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RESEARCH ARTICLE

STRUCTURAL AND OPTICAL PROPERTIES OF ZNS/PVA AND PB DOPED ZNS/PVA NANOCOMPOSITE FILMS

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ABSTRACT

ZnS/PVA and Pb doped ZnS/PVA nanocomposite films were synthesized using in-situ chemical method. X-ray diffraction patterns of the films confirm the cubic structure of ZnS. Optical absorption studies exhibit the red shifted phenomenon with the comparison of absorption peak of bulk ZnS. The optical band gap energy increases with increasing Pb dopant concentration. Photoluminescence spectra of the ZnS/PVA and Pb doped ZnS/PVA nanocomposite films show the two emission peaks in the visible region.

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INTRODUCTION

During the past two decades, semiconductor nanoparticles have been studied extensively for their tremendous optoelectronic applications in display screens, cathode-ray tubes (CRT), fluorescent lamps, X-ray detectors, light-emitting diodes (LEDs), laser materials, etc., as well as in spintronics and visible light photocatalysis. Semiconducting nanoparticles are known to exhibit exotic physicochemical properties due to quantum confinement effects. Among the semiconductors, ZnS is an important II-VI group wide band gap polar semiconductor and has been most widely used for phosphor host, optical coating, and solar cells. Due to the wide band gap (3.68 eV for cubic phase and 3.70 eV for hexagonal-wurtzite phase at room temperature) and relatively large exciton binding energy (40 meV), ZnS is recognized as one of the most promising materials for a number of optoelectronic applications (Rui Chen *et al*., 2010; Haiying Wang *et al*., 2006). Especially, ZnS nanoparticles doped with Ag^{+}, Ce^{3+}, Cu^{2+} and Sn^{4+} have received much attention for their improved optical properties due to their luminescence efficiency, decay time, and band edge emission with respect to particle size variation. A detailed exploratory study of room-temperature optical properties of ZnS nanoparticles can be more interesting due to their technological importance and the growing need for efficient phosphors in industry, and hence need more attention (Huaming Yang *et al*., 2005). In view of the above factors, we have prepared the nanocomposite films of ZnS/polyvinyl alcohol (PVA) and Pb doped ZnS/PVA by in-situ chemical method. Structural and optical properties of the films have been studied in detail.

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Experimental Details

A solution containing 0.6g of PVA in 10 ml de-ionized water was prepared by constant stirring and heating the mixture up to 70° C for an hour. Then the mixture was left to cool down to laboratory temperature while the stirring of the mixture was carried out to ensure a homogenous composition. (1:3) ratio of zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$) and sodium sulphide (Na_2S) were taken to prepare aqueous solution. Various concentration of (2 M % and 5 M %) lead nitrate ($Pb(NO_3)_2$) was added in the aqueous solution of Zinc acetate. The mixture solution was stirred vigorously for half hour, and thenthis solution was added in the PVA solution, andstirred vigorously to obtain homogeneous solution. Then half hour stirred aqueous Na_2S solution was added drop by drop in above

solution, till the whole solution appears completely milky. Then final solution was stirred vigorously to obtain homogenous solution. This homogenous solution left in petri dish and kept at hot air oven at the temperature 70°C to form film. After two hours the film peeled off the petri dish for characterizations. The structural studies were carried by using a Rigaku X-ray diffractometer with CuKα radiation (λ = 1.54 Å) in the range of 20-60°. Optical absorption spectra of the films were recorded at room temperature in the wavelength region of 300-800 nm using PerkinElmer LAMBDA 35 UV-VIS-NIR spectrometer. Photoluminescence (PL) studies were characterized using PerkinElmer LS 45 fluorescence spectrophotometer in wavelength range of 300-800 nm at room temperature with an excitation wavelength of 320 nm.

RESULTS AND DISCUSSION

X-ray diffraction studies

X-ray diffraction patterns (XRD) of pure ZnS/PVA and 4 mol% Pb doped ZnS/PVP nanocomposite films are shown in Fig. 1. All the diffraction peaks (< 20°) are assigned to PVA whereas the diffraction peaks are found in the Bragg angles (2θ) of 28.7°, 47.8° and 56.8° corresponding to hkl planes of (111), (220) and (311) of the cubic structure of ZnS (JCPDS card no: 05-566). The Pb doped ZnS/PVA films show no additional peaks, which confirms the purity of Pb doped films but there is a small shift towards to lower angle side compared to undoped ZnS pattern.

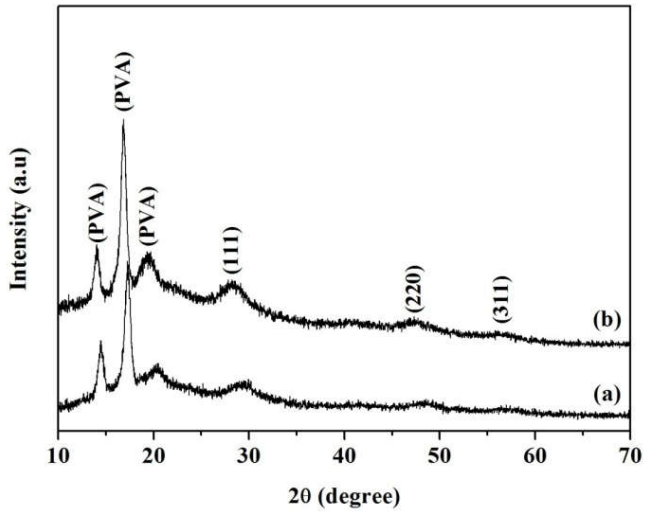

Fig. 1. XRD patterns of (a) ZnS/PVA and (b) Pb doped ZnS/PVA nanocomposite films

It is due to the fact the ionic radius of Pb^{2+} (1.49Å) is larger than the Zn^{2+} (0.74Å) i.e. the substitution of Pb in the Zn site and the change in the ionic radius will make the variation in interpalanar distance (*d*) induce this type of angle shift. The lattice constant (*a*) of three films can be calculated by using the relation, $d = a/(h^2+k^2+l^2)^{1/2}$ where *d* is the interplanar spacing and the values for undoped and 4 mol% Pb doped films are 5.409 Å and 5.414 Å respectively. The average crystallite size of prepared nanocomposite films can be calculated from the full width at half maximum of the characteristic peak using the Debye-Scherrer formula (Haiying Wang *et al*., 2006)

$$D = \frac{0.94\lambda}{\beta \cos\theta}$$

where D is the average crystallite size, λ is the wavelength of the X-rays, β is the full width at half maximum and θ is the diffraction angle. The crystallite size is calculated to be 3.25 nm for e ZnS/PVA and 4.18 nm for 4 mol% Pb doped ZnS/PVA nanocomposite films.

UV-VIS optical absorption studies

Fig. 2 shows the optical absorption spectra of ZnS/PVA and 4 mol% Pb doped ZnS/PVA nanocomposite films. As can be observed from Fig. 2, the absorption edge of ZnS/PVA film is at a wavelength of about wavelength of 338 nm which is shifted from that of bulk ZnS (345 nm) (Huaming Yang *et al*., 2005). It indicates the blue shift of ZnS nanoparticles in PVA. After the 4 mol% Pb doping, absorption edge shifted towards a longer wavelength of 385 nm. The shift in the absorption edge of 4 mol% Pb doped ZnS/PVA nanocomposite films towards longer wavelength, with increasing loading of Pb dopant concentration, is significantly demonstrated 'red-shifted' phenomenon. The optical band energy was calculated from the Tauc equation (Sangwook Lee *et al*., 2004)

$$(\alpha h\upsilon)^2 = A(h\upsilon - E_g)$$

where α is the absorption coefficient , $h\upsilon$ is the incident photon energy, E_g is the band gap of nanocrystals and A is a constant. Fig. 3 shows the $(\alpha h\upsilon)^2$ versus $h\upsilon$ plot to determine the band gap of ZnS/PVA and 4 mol% Pb doped ZnS/PVA nanocomposite films.

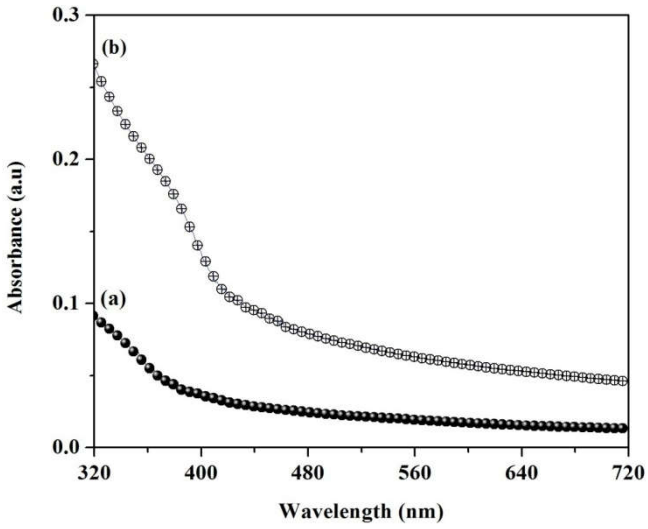

Fig. 2. UV-Vis Optical absorption spectra of (a) ZnS/PVA and (b) Pb doped ZnS/PVA nanocomposite films

The calculated E_g is found to be 3.25 and 2.85 eV for ZnS/PVA and 4 mol% Pb doped ZnS/PVA nanocomposite films, respectively. The values of energy band gap are considerably smaller than the bulk value of ZnS (3.65 eV), suggesting that the size of ZnS nanoparticles in the PVA matrix is very small. It is also observed that the decrease in band gap energy with increasing of Pb dopant concentration indicates an increase in the size of ZnS nanoparticles. The size

of nanoparticles can be calculated from the effective mass approximation theory (Peng *et al*., 2006) and is found to be 3.12 nm and 4.10 nm for ZnS/PVA and 4 mol% Pb doped ZnS/PVA nanocomposite films which are almost consistent with the size calculated from the XRD.

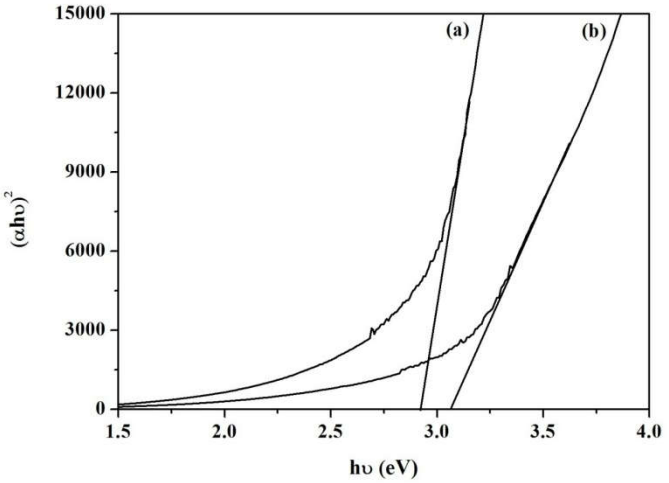

Fig. 3. $(\alpha h\upsilon)^2$ vs hυ plot of (a) Pb doped ZnS/PVA and (b) ZnS/PVA nanocomposite films

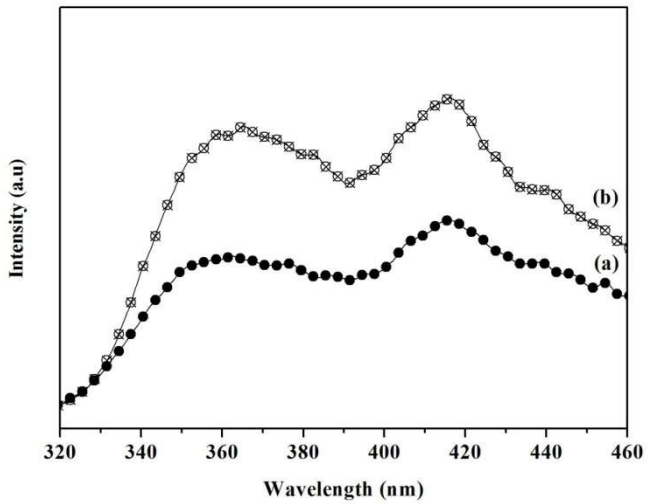

Fig. 4. PL spectra of (a) ZnS/PVA and (b) Pb doped ZnS/PVA nanocomposite films

Photoluminescence Studies

The PL spectra of ZnS/PVA and 4 mol% Pb doped ZnS/PVA films are shown in Fig. 3. Their excitation wavelength is at 320 nm. The PL spectra of ZnS/PVA and Pb doped ZnS/PVA nanocomposite films consist of two emission bands. One is at 364 nm while the other is at 417 nm. The emission peak at 364 nm is due to the near band edge emission of ZnS whereas the other peak at 417 nm is known as the blue emission of ZnS. The blue emission peak is attributed to the recombination between the sulfur vacancy-related donor and valance band. The intensity of PL peaks increases with increasing of Pb dopant concentration and the position of PL peaks also shifted towards longer wavelength with Pb dopant concentration which prove the increase in size of particles as discussed in XRD and optical absorption studies. It is also observed that the broadening of PL peaks indicates the presence of nanometer-sized ZnS particles (Sangwook Lee *et al*., 2004; W. Q. Peng *et al*., 2006; Tran Thi Quynh Hoae *et al*., 2011; Subhajit Biswas *et al*., 2005).

Conclusions

Undoped and Pb doped ZnS/PVA nanocomposite films were prepared using in-situ chemical method. XRD patterns of films confirmed the cubic structure of ZnS in the polymer matrix and the size of nanostructured ZnS in the polymer matrix is 3.25 nm for ZnS/PVA and 4.18 nm for Pb doped ZnS/PVA nanocomposite films. Optical absorption studies exhibited the blue shift in the absorbance band with the comparison of bulk ZnS. The optical band gap energy decreased with increasing of Pb dopant which indicates the increase of particle size and is found to be 3.25 eV for ZnS/PVA and 2.85 eV for Pb doped ZnS/PVA nanocomposite films. Photoluminescence spectra showed two emission peaks at 364 nm for band edge emission and 417 nm for blue emission of ZnS nanoparticles.

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