Chapter 5

Size dependent nonlinear optical properties of Zinc Oxide-Polystyrene nanocomposite films

5.1 Introduction

5.2 Optical Characterization

5.3 Nonlinear optical (NLO) studies

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The investigations carried out on the third-order nonlinear behavior of ZnO/PS nanocomposite films, containing ZnO particles with size in the range 6.5–35 nm, by Z-scan technique are included in this chapter. ZnO/PS nanocomposite shows a self-defocusing type nonlinearity and good nonlinear absorption at 532 nm. The observed optical nonlinearity is explained based on two-photon absorption. The third-order optical susceptibility ($\chi^{(3)}$) increases with increasing particle size (R) due to the size dependent enhancement of exciton oscillator strength. These films also show a self-defocusing type negative nonlinear refraction in closed aperture Z-scan experiment. The good nonlinear response of these composite films, combined with the improved stability of ZnO nanoparticles in the polymer matrix offer prospects of application of these composite films in the fabrication of stable non-linear optical devices.
5.1 Introduction

Nanoscale materials are under active research over the past few decades, owing to their interesting versatile properties, quite different from those of the bulk form [1]. Semiconductor nanocrystals have been investigated extensively due to their promising applications in optoelectronics and photonics. The effects of particle size on optical properties are more pronounced in semiconductor nanoparticles.

Specifically, oxide semiconductor nanocrystals are currently being studied widely, considering their tunable electrical and optical properties and the potential applications in many areas, such as field emission displays, solar cells and gas sensors [2-4]. The linear and nonlinear optical properties of nanostructured semiconductors are the topics of current theoretical and experimental interest [5]. With the advent of the widespread usage of optical detectors and sensors for scientific and industrial purposes, the need has rapidly arisen for optical limiting devices that protect the photosensitive components from intense optical radiation while remaining inactive for low intensity levels. Amongst the various nonlinear optical (NLO) materials investigated, direct band gap semiconductors, such as zinc oxide have attractive nonlinear properties that make them ideal candidates for NLO based devices. Zinc oxide is having many applications in transparent electronics, photovoltaics, display devices and laser fabrication [4, 6].

Investigations into the nonlinear optical properties of the composite films containing semiconductor nanoparticles have attracted considerable attention due to their practical applications in optical switching and optoelectronic devices [7-11]. Polymers are chosen as
suitable host materials because they usually exhibit long-term stability and possess flexible reprocessability. Attractive optical properties such as fluorescence, electroluminescence and optical nonlinearity have been observed in these organic-inorganic composites.

The studies of nonlinear processes in photonic materials are significant in the context of their technological applications, especially in areas such as passive optical power limiting, optical switching, and the design of logic gates. Optical limiting (OL) is an important application of nonlinear optics, useful for the protection of human eyes, optical elements and optical sensors from intense laser pulses. Optical limiting occurs when the absolute transmittance of a material decreases with increase in input fluence. The optical limiting property occurs mostly due to absorptive nonlinearity which corresponds to the imaginary part of third order susceptibility [12]. ZnO based nanocomposites are good candidates for optical limiting against broadband laser pulses. Optical limiting can be achieved by one or more of the nonlinear optical mechanisms such as excited state absorption (ESA), free-carrier absorption (FCA), two photon absorption (TPA), thermal defocusing/scattering, photo refraction, nonlinear refraction, and induced scattering [13]. Optical limiting performance is enhanced by coupling two or more of the nonlinear optical mechanisms like self-defocusing in conjunction with TPA in semiconductors [14] or TPA of one molecule with ESA in another molecule [15].

Although optical nonlinearity has been reported in many semiconductor nano composites [16, 17], this phenomenon in ZnO/PS nanocomposite films has not been subjected to detailed investigations.
yet. Hence attempts have been made, in the present work, to investigate in detail, the optical nonlinearity of polymer-modified nanocrystalline ZnO, synthesized by a wet-chemical synthesis process. Polystyrene (PS) is chosen as the host polymer material because of its excellent solubility in ordinary solvents and chemical stability. In the present work, the nonlinear optical properties of the ZnO/PS nanocomposite films are investigated by employing the Z-scan technique using nanosecond laser pulses at 532 nm. The dependence of the non-linear effects on the size of the ZnO nanoparticles in the composite films is analyzed in detail.

5.2 Optical characterization

The UV-Visible transmission spectra of the films were recorded on a JASCO-V 570 spectrophotometer in the wavelength range 200 to 800 nm.

The transmission spectra of pure PS and ZnO/PS nanocomposite film are shown in figure 5.1. The composite film shows transparency around 70% in the visible region. The photograph of the freestanding ZnO/PS nanocomposite film with the printing beneath is shown in the inset of figure 5.1. It is clear that the absorption of the ZnO/PS nanocomposite film comes mainly from the ZnO nanoparticles, especially below 400 nm. ZnO/PS nanocomposite film exhibits strong absorption around 350 nm and the optical band gap of the composite films is estimated from the plot of $(\alpha h\nu)^2$ vs. $(h\nu)$ for the absorption coefficient $\alpha$ [20]. An increase in the band gap with decrease in particle size of ZnO is observed which is attributed to the quantum size effect [21]. The band gap of ZnO nanoparticles increases as the size decreases, with a decrease in the concentration of KOH solution (Figure 5.2).
Figure 5.1: The transmission spectra of (a) PS film (b) ZnO/PS nanocomposite film (Inset shows the photograph of ZnO/PS freestanding film with the printing beneath it).

Figure 5.2: Dependence of band gap energy and particle size of ZnO in the composite film on KOH concentration.
5.3 Nonlinear optical (NLO) studies

The optical nonlinearity of the nanocomposite films was studied by Z-scan technique. This method was used for measuring the sign and magnitude of nonlinear refractive index and nonlinear absorption coefficient [18, 19]. A Q-switched Nd-YAG laser with a pulse width of 7ns at 532 nm was used in the experiment. A lens of focal length 23 cm was used to focus the laser pulses. Samples in the form of thin film were used for the experiment. The sample was moved in the direction of light incidence near the focal spot of the lens. The transmitted beam energy, reference beam energy and their ratio were measured simultaneously by an energy ratio meter (Rj7620, Laser Probe Corp.) having two identical pyroelectric detector heads. The linear transmittance of the far field aperture S, defined as the ratio of the pulse energy passing the aperture to the total energy was measured to be approximately 0.21. The data was analyzed by using the procedure described by Sheik Bahae et al. [18] and the nonlinear coefficients were obtained by fitting the experimental Z-scan plot with the theoretical plots. The experimental set up and other details are given in chapter 2.

5.3.1 Open aperture Z-scan

Nonlinear optical properties of ZnO/PS nanocomposite films, containing ZnO nanoparticles having different particle size, were investigated by the Z-scan technique. Figure 5.3(a-e) shows the nonlinear absorption of ZnO/PS nanocomposite films at a typical laser energy of 25µJ for an irradiation wavelength of 532 nm. The open-aperture curve exhibits a normalized transmittance valley, indicating the presence of induced absorption. The observed nonlinearity is found to be
of the third-order, as it fits to a two photon absorption process (TPA). The corresponding net transmission is given by [18]

\[ T(z) = \frac{1}{q_0} \int_{-\infty}^{\infty} \ln(1 + q_0 e^{-\beta t}) dt \]  

(5.1)

where \( q_0(z, r, t) = \beta I_0(t) L_{\text{eff}} \).

Here, \( L_{\text{eff}} = 1 - e^{-\alpha L / \alpha} \), is the effective thickness with linear absorption coefficient \( \alpha \) and nonlinear absorption coefficient \( \beta \), and \( I_0 \) is the irradiance at focus. The solid curves in figure 5.3(a-e) represent the theoretical curves having best fit to the experimental data. The experimentally obtained values of nonlinear absorption coefficient \( \beta \) at a pulsed energy of 25µJ are shown in table 5.1.

From the open aperture Z-scan curves it is found that the ZnO/PS nanocomposite films do exhibit a large induced absorption behavior. It is observed that as the band gap decreases (that is, as the particle size increases) the rate of two photon absorption increases which is attributed to an inverse proportionality between \( \beta \) and the third power of band gap [13]. Hence the dip in the open aperture curve increases with increase in particle size leading to the observed increase in the limiting efficiency with increase in the particle size. Although similar investigations have been reported in ZnO/PMMA nanocomposite films [22], in the present case, the curves of ZnO/PS films show a better fit to the theoretical equations for TPA, compared to the former. The transmittance minimum reported is about 0.65 for ZnO/PMMA films. For ZnO/PS films of the present work, the transmittance minimum is about 0.43, which highlights the better optical limiting efficiency of the latter compared to the former.
The nonlinear coefficients are calculated as described in chapter 2 (given in table 5.1), and show fairly high values of nonlinear parameters. The nonlinear absorption coefficient substantially increases as the size of the ZnO particles in the nanocomposite increases.

Generally, induced absorption can occur due to a variety of processes, like two photon absorption, free carrier absorption, transient absorption, inter band absorption, photo ejection of electrons and nonlinear scattering, which are reported to be operative in nanoclusters. In the present study, the theory of two photon absorption (TPA) process fits well with the experimental curve and hence TPA can be established as the basic mechanism. The reduced normalized transmittance values obtained (Figure 5.3) for larger particles show that the samples can be used as efficient optical limiters. Optical limiting devices (optical limiters) protect light-sensitive detectors such as eye or CCD cameras, from possible damage caused by intense light exposure.
Size – dependent NLO properties of ZnO/PS nanocomposite films

Figure 5.3(a–e): Open aperture Z-scan curves of ZnO/PS nanocomposite films containing ZnO particles of different size.
5.3.2 Closed aperture Z-scan

The closed aperture Z-scan traces of ZnO/PS nanocomposite films for an irradiance wavelength of 532 nm from pulsed Nd-YAG laser of energy 25µJ are given in figure 5.4. The closed-aperture curve exhibits a peak to valley shape, indicating a negative value of the nonlinear refractive index \( n_2 \) [23]. For samples with appreciable refractive and absorptive nonlinearities, closed aperture measurements show contributions from both, i.e. the intensity-dependent changes in the transmission and in refractive index [18]. By dividing the normalized closed aperture transmittance data by the corresponding normalized open-aperture data, one can retrieve the phase distortion created due to the change in refractive index.

The value of the difference between the normalized peak and valley transmittance, \( T_{p-v} \), can be obtained by the best theoretical fit from the results of divided Z-scan curve. The nonlinear refractive index \( n_2 \) is calculated from \( T_{p-v} \) in closed aperture Z-scan using equation (5.2) and is tabulated in table 5.1,

\[
T_{p-v} = 0.406(1 - S)^{0.25} |\Delta \Phi_0|, \quad \text{where} \quad |\Delta \Phi_0| = \frac{2\pi}{\lambda} n_2 I_0 L_{\text{eff}} \quad \text{(5.2)}
\]

where \( S \) is the linear transmittance of the far field aperture and \( \lambda \) is the excitation wavelength. From the closed aperture Z-scan fit, \( \Delta \Phi_0 \) can be obtained.

The peak-valley trace in the closed aperture Z-scan shows that these samples have self-defocusing (negative, \( n_2 < 0 \)) nonlinearity, as reported for ZnO/PMMA nanocomposite [22].
The nonlinear refractive index is also found to increase as the size of the ZnO particles in the nanocomposite increases.

Figure 5.4 (a-e): Closed aperture Z-scan curves of ZnO/PS nanocomposite films containing ZnO particles of different size
5.3.3 Size dependent enhancement of third order nonlinear susceptibility

By analyzing the open aperture and closed aperture Z-scan data, using the procedure described in chapter 2, the nonlinear susceptibility is calculated.

The nonlinear refractive index \( n_2 \) is related to the real part of nonlinear susceptibility, \( \text{Re} (\chi^3) \) by the relation,

\[
\text{Re} (\chi^3) = \frac{n_0 n_2}{3\pi} \text{ (esu)} \quad \text{----------------------------- (5.3)}
\]

The imaginary part of third order susceptibility \( \text{Im} (\chi^3) \) determines the strength of the nonlinear absorption. The nonlinear absorption coefficient, \( \beta \) is related to \( \text{Im} (\chi^3) \) by the relation

\[
\text{Im} (\chi^3) = \varepsilon_0 n_0^2 c^2 \frac{\beta}{\omega} \text{ (m}^2 \text{ V}^{-2} \text{)}
= \frac{n_0^2 c^2 \beta}{240 \pi^2 \omega} \text{ (esu)} \quad \text{----------------------------- (5.4)}
\]

where \( n_0 \) is the linear refractive index, \( \varepsilon_0 \) is the permittivity of free space and \( c \) the velocity of light in vacuum.

From the real and imaginary parts of (\( \chi^3 \)), the modulus of third order nonlinear susceptibility can be found out using equation (5.5).

\[
| (\chi^3) | = \left[ \text{Re} (\chi^3))^2 + \text{Im} (\chi^3)]^2 \right]^{1/2} \quad \text{----------------------------- (5.5)}
\]

The magnitude of (\( \chi^3 \)) is significantly affected by the crystallite size and it determines the strength of nonlinearity of the material.

The third order nonlinear susceptibility values of ZnO/PS composite films at a pulsed energy of 25\( \mu \)J for a wavelength of 532 nm
are tabulated in table 5.1. These values are within an error of 7% arising mainly by the uncertainty in intensity measurements on the samples and the fitting error.

There is enhancement in the nonlinear susceptibility values with increase in particle size. The enhancement of nonlinear optical properties with increasing particle dimension in the weak confinement regime, essentially originates from the size dependent enhancement of oscillator strength of coherently generated excitons [24]. In the weak confinement regime the Coulomb interaction between the electron and hole yields an exciton which is confined as a quasiparticle. The optical nonlinearity arises from the exciton-exciton interaction. Theoretical studies have shown that the confinement of excitonic envelope wave function gives rise to the enhancement in oscillator strength for an exciton within the nanoparticle by a factor of \( R^3/a_B^3 \), where \( R \) is the radius of the nanoparticle and \( a_B \), the exciton Bohr radius [24]. The effect of large oscillator strength is brought out only in the weak confinement regime. This size dependent oscillator strength has been experimentally confirmed in CuCl quantum dots [25, 26]. Such oscillator strength effect will result in an enhancement of the nonlinear susceptibility, and hence \( \chi_3 \) depends on the crystallite size [27, 28]. Hence, in the present study, the observed enhancement of nonlinear optical properties with increase in particle size can be attributed to the size dependent enhancement of exciton oscillator strength.

The nonlinear susceptibility is found to be size dependent, without showing any saturation behaviour in the size range of the present investigation. The observed high susceptibility values measured by the
Z-scan technique establish the fact that the ZnO/PS nanocomposite films investigated in the present work have good nonlinear optical response and can be chosen as ideal candidates with high prospects of applications in nonlinear optics [29, 30].

Table 5.1: Variation of band gap and nonlinear parameters with the ZnO nanoparticle size in the composite

<table>
<thead>
<tr>
<th>KOH concentration (M)</th>
<th>Particle size nm</th>
<th>Band gap (eV)</th>
<th>$\beta$ (cm/GW)</th>
<th>$n_2$ (10$^{-10}$ m$^2$/W)</th>
<th>$(\chi^3) \times 10^{-12}$ esu</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>6.5</td>
<td>4.05</td>
<td>82</td>
<td>-4.30</td>
<td>5.71</td>
</tr>
<tr>
<td>0.10</td>
<td>15</td>
<td>3.55</td>
<td>89</td>
<td>-6.08</td>
<td>6.17</td>
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<tr>
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<td>3.42</td>
<td>258</td>
<td>-7.15</td>
<td>7.28</td>
</tr>
<tr>
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<td>-7.99</td>
<td>8.81</td>
</tr>
<tr>
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<td>35</td>
<td>3.30</td>
<td>281</td>
<td>-13.3</td>
<td>14.0</td>
</tr>
</tbody>
</table>

5.4 Conclusion

The nonlinear optical properties of ZnO/PS nanocomposite films are investigated for optical limiting application. The composite films show a self-defocusing type (negative refractive index, $n_2$) nonlinearity and good nonlinear absorption behaviour. The observed optical nonlinearity is explained based on two-photon absorption. The dependence of the nonlinear parameters like nonlinear absorption coefficient, nonlinear refractive index and third order susceptibility on the ZnO particle size has been investigated and these parameters are found to be enhanced for larger particle size in the range of 6.5 to 35 nm. The observed nonlinear behaviour of the nanocomposite films is much pronounced compared to that of bulk ZnO. The fairly low transmittance
of about 0.43 observed for these nanocomposite films is ideal for the fabrication of efficient optical limiters in sensor protection applications. The ZnO nanoparticles embedded in the polystyrene matrix are highly stable and stable optical devices can be fabricated.

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