Size-dependent enhancement of nonlinear optical properties in nanocolloids of ZnO

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We have investigated the third-order nonlinearity in ZnO nanocolloids with particle sizes in the range 6–18 nm by the z-scan technique. The third-order optical susceptibility $\chi^{(3)}$ increases with increasing particle size (R) within the range of our investigations. In the weak confinement regime, an R^2 dependence of $\chi^{(3)}$ is obtained for ZnO nanocolloids. The optical limiting response is also studied against particle size. © *2008 American Institute of Physics.* [DOI: 10.1063/1.2838178]

I. INTRODUCTION

The linear and nonlinear optical properties of semiconductors are the subject of much current theoretical and experimental interest.[1] Nanosemiconductor materials that exhibit peculiar properties which are not shown by their bulk counterparts have attracted much interest from both fundamental and technological researchers. Among the various nonlinear optical (NLO) materials investigated, wide band gap semiconductors, especially zinc oxide (ZnO), have attractive nonlinear properties that make them ideal candidates for NLO-based devices. Nanosized ZnO in the form of quantum dots, nanowires, nanobelts, etc. are referred to as the material of the 21st century.[2] They are finding applications as efficient UV emitters, random lasers, field emission displays, etc. Most of the nonlinear optical devices rely mainly on higher order susceptibility of materials, *viz.*, $\chi^{(3)}$. The second and third harmonic generation in ZnO microcrystalline thin films has been reported.[3] Bulk ZnO crystals have been investigated for NL properties by the z-scan technique itself.[4] However, very little work has been done on NL properties of ZnO quantum dots and its nanocolloids because semiconductor nanoparticles in solution with a well-controlled size, shape, and surface properties are difficult to obtain.[5] Moreover, the volume fraction of crystallites in a stable solution is usually very small. As a consequence, the resultant nonlinear response is relatively weak. Due to the special nature of the synthesis route adopted in our present investigation, the volume fraction of the nanoparticles increases with particle size; hence, high nonlinear absorption at a larger particle size occurs. This in turn intrigued our interest in investigating the nonlinear optical properties of semiconductor nanocolloids. Hence, in the present investigation our focus is on the third-order NLO susceptibility of this wide band gap semiconductor, employing the technique of z-scan.

When the crystallite size is reduced to the order of an exciton Bohr radius a_B, quantum size effects appear and drastic changes in optical properties are expected. The quantum confinement effect in semiconductor nanocrystals can be classified into two regimes, i.e., the strong and weak confinement regimes, according to the ratio of nanocrystal radius R to a_B.[1,6] Nonlinear optical properties in nanocrystals have also been investigated for the corresponding confinement regimes. In the strong-confinement regime, the photoexcited electron and hole are individually confined. Theoretical and experimental works have revealed that the state-filling effect accounts for the nonlinearity in this regime.[7] The size dependence of the third-order susceptibility $\chi^{(3)}$ has also been studied, but the results are inconsistent; a larger nonlinear susceptibility for a larger size has been found for CdS_xSe_{1-x} nanocrystals by the saturation spectroscopy and degenerate four-wave mixing (DFWM) measurements, while Roussignol *et al.* have shown that larger $\chi^{(3)}$ values are obtained with decreasing sizes.[7,8]

In the weak-confinement regime, the Coulomb interaction between the electron and hole yields an exciton and it is confined as a quasiparticle. The nonlinearity arises from the exciton-exciton interaction, which results in the deviation from harmony of the bosonlike exciton within the nanocrystal, and the size-dependent enhancement of nonlinear susceptibility has been investigated theoretically[9,10] and experimentally.[11,12] Theoretical studies have shown that the confinement of the excitonic envelope wave function due to the infinite barrier potential gives rise to the enhancement in oscillator strength for an exciton within the nanocrystal by a factor of R^3/a_B^3; hence $\chi^{(3)}$ depends on the crystallite size.[9] Such a giant oscillator strength effect has been confirmed for CuCl nanocrystals; the radiative decay rate of confined excitons is proportional to $R^{2.1}$ for the glass matrix[13] and R^3 for the NaCl crystal matrix.[14] The validity of the size-dependent enhancement effect is limited by the long wavelength approximation, and a nonlocal theory applicable to the mesoscopic system larger than the wavelength has been developed.[10] The important role of the giant oscillator

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strength effect in the size-dependent enhancement of nonlinearity has been experimentally shown for CuCl nanocrystals.[12]

In ZnO, the exciton Bohr radius is 2 nm, which is roughly 4 times that of CuCl, and one can investigate the confinement effects and size dependence of $\chi^{(3)}$ over a wide range of crystallite sizes.[15] The susceptibility is size dependent, without showing a saturation behavior in the size range studied in our investigation. In this paper we report a detailed study of the size-dependent optical nonlinearity in ZnO nanocolloids over a range of 6–18 nm.

II. EXPERIMENT

Colloids of ZnO are synthesized by a polyol precipitation method.[16] The method of preparation involves the hydrolysis of zinc acetate dihydrate (ZnAc; Merck) in diethylene glycol medium (DEG; Merck). Among the different polyols, diethylene glycol (DEG) is chosen because it is reported to give powders with a uniform shape and size distribution. The size of the particles and hence the stability of this colloidal suspension depends on the concentration of zinc acetate as well as on the rate of heating. The molar concentration of precursor solution is varied from 0.01 to 0.1 M and a heating rate of 4 °C per minute is employed. The ZnO colloids are characterized by optical absorption measurements carried out using a spectrophotometer (JascoV-570 UV/VIS/IR). The cluster sizes are calculated from the absorption spectra using the analytical formula given by Viswanatha *et al.*[17]

In the present investigation, we have employed the single-beam z-scan technique with nanosecond laser pulses to measure the nonlinear optical absorption and refraction properties of ZnO nanocolloids, and observed that the colloids exhibit large nonlinear effects. The z-scan technique developed by Bahae and his co-workers is a single-beam method for measuring the sign and magnitude of nonlinear refractive index, n_2, and has sensitivity comparable to interferometric methods.[18] 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 the light incidence near the focal spot of the lens with a focal length of 200 mm. The radius of the beam waist ω_o is calculated to be 35.4 μm. The Rayleigh length, $z_o = \pi \omega_o^2 / \lambda$, 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 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 a 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 Bahae *et al.* and the nonlinear coefficients are obtained by fitting the experimental z-scan plot with the theoretical plots.
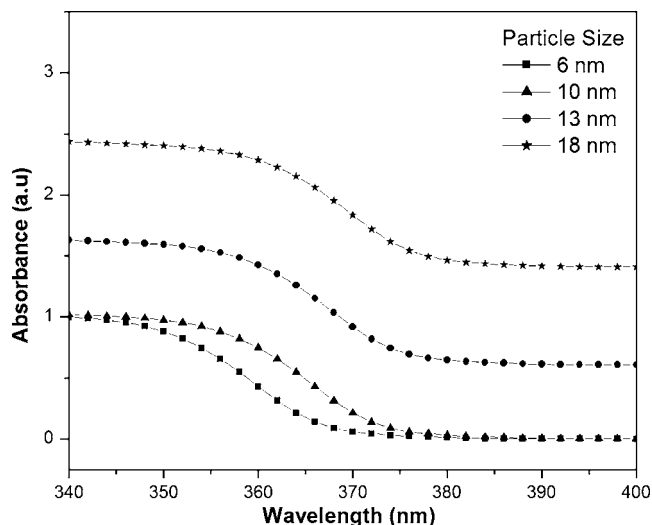

FIG. 1. Absorption spectra of ZnO colloids.

III. RESULTS AND DISCUSSION

Figure 1 gives the room-temperature absorption spectra of the ZnO colloids. The excitonic peak is found to be blueshifted with a decrease in particle size (370–350 nm) with respect to that of bulk ZnO, which could be attributed to the confinement effects.[19] The pronounced dependence of the absorption edge on the size of ZnO nanocrystals is used to determine the particle size.[17] To get a precise measure of the shift, the first derivative curve of the absorption spectrum is taken and the point of inflection is taken as the absorption edge. From the shift of the absorption edge, ΔE_g can be calculated and the particle size, d, is determined using the equation, $\Delta E_g = 100(18.1d^2 + 41.4d - 0.8)^{-1}$.

The direct band gap of ZnO colloids is estimated from the graph of $h\nu$ vs $(\alpha h\nu)^2$ for the absorption coefficient α that is related to the band gap E_g as $(\alpha h\nu)^2 = k(h\nu - E_g)$, where $h\nu$ is the incident light energy and k is a constant. The optical band gap (E_g) is found to be size dependent, and there is an increase in the band gap of the semiconductor with a decrease in the particle size as shown in Fig. 2. The
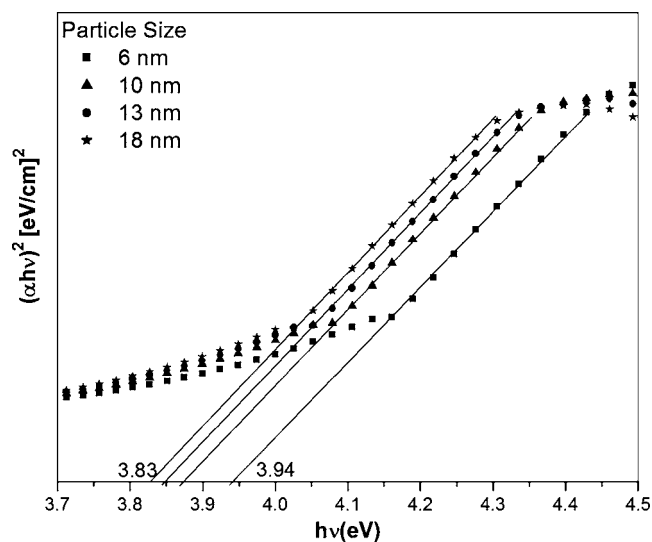

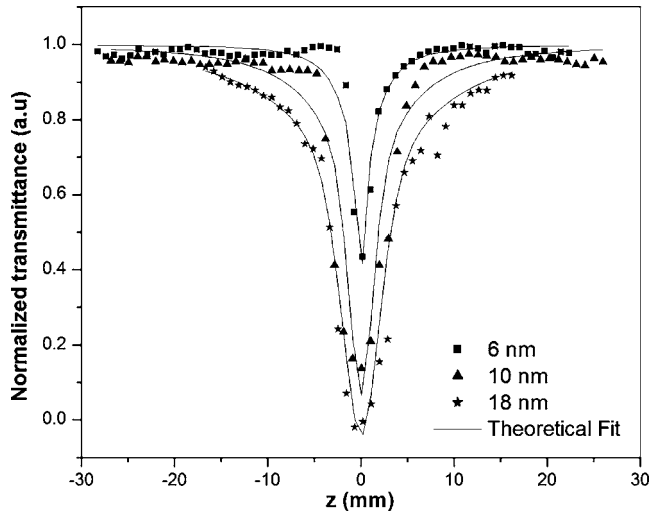FIG. 2. Optical band gap of ZnO colloids.

FIG. 3. The open-aperture z-scan traces of ZnO colloids of different particle sizes at a typical fluence of 866 MW/cm^2.

total change in the band gap of the material is contributed by both the shifts of the valence and the conduction band edges away from each other. In general, the shift of the top of the valence band (TVB) is not the same as that of the bottom of the conduction band (BCB). Moreover, there are recent studies, though few in number,[20] that report the individual shifts in TVB and BCB as a function of the size employing various forms of high-energy spectroscopies, such as the photoemission and the x-ray absorption spectroscopies. Thus, it is desirable to compute these shifts of the individual band edges with the size of the nanocrystallite. The shifts of the band edges decrease smoothly to zero for large-sized nanocrystals in every case, and the shift in the BCB is in general much larger compared to the shift in the TVB for any given size of the nanocrystal. This indicates that the shifts in the total band gap as a function of the nanocrystal size are always dominated by the shift of the conduction band edge in these systems. A larger shift for the BCB is indeed expected in view of the fact that the band-edge shifts are related inversely to the corresponding effective masses,[6] and the effective mass of the electron is always much smaller than that of the hole in these II–VI semiconductors. From the band-edge shifts, the electronic structure as a function of the nanocrystallite size was also calculated for semiconductors.[21] The band gap is found to be in the range 3.5–4 eV for the range of particles from 6–18 nm, agreeing well with the reported value.[22] This

makes the samples a two-photon absorber at 532 nm, since the incident photon energy is below, but close to, the band edge.

Figure 3 gives the open aperture z-scan traces of ZnO colloids of different particle sizes at a typical fluence of 866 MW/cm^2. The open-aperture curve exhibits a normalized transmittance valley, indicating the presence of a reverse saturable absorption in the colloids. The data are analyzed by using the procedure described by Bahae *et al.*[18] for a two-photon absorption process; the nonlinear absorption coefficient β is obtained by fitting the experimental z-scan plot to Eq. (1),

$$T(z) = \frac{C}{q_0\sqrt{\pi}} \int_{-\infty}^{\infty} \ln(1 + q_0 e^{-t^2}) dt, \tag{1}$$

where $q_o(z,r,t) = \beta I_o(t) L_{\text{eff}}$. Here, $L_{\text{eff}} = 1 - e^{-\alpha l}/\alpha$ is the effective thickness with linear absorption coefficient α, and I_o is the irradiance at focus. The solid curves in Fig. 3 are the theoretical fit to the experimental data. The imaginary part of the third-order susceptibility, Im $\chi^{(3)}$, is related to β through the equation Im $\chi^{(3)} = n_o^2 \varepsilon_o c^2 \beta/\omega$, where $n_o = 2.008$ is the linear refractive index of ZnO, ε_o is the permittivity of free space, c is the velocity of light in vacuum, ω is the angular frequency of the radiation used. The obtained values of the nonlinear absorption coefficient β and Im $\chi^{(3)}$ at an intensity of 866 MW/cm^2 are shown in Table I.

Figure 4 gives the closed-aperture z-scan traces of ZnO colloids of different particle sizes at a fluence of 866 MW/cm^2. The closed-aperture curve exhibited a peak-to-valley shape, indicating a negative value of the nonlinear refractive index n_2. For samples with sizable refractive and absorptive nonlinearities, closed-aperture measurements contain contributions from both the intensity-dependent changes in the transmission and in the refractive index.[18] By dividing the normalized closed-aperture transmittance by the corresponding normalized open-aperture data, we could retrieve the phase distortion created due to the change in refractive index; this result is depicted in Fig. 4.

It is observed that the peak-valley of the closed-aperture z-scan satisfied the condition $\Delta z \sim 1.7 \ z_0$, thus confirming the presence of cubic nonlinearity.[18] The value of ΔT_{p-v} i.e., the difference between the peak and valley transmittance, could be obtained by the best theoretical fit from the results

TABLE I. Measured values of nonlinear absorption, nonlinear refraction, and nonlinear susceptibility of ZnO colloids at an intensity of 866 MW/cm^2.

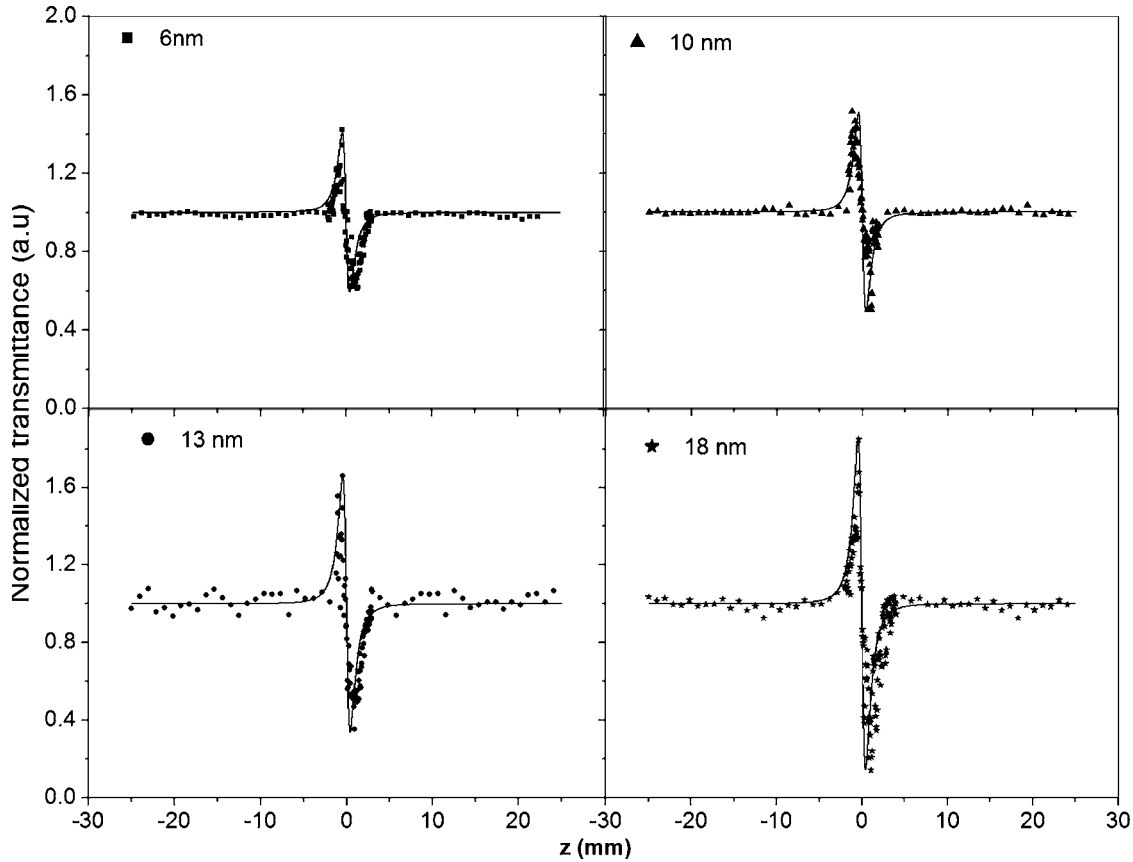| Average particle size R (nm)	Nonlinear absorption coefficient β (cm/GW)	Nonlinear refractive index n_2 $\times 10^{-10}$ esu	Imaginary part of nonlinear susceptibility Im $(\chi^{(3)})$ $\times 10^{-10}$ esu	Real part of nonlinear susceptibility Re $(\chi^{(3)})$ $\times 10^{-10}$ esu	Nonlinear susceptibility $\chi^{(3)}$ $\times 10^{-10}$ esu
6	42.4	−6.3	0.2	−1.3	1.3
10	231	−7.8	1.0	−1.7	2.0
13	487.2	−11.7	2.1	−2.5	3.3
18	2085.2	−13.1	9.0	−2.8	9.4

FIG. 4. The closed-aperture z-scan traces of ZnO colloids of different particle sizes at a fluence of 866 MW/cm^2.

of the divided z-scan curve. The nonlinear refractive index n_2 and the real part of the nonlinear susceptibility Re $\chi^{(3)}$ are given, respectively, by Eq. (2),

$$n_2(\text{esu}) = \frac{Cn_0}{40\pi^2}\frac{\lambda\Delta T_{p-v}}{0.812(1-S)^{0.25}L_{\text{eff}}I_0},$$

$$\text{(2)}$$

$$\text{Re }\chi^{(3)}(\text{esu}) = \frac{n_0 n_2(\text{esu})}{3\pi}.$$

The nonlinear refractive index n_2 and the real part of $\chi^{(3)}$ evaluated using the above equations are tabulated in Table I.

The enhancement of nonlinear optical properties with increasing dimension in the weak-confinement regime essentially originates from the size-dependent enhancement of the oscillator strength of coherently generated excitons. Since the exciton is confined in a quantum dot, the confinement of the excitonic wave function is expected to give rise to an enhancement of the oscillator strength per quantum dot by a factor of R^3/a_B^3.[9] This size-dependent oscillator strength was experimentally confirmed in CuCl quantum dots.[13,14] Such a giant oscillator strength effect will result in an enhancement of the nonlinear susceptibility.[12] In order to obtain the crystallite size dependence of the third-order susceptibility, the R dependence of $\chi^{(3)}$ is shown in Fig. 5. The data show a general trend of increasing $\chi^{(3)}$ values with increasing radius; the values range from 1.5×10^{-10} to 1.2×10^{-9} esu for R =6–18 nm. When we apply a least-squares fit, a size dependence of R^2 is obtained, indicating an enhancement of more

than two orders of magnitude. This dependence is in good agreement with that observed for CdS, CuCl, and CuBr nanocrystals.[12,23–25]

The open and closed-aperture z-scan curve of a ZnO colloid of size 6 nm at different input fluences is shown in Figs. 6 and 7, respectively. We can see that nonlinear optical properties are highly fluence dependent. The results show three orders of enhancement from the reported value of 5 cm/GW for bulk ZnO.[26] It has been reported that the reduced
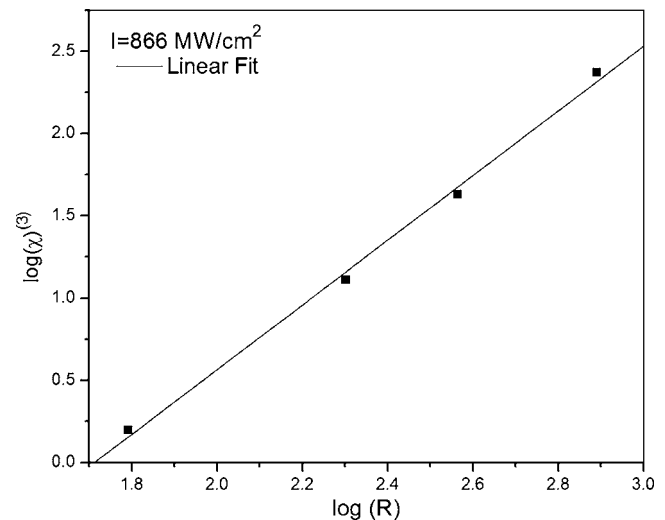

FIG. 5. The third-order susceptibility as a function of particle size for ZnO nanocolloids. The straight line indicates the result of a least-squares fit, which is the R^2 dependence.
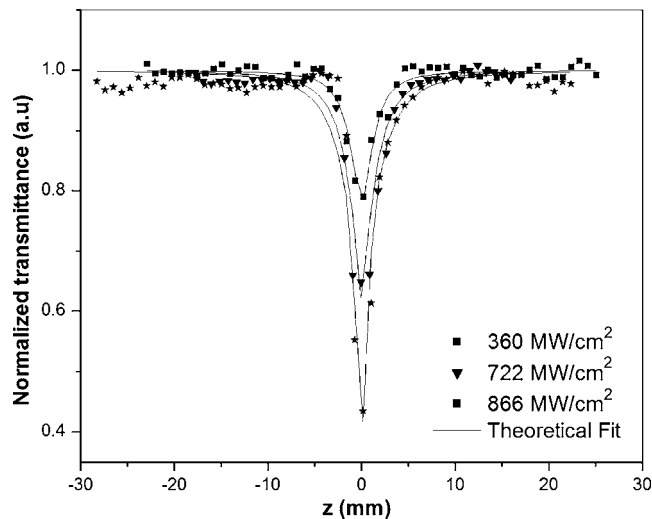
FIG. 6. The open-aperture z-scan curves of ZnO colloid of size 6 nm at different input fluences.

FIG. 8. Variation of nonlinear susceptibility with irradiance for ZnO colloids of different particle sizes.

dimensionality of the particles resulted in a considerable enhancement of the second-order susceptibility $\chi^{(2)}$ in thin films of ZnO.[3] Similar results in the third-order nonlinear parameters were evident in our measurements also. Figure 8 shows the variation of nonlinear susceptibility with irradiance for different colloids. Results show that $\chi^{(3)}$ is a function of intensity of the laser radiation which can be written as $\chi^{(3)} = \chi_0^{(3)} + \chi_1^{(3)} I + \chi_2^{(3)} I^2$. For a lower fluence and colloids with small size, $\chi^{(3)}$ is independent of intensity, indicating it is a
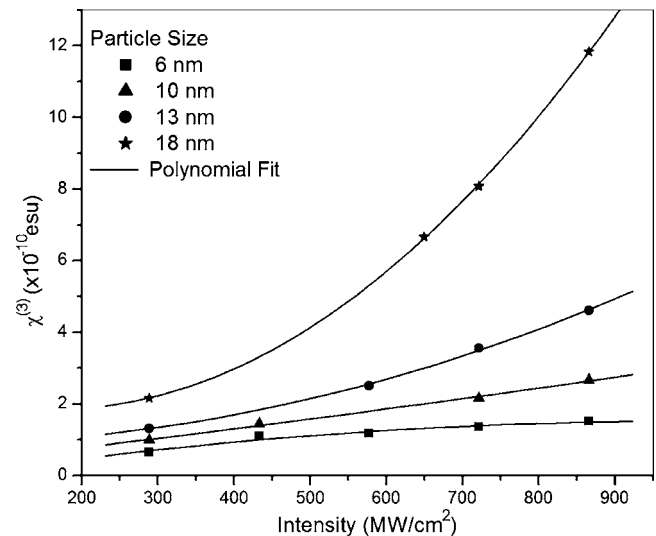
third-order effect resulting from two-photon absorption (TPA). For colloids of larger particle size and at higher fluences, $\chi^{(3)}$ becomes a nonlinear function of intensity. This quadratic dependence of $\chi^{(3)}$ with intensity is clearly shown in the figure, indicating the occurrence of higher order nonlinear processes such as free-carrier absorption. The free-carrier lifetime of ZnO is reported to be 2.8 ns.[4] Hence, there is a strong possibility that the 7 ns pulses used in the present
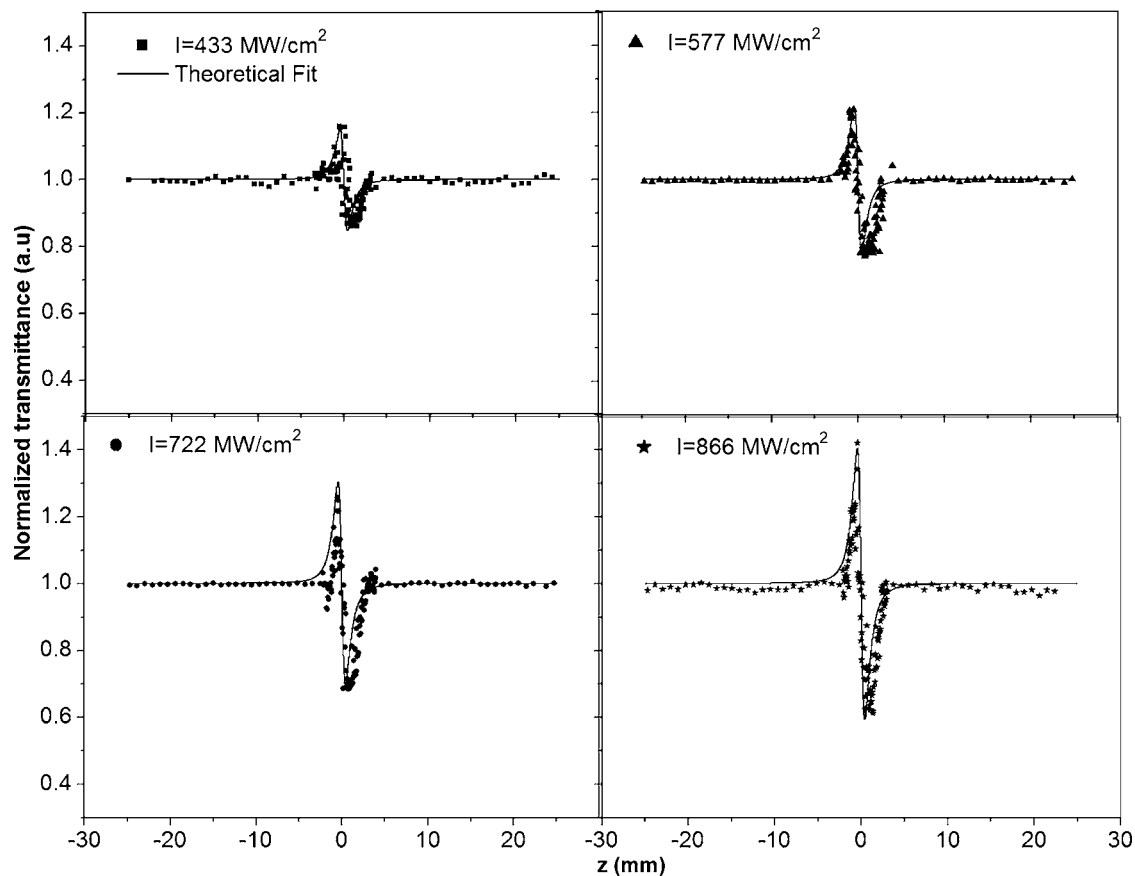

FIG. 7. The closed-aperture z-scan curves of ZnO colloid of size 6 nm at different input fluences.

study are exciting the accumulated free carriers generated by TPA by the rising edge of the pulse.

The values of $\chi^{(3)}$ measured at room temperature by the degenerate four-wave mixing technique on CuBr nanocrystals range from 8×10^{-11} to 1.1×10^{-9} esu for $R = 2.7–42$ nm and are comparable to the results presented here.[25] In this paper, we report the experimental evidence for the enhancement of third-order nonlinear susceptibility due to the size-dependent oscillator strength of confined excitons, which was theoretically predicted by Hanamura.[9] The enhancement of $\chi^{(3)}$ for thin nanocrystalline films compared to microcrystalline films of ZnO was attributed to the nanosized structure of the film.[27] Recently, a significant (~ 500 times) enhancement of the nonlinear refractive index with respect to the bulk value has been observed for polymer-capped ZnO nanocrystals with an estimated average size of 4 nm.[28] The third-order nonlinear optical response of these PVP-capped ZnO nanoparticles in a dilute solution was reported to be significantly larger and is of the order of 6.3×10^{-11} esu. This value is at least two orders of magnitude greater than that of the bulk ZnO. This remarkable enhancement in the third-order nonlinear optical response may be related to the exciton confinement and optical Stark effects.[5]

It is worth noting that certain representative third-order nonlinear optical materials, such as CuO chain compounds,[29] Ag_2S/CdS nanocomposites,[30] metallophthalocyanines,[31] porphrins,[32] organic dyes,[33] organic polymers,[34] organic coated quantum dots,[35] metal clusters,[36] etc., yielded values of the order of 10^{-10} to 10^{-14} esu for $\chi^{(3)}$ at a wavelength of 532 nm. These values are lower by one order of magnitude in comparison to the value of $\chi^{(3)}$ obtained in the present investigation. Thus, the real and imaginary parts of the third-order nonlinear optical susceptibility measured by the z-scan technique revealed that the ZnO colloids investigated in the present study have a good nonlinear optical response and could be chosen as ideal candidates with potential applications for nonlinear optics.

Recently, nanomaterials have drawn significant attention as optical limiters[37] for eyes or for sensor protection from laser terror in homeland or agile laser threats on the battlefield. Also, the nonlinear optical properties of nanomaterials are of great interest for optical switching, pulse power shaping of an 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 potentials of nanomaterials as optical power limiters have just begun to be recognized.

To examine the viability of nano-ZnO colloids as optical limiters, the nonlinear transmission of the colloid is studied as a function of the 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.[38] From the value of fluence at focus, the fluence values at
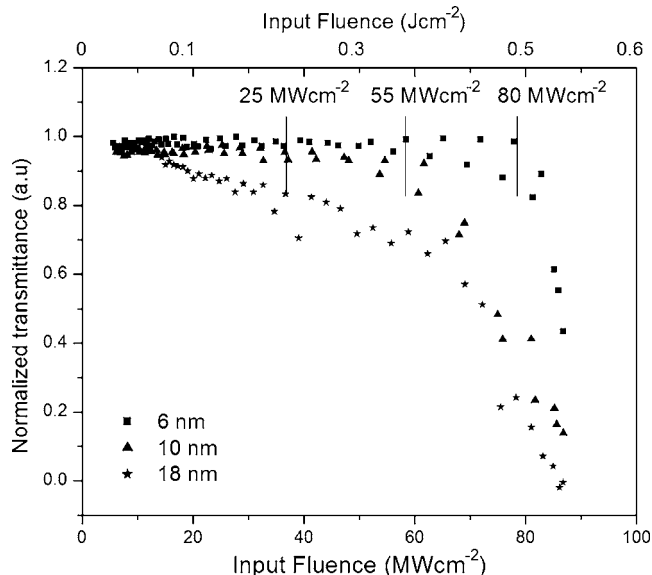

FIG. 9. Optical limiting curves of ZnO colloids of different particle sizes.

other positions could be calculated using the standard equations for a Gaussian beam waist. Such plots represent a better comparison of the nonlinear absorption or transmission in these samples and were generated from z-scan traces. Figure 9 illustrates the influence of nanoparticle size on the optical limiting response.

The fluence value corresponding to the onset of optical limiting (optical limiting threshold) is found to be high in the case of ZnO colloids of size 6 nm (80 MW/cm^2) in comparison to the ZnO colloids of size 10 nm (55 MW/cm^2) and ZnO colloids of size 18 nm (25 MW/cm^2). These values are comparable to the reported optical limiting threshold for CdS nanocolloids.[24] The arrow in the figure indicates the approximate fluence at which the normalized transmission begins to deviate from linearity. Particle size has a significant effect on the limiting performance of ZnO nanocolloids. Increasing the particle size reduces the limiting threshold and enhances the optical limiting performance. From the measured values of β for the colloids, it can be seen that the colloid with a larger particle size is a better nonlinear absorber and hence a good optical limiter.

IV. CONCLUSIONS

Nonlinear optical properties of ZnO semiconductor nanocolloids are investigated for optical power self-limiting application. We have experimentally demonstrated optical nonlinearity as a function of the size, and an R^2 dependence of nonlinear susceptibility is obtained for ZnO nanocolloids. Nonlinear susceptibility is highly fluence dependent and it becomes quadratic in nature for a large particle size. The observed nonlinearities are very high compared with those in bulk ZnO. The optical limiting response of ZnO nanocolloids, in the diameter range of 6–18 nm, increases with the increase of particle size.

ACKNOWLEDGMENTS

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