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Spectral and nonlinear optical characteristics of nanocomposites of ZnO–CdS

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In this article, we present the spectral and nonlinear optical properties of ZnO–CdS nanocomposites prepared by colloidal chemical synthesis. The optical band gap (E_g) of the material is tunable between 2.62 and 3.84 eV. The emission peaks of ZnO–CdS nanocomposites change from 385 to 520 nm almost in proportion to changes in E_g. It is possible to obtain a desired luminescence color from UV to green by simply adjusting the composition. The nonlinear optical response of these samples is studied by using nanosecond laser pulses from a tunable laser at the excitonic resonance and off-resonance wavelengths. The nonlinear response is wavelength dependent, and switching from saturable absorption (SA) to reverse SA (RSA) has been observed for samples as the excitation wavelength changes from the excitonic resonance to off-resonance wavelengths. Such a changeover in the sign of the nonlinearity of ZnO–CdS nanocomposites is related to the interplay of exciton bleach and optical limiting mechanisms. The ZnO–CdS nanocomposites show self-defocusing nonlinearity and good nonlinear absorption behavior at off-resonant wavelengths. The nonlinear refractive index and the nonlinear absorption increase with increasing CdS volume fraction at 532 nm. The observed nonlinear absorption is attributed to two photon absorption followed by weak free carrier absorption. The enhancement of the third-order nonlinearity in the composites can be attributed to the concentration of exciton oscillator strength. This study is important in identifying the spectral range and composition over which the nonlinear material acts as a RSA based optical limiter. ZnO–CdS is a potential nanocomposite material for the tunable light emission and for the development of nonlinear optical devices with a relatively small limiting threshold. [DOI: 10.1063/1.2919109]

I. INTRODUCTION

Semiconductor nanoparticles have been under continuous scientific interest because of their unique quantum nature, which changes the material solid-state properties. The linear and nonlinear optical properties of the semiconductors are the subject of much current theoretical and experimental interest.[1] Among the various nonlinear optical (NLO) materials investigated, the direct band gap semiconductors, especially zinc oxide (ZnO) and cadmium sulfide (Cds), have attractive nonlinear properties that make them ideal candidates for NLO based devices. ZnO is a wide and direct band gap II–VI semiconductor with a band gap of 3.37 eV and a high exciton binding energy of 60 meV having many applications, such as a transparent conductive contact, thin-film gas sensor, varistor, solar cell, luminescent material, surface electroacoustic wave device, heterojunction laser diode, UV laser, and others. Nanosized ZnO in the form of quantum dots, nanowires, nanobelts, etc, are referred to as the material of the 21st century.[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. There is a significant demand for high nonlinear optical materials, which can be integrated into an optoelectronic device.

In recent years, interest in the synthesis, characterization, and application of colloidal "quantum dot" semiconductor materials has markedly grown.[3] Nanocrystals of cadmium sulfide are by far the most studied system among all the semiconducting nanocrystals.[4] The bulk CdS has a direct band gap of 2.4 eV at 300 K, and the typical Bohr exciton diameter of CdS is around 5.8 nm; consequently, CdS nanocrystals in the size range of 1–6 nm show sizable quantum confinement effects with remarkably different optical properties. The size dependent, unusual optical, and electronic properties of these nanocrystals have been studied in detail by using a wide variety of experimental and theoretical techniques.[5]

The possibility of tailoring the bulk material properties by varying the size, structure, and composition of constituting nanoscale particles makes them candidates for various important applications in the field of material research. The field of nanocomposite materials has been widely recognized as one of the most promising and rapidly emerging research areas. Promising applications are expected or have already been realized in many fields of technology such as optical and electronic materials, solid electrolytes, coating technology, sensorics, catalysis, and separation science. Significant investigations have been done in the photophysical and photochemical behaviors of single and multicomponent metals and semiconductor nanoclusters.[6] Such composite materials are especially of interest in developing efficient light-energy conversion systems, optical devices, and microelectronics.

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For example, photoinduced deposition of noble metals such as Pt or Au on semiconductor nanoclusters has often been employed to enhance their photocatalytic activity.[7]

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,[8] while only a few reports can be found by using ZnO as the matrix for nanoparticle composite films.[9] These nanocomposites may lead to optically functional properties. 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 CdS and PbS particles can be easily tuned by selecting appropriate matrix materials.[10] Recently, a microemulsion technique has been developed to prepare semiconductor nanocomposites such as ZnS/CdSe, ZnSe/CdSe, or ZnS/CdS in a core-shell structure.[11] 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 NLO properties.[12] In this study, therefore, the nanocomposite techniques are applied to improve the spectral and optical properties of ZnO. In our continued efforts to explore the optical properties of various nanocomposites, we have now elucidated the spectral and nonlinear responses of ZnO–CdS nanocomposites.

Generally, photoluminescence spectrum of a single crystal ZnO mainly consists of two bands.[13] The one in the UV region corresponding to the near band edge emission at about 380 nm is mainly attributed to near band edge emission, and the other in the visible region is due to structural defects and impurities. Soon after the reporting of stimulated UV emission of ZnO at room temperature, it attracted the attention of the researchers as a UV laser material.[14] Thereafter, more and more investigators aimed at applications of ZnO emitting at the short wavelength. Several reviews elaborated the recent development of photoelectron applications of ZnO in a short wavelength.[15] Tsukazaki *et al.* reported the violet electroluminescence from homostructural ZnO *p-i-n* junctions at room temperature.[16] However, the improvement of UV emission and the simplification of growth techniques are still very important.

We report the wavelength dependent nonlinear absorption of ZnO–CdS nanocomposites with varying CdS content under nanosecond excitation. 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 occurs when the absolute transmittance of a material decreases with an increase in input fluence. One mechanism for optical limiting is provided by reverse saturable absorption (RSA), in which the excited state absorption cross section is higher than the ground state absorption cross section. It is also known that doping significantly improve the limiting performance of ZnO.

II. EXPERIMENT

Colloids of ZnO are synthesized by a modified polyol precipitation method.[17] The monodisperse 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 (DEG) medium. Among the different polyols, the DEG is chosen because it is reported to give particles with uniform shape and size distributions. The size of the particles and hence the stability of this colloidal suspension depend on the concentration of zinc acetate as well as on its rate of heating. The molar concentration of precursor solution is $0.025M$ and a heating rate of $4\ ^\circ\mathrm{C/min}$ is employed for the formation of ZnO at a temperature of $120\ ^\circ\mathrm{C}$. 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 to produce the monodisperse ZnO spheres. Prior to reaching the working temperature, typically at $115\ ^\circ\mathrm{C}$, some volume of the primary reaction supernatant is added to the solution. After reaching $120\ ^\circ\mathrm{C}$, it is stirred for 1 h to get a monodisperse stable colloid.

The CdS nanocolloids are prepared by chemical method.[18] $\mathrm{Cd(NO_3)_2\ 4H_2O}$ (Merck, India) and $\mathrm{NH_2CSNH_2}$ (Merck, India) are used as the precursors for the incorporation of Cd and S, respectively. These precursors are dissolved in 2-propanol and distilled water under stirring. The solution is kept on stirring for 1 h to get a monodisperse stable colloid. The molar concentration of the precursor solution is $0.025M$.

The ZnO–CdS nanocomposites are prepared by colloidal chemical synthesis by mixing a certain amount of CdS colloid to ZnO colloid and stirring for 1 h. The volume fraction of CdS is changed keeping the volume of ZnO constant. The samples having ZnO$-x$CdS composition with (x=) 0.1%, 0.5%, 1%, 1.5% 2%, and 5% are named as ZnO–0.1CdS, ZnO–0.5CdS, ZnO–1Cds, ZnO–1.5CdS, ZnO–2CdS, and ZnO–5CdS, respectively.

The ZnO–CdS nanocomposites are characterized by optical absorption measurements recorded by using a spectrophotometer (JascoV-570 UV/VIS/IR), and the fluorescence emission measurements are recorded by using a Cary Eclipse fluorescence spectrophotometer (VARIAN). In the present investigation, we have employed the single beam z scan technique with nanosecond laser pulses to measure the NLO absorptive and refractive properties of ZnO–CdS nanocomposites. Z scan technique developed by Bahae *et al.*[19,20] 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. A Q-switched neodymium doped yttrium aluminum garnet laser (Spectra Physics LAB-1760, 532 nm, 7 ns, 10 Hz) is used as the light source, and the wavelength dependences of the samples are studied by using a tunable laser (Quanta Ray MOPO, 5 ns, 10 Hz). 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 $35.4\ \mu\mathrm{m}$. The Rayleigh length $z_0=\pi w_0^2/\lambda$ is estimated to be 7.4 mm, much

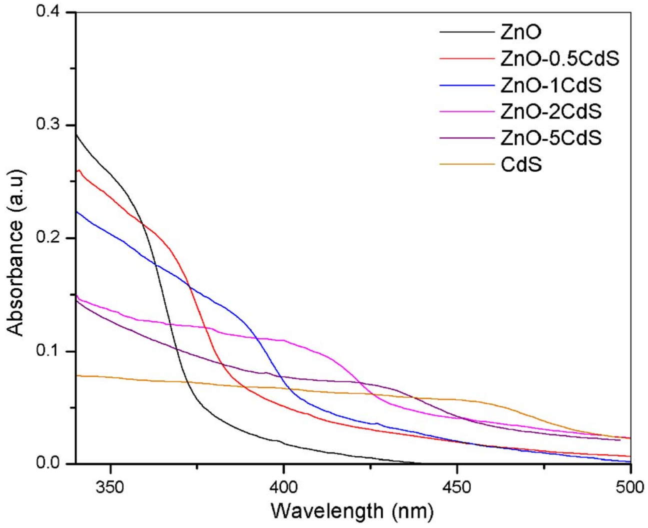

FIG. 1. (Color online) Absorption spectra of ZnO–CdS nanocomposites.

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 simultaneously measured by an energy ratiometer (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 by 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 Bahae *et al.*, and the nonlinear coefficients are obtained by fitting the experimental z scan plot with the theoretical plots.

III. RESULTS AND DISCUSSION

Optical absorption measurement is an initial step to observe the single colloid and nanocomposite behavior. Figure 1 gives the room temperature absorption spectra of the ZnO–CdS nanocomposites. The excitonic peaks of ZnO and that of CdS colloids are found to be blueshifted with respect to their bulk which could be attributed to the confinement effects.[21] The pronounced dependence of the absorption band gap on the size of semiconductor nanocrystals is used to determine the particle size. An order of magnitude estimate of the grain size is possible from the absorption spectra. From the shift of absorption edge, the size of the dots is calculated. The sizes of ZnO and Cds nanocolloids are in the range of 10–12 nm. The presence of excitonic peak itself indicates that the composites are of nanometer size. It is seen that the absorption edge corresponding to the nanocomposites gets redshifted as a function of the CdS content. The size evolution of nanocomposites may also have some relation with optical characteristics in addition to the composition, and the study is in progress.

The direct band gap of ZnO–CdS nanocomposites is estimated from the graph of $h\nu$ versus $(\alpha h\nu)^2$ 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 dependent on the composition, and there is a decrease in the band gap of the semiconductor with an increase in volume fraction of CdS in the nanocomposites, as shown in Fig. 2. E_g changes from 3.84 eV for ZnO to 2.62 eV for CdS almost in proportion to the composition of CdS. The total change in the band gap of the material is contributed by the shifts of the valence band as well as that of 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, although few in number that reported the individual shifts in TVB and BCB employing various forms of high-energy spectroscopies, such as the photoemission and the x-ray absorption spectroscopies.[22] The shifts of the band edges smoothly decrease to zero for large sized nanocrystals and the shift in the BCB is, in general, much larger compared to the shift in the TVB. Within the range of compositions

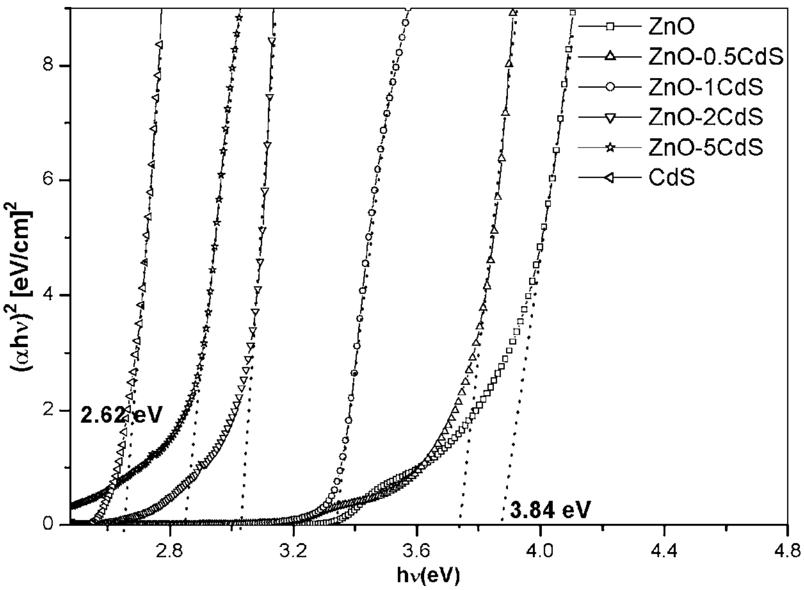

FIG. 2. Optical band gap of ZnO–CdS nanocomposites.

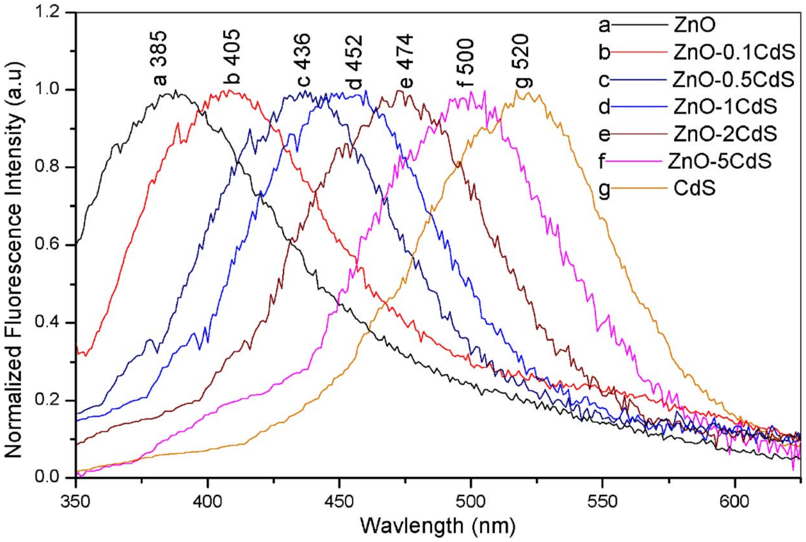

FIG. 3. (Color online) Fluorescence spectra of ZnO–CdS nanocomposites.

studied, the optical band gap is tunable from 2.62 to 3.84 eV. The band gap engineering in ZnS–CdS is reported to be from 2.58 to 3.91 eV.[23]

Photoluminescence spectra of all samples measured at room temperature are shown in Fig. 3. The 385 nm emission is the near band edge emission of ZnO and the 520 nm emission is the near band edge emission peak of CdS. Emission peaks of ZnO–CdS nanocomposites change from 385 to 520 nm almost in proportion to changes in E_g. It is possible to obtain a desired luminescence color from UV to green by simply adjusting the composition. The tuning of luminescence in ZnS–CdS is reported to be from blue to red in proportion to change in E_g.[23]

Figure 4 shows the nonlinear absorption of ZnO–CdS nanocomposites at a typical fluence of $300\ \mathrm{MW/cm^2}$ for an irradiation wavelength of 532 nm. The open-aperture curve exhibits a normalized transmittance valley, indicating the presence of reverse saturable absorption in the colloids. The obtained nonlinearity is found to be of the third order, as it fits to a two photon absorption (TPA) process. The corresponding net transmission is given in Ref. 19,

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

where

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

Here, $L_{\mathrm{eff}} = 1 - e^{-\alpha l}/\alpha$ is the effective thickness with linear absorption coefficient α, nonlinear absorption coefficient β, and I_0 is the irradiance at focus. The solid curves in Fig. 4 are the theoretical fit to the experimental data. The obtained values of nonlinear absorption coefficient β at an intensity of $300\ \mathrm{MW/cm^2}$ are shown in Table I.

Interestingly, ZnO and CdS colloids show a minimum nonlinearity, while the ZnO–CdS nanocomposites clearly exhibit a larger induced absorption behavior. The calculated nonlinear coefficients given in Table I show fairly high values of nonlinearity. The nonlinear absorption coefficient substantially increases in the nanocomposites, as compared to pure ZnO and CdS colloids. The enhancement of the third-order nonlinearity can be attributed to the concentration of exciton oscillator strength.[3]

Different processes, such as TPA, free carrier absorption, transient absorption, interband absorption, photoejection of electrons, and nonlinear scattering, are reported to be opera-

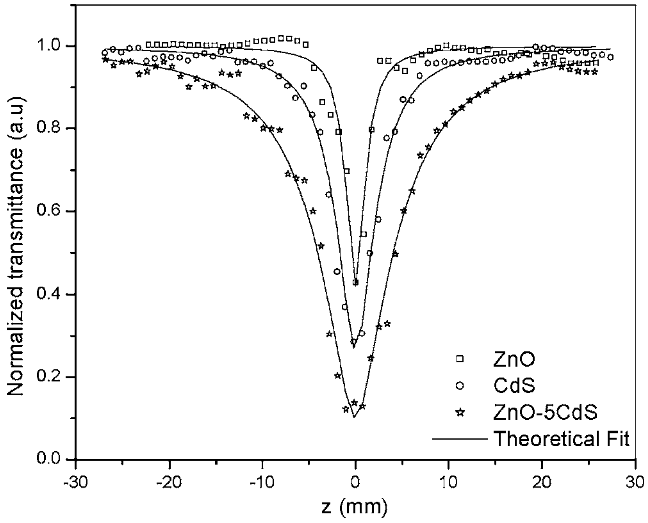

FIG. 4. Open-aperture z scan traces of ZnO–CdS nanocomposites at an intensity of $300\ \mathrm{MW/cm^2}$ for an irradiation wavelength of 532 nm.

TABLE I. Measured values of nonlinear absorption coefficient, saturation intensity, and refractive index of ZnO–CdS nanocomposites at an intensity of $300\ \mathrm{MW/cm^2}$ for different irradiation wavelengths.

	Nonlinear absorption coefficient			Nonlinear refractive index
	450 nm		532 nm	532 nm
ZnO–CdS nanocomposites	β (cm/GW)	I_s ($\mathrm{GW/cm^2}$)	β (cm/GW)	n_2 ($10^{-17}\ \mathrm{m^2/W}$)
ZnO	51.8		20.7	1.5
CdS		0.20	51.8	4.4
ZnO–0.5CdS	131.3		62.2	5.9
ZnO–1CdS	34.6		155.5	6.9
ZnO–2CdS	17.3		207.4	8.9
ZnO–5CdS		0.04	242.0	11.0

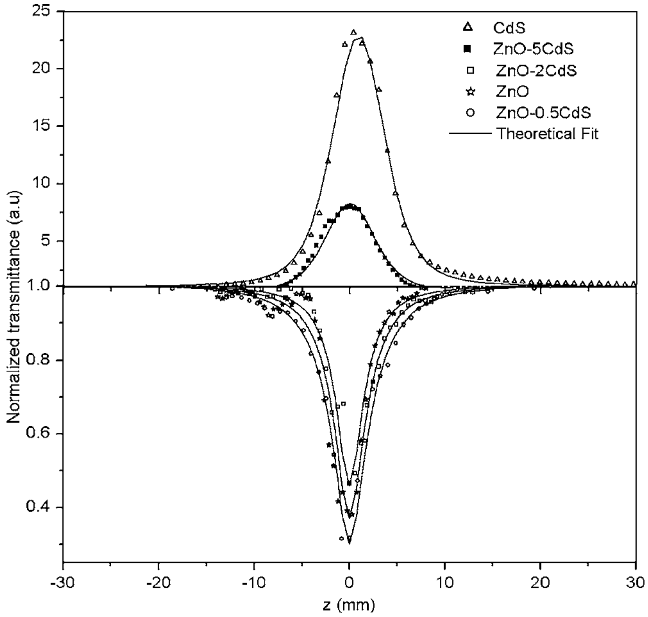

FIG. 5. Open-aperture z scan traces of ZnO–CdS nanocomposites at an intensity of 300 MW/cm^2 for an irradiation wavelength of 450 nm.

tive in nanoclusters. In general, induced absorption can occur due to a variety of processes. The theory of TPA process fitted well with the experimental curve establishes that TPA is the basic mechanism. There is a possibility of higher order nonlinear processes such as free carrier absorption contributing to induced absorption. The free carrier lifetime of ZnO is reported to be 2.8 ns.[24] 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. The larger nonlinear absorption in semiconductors such as ZnSe, ZnO, and ZnS is reported to be due to two photon induced free carrier absorption along with TPA.[24] The enhancement of nonlinear absorption in Ag_2S–CdS nanocomposites in comparison to the CdS nanoparticles is reported to be due to free-carrier absorption, and the free-carrier lifetime of ZnO is determined to be a few nanoseconds.[11] Thus, we propose that the observed nonlinearity is caused by TPA followed by weak free-carrier absorption in the nanocomposites.

Figure 5 shows the nonlinearity observed at 450 nm at a fluence of 300 MW/cm^2. An absorption saturation behavior is found in CdS colloid and ZnO–5CdS nanocomposites. However, all the other ZnO colloids and ZnO–CdS nanocomposites exhibit induced absorption at this wavelength. Such a changeover in the sign of the nonlinearity is related to the interplay of exciton band bleach and optical limiting mechanisms, as found from earlier studies of semiconductor nanoparticles.[25] Such a behavior can generally be modeled by defining a nonlinear absorption coefficient $\alpha(I)$, which is a sum of independent positive and negative transmission coefficients,[26]

$$\alpha(I) = \frac{\alpha}{1 + (I/I_S)} + \beta I, \tag{2}$$

where I_s is the saturation intensity. The obtained values of nonlinear absorption coefficient β and saturation intensity I_s at an intensity of 300 MW/cm^2 are shown in Table I.

The excitonic peak is sensitive to laser excitation. As the particle size is reduced, a series of nearby transitions occurring at slightly different energies in the bulk are compressed by quantum confinement into a single, intense transition in a quantum dot. Therefore, the oscillator strength of the nanoparticle is concentrated into just a few transitions and the strong exciton bleaching can be expected. Exciton bleach effects are seen when the CdS nanocolloids are excited at excitonic resonance with nanosecond laser pulses of 450 nm. So, increased transmission behavior is observed for CdS nanocolloids, which fits to a saturable absorption mechanism. On the other hand, ZnO colloids exhibit induced absorption at this wavelength. For a small volume fraction of CdS, the nonlinear absorption coefficient substantially increases in the nanocomposites, as compared to pure ZnO. ZnO–0.5CdS exhibits maximum nonlinear absorption at 450 nm. The enhancement of the third-order nonlinearity can be attributed to the concentration of exciton oscillator strength.[3] When the volume fraction of CdS increases beyond 0.5%, the nonlinear absorption coefficient decreases with the increase in the volume fraction of CdS and it becomes a saturable absorber at and above 5% CdS due to the interplay of exciton bleach and optical limiting mechanisms. The excitonic bleaching of the CdS nanocolloids originates from the transition between the ground state $1S(e)$ and the lowest excited state $1S3/2(h)$ since the excitation at 450 nm corresponds to the absorption close to the resonance of the $1S(e)$-$1S_{3/2}(h)$ excitonic transition.[25] Thus, the nonlinearity of the ZnO–CdS nanocomposites is related to the interplay of exciton bleach and optical limiting mechanisms at 450 nm. The great potential of using the ZnO–CdS nanocomposite lies in the fact that the composition of the constituent elements can readily be altered to optimize the desired NLO properties either as a saturable absorber or as a reverse saturable absorber.

Figure 6 gives the closed-aperture z scan traces of ZnO–CdS 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 sizable refractive and absorptive nonlinearities, closed-aperture measurements contain contributions from both the intensity-dependent changes in the transmission and in the refractive index.[19] 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 the 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.[19] The value of the difference between the normalized peak and valley transmittance $\Delta T_{p\text{-}v}$ 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 $\Delta T_{p\text{-}v}$ in a closed-aperture z scan by using Eq. (3) and is tabulated in Table I,

$$\Delta T_{p\text{-}v} = 0.406(1 - S)^{0.25}|\Delta\Phi_0|, \tag{3}$$

where

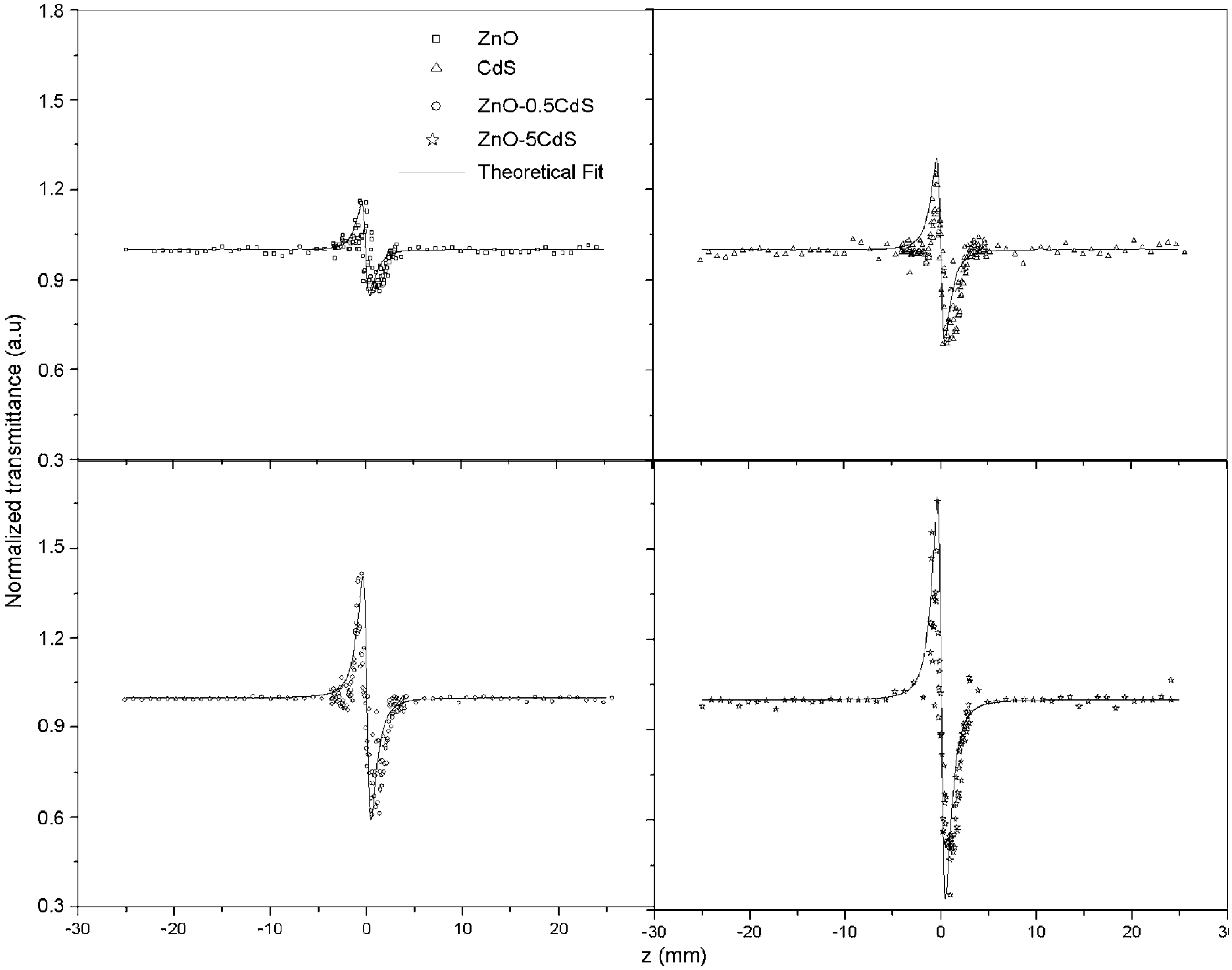

FIG. 6. Closed-aperture z scan traces of ZnO–CdS nanocomposites at an intensity of 300 $\mathrm{MW/cm^2}$ for an irradiation wavelength of 532 nm.

$$|\Delta\Phi_0| = \frac{2\pi}{\lambda} n_2 I_0 L_{\mathrm{eff}}.$$

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 have shown positive nonlinearity for individual CdS nanoclusters prepared by laser ablation.[27] The nonlinear refractive index substantially increases in the nanocomposites, as compared to pure ZnO and CdS colloids. The enhancement of the third-order nonlinearity can be attributed to the concentration of exciton oscillator strength.[3] 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 in absorption.[28] The figure of merit for the third-order nonlinearity measured by using z scan technique shows an increase in the particle size of ZnO as well as CdS.[25] We therefore attribute the steady increase in the n_2 values to the increase in third-order susceptibility as a function of particle size from ZnO–0.1CdS to ZnO–5CdS.

The significant optical nonlinearities of the pure semiconductor nanocolloid at 532 nm are reported to have the nonlinear refractive index of the order of 10^{-16}–10^{-17} $\mathrm{m^2/W}$. The third-order nonlinear absorption coefficients of CdS nanocrystals are reported to be of the order of 10^{-10} m/W.[29] It is worth noting that certain representative third-order NLO materials, such as CuO chain compounds, Ag_2S–CdS nanocomposites, organic coated quantum dots, metal clusters, etc., yielded values of the order of 10^{-9}–10^{-14} m/W for nonlinear absorption coefficient at a wavelength of 532 nm.[30,31] These values are comparable to the value of β obtained for nanocomposites in the present investigation. Thus, the nonlinear absorption coefficient and nonlinear refractive index measured by the z scan technique reveal that the ZnO–CdS nanocomposites investigated in the present study have good NLO response and could be chosen as ideal candidates with potential applications in nonlinear optics either as saturable absorber or as reverse saturable absorber.

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.[32] Also, the NLO properties of nanomaterials are of great interest for optical switching, pulse power shaping of optical parametric oscillator/optical parametric generator, and other

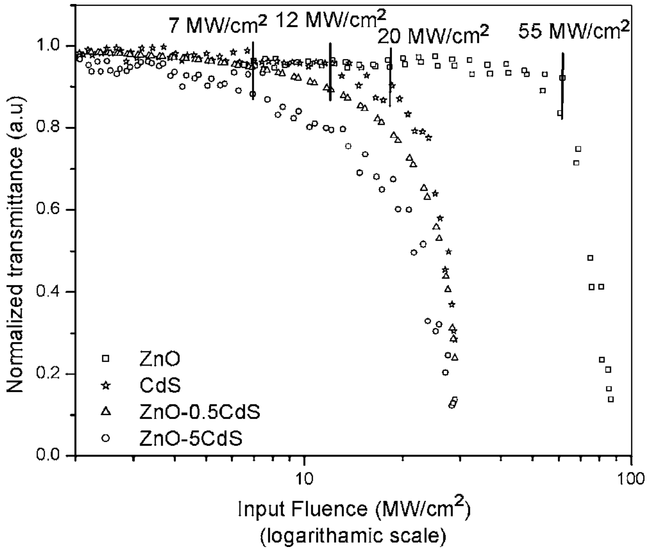

FIG. 7. Optical limiting response of ZnO–CdS nanocomposites at 532 nm.

NLO applications. Optical power limiting is operated through the NLO processes of nanomaterials. However, the great potentials of nanomaterials as optical power limiters have just begun to be recognized.

To examine the viability of ZnO–CdS 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 the third-order susceptibility.[33] From the value of fluence at focus, the fluence values at other positions could be calculated by using the standard equations for Gaussian beam waist. Such plots represent a better comparison of the nonlinear absorptions or transmissions in these samples and are generated from z scan traces. Figure 7 illustrates the influence of volume fraction of CdS in ZnO–CdS nanocomposites 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 ($55\ \mathrm{MW/cm^2}$) in comparison to the CdS colloids ($20\ \mathrm{MW/cm^2}$). These values are of the order of the reported optical limiting threshold for CdS nanocolloids.[34] ZnO–CdS nanocomposites are found to be good optical limiters compared to ZnO and CdS, and the optical limiting threshold of ZnO–5CdS nanocomposites is observed to be $7\ \mathrm{MW/cm^2}$. 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 CdS reduces the limiting threshold and enhances the optical limiting performance.

IV. CONCLUSION

The spectral and NLO properties of ZnO–CdS nanocomposites prepared by a colloidal chemical synthesis are investigated. The optical band gap is tunable between 2.62 and 3.84 eV. The emission peaks of ZnO–CdS nanocomposites change from 385 to 520 nm almost in proportion to changes in E_g. It is possible to obtain a desired luminescence color from UV to green by simply adjusting the composition. NLO response of these samples is studied by using nanosecond laser pulses from a tunable laser at excitonic resonance and off-resonance wavelengths. The nonlinear response is wavelength dependent, and switching from saturable absorption to reverse saturable absorption has been observed for samples as the excitation wavelength changes from the excitonic resonance to off-resonance wavelengths. Such a changeover in the sign of the nonlinearity of ZnO–CdS nanocomposites is related to the interplay of exciton bleach and optical limiting mechanisms. The ZnO–CdS nanocomposites show self-defocusing nonlinearity and good nonlinear absorption behavior at off-resonant wavelengths. The nonlinear refractive index and the nonlinear absorption increase with increasing CdS volume fraction at 532 nm. The observed nonlinear absorption is explained through TPA followed by weak free carrier absorption. The enhancement of the third-order nonlinearity in the composites can be attributed to the concentration of exciton oscillator strength. This study is important in identifying the spectral range and composition over which the nonlinear material acts as a RSA based optical limiter. It is shown that ZnO–CdS is a potential nanocomposite material for tunable light emission and for the development of NLO devices with a relatively small limiting threshold.

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