ZnSe/PVP nanocomposites: Synthesis, structural and nonlinear optical analysis

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Article history:
Received 29 December 2016
Received in revised form 21 March 2017
Accepted 17 April 2017
Available online 19 May 2017

Keywords:
Nonlinear optics
Nanocomposite
Pulsed laser ablation
Band gap
Optical limiting

1. Introduction

Inorganic semiconducting nanomaterials with controlled sizes, morphologies and uniform size distribution, are essential for optoelectronics and luminescent applications [1,2]. ZnSe is such an important II-VI semiconducting material with wide direct band gap (2.7 eV), large binding energy (22 meV) and small exciton Bohr radius of 3.8 nm at room temperature, which could be a part of the above-mentioned applications especially blue laser diode, light

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http://dx.doi.org/10.1016/j.matchemphys.2017.04.069
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emitting diodes, solar cells, IR optical windows etc [3–7]. Moreover, high third order nonlinearity of ZnSe nanoparticles makes them applicable for optical switches, digital signal restoration, optical storage media and optical limiters [8]. Many methods were reported for synthesizing ZnSe nanoparticles such as pulsed laser deposition, chemical bath deposition, sol-gel method, co-precipitation method, molecular beam epitaxy, reduction by ionising radiation etc [8–12]. Most of these methods are expensive and complex in nature. For the last few years, pulsed laser ablation (PLA) technique is turned to be one of the best physical methods for the preparation of nanocomposites (nc) due to the following advantages. It is simple and clean synthesis in which further purification is not required [13]. The liquid medium in which we place the ablating target itself act as the matrix or dispersive medium for the nanoparticles [14]. The particle size and morphology can be controlled by varying the laser parameters such as wavelength, fluence and pulse duration of the laser. Physical properties of the liquid medium chosen for the ablation also influences the size of the nanoparticle formed [15]. Anikin et al., reported the synthesis of ZnSe nc in diethylene glycol by PLA for the first time [16]. Mosmer et al., synthesized ZnSe ncs in acetone and ethyl alcohol and compared structural properties of the two ncs formed [7]. Here we report the synthesis of ZnSe nc in the polyvinyl pyrrolidone (PVP)/dimethyl formamide (DMF) solution by PLA and their detailed structural and nonlinear optical (NLO) investigations. For this organic-inorganic composite formation, PVP is chosen as the dispersive medium because of its less toxicity, excellent solubility and high chemical stability [17]. In the in situ synthesis of ZnSe/PVP nc by laser ablation, reduced particle size of ZnSe nanoparticles enhances the optical nonlinearity due to quantum confinement and the stabilizing polymer PVP enhances the optical properties of the nc altogether. The third order nonlinear parameters extracted from the z-scan analysis demonstrate the nc as an excellent candidate for nonlinear optical applications.

2. Experimental methods

2.1. Synthesis

ZnSe/PVP nc was synthesized by ablating a flat bulk ZnSe target (Alfa Aesar:99.995%) with thickness of 3 mm placed in the beaker containing 2 wt% PVP/DMF solution using a Q-switched Nd: YAG laser (Spectra Physics) of wavelength 532 nm, 7 ns pulse width and 10 Hz repetition rate. The laser beam with energy 30 mJ/pulse was focused on the target using a convex lens of focal length 50 mm for 20 min. A yellow colored colloidal solution was obtained.

During laser ablation, the laser beam is focused on the target through the liquid environment. The ablated species, which is a cloud of Zn, Se ions and neutral atoms, form a plasma plume on the top of the target and nucleation leads to the growth of the nano-clusters which occurs inside the plume and on the plume-liquid interfaces. On cooling the plasma plume by the surrounding liquid, Zn and Se form molecules and they combine to form the crystalline structures which disperse in the entire liquid to form nc [7,13].

2.2. Characterization

The nc formation is confirmed by FTIR analysis using FT-IR spectrometer (JASCO-FT/IR 4700). The absorption and the emission spectra were obtained using a UV-Vis spectrophotometer (Shimadzu-UV 2450) and a fluorometer (Perkin Elmer LS 45), respectively. The synthesized nc was drop casted on the glass slide for XRD characterization (RIGAKU-MINIFLEX 600) using CuKα radiation. After removing PVP/DMF by centrifugation, the sample was further characterized by TEM (JEOL, JEM-2100) at an accelerating voltage of 200 kV and SEM (HITACHI SU6600).

The nonlinear optical studies were performed by z-scan technique introduced by Sheik Bahae et al. [18]. The same laser system mentioned in the synthesis part was used as the excitation source of the z-scan experiment in ns regime and the experimental arrangement is given in Fig. 1. The laser beam having Gaussian profile is divided in to two, using a beam splitter and kept one as the reference beam and the other passes through the sample, which is moving along the focus of a convex lens (focal length 150 mm) with the help of computer controlled micrometer translational stage in steps of 1000 μm. The incident and transmitted laser energies were collected using two identical Pyroelectric detectors (RIJP-735 Laser Probe Inc, USA) and recorded by an energy ratio meter (RJ-7620, Laser Probe Inc, USA). To satisfy the thin sample approximation condition, the sample was taken in a quartz cuvette of 1 mm thickness which is less than the Rayleigh range. Rayleigh range is calculated to be 1.69 mm, using the equation, z₀ = πλω₀²/λ, where λ₀ is the beam radius at the focus (16.9 μm). The beam diameter at any position z = ω₀ can be calculated using the relation ω₀ = ω₀ [1 + (z/2z₀)²] and hence the laser beam fluence also can be determined. The linear transmittance of the nc is adjusted to be 70% for all z-scan experiments.

Nonlinear optical studies of ZnSe nc thin films were performed in the femtosecond (fs) temporal regime using Ti: Sapphire laser system (Chameleon, Coherent) delivering nearly transform-limited pulses of ~150 fs with a repetition rate of 80 MHz at 800 nm. Laser pulses with peak intensity 42 MW/cm² were used for the experiments. The beam was focused using a lens of 100 mm focal length into the sample. The beam waist (ω₀) estimated was ~25 μm with a Rayleigh range of 3.5 mm. The transmittance changes of the sample were measured with a sensitive power meter (Power Max, Coherent) in the far-field as the sample moves along the propagation axis with the help of translational stage. We kept the pulse energy lower in order to avoid contribution from higher order nonlinearities.

3. Results and discussions

3.1. Linear optical analysis

UV-Visible absorption spectrum of ZnSe/PVP nc, shows a sharp absorption peak around 269 nm (Fig. 2(a)). The optical band gap can be estimated from the classical Tauc equation 2hν = A(hν−Eg)², where z is the absorption coefficient, hν is the photon energy, Eg is band gap energy, A is a constant and n is having different values like 1/2, 1, 3/2, or 2 for allowed direct, allowed indirect, forbidden direct and forbidden indirect electronic transitions. The band gap of the nc is obtained as 3.87 eV from the Tauc plot, on extrapolating the linear portion of (zhν)² to the hν axis (Fig. 2(b)). The large band gap value ensures the potentiality of the synthesized ZnSe nc in optoelectronic devices as it can withstand high voltage, high frequency, and high temperature. The photoluminescence spectrum of the sample is given in Fig. 3, which is a broad, but intense emission spectrum centered at 374 nm for an excitation wavelength of 270 nm and this UV emission is due to electron hole recombination [19]. The increased band gap value and the blue shift in both absorption and emission spectra compared to the bulk ZnSe can be accredited to the quantum confinement effect which is due to the changes in atomic structure by the direct influence of ultra reduced size of the nanoparticles on the energy band structure. The particle size corresponds to quantum confinement ranges from 1 to 25 nm for II-VI group semiconductors in which the spatial extent of the electronic wave function is comparable with the mentioned particle size and the electrons respond to changes in particle size by
adjusting their energy [4,5]. The photographic image of the synthesized sample taken under UV light is shown inset of Fig. 3.

### 3.2. Structural and morphological analysis

The interaction between ZnSe nanocrystals and PVP in the formation of nc is evident from the FTIR spectrum of both PVP and ZnSe/PVP given in Fig. 4. The observed shift in the peaks 3497.27 cm\(^{-1}\)/C\(_0\) 1, 2339.23 cm\(^{-1}\)/C\(_0\) 1, 1660.41 cm\(^{-1}\)/C\(_0\) 1 and 1254.47 cm\(^{-1}\)/C\(_0\) 1 of PVP on nc formation assures the strong interaction of ZnSe nanocrystals with PVP, and the peak at 524.54 cm\(^{-1}\)/C\(_0\) indicates Zn and Se vibrations [20,21]. The crystalline structure of the composite is analysed by the XRD spectrum of ZnSe nc is given in Fig. 5. The prominent diffraction peaks correspond to the lattice planes (111), (220) and (311) are at 27.23°, 45.22° and 53.59° respectively.

According to the JCPDS no: 65-9602, the synthesized ZnSe nc is of cubic Zinc blend structure and it belongs to the F\(_{43}m\) space group [22]. The average size of the nc is calculated as 62.7 nm using Debye-Scherrer formula, \(D = \frac{0.9\lambda}{\beta \cos \theta}\), where \(\lambda\) is the wavelength of X-ray radiation (1.5418 Å), \(\beta\) is the full width at half maximum (FWHM) in radians of the peak corresponding to the lattice plane (111) and \(\theta\) is the angle of diffraction [21]. The lattice parameter, \(a\) is calculated as 5.71 Å, from the \(d\) values corresponding to (111), (220) and (311) planes, using equation (1)/

\[
d^2 = \frac{(h^2 + k^2 + l^2)}{a^2}
\]

No other peaks are observed in the spectrum, implying the purity of the synthesized sample. The Sharp and narrow peak are due to the relatively larger size and crystalline quality of the nc thus formed [23].

TEM image of the ZnSe nc and the Gaussian fitted histogram (inset) are shown in Fig. 6(a). The size of the formed nanoparticles varies from 5 nm to 80 nm range where most of the particles have the size <20 nm. The average particle size is found to be 12.69 ± 0.14 nm. The larger size of the nc obtained from the XRD spectrum could be due to the presence of PVP in the drop casted sample. Grain size image of ZnSe nc is given in Fig. 6(b) and the
The lattice spacing corresponding to the plane (111) is 0.32 nm which is in accordance with the XRD spectrum. The selected area electron diffraction pattern (SAED) is given inset. Bright spheres in the SAED pattern correspond to the lattice planes (111), (220) and (311), indicate the good crystalline nature of the sample. The d values corresponding to (220) and (311) planes are 0.17 nm and 0.16 nm. The SEM image of the nc is shown in Fig. 7 and it ensures the spherical morphology of the ZnSe nc.

3.3. Nonlinear optical analysis

The open aperture z-scan signature of the ZnSe/PVP nc and the PVP/DMF solution using ns pulses at a peak intensity of 0.27 GW/cm$^2$ is given in Fig. 8. It is found that the nc exhibits good nonlinear absorption (NLA) and PVP/DMF solution shows negligible NLA, hence the solvent effect can be discarded. The transmittance of the sample is symmetric about the focus ($z = 0$). Experimental data are shown by circles and its corresponding theoretical fit is shown by solid line. The theoretical fitting is done based on the nonlinear propagation equation involving two-photon absorption (2PA) and is given by

$$\alpha(I) = \frac{\alpha_0}{1 + \left(\frac{I}{I_0}\right)} + \beta I$$

(1)

where, $\alpha(I)$ the intensity dependent absorption, $\alpha_0$ the linear absorption coefficient, $I_s$ saturation intensity and $I$ the incident beam intensity [24]. The modified transmittance equation for temporal and spatial Gaussian beam can be written as,

$$T(z) = \frac{Q_0}{\pi^{1/2} q_0(z)} \int_{-\infty}^{\infty} \ln(1 + q_0(z))e^{-r^2} dt$$

(2)

where, $Q_0(z) = \exp(\alpha_0 I/(I + I_s))$ and $q_0(z) = \alpha_0 \beta_{eff}(1/(1 + z/z_0)^2)$ in which, $I_0$ is the on-axis input intensity, $z$ is the position of the sample, $z_0$ is the Rayleigh range and $\beta_{eff}$ is the effective optical path length given by $(1-\exp(-\alpha_0 L))/\alpha_0$ and $L$ is the sample length. The NLA coefficient $\beta_{eff}$ which is a measure of the overall nonlinear absorption including excited state absorption (ESA) and 2PA, is obtained as $2.6 \times 10^{-10}$ mW$^{-1}$ from the theoretical fitting of the z-scan data and the value is found to be comparable with NLA coefficients of many of the semiconductor and metal nanoparticles [25–28].

NLA can arise due to many absorption mechanisms such as multiphoton absorption, ESA, free carrier absorption etc. For ZnSe nc, the linear absorption peak is obtained at 269 nm, which is twice the excitation frequency and it implies the chance of 2 PA as NLA.
mechanism. We have done the open aperture analysis for different peak intensities; 0.14 GW/cm², 0.27 GW/cm², 0.82 GW/cm² and 1.37 GW/cm² (Fig. 9(a)). It is found that the $\beta_{\text{eff}}$ values were decreasing with increasing peak intensities (in Fig. 9(b)), which confirms the absorption mechanism as reverse saturable absorption (RSA) i.e., 2PA followed by ESA, that involves two real energy states and considerable ground state depletion. Therefore on increasing intensity, depletion of the ground state population increases, which leads to decrease in $\beta_{\text{eff}}$ values [29]. The observed NLA point towards strong optical limiting behavior and their immense applications in eye and sensor protection from intense lasers lights [30]. To determine the photo-thermal stability of the synthesized sample, we have irradiated the nc at a very high peak intensity of 5.55 GW/cm² for 20 min and checked the absorption spectrum of the sample before and after irradiation. The consistency of the absorption peak pronounced the photo-thermal stability of the sample.

The closed aperture (CA) z-scan analysis extracts the nonlinear refractive property of the sample, in which an aperture of diameter 3 mm is kept in front of the detector in the far field. To recapture the phase distortion due to intensity dependent nonlinear refractive index, normalized CA data can be divided by the corresponding normalized OA data [31]. Fig. 10 shows the pure nonlinear refraction signature obtained by the above-mentioned division method. The post-focal valley followed by pre-focal peak indicates negative nonlinear refractive index coefficient. The obtained signature is fitted using the following equation [32].

Fig. 8. Open aperture Z scan signature of ZnSe/PVP NC at 0.27 GW/cm².

Fig. 9. (a) Normalized open aperture z scan signatures of ZnSe/PVP nc at different energies and (b) $\beta_{\text{eff}}$ versus on-axis intensity $I_0$.

Fig. 10. Closed by open aperture z scan signature of ZnSe/PVP nc at 0.27 GW/cm².

Fig. 11. Input fluence versus normalized transmittance of ZnSe/PVP nc at 1.37 GW/cm².
In which, $T$ is the normalized transmittance for the pure refractive nonlinearity, $\Delta \phi_0$ is the on-axis nonlinear phase shift at the focus. The nonlinear refraction coefficient $n_2$ was obtained as $1.45 \times 10^{-11}$ esu, using the relation $n_2 \text{ (esu)} = |c|n_0/40\pi \gamma (\text{m}^2\text{W}^{-1})$ where $\gamma = \Delta \phi_0/l_2 n_0 \Delta \phi_{\text{off}}$, $c$ is the velocity of light in $\text{ms}^{-1}$ and $n_0$ is the linear refractive index ($n_0 = 1.42$). The real and imaginary parts of third order nonlinear susceptibility were calculated using the relations $\text{Re}(X^{(3)}) = 2n_0\epsilon_0c\gamma \beta$ and $\text{Im}(X^{(3)}) = n_0\epsilon_0c\beta l_2 \gamma$. The values were obtained as $1.5 \times 10^{-12}$ esu and $1.12 \times 10^{-11}$ esu. Then the total $X^{(3)}$ is $1.16 \times 10^{-11}$ esu. All the nonlinear parameters were measured within the error limit of $7\%$, which could be due to laser energy fluctuations and data fitting errors. The value of the third order nonlinear susceptibility is comparable to the reported values [33].

The optical limiters are meant for minimizing the threat by high intense lasers and they reduce the transmittance as input intensity increases. The optical limiting property of the sample at 1.37GW/cm$^2$ is extracted from the OA z-scan data by plotting normalized transmittance versus input fluence as shown in Fig. 11, in which the transmittance decreases as the fluence increases. The value of input fluence at which it starts decreasing (onset value), and at which the transmittance becomes half (limiting threshold) are the parameters deciding the optical limiting quality of the sample. Here the onset value of the ZnSe nc is 0.47 J/cm$^2$ and the threshold value of optical limiting is 6.8 J/cm$^2$ which are comparable with many of the reported values [34,35].

Z-scan measurements of ZnSe nc thin film in the fs regime also reveal the optical limiting nature of the composite. The open aperture signature and the optical limiting curve of the nc film using laser with fs pulse width is given in Fig. 12(a) and (b).

The data was fitted using the following equation (equation (4)) derived from the propagation equation [18],

$$T = \frac{1}{1 + \beta L_{\text{off}} \left( \frac{l_{\text{off}}}{l_0} \right)^{1/3}}$$  

where $\beta$ is the effective third order nonlinear absorption coefficient, $l_{\text{off}}$ is the peak intensity. On fitting the experimental data using equation (4), $\beta$ and $l_{\text{off}}$ were obtained as $4.5 \times 10^{-7}$ cm$^2$W and 42 MW/cm$^2$ respectively. The optical limiting graph is extracted from the OA plot just as in the case of ns z-scan analysis and the limiting threshold is obtained as $0.048$ J/m$^2$. Further measurements need to be performed for understanding the excited state dynamics. However, the sample is showing good optical limiting property in the fs regime. Among the number of causes for third-order nonlinearities, thermal nonlinearity which leads to thermo refraction needs to be considered while using high repetition rate (MHz) laser sources. This may occur when the thermal diffusion time is larger than the temporal spacing between the pulses [36].

We have estimated the thermal diffusion time for ZnSe/PVP case, and was found to be $7.7$ ns, which is lower than the temporal spacing (13 ns) between consecutive pulses. We still cannot completely rule out the possibility of small contribution of thermal nonlinearity to the overall observed nonlinear absorption coefficient. Recent studies on Zinc(II) phthalocyanine molecules performed at 800 nm with fs, MHz pulses and 1.5 ps, kHz pulses clearly demonstrated a two orders of magnitude difference in the 2PA coefficient [37]. Fs/kHz z-scan measurements will be performed to measure the NLA coefficients devoid of any thermal nonlinearity in near future.

4. Conclusion

We report the synthesis of ZnSe/PVP nc by pulsed laser ablation technique in the liquid phase using Q-switched Nd: YAG laser of 532 nm wavelength. Absorption and emission spectra guaranteed the optical and crystalline quality of the nc. The large band gap value of the nc is making it a promising candidate for optoelectronic applications. Formation of the nc is confirmed by FTIR analysis. The structural and morphological characterizations were done by XRD, TEM and SEM and the average particle size is found to be 12.69 ± 0.14 nm. The nonlinear optical investigations were done by z-scan analysis in both ns and fs regime, and it is found that the nc exhibits good optical limiting property in both excitation regime.

Acknowledgement

Authors acknowledge NIT Calicut, Kozhikode, Kerala, India for the financial support. MCD expresses her gratitude towards Ms. Dijo Prasannan, Mr. Muhammed Sabeer and her colleagues Dr. N. K. Siji Narendra, Mrs. M. V. Vijisha and Mr. K. Vasudevan for their valid suggestions and support. SVR and PTA acknowledge DRDO for financial assistance.

References
