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Structural and optical properties of PbS-PVA, CdS-PVA and PbS-CdS-PVA nanocomposite films

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Abstract : Freestanding nanocomposite films of PbS-PVA, CdS-PVA and PbS-CdS-PVA were synthesized using in-situ chemical method. All the nanocomposite films were characterized by XRD, SEM, FTIR and UV-Visible optical absorption studies. XRD patterns of all the nanocomposite films confirmed the cubic phase of PbS and CdS nanoparticles in PVA matrix. SEM images showed the mono-dispersion of PbS and CdS nanoparticles in PVA matrix.FTIR studies exhibited the shift in the peak position of functional groups of PVA matrix which indicates the interaction of nanoparticles and PVA polymer. UV-Visible optical absorption spectroscopy revealed the blue shift in absorption onset of PbS nanoparticles and CdS nanoparticles in PVA with the comparison of absorption onset of bulk PbS and CdS. The optical band gap energy of all the nanocomposite films were calculated and found to be 2.10, 2.84 and 2.22 eV for PbS-PVA, CdS-PVA and PbS-CdS-PVA films. The optical band gap energy of PbS-CdS-PVA nanocomposite film lies between the optical band gap energy of PbS/PVA and CdS/PVA films and is closer to the optical band gap energy of PbS/PVA film which indicates that the PbS nanoparticles are good candidates for the fabrication of future opto-electronic devices with the comparison of CdS nanoparticles.

Keywords: Nanocomposite films, Lead sulphide, Cadmium sulphide, Polyvinyl alcohol, Optical properties.

1. Introduction

In recent years, semiconductor nanoparticles have been extensively studied due to their novel properties which are greatly different from those of their bulk materials. Nowadays, semiconductor-polymer nancomposites have attracted growing interest because these materials offer new performance by combining properties from both the semiconductor and the polymer matrix. The nanoparticles exhibit unique properties, due to quantum size effects and the large number of unsaturated surface atoms. The polymeric matrix provides additional qualities such as the processability, solubility and thermal stability of the systems. In this way, nanocomposite materials possessing novel catalytic, conductive, magnetic and optical properties can be obtained. The polymers are selected on the basis of their specific properties such as nonlinearity, electrical conduction, properties related to oxidation resistance of sulphide nanopaticles and they form a nanoreactor to restrict the growth of nanoparticle and prevent aggregation [1-12]. Among the polymers, poly vinyl alcohol (PVA) is highly water soluble hydrophilic polymer and has been wide range of applications in optical and electrical properties of nanoparticles. PVA also posses important advantages of good mechanical strength, long term temperature stability, acousto-optical, excellent film forming properties and surfactant materials of nanoparticles [2-6].

Lead sulphide (PbS) and cadmium sulphide (CdS) nanoparticles have received a lot of attention in the last two decades due to their potential applications in the fabrication of optoelectronic devices.PbS is a IV-VI group of semiconductor having cubic crystal structure with a small band gap (0.41 eV, at 300 K) and a large exciton Bohr radius of 18 nm, which contribute to the strong quantum confinement effect over a large nanocrystalline size range. Therefore, nanostructured PbS has shown some novel and excellent optical and electronic properties, such as IR photodetectors, photovoltaics, and mode-locked lasers. CdS is a II-VI group of semiconductor having direct energy band gap of 2.42 eV at room temperature, which is one of the important material for applications in electro-optic devices such as laser materials, transducers, photoconducting cells, photosensors, optical wave-guides and non-linear integrated optical devices [2-12]. Although a large third-order nonlinear optical property can be obtained in PbS and CdS nanoparticles for optical applications, no one article has reported on structural and optical properties of PbS-CdS-PVA nanocomposite film. In this manuscript, we have synthesized the nanocomposite films of PbS-PVA, CdS-PVA and PbS-CdS-PVAusing in-situ chemical method. Structural and opticalproperties of PbS-PVA, CdS-PVA and PbS-CdS-PVA nanocomposite films have been studied in detail.

2. Experimental

For the fabrication of nanocomposite films, PVA aqueous solution (5 wt%) in distilled water was prepared by magnetic stirrer for an hour at 70˚C. After ageing, $Pb(NO_3)_2$dissolved in distilled water was added to the PVA solution. Then an appropriate quantity of aqueous solution of Na_2S solution was added to the above solution with continuous stirrer at room temperature for few hours until the solution turns into brown colour, indicating the formation of PbS nanoparticles. The resultant solution was poured into petri-dish and dried at 100˚C for 1 hour in order to evaporate the solvent. After drying, the films were peeled off from the petri-dishes for further characterization. CdS-PVA nanocomposite film was synthesized using $Cd(NO_3)_2$ precursor. The formation of CdS nanoparticles in PVA matrix identified when mixture solution of $Cd(NO_3)_2$, Na_2S and PVA turns into yellow colour. Similarly, PbS-CdS-PVA nanocomposite film was prepared by adding the same amount of $Pb(NO_3)_2$ and $Cd(NO_3)_2$ in PVA solution. X-ray diffraction (XRD) studies were carried out of PbS-CdS-PVA nanocomposite film using Shimadzu XRD-6000 diffraction in the 2θ range 10˚-60˚ using CuKα radiation of wavelength λ=1.5405Å. The surface morphology of PbS-PVA and CdS-PVA and PbS-CdS-PVA nanocomposite films was studied by scanning microscopy (SEM) using a JSM-6390 microscopy. The Fourier transform infrared (FT-IR) spectrum was recorded for PbS-PVA and CdS-PVA and PbS-CdS-PVA nanocomposite films in the wavenumber range of 4000-400 cm^{-1} at room temperature using Perkin Elmer spectrum EXD FTIR spectrophotometer with a resolution of 2 cm^{-1}. The linear optical absorption spectra were recorded for all the nanocomposite films in the range of wavelength from 200 to 1000 nm at room temperature using a PerkinElmer Lambda35 spectrometer.

3. Results and discussion:

3.1. X-ray diffraction

Figure 3.1 shows the x-ray diffraction pattern of all the nanocomposite film. All the diffraction pattern exhibits a peak at 19.86˚which corresponds to semi crystalline nature of PVA [2]. In the diffraction pattern of PbS-PVA, the broad peak observed at 30.07˚ which corresponds to the hkl plane of (200) and agreed with standard data of JCPDS film no.05-592, indicating cubic structure of PbS [2-7]. XRD pattern of CdS-PVA nanocomposite film exhibit a peak at 25.4˚, corresponding to the hkl plane of (111) which matches well with the standard data of JCPDS file no. 80-0019 and It confirms cubic structure of CdS [8-12]. XRD pattern of PbS-CdS-PVA nanocomposite film shows only one diffraction peak at 25.8˚, which might be attributed to cubic structure of PbS and agreed with JCPDS file no. 05-592. No one diffraction peak is found for CdS in XRD pattern of PbS-CdS-PVA due to the amorphous nature of CdS. The average crystalline size of all the nanocomposite films was calculated using Debye Scherer equation [4],$D=k\lambda/\beta\cos\theta$, Where, D is the average particle size, K is a geometric factor (which is equal to 0.94), λis the wavelength of X-ray (1.5406Å), β is the full width half maximum of the diffraction peak. The calculated nanocrystallite size is found to be 9.7, 4.8 and 6.3 nm for PbS-PVA, CdS-PVA and PbS-CdS-PVA freestanding nanocomposite films.

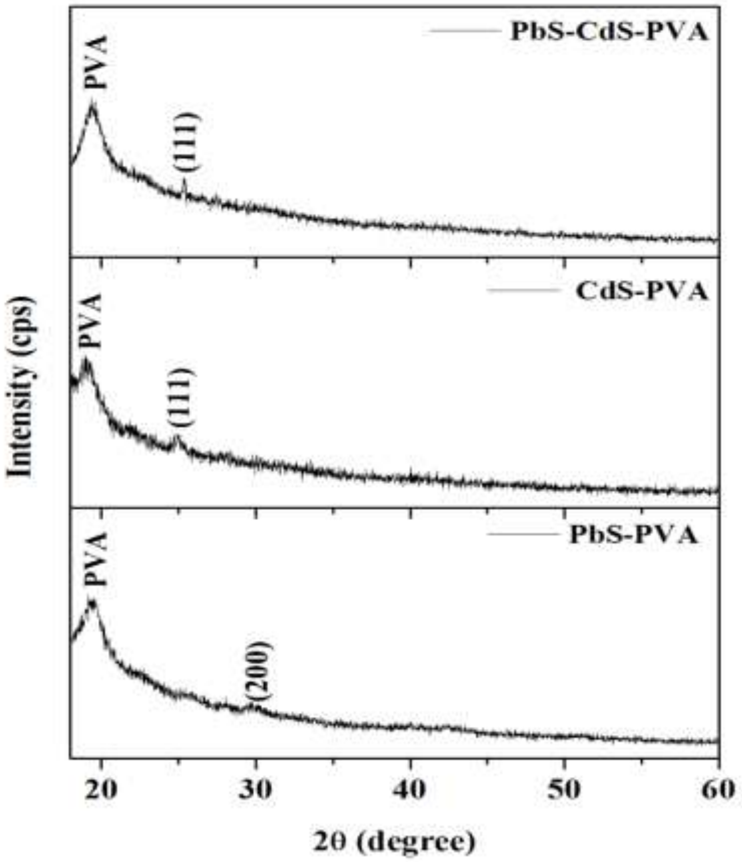

Fig. 3.1 XRD pattern of PbS-PVA and CdS-PVA and PbS-CdS-PVA nanocomposite films

3.2. SEM analysis:

Figure 3.2 (a-c) shows the surface of morphology of PbS-PVA, CdS-PVA, and PbS-CdS-PVA nanocomposite films. SEM micrograph of PbS-PVA shows that the PbS nanoparticles are well mono-dispersed in polymer matrix whereas the SEM micrograph of CdS-PVA nanocomposite film shows the aggregation of CdS nanoparticles in polymer matrix. In the SEM micrograph of PbS-CdS-PVA nanocomposite film, the size of the nanoparticle are small and theyare well mono-dispersed as compared with SEM of PbS-PVA and CdS-PVA nanocomposite .

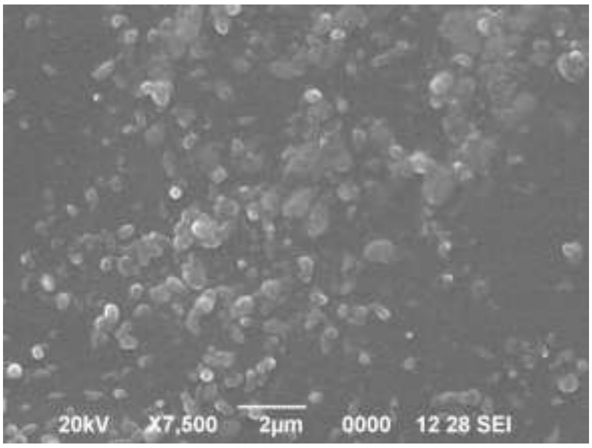

Fig.2 SEM micrograph of (a) PbS-PVA

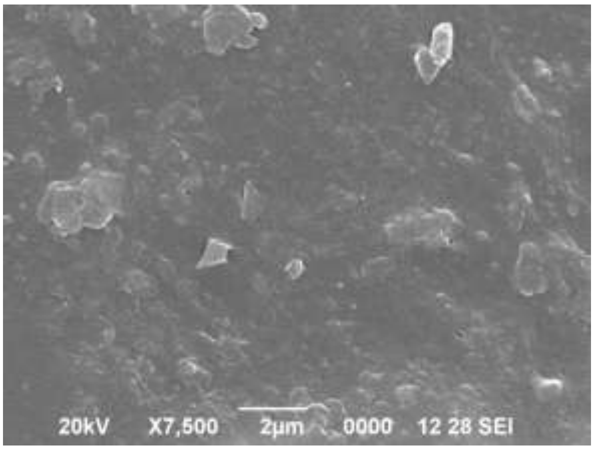

Fig 2. SEM micrograph of (b) CdS-PVA

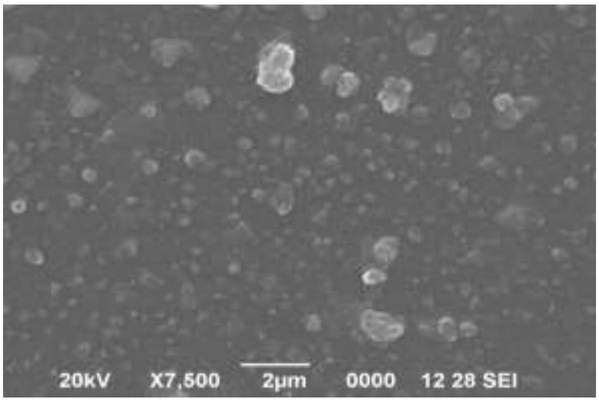

Fig .2 SEM micrograph of (c) PbS-CdS-PVA

3.3. FTIR studies:

Figure 3.3 shows the FTIR spectra of PbS-PVA, CdS-PVA and PbS-CdS-PVA nanocomposite films. FTIR spectrum of PbS-PVA nanocomposite film shows the peaks at 3420, 3338, 2922, 1721, 1430, 1373, 1330, 1251 and 1105 cm^{-1}which are attributed to O-H stretching, primary amide NH_2 asymmetric stretching, asymmetric C-H stretch band of CH_3group, C=O stretching, C-O-H in plane bending, C-O stretching, aromatic C-N stretching, aliphatic C-N stretching and second overtone C-H stretching. The other three peaks of PbS-PVAnanocomposite film at 943, 844 and 611 cm^{-1} are assigned to out-of-plane C-H bending.

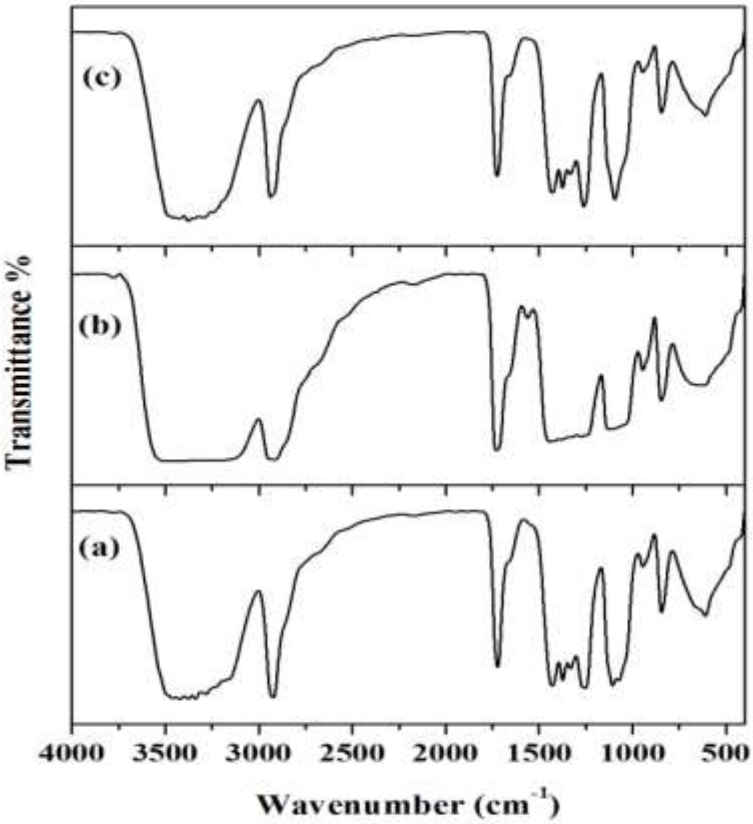

Fig.3.3 FTIR spectra of (a) PbS-PVA, (b) CdS-PVA and (c) PbS-CdS PVA nanocomposite films

FTIR spectrum of CdS-PVA film shows the peaks of asymmetric C-H stretch band of CH3 group, C=O stretching, C-O-H in plane bending, C-H stretching at 2913, 1726, 1442 and 1130 cm-1, respectively. The other three peaks of CdS-PVA film at 944, 847 and 614 cm-1 are assigned to out-of-plane C-H bending [1, 3-12]. FTIR spectrum of PbS-CdS-PVA nanocomposite film exhibits all the peaks observed in the FTIR spectrum of PbS-PVA film with small shift in the position of peaks which indicates the dominate role of PbS nanoparticles in PVA matrix and strong interaction of PbS nanoparticles than the interaction of CdS nanoparticles in PVA matrix.

3.4. UV-Visible optical absorption studies

Figure 3.4 shows the optical absorption spectra of PbS-PVA, CdS-PVA and PbS-CdS-PVA nanocomposite films. The optical absorptionspectrum of PbS-PVA nanocomposite film exhibits the absorption onset at 589 nm and causes the blue shift in absorption onset in comparison with absorption onset of bulk PbS (3020 nm) whereas the optical absorption spectra of CdS-PVA nanocomposite film exhibits the absorption onset at 437 nm and causes the blue shift in absorption onset with the comparison of absorption onset of bulk CdS (517 nm) [3-12]. The optical absorption spectrum of PbS-CdS-PVA nanocomposite film exhibits the absorption onset at 559 nm which lies between the absorption onset of PbS-PVA and CdS-PVA nanocomposite films as expected. The absorption onset of PbS-CdS-PVA nanocomposite film shows the blue shift in comparison of absorption onset of PbS-PVA nanocomposite film and red shift in comparison of absorption onset of CdS-PVA nanocomposite film which confirms the size of the nanocrystallites of PbS-CdS-PVA film lies between the size of the nanocrystallites of PbS-PVA and CdS-PVA films and agreed well with the size of nanocrystallites estimated from XRD. The optical band gap energy of all the films was estimated using the equation, E=hυ (where h is plank's constant and υ is a frequency), and is found to be 2.10, 2.84 and 2.22 eV for PbS-PVA, CdS-PVA and PbS-CdS-PVA nanocomposite films respectively. The optical band gap energy of PbS-CdS-PVA film lies between the optical band gap energy of PbS-PVA and CdS-PVA films and is closer to the optical band gap energy of PbS-PVA film which indicates that the PbS nanoparticles are suitable candidates for the fabrication of optoelectronic devices than the CdS nanoparticles. The size of nanocrystallites using Brus equation [4]is found to be 9.2, 4.1 and 6 nm for PbS-PVA, CdS-PVA and PbS-CdS-PVA nanocomposite films. These values are almost consistent with the nanocrystallite size calculated from the XRD.

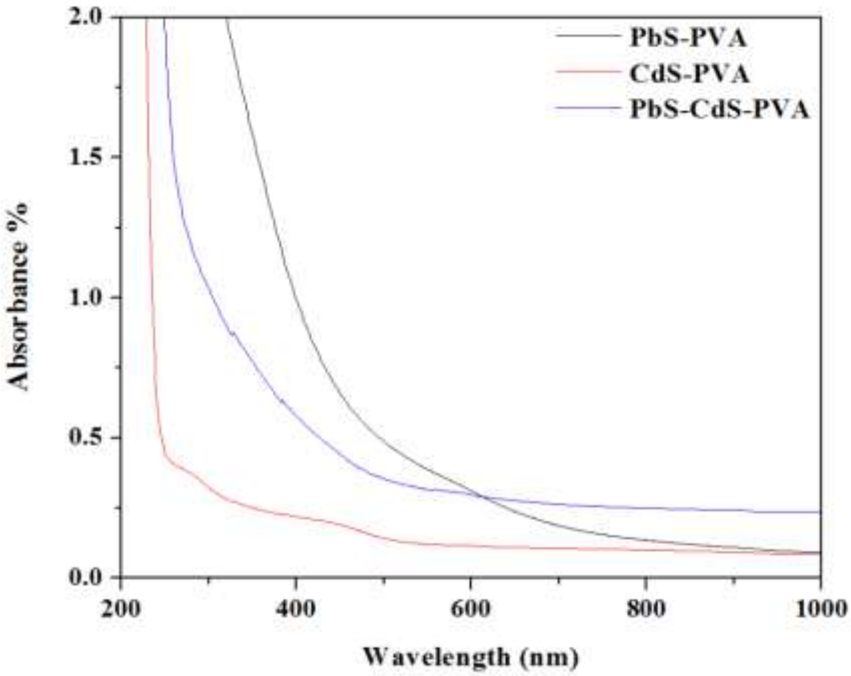

Fig. 3.4Optical absorption spectra of PbS-PVA and CdS-PVAand PbS-CdS-PVA nanocomposite films

3.5 Conclusion

PbS-PVA, CdS-PVA and PbS-CdS-PVA nanocomposite films were successfully synthesized by in-situ chemical method. XRD pattern confirms the cubic phase structure of all the films. Also the nanocrystallite size was determined using Debye Scherer’s formula and is found to be 9.7, 4.8 and 6.3 nm for PbS-PVA, CdS-PVA and PbS-CdS-PVA free standing nanocomposite films. Scanning electron microscopy shows that PbS and CdS nanoparticles are well monidispersed in the PVA matrix. The formation of all the films was confirmed by FTIR spectra. UV-Visible optical absorption spectra revealed the blue shift and red shift in PbS-CdS-PVA with the comparison of optical absorption spectrum of PbS-PVA and CdS-PVA nanocomposite films.

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