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Structural and optical properties of Ce doped CdS/PEG nanocomposite films

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Abstract

Ce doped CdS/PEG nanocomposite films were synthesized by in-situ method. XRD patterns confirm that all the nanocomposite films exhibits the cubic phase of CdS nanoparticles and the size of the nanoparticles are varying from 4.13 to 4.64 nm with Ce doping. FTIR spectra confirm the formation of CdS/PEG nanocomposite films. UV-Visible optical absorption studies exhibit the blue shifted phenomenon of title samples with the comparison of bulk CdS. The optical band gap energy is found to be decrease with increasing Ce dopant concentrations.

Keywords: *Nanocomposite, thick films, x-ray diffraction, optical properties*

1. Introduction

Among the group of II-VI semiconductor nanocrystals, CdS nanocrystals find possible applications in optical switches, sensors, electro-luminescent devices and biomedical tags due to their band gap energy of 2.4 eV and Bohr exciton diameter of 6 nm. CdS nanocrystals exhibit size dependent physical properties stemming from quantum confinement effects, which can be successfully exploited by their incorporation into the suitable polymer matrix [1-5]. Among the polymers, Poly ethylene glycol (PEG), water soluble polymer, has several advantages such as good mechanical strength, long term temperature stability, optical, electrical, excellent film forming properties and surfactant materials of nanoparticles [4-6]. Use of Ce as dopant certainly improves the luminescent properties of nanoparticles. Ce^{3+} ions were also widely used as activators for its allowed optical transitions of 4f-5d. A strong overlap of the activator 5d-orbitals with ligand orbital causes high sensitivity of their spectral characteristics to the local environment structure [7,8]. In this paper, nanocomposite films of Ce doped CdS/PEG have synthesized using in-situ chemical method. Their structural and optical properties are discussed in detail with varying the Ce concentration.

2. Materials and methods

2.1. Preparation of nanocomposite films

The synthesis process involved the preparation of an aqueous solution of cadmium nitrate and cerium nitrate in distilled water by magnetic stirring for about 20 min and mixed with each other to form a homogeneous solution. 10 wt% of PEG powders were added to the above solution with constant stirring till the solution becomes transparent and colourless. The resultant solution is so called Sol A. An aquous solution of sodium sulphide (Na_2S) was prepared by dissolving an appropriate amount of Na_2S in distilled water and this solution was added to Sol A and then vigorously stirred at room temperature until the solution turns into yellow colour which indicates the formation of CdS nanoparticles in PEG matrix. The resultant solution was stirred for 2-3 h. The solution was poured into cleaned glass petri-dish and then kept into hot air oven at 120°C for 1 h to allow the removal of solvent, residual organics and film densification. Similarly, three films of Ce doped CdS/PEG were prepared by varying the concentration of Ce dopant as 0, 4 and 7 mol%.

2.2. Characterization

X-ray powder diffraction (XRD) studies of CdS/PEG and Ce doped CdS/PEG nanocomposite films were carried out using a Rigaku x-ray diffractometer with CuKα radiation (λ = 1.54 Å) in the range of 20-60°. The FTIR spectra of Ce doped CdS/PEG nanocomposite films were carried out using a PerkinElmer Spectrum GX Fourier transform infrared (FTIR) spectrophotometer in the wavenumber range of 4000-400 cm^{-1}. The optical absorption spectra of CdS/PEG and Ce doped CdS/PEG nanocomposite films were recorded in the range of wavelength from 300 to 800 nm at room temperature using a PerkinElmer Lambda 35 spectrometer.

3. Results and discussion

3.1. X-ray diffraction studies

Fig. 1 shows the XRD patterns of (a) CdS/PEG (b) 4 and (c) 7 mol% Ce doped CdS/PEG nanocomposite films. The broadening of diffraction peaks indicates the presence of nanometer-sized particles in the samples. The diffraction patterns of CdS/PEG nanocomposite film exhibit three peaks at 2θ value of 26.5°, 44.1° and 52.1° corresponding to the (111), (220) and (311) planes of cubic CdS structure, which is well consistent with the standard data (JCPDS card no.80-0019). All the diffraction peaks get shifted towards to lower angle side in the Ce doped CdS/PEG nanocomposite films. It is also worthy to notify that no diffraction peaks assigned to the Ce related impurity phase or secondary phase were found in the Ce doped films. The lattice constant '*a*' has been calculated and is found to be 5.807 Å for CdS/PEG whereas for 4 and 7 mol% Ce doped CdS/PEG nanocomposite films; these values are found to be 5.811 and 5.814Å. It can be observed that the increase in lattice constant with increasing Ce dopant concentration which confirms that the occupation of Ce^{3+} into Cd^{2+} lattice sites [9].

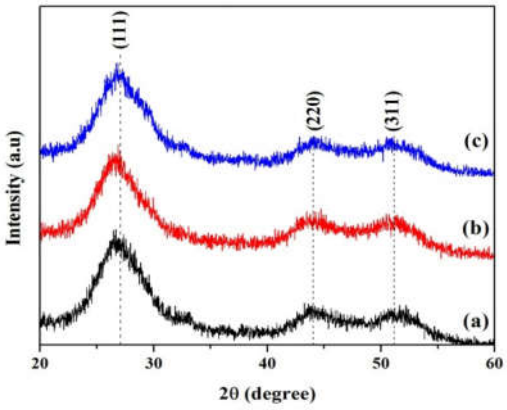

Fig. 1. *XRD patterns of (a) CdS/PEG, (b) 4 and (c) 7 mol% Ce doped CdS/PEG nanocomposites*

The average crystallite size of nanostructured CdS crystallite was calculated using Debye Scherrer formula:

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

where d is the average crystallite size, λ is the X-ray wavelength (1.54 Å), θ is Bragg diffraction angle, and β is full width at half maximum, respectively [10]. The calculated crystallite size was found to be 4.13 nm for CdS/PEG, 4.36 and 4.64 nm, for 4 mol% and 7 mol% Ce doped CdS/PEG nanocomposite films, which are about 7 to 20 times of smaller than the size estimated for CdS thin films using chemical bath deposition technique with the variation of pH range from 12 to 10 reported by Kariper et al [11].

3.2. FTIR analysis

FTIR spectra are used to investigate the type of chemical bonding between CdS nanoparticles and PEG host polymer. FTIR spectra of (a) CdS/PEG, (b) 4 and (c) 7 mol% Ce doped CdS/PEG nanocomposite films are shown in Fig. 2. As shown in Fig. 2(a), the spectrum of CdS/PEG exhibits a several bands of stretching and vibrations i. e. 3430, 2914, 1654, 1428, 1281, 1166, 1005 and 842 cm^{-1} which are assigned to the OH group, -C-H asymmetrical stretching, -C=O stretching, C-H bending, C-O-C stretching, -C-N stretching, cyclic –C-C- stretching and amide or CH_2 rocking band respectively. These FTIR peaks are almost similar to the FTIR spectra of PEG observed by Andrea Leon et al [12] and Shanmugam Cholan et al [13]. The peak at 628 cm^{-1} is attributed to the Cd-S stretching [5]. From the Fig. 2(b), It can be observed that the shift in the peaks towards to lower wavenumber with the comparision of FTIR spectra of CdS/PEG film which confirms the influence of Ce dopant concentrations into CdS lattice site for increasing the size of CdS nanoparticles which cause the strong interaction with the PEG polymer matrix and also show a new peak at 2350 cm^{-1} in 7 mol% Ce doped CdS/PEG nanocomposite film. However, the increase in absorbance with increasing of Ce dopant concentration, suggesting the increase in particle size within polymer matrix.

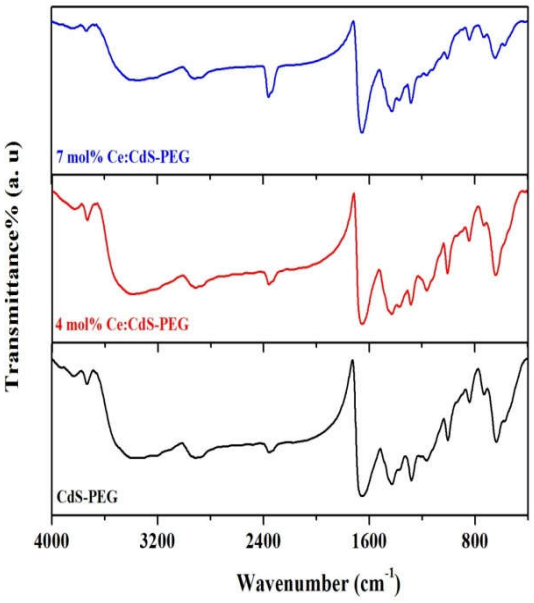

Fig. 2. *FTIR spectra of all the nanocomposite films*

3.3. Optical absorption studies

Fig. 3(a) shows the optical absorption of CdS/PEG, 4 and 7 mol% Ce doped CdS/PEG nanocomposite films. The absorption spectrum of CdS/PEG nanocomposite film shows an absorption edge at 434 nm which is shifted towards shorter wavelength, compared with absorption edge of bulk CdS (517 nm) [1], indicating the blue shift whereas in Ce doped CdS/PEG nanocomposite films, the absorption edge showed a red shift from 440 to 447 nm. The absorption edge of CdS/PEG nanocomposite films observed in this work is almost shifted about 40 nm towards shorter wavelength with the comparison of the absorption edge of CdS/PVA nanocomposites observed by Elashmawi et al [13]. The optical band gap values have been estimated using the following relation:

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

Where, h is Planck's constant, α is the linear absorption coefficient and ν is the transition frequency of incident photon. The exponent n tells about the nature of band transition, n = 1/2 and n = 3/2 and corresponds to direct allowed and direct forbidden transitions and n = 2 and 3 corresponds to indirect allowed and indirect forbidden transitions respectively [11]. The optical band gap of the films is estimated by plotting graph of $h\nu$ vs. $(\alpha h\nu)^2$ for the linear absorption coefficient α as shown inset of Fig. 3.

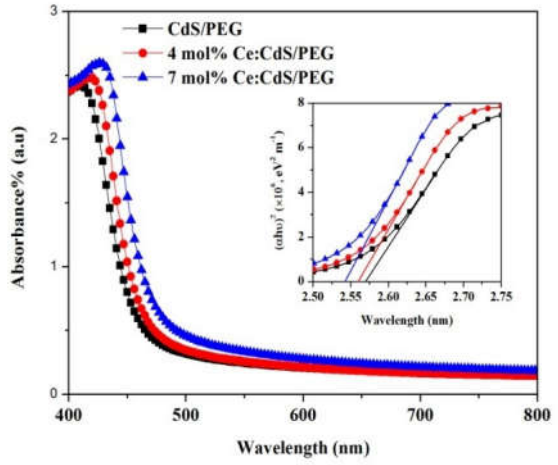

Fig. 3. *UV-Visible optical absorption spectra of all the nanocomposite films and inset shows $(\alpha h\upsilon)^2$ vs $h\upsilon$ plot for determining the E_g value of all the nanocomposite films*

By extrapolating the straight portion of the graph on $h\nu$ axis at α = 0, the band gaps of the CdS/PEG, 4 mol% Ce doped CdS/PEG and 7 mol% Ce doped CdS/PEG nanocomposite films found to be 2.572, 2.565 and 2.541 eV, respectively. The decrease in band gap values reveals that the size of the CdS nanocrystals has been increased on Ce doping. The size of the CdS nanoparticles can be calculated using the Brus equation as follows

$$E_{np} = E_g + \frac{h^2}{8r^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) \qquad (3)$$

where E_{np} is the band gap of the CdS nanoparticles, E_g is the band gap of bulk CdS (2.42 eV), m_e^* is the effective mass of electron (=0.19m_e), m_h^* is the effective mass of hole (0.8m_e) and r is the radius of CdS particles [13]. Employing the calculated optical band gap values in the Brus equation, the CdS nanoparticles size can be calculated and is found to be 4.20, 4.41 nm and 4.59 nm for CdS/PEG, 4 and 7 mol% Ce doped CdS/PEG nanocomposite films, respectively. The estimated size of CdS nanoparticles from optical studies is almost consistent with the size calculated from XRD pattern.

4. Conclusion

We have successfully synthesized CdS/PEG and various concentrations of Ce doped CdS/PEG nanocomposite films by in-situ method. XRD patterns confirm that the synthesized nanocrystallites belong to the cubic structure of CdS nanoparticles and size of the nanoparticles determined using Debye-Scherrer formula are found to be ranging of 4.13 to 4.64 nm with Ce doping. The formation of CdS/PEG nanocomposite thin films and the effect of Ce dopant concentration in CdS/PEG films was analyzed using FTIR spectra. The blue shifted phenomenon was found in UV-Visible optical absorption studies of title samples with comparison of bulk CdS. The decrease in optical band gap energy with increasing Ce dopant concentrations is attributed to red shift which indicates the increase in the size of CdS nanoparticles.

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