Nonlinear optical characteristics of nanocomposites of ZnO–TiO$_2$–SiO$_2$

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Abstract

In this article we present the nonlinear optical properties of ZnO–TiO$_2$–SiO$_2$ nanocomposites prepared by colloidal chemical synthesis. Nonlinear optical response of these samples is studied using nanosecond laser pulses at an off-resonance wavelength. The nonlinearity of the silica colloid is low and its nonlinear response can be improved by making composites with ZnO and TiO$_2$. These nanocomposites show self-defocusing nonlinearity and good nonlinear absorption behaviour. The nonlinear refractive index and the nonlinear absorption increases with increasing ZnO volume fraction. The observed nonlinear absorption is explained by two photon absorption followed by weak free carrier absorption and nonlinear scattering. ZnO–TiO$_2$–SiO$_2$ is a potential nanocomposite material for the development of nonlinear optical devices with a relatively small limiting threshold.

1. Introduction

The field of nanocomposite materials has been widely recognized as one of the most promising and rapidly emerging research areas [1]. There are some material designs to strengthen and toughen ceramics by using composite techniques to incorporate particulate, whisker or platelet reinforcement. Recent investigations have shown that ceramic composites having nano-sized metal particulate dispersions show excellent optical, electrical and mechanical properties [2]. Promising applications are expected or have already been realized in many fields of technology such as optical and electronic materials, solid electrolytes, coating technology and catalysis. Significant investigations have been done in the photophysical and photochemical behavior of single and multi-component metal and semiconductor nanoclusters [1]. Such composite materials are especially of interest in developing efficient light-energy conversion systems and optical devices.

With many advantages such as low cost, nontoxicity and stability, ZnO is becoming a very promising n-type oxide semiconductor. Most of the work has been devoted to the electrical and fluorescent properties of ion-doped zinc oxide materials, while only a few reports can be found using ZnO as the matrix for nanoparticle composite films [3]. These nanocomposites may lead to optically functional properties.

In recent years, interest in the synthesis, characterization, and application of colloidal “quantum dot” semiconductor materials has grown markedly [4]. Nanoscale composite materials containing titanium oxides are interesting because of their potential applications in optoelectronic devices and the bulk TiO$_2$ has a direct band gap of 3.2 eV. A great deal of research effort has been focused on both synthesis of TiO$_2$ nanocomposites, and on their linear optical properties. Recently the nonlinear optical properties of such materials have also received attention. A large, reverse saturable type of nonlinear absorption is observed in polystyrene maleic anhydride–TiO$_2$ nanocomposites with a continuous wave He–Ne laser beam [5].

Extensive investigations of the photoluminescence and the third-order optical nonlinearities of nanometer-sized semiconductor materials have demonstrated interesting physical properties and potential applications. The absorption and luminescent properties of TiO$_2$, CdS and PbS particles can be easily tuned by...
selecting appropriate matrix materials. Recently, a microemulsion technique has been developed to prepare semiconductor nanocomposites such as ZnS/CdSe, ZnSe/CdSe, ZnS/CdS or TiO_2–SiO_2 in a core-shell structure [6]. Chemically synthesized semiconductor nanocomposites offer necessary and basic materials promising color-tunable, flexible, all-purpose chromophore systems, in which the strong quantum confinement effect of the carriers leads to unique, size dependent linear and nonlinear optical properties.

The synthesis of new nonlinear optical materials based on transparent semiconductor and insulator that contain metal nanoparticles is nowadays of great interest for applications in nonlinear optics [1]. For optical limiting applications it is necessary that the sample possess low linear losses and high nonlinear losses. Nonlinear losses can be due to multiphoton absorption, reverse saturable absorption, nonlinear scattering, and self-action of laser radiation (Kerr and thermal self-focusing and self-defocusing) [7]. The nonlinearity of the silica colloid is low and its optical limiting response can be improved by making composites with ZnO and TiO_2–SiO_2 which gives rise to wide applications in optoelectronic devices.

Different metal particles, organic nanocrystals and fullerenes doped in sol–gel glasses and silica composites are well studied for optical limiting applications [1,2]. It is also known that doping significantly improve the limiting performance of ZnO. In this paper we present the nonlinear optical properties of ZnO–TiO_2–SiO_2 nanocomposites.

2. Experimental

Colloids of ZnO are synthesized by a modified polyol precipitation method [7]. The ZnO colloidal spheres are produced by a two-stage reaction process. The method of preparation involves the hydrolysis of zinc acetate dihydrate (ZnAc) in diethylene glycol medium (DEG). Among the different polyols, diethylene glycol (DEG) is chosen because it is reported to give particles with uniform shape and size distribution. The size of the particles and hence the stability of this colloidal suspension depend on the concentration of zinc acetate as well as on the rate of heating. The molar concentration of precursor solution is 0.025 M and a heating rate of 4 °C per minute is employed for the formation of ZnO at a temperature of 120 °C. The product from the primary reaction is placed in a centrifuge and the supernatant (DEG, dissolved reaction products, and unreacted ZnAc and water) is decanted off and saved. A secondary reaction is then performed similar to the primary reaction. Prior to reaching the working temperature, typically at 115 °C, some volume of the primary reaction supernatant, say 5 ml, is added to the solution. After reaching 120 °C, it is stirred for one hour, to get a stable colloid.

The TiO_2 nanocolloids are prepared by hydrolysis method [8]. Titanium tetrabutoxide (Aldrich) is used as the precursor. In a typical synthesis, 0.025 M titanium tetrabutoxide is dispersed in distilled water under stirring. The solution is kept on stirring for one hour to get a stable colloid. A stable nanocolloid of SiO_2 particles dispersed in water has been obtained from Aldrich Chemical Company.

The ZnO–TiO_2–SiO_2 nanocomposites are prepared by colloidal chemical synthesis by mixing fixed amount of TiO_2 and SiO_2 colloids to ZnO colloid at 120 °C during its preparation stage and stirred for 1 h at that temperature. The concentration of all the 3 nanocolloids is 0.025 M. The volume fraction of ZnO is changed keeping the volume of TiO_2 and SiO_2 a constant, typically 50 ml. The samples having xZnO–TiO_2–SiO_2 composition of (x=) 1%, 2%, 3% 5% are named as 1ZnO–TiO_2–SiO_2, 2ZnO–TiO_2–SiO_2, 3ZnO–TiO_2–SiO_2 and 5ZnO–TiO_2–SiO_2 respectively. The ZnO–TiO_2–SiO_2 nanocomposites are characterized by optical absorption measurements recorded using a spectrophotometer (Jasco-570 UV/VIS/IR).

In the present investigation, we have employed the single colloid z scan technique with nanosecond laser pulses to measure nonlinear optical absorptive and refractive properties of ZnO–TiO_2–SiO_2 nanocomposites. z Scan technique developed by Sheik Bahae and his co-workers is a single beam method for measuring the sign and magnitude of nonlinear refractive index, n_2, and has a sensitivity comparable to interferometric methods [9,10]. A Q-switched Nd:YAG laser (Spectra Physics LAB-1760, 532 nm, 7 ns, 10 Hz) is used as the light source. The sample is moved in the direction of light incidence near the focal spot of the lens with a focal length of 200 mm. The radius of the beam waist w_0 is calculated to be 35.4 μm. The Rayleigh length, z_R is estimated to be 7.4 mm, much greater than the thickness of the sample cuvette (1 mm), which is an essential prerequisite for z scan experiments. The transmitted beam energy, reference beam energy and their ratio are measured simultaneously by an energy ratio meter (RJ7620, Laser Probe Corp.) having two identical pyroelectric detector heads (Rjp735). The linear transmittance of the far field aperture S, defined as the ratio of the pulse energy passing the aperture to the total energy is measured to be approximately 0.21. The z scan system is calibrated using Cs_2 as the standard. The effect of fluctuations of laser power is eliminated by dividing the transmitted power by the power obtained at the reference detector. The data are analyzed by using the procedure described by Sheik Bahae et al. and the nonlinear coefficients are obtained by fitting the experimental z scan plot with the theoretical plots.

3. Results and discussion

Optical absorption measurement is an initial step to observe the single colloid and metal-semiconductor nanocomposite behaviour. Fig. 1 gives the room temperature absorption spectra of the ZnO–TiO_2–SiO_2 nanocomposites. There is a change in absorption with the ZnO content and as the volume fraction of ZnO increases, the excitonic peak exhibits its signature. It is seen that the absorption edge corresponding to the nanocomposites gets red shifted and the exciton oscillator strength increases as a function of the ZnO content consistent with published reports [11,12]. The structure and size evolution of the nanocomposites may also have some relation with optical characteristics in addition to the composition and the study is in progress.

Fig. 2 shows the nonlinear absorption of ZnO–TiO_2–SiO_2 nanocomposites at a typical fluence of 300 MW/cm² for an irradiation

![Fig. 2](image-url)
nanocomposites, as compared to pure nanoparticles [13]. The large values of the third-order nonlinearity in our samples are expected to be very small in silica colloids because the total input intensity is relatively small compared to the breakdown threshold. Hence we propose that this nonlinearity in our samples is caused by two photon absorption followed by weak free carrier absorption and nonlinear scattering.

It is possible that nonlinear scattering dominates two photon absorption on the silica colloids and the presence of nonlinear scattering reduces the two photon absorption coefficient in silica colloids. Both the linear and the nonlinear absorption of wide-band silica colloids in the visible and the near-infrared ranges are known to be negligible if the input intensity is well below the breakdown threshold. Therefore, two-photon absorption contribution is expected to be negligible if the input intensity is well below the breakdown threshold. Hence we propose that this nonlinearity in our samples is caused by two photon absorption followed by weak free carrier absorption and nonlinear scattering.

Fig. 3 gives the closed aperture z scan traces of ZnO–TiO$_2$–SiO$_2$ nanocomposites at a fluence of 300 MW/cm$^2$ for an irradiation wavelength of 532 nm. The closed-aperture curve exhibits a peak-valley shape, indicating a negative value of the nonlinear refractive index $n_2$. For samples with sizeable refractive and absorptive nonlinearities, closed-aperture measurements contain contributions from both the intensity-dependent changes in the transmission and in refractive index [9]. By dividing the normalized closed-aperture transmittance by the corresponding normalized open-aperture data we can retrieve the phase distortion created due to the change in refractive index.

It is observed that the peak-valley of closed-aperture z scan satisfied the condition $\Delta \approx 1.7z_0$, thus confirming the presence of pure electronic third-order nonlinearity [9]. The value of the difference between the normalised peak and valley transmittance, $\Delta T_{p-v}$, 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 $\Delta T_{p-v}$ in closed aperture z scan using Eq. (2) and is tabulated in Table 1.

$$\Delta T_{p-v} = 0.406(1-S)^{0.25} |\Phi_0| \text{ where } |\Phi_0| = \frac{2\pi}{\lambda} n_2I_t L_{\text{eff}}$$

Table 1

<table>
<thead>
<tr>
<th>ZnO–TiO$_2$–SiO$_2$ nanocomposites</th>
<th>$\beta$ (cm/GW)</th>
<th>$N_2$ ($10^{-12}$ m$^2$/W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>1.7</td>
<td>0.9</td>
</tr>
<tr>
<td>TiO$_2$–SiO$_2$</td>
<td>27.7</td>
<td>3.1</td>
</tr>
<tr>
<td>ZnO–TiO$_2$–SiO$_2$</td>
<td>51.8</td>
<td>3.8</td>
</tr>
<tr>
<td>ZnO–TiO$_2$–SiO$_2$</td>
<td>86.4</td>
<td>5.0</td>
</tr>
<tr>
<td>ZnO–TiO$_2$–SiO$_2$</td>
<td>110.6</td>
<td>6.7</td>
</tr>
<tr>
<td>ZnO–TiO$_2$–SiO$_2$</td>
<td>155.5</td>
<td>9.5</td>
</tr>
</tbody>
</table>

The peak–valley trace in a closed aperture z scan shows that these samples have self-defocusing (negative, $n_2 < 0$) nonlinearity, though earlier reports with nanosecond pulsed lasers have shown positive nonlinearity for fused silica due to the mechanism of electrostriction [18]. We suggest that the possible physical origin of the nonlinear refraction of ZnO–TiO$_2$–SiO$_2$ nanocomposites is mainly a two photon absorption process and partially nonlinear scattering and a weak thermal effects in the nanosecond time domain. It is reported that the difference between the third-order optical susceptibilities for z scan and four wave mixing (FWM) is due to scattering from the surface of silica nanoaerogels in the z scan measurements [19]. We have not observed any sign reversal of the nonlinear refractive index either in the intensity ranges (150–400 MW/cm$^2$) studied using the second harmonics of a Q-switched Nd:YAG laser or within the wavelength range 450–650 nm studied using a tunable laser (Quanta Ray MOP, 5 ns, 10 Hz). The nanocomposites exhibit reverse saturable absorption at all wavelengths and good nonlinear absorption, which increases with increase in input intensity. The nonlinear refractive index increases substantially in the nanocomposites, as compared to pure SiO$_2$ colloids. The large enhancement of the third-order...
The nonlinearity of the silica aerogel is reported to be due to the quantum confinement effect of bound electrons, which is induced by the nanostructure nature of the sample [19]. Since $n_2$ increases with absorption, thermal nonlinearity is also taken into account. It is reported that if the thermal contributions are to dominate, then there will be an increase in $n_2$ with increase of absorption [20]. The third-order nonlinear susceptibility of silica nanoaerogels is estimated to be $9.6 \times 10^{-10} \text{m}^2/\text{V}^2$ ($6.9 \times 10^{-11} \text{esu}$) from FWM measurements [19]. In the case of fused silica, the nonlinear refractive index is reported to be quite small, roughly $3 \times 10^{-20} \text{m}^2/\text{W}$, which is about two orders of magnitude below the nonlinear refractive index of most of the materials usually studied with the z scan method [18]. The third-order optical nonlinearity, $n_2$ of TiO$_2$ nanocystalline particles dispersed in SiO$_2$ is found to be $10^{-12} \text{esu}$ at 532 nm with nanosecond laser pulses [21,22]. The significant optical nonlinearities of the pure semiconductor nano colloid at 532 nm are reported to have the nonlinear refractive index of the order of $10^{-16}$–$10^{-17} \text{m}^2/\text{W}$. It is worth noting that certain representative third-order nonlinear optical materials, such as CuO chain compounds, Ag$_2$S/CdS nanocomposites, organic coated quantum dots, core-shell silica nanocomposites etc., yielded values of the order of $10^{-9}$–$10^{-14} \text{mW}$ for nonlinear absorption coefficient and $10^{-16}$–$10^{-20} \text{m}^2/\text{W}$ for nonlinear refractive index at a wavelength of 532 nm [6]. These values are comparable to the value of $n_2$ obtained for nanocomposites in the present investigation. Thus, the nonlinear absorption coefficient and nonlinear refractive index measured by the z scan technique reveals that the ZnO–TiO$_2$–SiO$_2$ nanocomposites investigated in the present study have good nonlinear optical response and could be chosen as ideal candidates with potential applications in nonlinear optics.

Recently, nanomaterials have drawn significant attention as optical limiters for eyes or for sensor protection from laser terror in homeland or agile laser threats on the battlefield [23]. Also, the nonlinear optical properties of nanomaterials are of great interest for optical switching, pulse power shaping of OPO (optical parametric oscillator)/OPG (optical parametric generator), and other nonlinear optical applications. Optical power limiting is operated through the nonlinear optical processes of nanomaterials. However, the great potential of nanomaterials as optical power limiters have just begun to be recognized.

To examine the viability of ZnO–TiO$_2$–SiO$_2$ nanocomposites as optical limiters, the nonlinear transmission of the colloid is studied as a function of input fluence. An important term in the optical limiting measurement is the limiting threshold. It is obvious that the lower the optical limiting threshold, the better the optical limiting material. Optical limiters are devices that transmit light at low input fluences or intensities, but become opaque at high inputs. The optical limiting property occurs mostly due to absorptive nonlinearity which corresponds to the imaginary part of third-order susceptibility [24]. From the value of fluence at focus, the fluence values at other positions could be calculated using the standard equations for Gaussian beam waist. Such plots represent a better...
comparison of the nonlinear absorption or transmission in these samples and are generated from z scan traces. Fig. 4 illustrates the influence of volume fraction of ZnO in ZnO–TiO$_2$–SiO$_2$ nanocomposites on the optical limiting response.

The fluence value corresponding to the onset of optical limiting (optical limiting threshold) is found to be very low in the case of TiO$_2$–SiO$_2$ colloids (21 MW/cm$^2$) in comparison with that of the silica colloids (120 MW/cm$^2$). These values are comparable to the reported optical limiting threshold for CdS and ZnO nano colloids [25]. ZnO–TiO$_2$–SiO$_2$ nanocomposites are found to be good optical limiters compared to ZnO, TiO$_2$ and SiO$_2$ and the optical limiting threshold of 5ZnO–TiO$_2$–SiO$_2$ nanocomposites is observed to be 11 MW/cm$^2$. The arrow in the figure indicates the approximate fluence at which the normalized transmission begins to deviate from linearity. Nanocomposites have a significant effect on the limiting performance and increasing the volume fraction of ZnO reduces the limiting threshold and enhances the optical limiting performance.

4. Conclusion

The nonlinear optical properties of ZnO–TiO$_2$–SiO$_2$ nanocomposites prepared by a colloidal chemical synthesis are investigated. These nanocomposites show self-defocusing nonlinearity and good nonlinear absorption behaviour. The nonlinear refractive index and the nonlinear absorption increases with increasing ZnO volume fraction. The observed nonlinear absorption is explained by two photon absorption followed by weak free carrier absorption and nonlinear scattering. These materials can be used as optical limiters and ZnO–TiO$_2$–SiO$_2$ is a potential nanocomposite material for the development of nonlinear optical devices with a relatively small limiting threshold.

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References