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Study on the third-order nonlinear optical properties of Cd\(^{2+}\) ion doped ZnS/PVP nanocomposite films

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Abstract

Cd\(^{2+}\) ion doped ZnS/PVP nanocomposite films have been prepared using in-situ chemical method. XRD studies confirm the cubic structure of ZnS for all the films and the nanocrystallite size of ZnS is found to varying from 3.82 to 4.07 nm with Cd doping. The morphology of the films has been analyzed using SEM micrograph which shows the mono dispersion of ZnS nanoparticles in PVP matrix. The interaction between ZnS nanoparticles and PVP polymer matrix has been discussed using FTIR spectra. Optical absorption spectra of the films reveal the blue shift on the absorbance onset with the comparison of bulk ZnS and the estimated optical band gap energy decreases with increasing the concentration of Cd dopant. Photoluminescence spectra show a blue emission peak for all the films. The Z-scan results of three samples show a reverse saturation absorption process in open Z-scan experiment and self-focusing behavior in closed Z-scan experiment. Both ZnS/PVP and Cd\(^{2+}\) ion doped ZnS/PVP films exhibited the large optical nonlinearity and the value of nonlinear refractive index (n\(^2\)), nonlinear absorption coefficient (\(\beta\)), third-order nonlinear optical susceptibility (\(\chi^{(3)}\)) and figure of merit (FOM) increase with Cd doping. The estimated n\(^2\), \(\beta\), \(\chi^{(3)}\) and FOM values were found to be high for 6 mol% Cd doped ZnS/PVP nanocomposite film and they are about 1.771×10\(^{-10}\) m\(^2\) W\(^{-1}\), 4.148×10\(^{-3}\) mW\(^{-1}\), 1.603×10\(^{-4}\) esu and 9.576×10\(^{-6}\) esu m respectively. The experimental results clearly showed that the Cd\(^{2+}\) ion doped ZnS/PVP nanocomposite film is a worthy candidate for the future nonlinear optical device fabrication.

Keywords: Nanocomposite, ZnS, Polymer, Structural properties, Third-order nonlinear optical properties

1. Introduction

In recent years, semiconducting nanoparticles have been widely investigated by many researchers due to the quantum confinement effect and notable changes in the chemical and physical properties of these particles with the comparison of those of bulk solids. They doped with different metal ions produce new door for optical studies and potential applications in optical device fabrication. Among the semiconductors, ZnS is a well known II-VI group semiconductor with an energy band gap of 3.6 eV and is widely used as a phosphor and in luminescent device [1-5].
Transition metal ions doped ZnS nanoparticles have received much attention due to their exceptional luminescent properties. During the past decades, luminescent properties have been extensively investigated on Mn doped ZnS [1], Cu doped ZnS [2], Ag doped ZnS [3], Ce doped ZnS [4] and Pb doped ZnS nanoparticles [5]. Large third-order optical nonlinearity can be expected from ZnS nanoparticles due to its exceptional luminescent properties. Initially, third-order nonlinear optical studies have been carried out on ZnS nanoparticles dispersed in solution [6, 7]. Later, this study has been carried out on ZnS thin films using different substrates due to the instability of ZnS nanoparticles in solution. During the Z-scan measurements on substrate supported ZnS thin films, it was very difficult to determine the accurate nonlinear optical coefficients of ZnS nanoparticles due to the contribution of optical nonlinearity of substrates. In order to resolve it, different substrates were used for making ZnS thin films to extract the true values of nonlinear optical coefficients of ZnS nanoparticles [8-11]. In recent years, self standing nanocomposite films containing semiconducting nanoparticles embedded in polymer matrix have been widely attracted by many researchers due to the following factors: (a) mono-dispersion of nanoparticles can be easily achieved in polymer matrix, (b) true nonlinear optical coefficients of nanoparticles can be obtained, (c) easy preparation and estimation of nonlinear optical coefficients, (d) improved thermal and mechanical stabilities [12-16].

In this paper, third-order nonlinear optical properties of Cd doped ZnS/poly vinyl pyrrolidone (Cd:ZnS/PVP) nanocomposite films have been reported. PVP was chosen as polymer matrix due to its outstanding film forming property, biocompatible and biodegradable polymer, non-toxic, high solubility in water, good mechanical strength, high thermal stability, high transparency (from ultraviolet to near infrared regions) and easy processability [16-19]. To our best of our knowledge, this is the first report on nonlinear optical properties of Cd doped ZnS/PVP nanocomposite films using Z-scan technique. During the Z-scan measurements, large value of third-order optical nonlinear coefficients was obtained. They are about two orders of magnitude larger than that of ZnS nanoparticles dispersed in solution and ZnS thin films using different substrates.

2. Experimental

2.1. Preparation of Cd doped ZnS/PVP nanocomposite films

For synthesis of nanocomposite films, 1 g of PVP polymer dissolved in double distilled water was constantly stirred using magnetic stirrer until the solution turns into transparent and colorless. Zinc acetate dihydrate and sodium sulfide with concentrations of the molar ratio of 1:1 were fixed for preparation of all the films. An aqueous solution of zinc nitrate (solution A) and cadmium nitrate (solution B) in double distilled water was prepared at room
temperature. Then solutions (A and B) were stirred vigorously for 20 min using magnetic stirrer until the mixture solution turns into transparent solution. The mixture solution of zinc nitrate and cadmium nitrate was added into the PVP solution. Then sodium sulfide aqueous solution was slowly mixed with above solution with constant stirring until the whole solution becomes to milky white color, representing the initial formation of ZnS. The stirred solution was cast on the glass slide and then dried at 70°C for 1 h in vacuum oven to evaporate the solvent contents from the Cd doped ZnS/PVP nanocomposite films. Similarly, 0, 4 and 8 mol% Cd doped ZnS/PVP nanocomposite films were synthesized. The film thickness of all the films was in the range of 65-125µm.

2.2. Characterization

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°. The surface morphologies were carried out by using JEOL Model JSM-6390LV scanning electron microscope. The FTIR spectra of three films were recorded using a PerkinElmer Spectrum GX FTIR spectrophotometer in the wavenumber range of 4000-400 cm\(^{-1}\). The room temperature optical absorption spectra were recorded using a PerkinElmer Lambda 35 spectrometer in the range of wavelength from 250 to 1000 nm. Photoluminescence (PL) studies were characterized using PerkinElmer LS 45 fluorescence spectrophotometer in wavelength range of 300-800 nm at room temperature. The Z-scan experiment was carried out using light source with a light pulse width of 5 ns illuminated by a Nd:YAG laser with a frequency doubled at 532 nm of energy per pulse of 8.0 µJ at the focus and repetition rate of 1 Hz at room temperature. A small spot of the sample was focused by the light beam using a lens having focal length 120 mm along the z axis. The sample was scanned along the Z-axis through the focal point. The transmitted light was measured as a function of position of the sample in the Z-direction through the locality of focal plane. Both open aperture (OA) and closed aperture (CA) Z-scan experiments were carried to determine the nonlinear absorption coefficient and nonlinear refractive index. The Rayleigh length (Z\(_R\)) and the beam waist (ω\(_0\)) were estimated and are found to be 2.8 mm and 25 µm.

3. Results and discussions

3.1. X-ray diffraction studies

X-ray diffraction patterns (XRD) of ZnS/PVP and various concentrations of Cd doped ZnS/PVP nanocomposite films are shown in Fig. 1. The diffraction peaks found in the Bragg angles (2θ) of 28.7°, 47.8° and 56.8° corresponding to hkl planes of (111), (220) and (311) could be assigned to cubic structure of ZnS (JCPDS card no: 05-566). From the XRD patterns of Cd doped ZnS/PVP films, no additional peaks were found and it confirms
the purity of Cd doped films. It can be seen in Fig. 1, the position of diffraction patterns shifted towards lower angle side with Cd doping in ZnS/PVP which is due to the fact that the ionic radius of Cd\(^{2+}\) (0.95 Å) is larger than the Zn\(^{2+}\) (0.74Å), i.e. the doping of Cd in the Zn site and the change in the ionic radius will make the variation in interplanar distance \((d)\) induce this type of angle shift [4]. The lattice constant \((a)\) of three films can be calculated by using the relation, 
\[
d = \frac{a}{(h^2+k^2+l^2)^{1/2}}
\]
where \(d\) is the interplanar spacing and the values for undoped, 3 and 6 mol% Cd doped films are 5.422 Å, 5.416Å and 5.11Å respectively. The lattice constant value decreases with increasing Cd doping. The average crystallite size of all the films can be calculated using the Debye-Scherrer formula:

\[
D = \frac{0.9 \lambda}{\beta \cos \theta}
\]

where \(D\) is the average crystallite size, \(\lambda\) is the wavelength of the X-rays, \(\beta\) is the full width at half maximum and \(\theta\) is the diffraction angle [4, 12]. The nanocrystallite size is found to be 3.82 nm for ZnS/PVP, 3.97 nm for 3 mol% Cd doped ZnS/PVP and 4.07 nm for 6 mol% Cd doped ZnS/PVP nanocomposite films.

3.2. SEM analysis

The SEM images of (a) ZnS/PVP, (b) 3 mol% Cd doped ZnS/PVP and (c) 6 mol% Cd doped ZnS/PVP films are shown in Fig. 2. The surface morphologies of three films are smooth which is due to the presence of PVP matrix. The ZnS nanoparticles and Cd doped ZnS nanoparticles are well mono-dispersed in PVP polymer matrix. From the Fig. 2, it can be clearly observed that the size of ZnS nanoparticles is increased with increasing of Cd dopant concentrations which might be attributed to the effect of Cd dopant in ZnS.

3.3. FTIR analysis

FTIR spectra of (a) ZnS/PVP, (b) 3 and (c) 6 mol% Cd doped ZnS/PVP nanocomposite films are shown in Fig. 3. The broad peak at 3340 cm\(^{-1}\) observed in ZnS/PVP film is attributed to the vibration of the N-H stretching of covalent bond. The other peaks of ZnS/PVP film at 2920, 1716, 1435, 1100, 928, and 847 cm\(^{-1}\) can be assigned to the C-H stretching, C=O stretching, bending of CH\(_2\), C-O stretching, CH\(_2\) rocking and CH\(_2\) stretching, respectively [18, 19]. The FTIR spectrum of the ZnS/PVP nanocomposite film after doping Cd\(^{2+}\) ion into ZnS nanoparticles shows the significant changes with respect to decrease in intensity, shift in the position of absorption peaks and disappearance of the peaks which suggest the strong interaction between ZnS nanoparticles with Cd doping and PVP. The signification changes mentioned above causes an increase in the size of ZnS nanoparticles in PVP polymer matrix with Cd doping.
3.4. UV-Vis optical absorption studies

Fig. 4 shows the optical absorption spectra of ZnS/PVP and Cd doped ZnS/PVP films. As can be observed from Fig. 4, the absorption onset of ZnS/PVP film is observed at 315 nm which exhibits the blue shift with the comparison of the absorption onset of bulk ZnS (340 nm) [2]. In optical absorption spectra of Cd doped ZnS/PVP films, the absorption onset shifted towards a longer wavelength of 320 nm for 3 mol% Cd doped ZnS/PVP film while it is shifted to 326 nm for the 6 mol% Cd doped ZnS/PVP film. The shift in the absorption onset of nanocomposite films towards longer wavelength with increasing of Cd dopant is significantly indicated ‘red-shifted’ phenomenon which causes the decrease in optical band gap energy of ZnS nanoparticles. The optical band gap energy of nanocomposite films can be calculated using the Tauc equation:

\[(\alpha h\nu)^2 = A(h\nu - E_g)\]

where \(\alpha\) is the absorption coefficient, \(h\nu\) is the incident photon energy, \(E_g\) is the band gap of ZnS nanoparticles and \(A\) is a constant [12]. Fig. 5 shows the \((\alpha h\nu)^2\) versus \(h\nu\) plot of ZnS/PVP and Cd doped ZnS/PVP nanocomposite films to determine the value of \(E_g\). The \(E_g\) values were estimated by extrapolating the linear portions of the curves to zero absorption value. The calculated \(E_g\) is found to be 3.27, 3.17 and 3.08 eV for undoped, 3 and 6 mol% Cd doped ZnS/PVP film, respectively. It is also observed that the decrease in band gap energy with increasing of Cd dopant concentration indicates an increase in the size of ZnS nanoparticles. The size of ZnS nanoparticles can be calculated using Brus equation:

\[E_{gn} = E_g + \frac{\hbar^2 \pi^2}{2R^2} \left( \frac{1}{m_e} + \frac{1}{m_h} \right)\]

where \(m_e\) and \(m_h\) are electron and hole effective masses and \(R\) is the particle size [20]. For cubic ZnS, \(m_e = 0.34 m_o\) and \(m_h = 0.23 m_o\) (\(m_o\) is the free electron rest mass). The size of ZnS nanoparticles in PVP matrix is found to be 3.79 nm, 3.91 nm and 4.03 nm for ZnS/PVP, 3 and 6 mol% Cd doped ZnS/PVP nanocomposite films. The values are well agreed with the results of XRD pattern.

3.5. Photoluminescence studies

The PL spectra of (a) ZnS/PVP, (b) 3 and (c) 6 mol% Cd doped ZnS/PVP films are shown in Fig. 6. The excitation wavelength is 310 nm. The PL spectrum of undoped ZnS/PVP film shows a blue emission peak centered around 449 nm while the PL spectra of 3 and 6 mol% Cd doped ZnS/PVP films exhibit the same blue emission peak centered on 445 nm and 439 nm, respectively. The blue emission peak ranging from 449 to 439 nm with Cd doping
is attributed to defect states such as sulfur vacancies located at the surface of ZnS nanoparticles of ZnS. The transition of electrons from a shallow state near the conduction band to the sulfur vacancies present near the valence band is the major reason for the emission observed at 445 nm [5]. Similar result has been reported by Poornaprakash et al for Co doped ZnS nanoparticles at 442 nm [20] and Esmaeil Shahriari et al for Ag doped ZnS thin film at 450 nm [8]. Upon increasing the Cd dopant concentration from 0 to 6 mol%, it has been noticed the enhancement in the intensity of emission peak. The intensity of PL peaks increases and the shift in the position of the emission peak towards shorter wavelength with increasing of Cd dopant concentration proves the increase in size of ZnS particles as discussed in XRD and optical absorption studies.

3.6. Z-scan results

Open aperture Z-scan plot of all the nanocomposite films is shown in Fig. 7(a). The open aperture (OA) plot shows a normalized transmittance valley which represents reverse saturable absorption behavior with positive nonlinear absorption. A closed aperture Z-scan plot of all the nanocomposite films is shown in Fig. 7(b). The closed aperture (CA) plot shows a valley to peak nature which exhibits strong self-focusing with positive nonlinear refraction [12-16]. The data were analysed using the procedures described by Sheik-Bahae et al [22]. The nonlinear refractive index \( n_2 \) (esu) can be calculated using the following equation:

\[
    n_2(\text{esu}) = \frac{cn_0\lambda\Delta T_{p-v}}{40\pi^20.812(1-S)^{0.25}L_{\text{eff}}I_0}
\]  

(4)

where \( c \) is the velocity of light, \( n_0 \) is the linear refractive index of the sample, \( \lambda \) is the wavelength of light, \( \Delta T_{p-v} \) is the difference between the normalized peak and valley transmittance, \( S \) is the aperture transmittance and \( L_{\text{eff}} = 1 - \exp(-\alpha L) / \alpha \) is the effective thickness of the sample (\( L \) is the sample thickness, \( \alpha \) is the linear optical absorption coefficient), and \( I_0 \) is the intensity of laser at the focal point. The calculated nonlinear refractive indices are found to be \( 8.14 \times 10^{-10} \), \( 1.341 \times 10^{-10} \) and \( 1.771 \times 10^{-10} \) m² W⁻¹ for ZnS/PVP, 3 mol% Cd doped ZnS/PVP and 6 mol% Cd doped ZnS/PVP nanocomposite films respectively. The nonlinear absorption coefficient (\( \beta, \text{mW}^{-1} \)) of all the nanocomposite films can be calculated by nonlinear curve fitting on the data of open aperture curve by the following equation:

\[
    T(z,S = 1) = \sum_{m=0}^{a} \left[ \frac{-\beta I_0 L_{\text{eff}}}{1 + z^2 / z_n^2} \right]^{m} \times \left[ \frac{1}{(m+1)^{1/2}} \right]
\]  

(6)
The calculated nonlinear absorption coefficients are found to be $1.470 \times 10^{-3}$, $2.946 \times 10^{-3}$ and $4.148 \times 10^{-3}$ mW$^{-1}$ for ZnS/PVP, 3 and 6 mol% Cd doped ZnS/PVP nanocomposite films, respectively. The estimated $\beta$ values are two orders of magnitude larger than that of the Co doped ZnS thin film [23]. The real $(\text{Re}\chi^{(3)}, \text{esu})$ and imaginary $(\text{Im}\chi^{(3)}, \text{esu})$ parts of the third-order nonlinear susceptibility can be estimated using the following equations:

$$\text{Re}\chi^{(3)}(\text{esu}) = \frac{n_2n_z}{3\pi}$$ (5)

$$\text{Im}\chi^{(3)}(\text{esu}) = \frac{n_2^2c^2\beta}{240\pi^2\omega}(\text{mW}^{-1})$$ (7)

where $\omega$ is the angular frequency of light field. The real part of the third-order nonlinear susceptibility, $\text{Re}\chi^{(3)}$, is about $6.280 \times 10^{-5}$, $8.941 \times 10^{-5}$ and $1.037 \times 10^{-4}$ esu for ZnS/PVP, 3 and 6 mol% Cd doped ZnS/PVP nanocomposite films respectively whereas the imaginary part of the third-order nonlinear susceptibility, $\text{Im}\chi^{(3)}$, is about $5.709 \times 10^{-5}$, $9.887 \times 10^{-5}$ and $1.222 \times 10^{-4}$ esu for ZnS/PVP, 3 and 6 mol% Cd doped ZnS/PVP nanocomposite films respectively. The absolute value, $\chi^{(3)}$, of third-order nonlinear optical susceptibility of all the nanocomposite films can be estimated using the following equation:

$$\left|\chi^{(3)}\right| = \left[\left(\text{Re}\chi^{(3)}\right)^2 + (\text{Im}\chi^{(3)})^2\right]^{1/2}$$ (9)

The value of $\chi^{(3)}$ is found to be $8.488 \times 10^{-5}$, $1.333 \times 10^{-4}$ and $1.603 \times 10^{-4}$ esu for ZnS/PVP, 3 mol% Cd doped ZnS/PVP and 6 mol% Cd doped ZnS/PVP nanocomposite films respectively. The $\chi^{(3)}$ values are four orders of magnitude larger than the reported value of some other representative nonlinear optical material cobalt phthalocyanine multilayer films [25] and N-doped graphene oxide nanocomposites [26].

From the Z-scan measurements, it can be clearly observed that the nonlinear optical coefficients of ZnS nanoparticles in PVP polymer matrix increase with increasing of Cd dopant concentration and Cd$^{2+}$ metal ion is a worthy candidate as the dopant to improve the nonlinear optical properties of semiconducting nanoparticles. The results obtained in the present work exhibit the reverse saturable absorption in open aperture Z-scan and self-focusing effect in closed aperture Z-scan for Cd doped ZnS/PVP nanocomposite films with varying the dopant concentration of Cd dopant from 0 to 6 mol%. Similar results have been observed for Ag doped ZnS thin films by Esmaeil Shahriari et al [8]. They have also shown that the more concentration of Ag dopant would also increase the nonlinear optical parameters of ZnS thin films. Similarly, Ganesha Krishna et al have reported that the spray
deposited ZnS thin film exhibited the maximum nonlinear absorption coefficient. i.e., $\beta = 31.9 \times 10^{-4} \text{m/W}^{-1}$ [9]. Third-order nonlinear optical properties of Nd$^{3+}$-Li$^+$ co-doped ZnS-PVP nanocomposite thin films were studied by Talwatkar et al using a continuous wave He-Ne laser at the wavelength of 632.8 nm. They have reported that the Nd$^{3+}$-Li$^+$ co-doped ZnS-PVP nanocomposite thin films showed the large refractive index ($n_2 = 10^{-7} \text{cm}^2/\text{W}$), absorption coefficient ($\beta = 10^{-6} \text{cm/W}$) and third order nonlinear susceptibility ($\chi^{(3)} = 10^{-7} \text{esu}$) [10].

On other hand, Dehghani et al have reported the nonlinear optical properties of ZnS nanoparticles in aqueous solution using CW He-Ne laser at 632.8 nm with nonlinear absorption coefficient ($\beta = 3.2 \times 10^{-5} \text{m/W}$) and nonlinear refractive index ($n_2 = 10^{-12} \text{m}^2/\text{W}$). In this report, the PVP polymer has been used as the capping agent for stability of ZnS nanoparticles in aqueous solution. However, they have not reported the complete study of nonlinear optical properties of ZnS nanoparticles in aqueous solution by determining the third-order nonlinear optical susceptibility and figure of merit [6]. Wang et al have reported the third-order nonlinear optical susceptibility in the order of $10^{-9} \text{esu}$ for ZnS-PVP nanocomposite suspension [7]. From this, it can be confirmed that the self-standing nanocomposite films containing semiconductor nanoparticles with a suitable polymer matrix as the nonlinear optical materials would certainly exhibit the large third-order nonlinearity than the substrate supported films using a glass substrate or any other substrate.

The estimated value of nonlinear optical parameters of Cd$^{2+}$ doped ZnS/PVP nanocomposite film in this work is more than one order of magnitude greater than the value reported for Ag doped ZnS thin films, spray deposited ZnS thin films, Nd$^{3+}$-Li$^+$ co-doped ZnS-PVP nanocomposite thin films and ZnS nanoparticles in aqueous solution using different capping agents. Recently, Sezen Tekin et al have reported tunable nonlinear optical absorption studies of ZnS nanocomposite thin films using silicon substrate by varying the concentration of nanoparticles using hydrothermal carbonization method. In this report, they have found that the nonlinear absorption coefficient of ZnS nanocomposite thin films was varied from the order of $10^3 \text{cm/GW}$ to $10^5 \text{cm/W}$ by varying the concentration of ZnS nanoparticles in PMMA and the addition of carbon. Finally, they have concluded the report with the statement of optical band gap energy and nonlinear absorption coefficient which depend on the aggregation of nanoparticles in the nanocomposites [11]. The reports of nonlinear optical studies on ZnS thin films and ZnS nanoparticles dispersed in aqueous solution mentioned above have been stimulated to investigate the complete study of third-order nonlinear optical properties of ZnS using suitable dopant in suitable polymer matrix. Based on this, the complete study of nonlinear optical parameters such as the nonlinear absorption coefficient, nonlinear refractive index, third-order

nonlinear optical susceptibility and figure of merit have been investigated on the Cd$^{2+}$ doped ZnS/PVP self-standing nanocomposite films in this report. In order to find the effectiveness of the Cd doped ZnS/PVP nanocomposite films for practical use in nonlinear optical devices, Figure of merit (FOM) has been calculated for all the films using the following relation, $\chi(3)/\alpha$ (where $\alpha$ is the linear absorption coefficient). The calculated FOM value is $4.042 \times 10^{-9}$, $7.152 \times 10^{-9}$ and $9.576 \times 10^{-6}$ esu m for ZnS/PVP, 3 mol% Cd doped ZnS/PVP and 6 mol% Cd doped ZnS/PVP nanocomposite films, respectively. The FOM values are eleven orders of magnitude greater than that of nanocrystalline benzimidazole thin films reported by Praveen et al [24]. The large value of nonlinear optical parameters obtained in this present study strongly recommends that the Cd$^{2+}$ doped ZnS/PVP self-standing nanocomposite films are promising candidate for the fabrication of future nonlinear optical devices.

4. Conclusions

ZnS/PVP and Cd doped ZnS/PVP nanocomposite films were prepared using in-situ chemical method. XRD patterns of all the films confirm the cubic structure of ZnS in the polymer matrix and the size of nanostructured ZnS in the polymer matrix is varying from 3.82 to 4.07 nm. SEM micrograph show smooth surface of the films and the mono dispersion ZnS nanoparticles in PVP matrix. FTIR spectra confirm the formation of Cd doped ZnS/PVP nanocomposite films. Optical absorption studies exhibited the blue shift in the absorbance onset, with the comparison of bulk ZnS. It is found that the decrease in optical band gap energy with increasing Cd dopant indicates the increase of particle size. Photoluminescence spectra of all the films exhibited a well known blue emission peak ranging from the wavelength of 449 to 439 nm with Cd doping. The Z-scan measurements represented that the Cd doped ZnS/PVP nanocomposite films exhibited large optical nonlinearity. For 6 mol% Cd doped ZnS/PVP nanocomposite film, the $n_2$, $\beta$, $\chi^{(3)}$ and figure of merit values were found to be $1.771 \times 10^{-10}$ m$^2$ W$^{-1}$, $4.148 \times 10^{-3}$ mW$^{-1}$, $1.603 \times 10^{-4}$ esu and $9.576 \times 10^{-6}$ esu m respectively. The Z-scan results of all the films have shown that the nonlinear absorption can be attributed to a reverse saturation absorption process, while the nonlinear refraction leads to self-focusing. The present report strongly recommends that the Cd doped ZnS/PVP nanocomposite film is a promising material for applications in the fabrication of nonlinear optical devices.

Conflict of Interest

The authors declare that they have no conflict of interest

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Fig. 1. X-ray diffraction of ZnS/PVP and Cd doped ZnS/PVP nanocomposite films.
Fig. 2 SEM image of (a) ZnS/PVP, (b) 3 and (c) 6 mol% Cd doped ZnS/PVP nanocomposite films
Fig. 3. FTIR spectra of (a) ZnS/PVP, (b) 3 and (c) 6 mol% Cd doped ZnS/PVP nanocomposite films.
Fig. 4. UV-Visible optical absorption spectra of ZnS/PVP and Cd doped ZnS/PVP nanocomposite films
Fig. 5. $(\alpha h\nu)^2 \times 10^9 (\text{eV}^2 \text{m}^{-1})$ vs $h\nu$ plot of ZnS/PVP and Cd doped ZnS/PVP nanocomposite films to determine $E_g$. 
Fig. 6. PL spectra of ZnS/PVA and Cd doped ZnS/PVA nanocomposite films.
Fig. 7. (a) open aperture and (b) closed aperture Z-scan plots of all the nanocomposite films
Figures

Figure 1

X-ray diffraction of ZnS/PVP and Cd doped ZnS/PVP nanocomposite films.
Figure 2

SEM image of (a) ZnS/PVP, (b) 3 and (c) 6 mol% Cd doped ZnS/PVP nanocomposite films
Figure 3
FTIR spectra of (a) ZnS/PVP, (b) 3 and (c) 6 mol% Cd doped ZnS/PVP nanocomposite films.

Figure 4
UV-Visible optical absorption spectra of ZnS/PVP and Cd doped ZnS/PVP nanocomposite films
Figure 5

\((\alpha h \nu)^2 \times 10^9 \text{ (eV}^2\text{m}^{-1})\) vs \(h \nu\) plot of ZnS/PVP and Cd doped ZnS/PVP nanocomposite films to determine \(E_g\)
Figure 6

PL spectra of ZnS/PVA and Cd doped ZnS/PVA nanocomposite films.
Figure 7

(a) open aperture and (b) closed aperture Z-scan plots of all the nanocomposite films