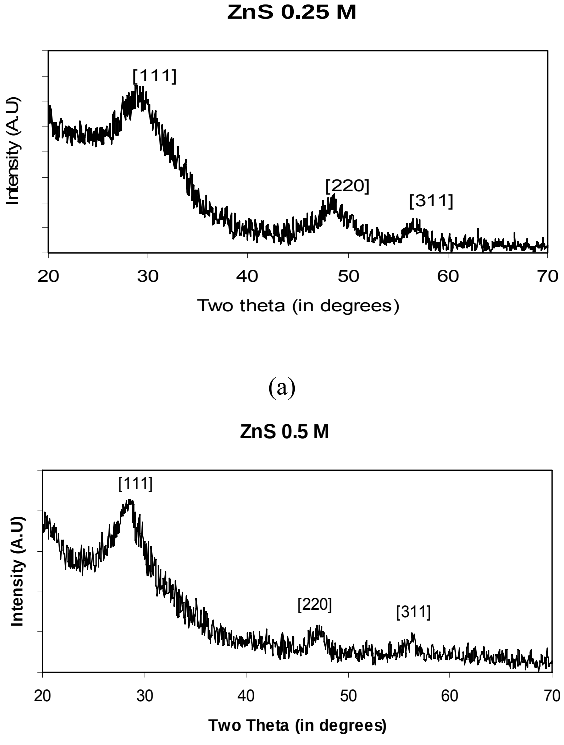
ZnS nanocrystalline thin films are synthesized using polyvinyl alcohol (PVA) as a matrix by an ion exchange reaction. PVA being a good solute to multiple phase system provides uniform gaps that are very close to each other and distributes in the form of array. 2 wt% solutions of PVA and $ZnCl_2$ were mixed with different concentration (0.25M, 0.5M,) under high stirring rate (200 rpm) condition using magnetic stirrer. A constant temperature of 70^0C was maintained during the process of stirring for three hours. The sample under preparation was kept for 12 hours for complete dissolution to get a transparent solution. Equimolar solution of Na_2S was added drop by drop to make the solution completely milky. The ZnS nanoparticles containing PVA were cast over properly cleaned glass substrate to produce the thin film form and successive experiments for characterization were carried out. The chemical reaction occurs as follows

$$ZnCl_2 + Na_2S \rightarrow ZnS + 2\,NaCl \qquad (1)$$

3. Results and discussion

3.1. XRD measurements

To identify the structure and phase, the diffraction patterns of as prepared samples were taken by Seifert XRD (3003TT) operating at 40 kV-30 mA. The radiation source used was CuK_α (λ=1.542Å) and Nickel filter was used to block K_β radiation. Prior to XRD observation, the XRD instrument was calibrated using standard silicon sample. The samples were synthesized by above technique and differs only in molarity (0.25M and 0.5M). Fig. 1(a) shows broad peak at 2θ = 28.85^0, 48.41^0 and 56.5^0 for 0.25M and Fig. 1(b) shows broad peak at 2θ = 28.68^0, 47.29^0 and 56.36^0 for 0.5M sample corresponding to the (111), (220) and (311) planes of cubic Zinc blende structure respectively (JCPDS card no 5-0566).



(a)

(b)

Fig.1. XRD pattern of ZnS nanocrystalline thin films for 0.25M and 0.5M.

From XRD pattern it is seen that the broaden peak shifts to the higher diffraction angle due to lattice contraction with respect to bulk. The lattice contraction occurs because of higher surface to volume ratio [23]. The crystallite sizes of the nanocrystalline films are estimated using Scherrer's formula [24] given by

$$D = K\lambda / \beta_{2\theta}\cos\theta \qquad (2)$$

where K is a constant which is taken to be 0.89, λ is the wavelength of X-ray used, $\beta_{2\theta}$ is the full width at half maximum of peak intensity and θ is the Bragg's angle. The calculation of $\beta_{2\theta}$ is done by zooming the peak position using Origin graphics software. The values of crystallite sizes of the films are shown in Table 1. The crystallite sizes are found to be within the range of 4-5 nm. It is observed that the crystallite size decreases with increase in molarity.

Table 1. Values of crystallite sizes and band gaps for ZnS nanoparticles for 0.25M and 0.5M.

Molarity	Grain size from XRD (nm)	Energy band gap (eV)	Blueshift (eV)
0.25 M	4.7	3.82	0.14
0.5 M	4.4	3.89	0.21

3.2. Optical measurements

The optical absorbances were recorded at room temperature using double beam automated spectrometer (HITACHI-U3210).

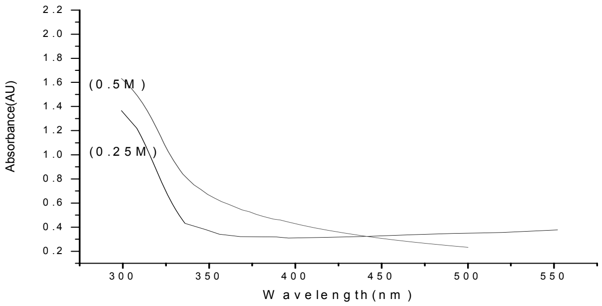


Fig. 2. UV spectra of ZnS samples for 0.25M and 0.5M.

The UV absorption spectra of ZnS nanoparticles for different molarities taken at room temperature are shown in Fig. 2. The sharp absorption edge is at 308.4 nm for 0.5M and 299.6 nm for 0.25M which is at a shorter wavelength than that of bulk ZnS as a consequence of quantum confinement effect [25]. The band gap energy of the corresponding samples are calculated by plotting $(\alpha h\upsilon)^2$ versus hυ using the relation

$$\alpha = C(h\upsilon - E_g)^{1/2} / h\upsilon \qquad (3)$$

where α is the absorption coefficient, C is a constant, hυ is the photon energy and E_g is the band gap energy.

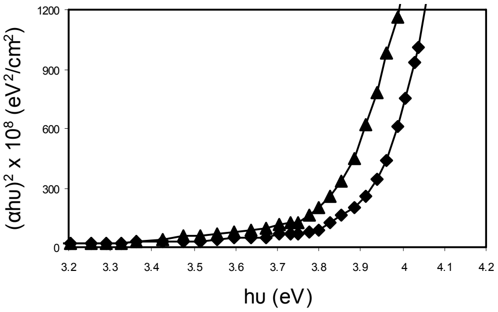


Fig. 3. Band gap determination of ZnS samples for 0.25M and 0.5M.

The exact value of the band gap is determined by extraploting the straight line portion of $(\alpha h\upsilon)^2$ versus hυ graph to the hυ axis. The value of band gap has been found to increase with the decrease of crystallite size which is blueshifted as compared to the bulk band gap value due to the effect of quantum confinement of nanoparticles [26, 27].

3.3. Photoluminescence (PL) spectra

Photoluminescence spectra of ZnS sample measured at room temperature (300 K) is shown in Fig. 4.

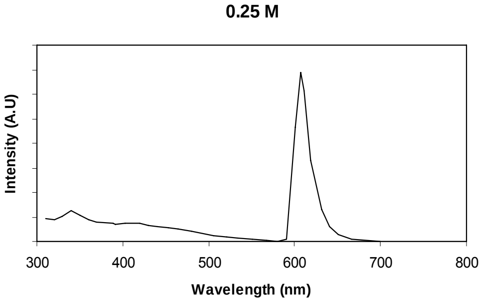


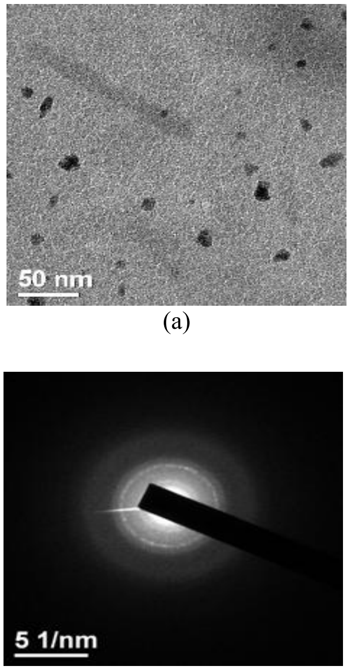
Fig. 4. Photoluminescence spectra for 0.25M ZnS sample.

The spectra were recorded using (F2500) FL spectrometer. The plot contains two peaks at 340 nm and 607 nm. The excitation wavelength was 300 nm. The luminescence spectra clearly shows that prepared zinc sulphide quantum dot has emission peak with high intensity at longer wavelength region. Another peak of less intensity is also observed at shorter wavelength side may be due to recombination of electrons at the sulpher vacancy donor level [28, 29]. The intense sharp peak at 607 nm clearly shows red shift from the absorption edge which is observed in almost all the semiconductor nanoparticles studied so far and are generally assigned to defect states [30]. The red shifts are usually associated with trapped state such as vacancies, interstitial, impurities and surface defects.

3.4. TEM observation

The nanostructure observed from High Resolution Transmission Electron Microscopy (HRTEM) [Model JEOL JEM 2100] shows particle size distribution of prepared 0.25M sample. The TEM was operated at 200 kV.

Fig. 5(a) indicates that the distribution of particles are roughly spherical while Fig. 5(b) shows the selected area of electron diffraction pattern of the sample consisting of a central halo with concentric rings, corresponding to (111), (220) and (311) planes. This confirms the cubic Zinc blende structure of ZnS nanoparticles. The average particle size from TEM is found to be 5 nm which is in close agreement with XRD results.



(a)

(b)

Fig. 5. TEM images of 0.25M ZnS sample.

4. Conclusions

The ZnS thin films prepared by chemical method in PVA matrix are found to be nanocrystalline. X-ray diffraction patterns and selected area electron diffraction patterns studied by TEM confirms the nanocrystalline cubic ZnS phase formation. The crystallite sizes are found in the range 4-5 nm. The UV absorptions show an increase in optical band gap which exhibits a strong quantum confinement effect. At room temperature PL spectra of the sample shows two peaks at 340 nm and 607 nm. The first peak is due to the sulpher vacancy while the later is due to the defect states. The particle sizes calculated from XRD are nearly equal to that of TEM observation.

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