

Phenomenal enhancement of optical nonlinearity in PTZ-I based ZnS/ZnSe nanocomposites

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ABSTRACT

The enhanced nonlinear optical properties of phenothiazine-iodine (PTZ-I) charge transfer complex (CTC) on composite formation with ZnS/ZnSe nanostructures are reported. The interaction between the components was confirmed by the FTIR spectra. Structural and morphological changes on nanocomposite formation were analyzed by scanning electron microscopy and X-ray diffraction spectra. The absorption and emission features of both the nanocomposites and their constituent components were studied. Nonlinear optical properties of all the samples in nanosecond regime were investigated by the Z-scan technique using Nd: YAG laser with 532 nm wavelength and 7 ns pulse width. The optical nonlinearity of PTZ-I CTC was found to be improved considerably on composite formation and the new systems can be proposed as excellent candidates for photonic devices. Enhanced optical nonlinearity of the composites could be attributed to charge/energy transfer mechanism between PTZ-I CTC and the nanostructures.

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1. Introduction

Blending different materials to form composites and thus to extract properties superior to starting materials is a current trend in the field of nonlinear optics. In a nanocomposite (NC), one of the phases being of nanometer size, the interplay between the phase interfaces is increased extensively, resulting the enhancement in material properties [1–4]. Optical nonlinearity of organic compounds can be varied by the structural alteration [5] and that of nanomaterials by varying the size and shape [6]. Both are largely investigated for their nonlinear optical (NLO) properties, but only a few studies have been reported on the NLO properties of systems comprising charge transfer complex when compared to above two categories [7]. The architecture of fusing the nanostructure (NS) with a complex organic compound is expected to result in promising candidates for applications such as optical limiters, bio imaging, solar cells, catalysis, fuels, etc. [3,8]. So far various NC systems are explored for NLO applications [9–13]. Here, NC systems of II-VI semiconductor NS with phenothiazine-iodine (PTZ-I) charge transfer complex (CTC) are studied in detail and the composite exhibited enhanced NLO properties compared to the pristine

compounds. PTZ-I CTC is a semiconductor molecular structure with excellent electronic, magnetic and optical properties [14,15]. In PTZ-I CTC, phenothiazine acts as an electron donor and iodine as an electron acceptor and forms a single system with a charge transfer absorption band in the UV–Visible region [16,17]. The induced dipole moment and delocalization of electrons on charge transfer between PTZ and iodine are expected to contribute to the optical nonlinearity of CTC [7,18]. In an attempt to improvise the exhibited NLO behavior of PTZ-I CTC, ZnS/ZnSe NS were incorporated to the CTC by the method of stirring. ZnS and ZnSe NS were synthesized by pulsed laser ablation as dispersed in the solution of polyvinylpyrrolidone/dimethylformamide (PVP/DMF) and their structural and nonlinear optical properties are reported elsewhere [19,20]. In this work, two NC systems were prepared by incorporating both ZnS and ZnSe separately with CTC, namely ZnS-PTZ and ZnSe-PTZ. The improved optical nonlinearity of the NC could be ascribed due to the charge/energy transfer between the components.

2. Experimental methods

2.1. Synthesis

Phenothiazine-iodine CTC in 1:3 M ratio was synthesized by stirring the mixture of 0.5 g of PTZ (>98% Sigma Aldrich) in 50 ml of

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DMF and 1.95 g of iodine in 150 ml of DMF continuously for 3 h [17]. The resultant dark-colored solution was found to be stable for several months. ZnS and ZnSe nanostructures were synthesized by ablating the respective targets placed in the PVP/DMF solution. The targets were irradiated by a focused laser beam having pulse energy 30 mJ/pulse for 20 minutes [19,20]. Both CTC and synthesized nanostructures in the solution form were mixed separately in an equal proportion and then stirred for 2 hours continuously to form corresponding nanocomposites.

2.2. Characterization

The absorption and emission spectra of individual components and the composites were recorded using a UV–Visible spectrophotometer (Shimadzu-UV 2450) and a fluorometer (Perkin Elmer LS 45) respectively. Morphological analysis of the NC was carried out using scanning electron microscope (SEM- HITACHI SU6600). The composite formation was confirmed with the help of FTIR spectrometer (JASCO-FT/IR 4700). The structural characterization of the samples was done by X-ray diffractometer (RIGAKU-MINIFLEX 600) using CuK_α radiation.

Z-scan experimental set up introduced by Sheik Bahae et al. was used for NLO studies [21] and the schematic diagram is given in Fig. 1. The Z-scan method is widely used for measuring both the sign and magnitude of the nonlinearity and the method is very simple and highly sensitive. The open aperture (OA) Z-scan method is used to study nonlinear absorption (NLA) and closed aperture (CA) Z-scan is used for nonlinear refraction (NLR) studies. Linear transmission of all the samples viz., ZnS NS, ZnSe NS, PTZ-I CTC, ZnS-PTZ, and ZnSe-PTZ were kept around 70%.

A tightly focussed spatial and temporal Gaussian (TEM_{00}) laser beam (Nd: YAG laser: 532 nm, 7 ns, 10 Hz) was used as the excitation source for the Z-scan experiment. The beam is split into two using a beam splitter, in which one beam is taken as the reference beam and the other beam is focused using a convex lens of focal length 150 mm and is allowed to transmit through the sample taken in a 1 mm thick quartz cuvette. The sample is moving from $-z$ to $+z$ through the focus of the lens in steps of 1000 μm with the help of a motorized translational stage which is controlled by a computer program. Both the reference beam and the transmitted beam are detected using two pyroelectric detectors (RjP-735 Laser Probe Inc, USA) and are recorded in the energy meter (Rj-7620, Laser Probe Inc, USA). The thickness of the sample is less than Rayleigh range, $z_0 = 1.69 \text{ mm}$, (which is calculated using the formula, $z_0 = \pi\omega_0^2/\lambda$) and hence the thin sample approximation can be applied. The intensity dependent transmittance measured using detectors are plotted against the position of the sample. In CA Z-scan method, a small aperture of 4 mm diameter is placed in front

of the detector to detect the intensity dependent phase distortion of the core portion of the beam. But in OA Z-scan method the whole beam profile is detected in the detector as there is no aperture in the path of the beam [19].

3. Results and discussions

3.1. Optical analysis

The linear absorption spectra of ZnS-PTZ and ZnSe-PTZ are given along with that of PTZ-I and the corresponding NS respectively in Fig. 2(a) and (b). PTZ-I showed strong absorption of a charge-transfer band in the UV–Visible region (250 nm– 450 nm) and it didn't show any absorption peak of either PTZ or iodine [7,15]. This charge transfer band is due to the charge transfer of electrons from the highest occupied orbital of PTZ to the lowest unoccupied orbital of iodine [22]. The absorption peaks of both ZnS and ZnSe NS were found to be red shifted by nanocomposite formation [4,23].

The photoluminescence spectra of the two composites were analyzed to find the changes in emission properties with that of individual components and are given in Fig. 3. The composites and PTZ-I were excited at a wavelength of 350 nm and the pristine ZnS or ZnSe were excited at a wavelength of 270 nm to record the corresponding emission spectra. Both ZnS and ZnSe showed the strong emission peaks in the UV region (344 nm and 374 nm respectively), whereas the emission from PTZ-I consists of two visible peaks at 408 nm and 425 nm. Both the composites possessed smooth and narrow emission spectra with their emission peaks at 412 nm and 414 nm for ZnS-PTZ and ZnSe-PTZ respectively.

3.2. FTIR analysis

The FTIR spectra of the phenothiazine-iodine complex and their composites of ZnS and ZnSe are given in Fig. 4. The PTZ-I showed a strong and broad peak at 3384 cm^{-1} , which is the characteristic N–H bond of PTZ-I complex [24]. The N–H band of PTZ at 3384 cm^{-1} was found to be shifting to a higher wavenumber at 3404 cm^{-1} and 3414 cm^{-1} on the composite formation with ZnSe and ZnS respectively. The aromatic C=C stretching vibration was observed around 1435 cm^{-1} and found to be shifted to 1496 cm^{-1} on composite formation. These shifts in absorption frequencies of composite as compared to pure PTZ-I was attributed to the interfacial interactions between the NS and the polar segment of PTZ-I. The new absorption peaks observed at 657 cm^{-1} and 1099 cm^{-1} for ZnS-PTZ and at 655 cm^{-1} and 1098 cm^{-1} for ZnSe-PTZ, also indicate the interaction between the components and the composite formation.

3.3. Structural and phase analysis

SEM images of PTZ-I, ZnS-PTZ and ZnSe-PTZ composites are shown in Fig. 5 (a), 5 (b) and 5 (c) respectively. The surface morphology of pure PTZ-I was globuloidal. From the SEM images, the spherical morphologies of nanocomposites were also revealed.

The XRD spectra of PTZ-I, ZnS-PTZ, and ZnSe-PTZ are given in Fig. 6. It can be seen from the figure that the PTZ-I shows the diffraction peaks at $2\theta = 8.26^\circ, 12.52^\circ, 16.75^\circ, 21.03^\circ, 33.53^\circ, 38.46^\circ$ indicating the crystalline behavior of the charge transfer complex. ZnS NS shows the crystalline diffraction peaks at 2θ values of $28.47^\circ, 47.43^\circ$ and 56.31° and possesses hexagonal wurtzite structure (JCPDS card no: 39–1363) with planes (008), (110) and (118) for ZnS NS [20], whereas the diffraction peaks of ZnSe NS are at $27.23^\circ, 45.22^\circ$ and 53.59° corresponding to crystalline planes (111), (220) and (311) which is of cubic zinc blend structure (JCPDS no:

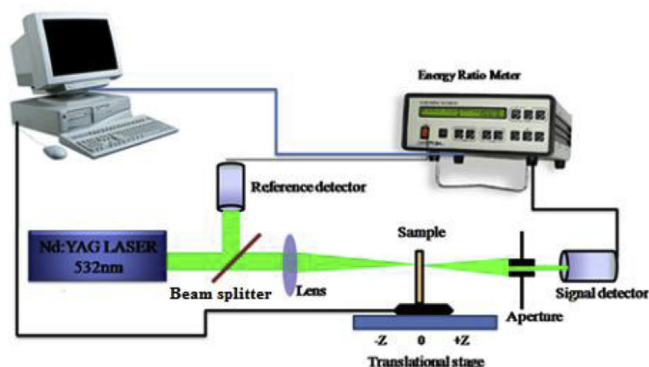


Fig. 1. Z-scan experimental set up.

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