Linear and nonlinear optical characteristics of $ZnO–SiO_2$ nanocomposites

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We present the spectral and nonlinear optical properties of $ZnO–SiO_2$ nanocomposites prepared by colloidal chemical synthesis. Obvious enhancement of ultraviolet (UV) emission of the samples is observed, and the strongest UV emission of a typical $ZnO–SiO_2$ nanocomposite is over three times stronger than that of pure ZnO. The nonlinearity of the silica colloid is low, and its nonlinear response can be improved by making composites with ZnO. These nanocomposites show self-defocusing nonlinearity and good nonlinear absorption behavior. The observed nonlinear absorption is explained through two photon absorption followed by weak free carrier absoption and nonlinear scattering. The nonlinear refractive index and the nonlinear absorption increase with increasing ZnO volume fraction and can be attributed to the enhancement of exciton oscillator strength. $ZnO–SiO_2$ is a potential nanocomposite material for the UV light emission and for the development of nonlinear optical devices with a relatively small limiting threshold.

OCIS codes: 190.4400, 300.1030, 300.2140, 300.6280.

1. Introduction

The linear and nonlinear optical properties of semiconductors are the subject of much current theoretical and experimental interest [1]. Among the various nonlinear optical (NLO) materials investigated, wide bandgap semiconductors, especially zinc oxide (ZnO), have attractive nonlinear properties that make them ideal candidates for NLO based devices. ZnO is a wide and direct bandgap II–VI semiconductor with a bandgap of 3.37 eV and a high exciton binding energy of 60 meV and having many applications, such as solar cell, luminescent material, heterojunction laser diode, and UV laser [2]. The optical properties of this material are currently the subject of tremendous investigations, in response to the industrial demand for optoelectronic devices that could operate at short wavelengths. Also, there is a significant demand for high nonlinear optical materials, which can be integrated into an optoelectronic device with a relatively small limiting threshold.

The field of nanocomposite materials has been widely recognized as one of the most promising and rapidly emerging research areas because of their enhanced luminescence and fast nonlinear response that can be utilized in making them as potential optical devices [3]. Significant investigations have been done in the photophysical and photochemical behavior of single and multicomponent metal, semiconductor and dielectric nanoclusters. Such composite materials are especially of interest in developing efficient light-energy conversion systems and optical and microelectronic devices [4]. Recent investigations have shown that ceramic composites having nano-sized metal particulate dispersions show excellent optical, electrical, and mechanical properties [5].

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 and optoelectronics because of the high polarizability and

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ast nonlinear response [3]. For optical limiting appliations it is necessary that the sample possess low linar losses and high nonlinear losses. Nonlinear losses an be due to multiphoton absorption, reverse saturble absorption, nonlinear scattering, and self-action f laser radiation (Kerr and thermal self-focusing and elf-defocusing) [6]. The nonlinearity of the silica coloid is low and its optical limiting response can be imroved by making composites with ZnO, which gives ise to wide applications in optoelectronic devices. In our continued efforts to explore the optical properties f various nanocomposites, we have now elucidated the spectral and nonlinear response of ZnO–SiO$_2$ nanocomposites.

Generally, the photoluminescence (PL) spectrum of a single crystal ZnO consists mainly of two bands [7]. Soon after the reporting of stimulated UV emission of ZnO at room temperature, ZnO attracted attention as an UV laser material [8]. Thereafter, more and more researchers aimed at applications of ZnO emitting at the short wavelength [9]. Several reviews elaborated the recent development of photoelectron applications of ZnO in short wavelength. Tsukazaki *et al.* reported the violet electroluminescence from homostructural ZnO *p-i-n* junctions at room temperature [10]. Effective UV random lasing has been observed from patterned p-SiC(4H)/i-ZnO–SiO$_2$ nanocomposite films under optical excitation [11]. UV random lasing can be achieved in these composites because the appropriate patterning of ZnO clusters enhances the optical quality (i.e., higher gain and lower loss) of the random media. However, the improvement of UV emission and the simplification of growth techniques are still very important. In this study, the UV emission from ZnO–SiO$_2$ nanocomposites is observed to be enhanced by ZnO doping. It is suggested that the enhancement of UV emission is mainly caused by the excitons formed at the interface between SiO$_2$ and ZnO.

Different metal particles, organic nanocrystals, and fullerenes doped in solgel glasses and silica composites are well studied for optical limiting applications [3,5]. We present the nonlinear optical properties of ZnO–SiO$_2$ nanocomposites with varying ZnO content.

2. Experiment

Colloids of ZnO are synthesized by a modified polyol precipitation method [12]. The stable 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 that is similar to the above procedure to produce stable ZnO spheres. Prior to reaching the working temperature, typically at 115 °C, some volume of the primary reaction supernatant is added to the solution. After reaching 120 °C, it is stirred 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–SiO$_2$ nanocomposites are prepared by colloidal chemical synthesis by mixing a certain amount of SiO$_2$ colloid to ZnO colloid at 120 °C during its preparation stage and stirred for 1 hour at that temperature. The volume fraction of ZnO is changed, keeping the volume of SiO$_2$ a constant. The samples having xZnO–SiO$_2$ composition of ($x =$) 0.1–5% are named as 0.1ZnO–SiO$_2$ to 5ZnO–SiO$_2$, respectively.

The ZnO–SiO$_2$ nanocomposites are characterized by optical absorption measurements recorded using a spectrophotometer (JascoV-570 UV/VIS/IR), and the fluorescence emission measurements are recorded using a fluorescence spectrometer (Varian-Cary eclipse). In the present investigation, we have employed the single beam z-scan technique with nanosecond laser pulses to measure nonlinear optical absorptive and refractive properties of ZnO–SiO$_2$ nanocomposites. The z-scan technique developed by Sheik Bahae and his coworkers 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 [13,14]. 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 ω_0 is calculated to be 35.4 μm. The Rayleigh length, $z_0 = \pi w_0^2/\lambda$ 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 ratiometer (Rj7620, Laser Probe Corporation) 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 nanocomposite behavior. Figure 1 gives the room temperature absorption spectra of the ZnO–SiO_2 nanocomposites. The excitonic peak of ZnO colloid is found to be blue shifted with respect to that of bulk ZnO, which could be attributed to the confinement effects [15]. There is a change in absorption with the ZnO content, and as the volume fraction of ZnO increases beyond 2%, 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 [16]. 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.

Photoluminescence spectra of all the samples measured at room temperature are shown in Fig. 2. The intensities of the emission peaks depend on the volume fraction of ZnO present in the samples. ZnO and ZnO–SiO_2 composites exhibit emissions at 385 nm, but the fluorescence intensity of the composites is much stronger than that of ZnO. 1ZnO–SiO_2 has the strongest UV emission centered at 385 nm. The increase of the UV emission can be attributed to the enhancement of exciton oscillator strength [17]. Figure 3 shows the PL intensity as a function of the ZnO content. It is clear that the intensity of this peak increases with the increasing amount of the Zn acceptors. As the volume fraction of ZnO increases, the formation of aggregates decreases the fluorescence emission [18]. This can be related to the phenomenon of reabsorption and emission at higher concentrations, which ultimately reduces the fluorescence emission. As the volume fraction increases, the low frequency tail of the absorption spectrum of the sample overlaps with the high frequency end of its fluorescence spectrum. The fluorescence from the excited state is reabsorbed by the ground state. This process increases with increase in volume fraction, which results in decrease of fluorescence. The formation of aggregates quenches the fluorescence emission by collision or long range nonradiative energy transfer. The emission of ZnO at 385 nm can be attributed to exciton transition. As the volume fraction of ZnO increases, the exciton oscillator strength increases, so that the UV emission is enhanced accordingly, as shown in Fig. 2. Nanostructural semiconductor materials generally have more holes accumulated on its surface or in the interface than common semiconductor materials [19].

Figure 4 shows the nonlinear absorption of ZnO–SiO_2 nanocomposites at a typical fluence of 300 MW/cm^2. The open-aperture curve exhibits a normalized transmittance valley, indicating the presence of induced absorption in the colloids. The obtained 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 [13]

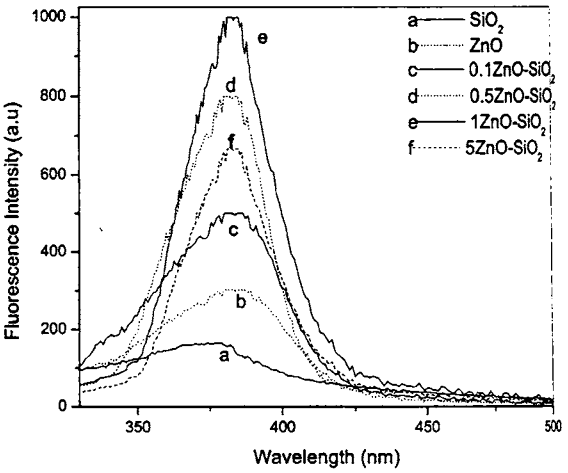

Fig. 2. Fluorescence spectra of ZnO–SiO_2 nanocomposites.

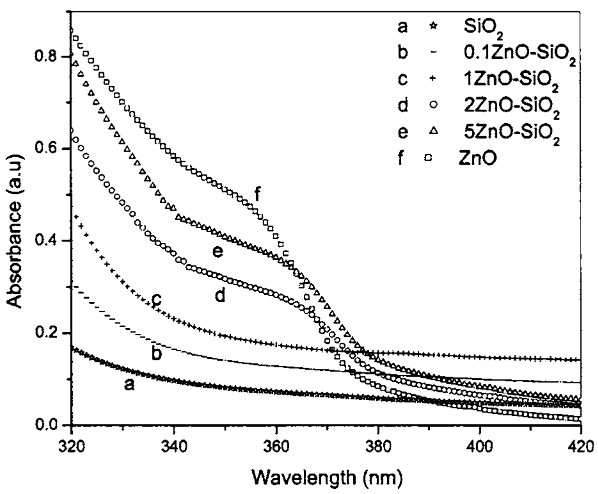

Fig. 1. Absorption spectra of ZnO–SiO_2 nanocomposites.

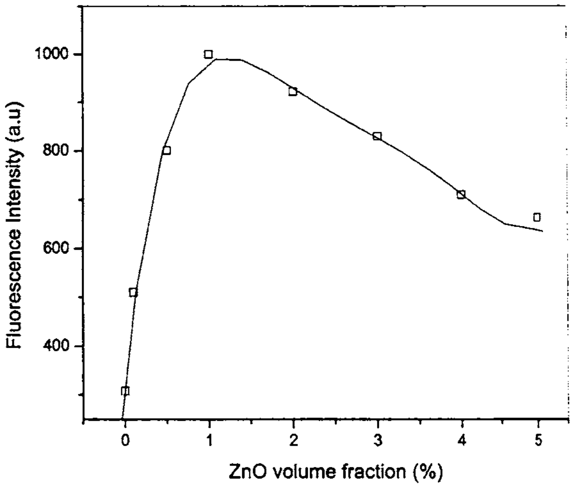

Fig. 3. Fluorescence intensity of UV peak as a function of the volume fraction of ZnO in ZnO–SiO_2 nanocomposites.

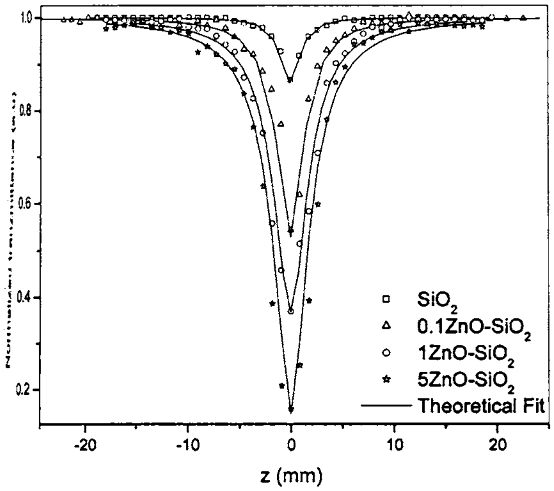

Fig. 4. Open aperture z-scan traces of ZnO–SiO$_2$ nanocomposites at an intensity of 300 MW/cm^2 for an irradiation wavelength of 532 nm.

$$T(z) = \frac{1}{q_0\sqrt{\pi}}\int_{-\infty}^{\infty}\ln(1+q_0 e^{-t^2})\mathrm{d}t,$$
$$q_o(z,r,t) = \beta I_o(t)L_{\mathrm{eff}}. \qquad (1)$$

Here, $L_{\mathrm{eff}} = 1 - e^{-\alpha l}/\alpha$ is the effective thickness with linear absorption coefficient α and nonlinear absorption coefficient β, and I_o is the irradiance at focus. The solid curves in Fig. 4 are the theoretical fit to the experimental data. The experimentally obtained values of nonlinear absorption coefficient β at an intensity of 300 MW/cm^2 are shown in Table 1.

Interestingly, SiO$_2$ colloids show a minimum nonlinearity, while the ZnO–SiO$_2$ nanocomposites clearly exhibit a larger induced absorption behavior. The calculated nonlinear coefficients given in Table 1 show fairly high values of nonlinearity. The nonlinear absorption coefficient increases substantially in the nanocomposites, as compared to pure ZnO and SiO$_2$ colloids. It is reported that the nonlinear absorption coefficient increases in the core-shell silica nanocomposites, as compared to pure nanoparticles [20]. The large values of the third-order nonlinearity can be attributed to the enhancement of exciton oscillator strength [17].

Table 1. Measured Values of Nonlinear Absorption Coefficient and Refractive Index of ZnO–SiO$_2$ Nanocomposites at Intensity of 300 MW/cm^2 for Irradiation Wavelength of 532 nm

ZnO–SiO$_2$ Nanocomposites	β [cm/GW]	n_2 [$\times 10^{-17}$ m^2/W]
ZnO	20.7	−1.5
SiO$_2$	1.7	−0.9
0.1ZnO–SiO$_2$	12.1	−2.2
0.5ZnO–SiO$_2$	27.7	−3.1
1ZnO–SiO$_2$	41.5	−4.4
2ZnO–SiO$_2$	86.4	−5.0
5ZnO–SiO$_2$	138.2	−5.9

Different processes, like two photon absorption, free carrier absorption, transient absorption, interband absorption, photoejection of electrons and nonlinear scattering are reported to be operative in nanoclusters. In general, induced absorption can occur due to a variety of processes. The theory of two photon absorption process fitted well with the experimental curve infers that TPA is the basic mechanism. There is a possibility of higher order nonlinear processes such as free carrier absorption (FCA) contributing to induced absorption. The free carrier lifetime of ZnO is reported to be 2.8 ns [21]. Hence the 7 ns pulses used in the present study can excite the accumulated free carriers generated by TPA by the rising edge of the pulse. But the free carrier absorption is weak compared to TPA, and hence the corresponding contribution in the z-scan curves is relatively less.

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 [22]. Therefore the two-photon absorption contribution is 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 is caused by two photon absorption followed by weak free carrier absorption and nonlinear scattering occurring in the nanocomposites.

Figure 5 gives the closed-aperture z-scan traces of ZnO–SiO$_2$ nanocomposites at a fluence of 300 MW/cm^2. 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

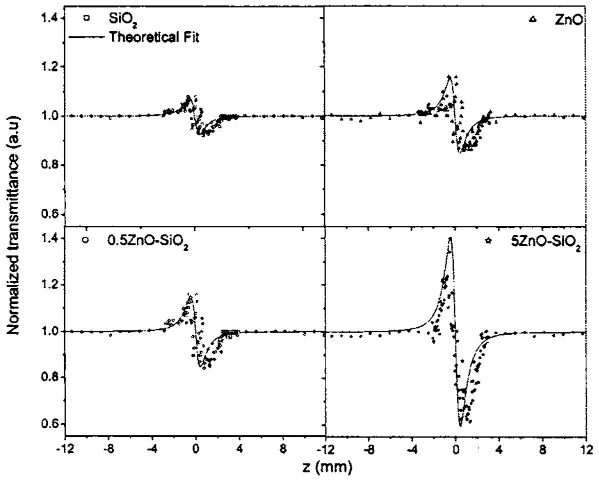

Fig. 5. Closed-aperture z-scan traces of ZnO–SiO$_2$ nanocomposites at an intensity of 300 MW/cm^2 for an irradiation wavelength of 532 nm.

intensity-dependent changes in the transmission and in refractive index [13]. 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 $\Delta z \sim 1.7\, z_0$, thus confirming the presence of pure electronic third-order nonlinearity [13]. The value of the difference between the normalized peak and valley transmittance, ΔT_{p-v}, can be obtained by the best theoretical fit from the results of a divided z-scan curve. The nonlinear refractive index n_2 is calculated from ΔT_{p-v} in closed-aperture z-scan using Eq. (2) and is tabulated in Table 1:

$$\begin{aligned} \Delta T_{p-v} &= 0.406(1-S)^{0.25}|\Delta\Phi_0|, \\ |\Delta\Phi_0| &= \frac{2\pi}{\lambda} n_2 I_0 L_{\mathrm{eff}}. \end{aligned} \qquad (2)$$

The peak–valley trace in a closed-aperture z-scan shows that these samples have self-defocusing (negative, $n_2 < 0$) nonlinearity, although earlier reports with nanosecond pulsed lasers have shown positive nonlinearity for fused silica due to the mechanism of electrostriction [23]. We suggest that the possible physical origin of the nonlinear refraction of $ZnO–SiO_2$ composites 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 [24]. We have not observed any sign reversal of the nonlinear refractive index, either in the intensity ranges (150–400 $\mathrm{MW/cm^2}$) 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 MOPO, 5 ns, 10 Hz). The nanocomposites exhibit induced 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 ZnO and SiO_2 colloids. The large enhancement of the third-order 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 [24]. 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 an increase of absorption [25].

The third-order nonlinear susceptibility of silica nanoaerogels is estimated to be $9.6 \times 10^{-19}\,\mathrm{m^2/V^2}$ $(6.9 \times 10^{-11}\,\mathrm{esu})$ from FWM measurements [24]. In the case of fused silica, the nonlinear refractive index is reported to be quite small, roughly $3 \times 10^{-20}\,\mathrm{m^2/W}$, which is about two order of magnitude below the nonlinear refractive index of most of the materials usually studied with the z-scan method [23]. It is worth noting that certain representative third-order nonlinear optical materials, such as CuO chain compounds, Ag_2S/CdS nanocomposites, organic coated quantum dots, and core-shell silica nanocomposites, yielded values of the order of 10^{-9} to 10^{-14} m/W for nonlinear absorption coefficient and 10^{-16} to $10^{-20}\,\mathrm{m^2/W}$ for nonlinear refractive index at a wavelength of 532 nm [26,27]. These values are comparable to the value of β and 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 $ZnO–SiO_2$ nanocomposites investigated in the present study have good nonlinear optical response and could be chosen as a material 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 laser threats on the battlefield [28]. Also, the nonlinear optical properties of nanomaterials are of great interest for optical switching, pulse power shaping of optical parametric oscillator)/optical parametric generator (OPO/OPG), 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.

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 [29]. 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.

Figure 6 illustrates the influence of volume fraction of ZnO in $ZnO–SiO_2$ nanocomposites on the optical limiting response. The arrow in the figure indicates the optical limiting threshold, which is the approximate fluence at which the normalized transmission begins to deviate from linearity. The optical limiting threshold is found to be very low in the case of ZnO colloids (55 $\mathrm{MW/cm^2}$) in comparison with that of the silica colloids (120 $\mathrm{MW/cm^2}$). These values are comparable to the reported optical limiting threshold for CdS and ZnO nanocolloids [26,30]. $ZnO–SiO_2$ nanocomposites are found to be good optical limiters compared to ZnO and SiO_2, and the optical limiting threshold of $5ZnO–SiO_2$ nanocomposites is observed to be 20 $\mathrm{MW/cm^2}$. Nanocomposites have a significant effect on the limiting performance, and increasing the

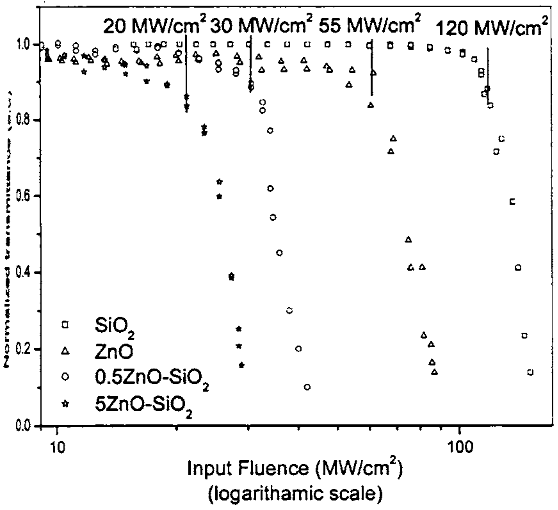

Fig. 6. Optical limiting response of ZnO–SiO_2 nanocomposites generated from open-aperture z-scan traces at 532 nm.

volume fraction of silica reduces the limiting threshold and enhances the optical limiting performance.

4. Conclusions

The spectral and nonlinear optical properties of ZnO–SiO_2 nanocomposites prepared by a colloidal chemical synthesis are investigated. Very strong UV emissions at room temperature are observed from ZnO–SiO_2 nanocomposites. Compared to regular ZnO colloid, ZnO–SiO_2 nanocomposite is advantageous due to its stronger UV emission. The strongest UV emission is observed to be over three times that of a pure ZnO. The increase of UV emission can be attributed to the enhancement of exciton oscillator strength. These nanocomposites show self-defocusing nonlinearity and good nonlinear absorption behavior. 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–SiO_2 is a potential nanocomposite material for the UV light emission and for the development of nonlinear optical devices with a relatively small limiting threshold.

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