

## Enhanced luminescence and nonlinear optical properties of nanocomposites of ZnO–Cu

Litty Irimpan,<sup>a)</sup> V.P.N. Nampoori, and P. Radhakrishnan

*International School of Photonics, Cochin University of Science and Technology, Cochin, Kerala 682022, India*

(Received 6 February 2008; accepted 29 April 2008)

In this article, we present the spectral and nonlinear optical properties of ZnO–Cu nanocomposites prepared by colloidal chemical synthesis. The emission consisted of two peaks. The 385-nm ultraviolet (UV) peak is attributed to ZnO and the 550-nm visible peak is attributed to Cu nanocolloids. Obvious enhancement of UV and visible emission of the samples is observed and the strongest UV emission of a typical ZnO–Cu nanocomposite is over three times stronger than that of pure ZnO. Cu acts as a sensitizer and the enhancement of UV emission are caused by excitons formed at the interface between Cu and ZnO. As the volume fraction of Cu increases beyond a particular value, the intensity of the UV peak decreases while the intensity of the visible peak increases, and the strongest visible emission of a typical ZnO–Cu nanocomposite is over ten times stronger than that of pure Cu. The emission mechanism is discussed. Nonlinear optical response of these samples is studied using nanosecond laser pulses from a tunable laser in the wavelength range of 450–650 nm, which includes the surface plasmon absorption (SPA) band. The nonlinear response is wavelength dependent and switching from reverse saturable absorption (RSA) to saturable absorption (SA) has been observed for Cu nanocolloids as the excitation wavelength changes from the low absorption window region to higher absorption regime near the SPA band. However, ZnO colloids and ZnO–Cu nanocomposites exhibit induced absorption at this wavelength. Such a changeover in the sign of the nonlinearity of ZnO–Cu nanocomposites, with respect to Cu nanocolloids, is related to the interplay of plasmon band bleach and optical limiting mechanisms. The SA again changes back to RSA when we move over to the infrared region. The ZnO–Cu nanocomposites show self-defocusing nonlinearity and good nonlinear absorption behavior. The nonlinear refractive index and the nonlinear absorption increases with increasing Cu volume fraction at 532 nm. The observed nonlinear absorption is explained through two-photon absorption followed by weak free-carrier absorption and interband absorption mechanisms. This study is important in identifying the spectral range and composition over which the nonlinear material acts as a RSA-based optical limiter. ZnO–Cu is a potential nanocomposite material for the light emission and for the development of nonlinear optical devices with a relatively small limiting threshold.

### 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 semiconductors are the subject of much current theoretical and experi-

mental interest.<sup>1</sup> 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. 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, ultraviolet (UV) laser, and others. Nano-sized ZnO in the form of quantum dots, nanowires,

<sup>a)</sup>Address all correspondence to this author.  
e-mail: littyirimpan@yahoo.co.in  
DOI: 10.1557/JMR.2008.0364

nanobelts, etc., are referred to as the material of the 21st century.<sup>2</sup> 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.

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 behavior of single and multicomponent metal and semiconductor nanoclusters.<sup>3</sup> Such composite materials are especially of interest in developing efficient light-energy conversion systems, optical devices, and microelectronics. For example, photo-induced deposition of noble metals, such as Pt or Au on semiconductor nanoclusters, has often been used to enhance their photocatalytic activity.<sup>4</sup>

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 nanosized metal particulate dispersions show excellent optical, electrical, and mechanical properties.<sup>5</sup> In this study, therefore, the nanocomposite techniques are applied to improve the spectral and optical properties of ZnO. Optical nonlinearity of metal nanoparticles in a semiconductor has attracted much attention because of the high polarisability and fast nonlinear response that can be used in making them as potential optical devices.<sup>3</sup> Metal clusters and nanoparticles are promising materials for different nonlinear optical processes, like optical limiting, optical switching, and computing, because of their ultrafast nonlinear response.<sup>6</sup> It is well known that noble metal nanoparticles show an absorption due to surface plasmon resonance (SPR) in the visible region.<sup>3</sup> Out of various metal nanoparticles, silver, copper, and gold are extensively studied in colloids, thin films, and in different glass matrices for their nonlinear optical properties.<sup>7</sup> In this work, Cu is selected to prepare metal-semiconductor nanocomposite with ZnO because of their interesting optical properties in the visible range, which gives rise to wide applications in optoelectronic devices. In our continued efforts to explore the optical properties of various nanocomposites, we have now elucidated the spectral and nonlinear response of ZnO–Cu nanocomposites.

Generally, photoluminescence (PL) spectrum of a single crystal ZnO consists mainly of two bands.<sup>8</sup> The one in the UV region corresponding to the near-band-edge emission at about 380 nm is mainly attributed to exciton states, 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, ZnO attracted the attention of the researchers as a UV laser material.<sup>9</sup> Thereafter, more and more investigators aimed at applications of ZnO emitting at the short wavelength. Several reviews elaborated on the recent development of photoelectron applications of ZnO in short wavelength.<sup>10</sup> Tsukazaki et al. reported the violet electroluminescence from homostructural ZnO *p-i-n* junctions at room temperature.<sup>11</sup> However, the improvement of UV emission and the simplification of growth techniques are still very important.

We report the wavelength dependence of nonlinear absorption of ZnO–Cu nanocomposites with varying Cu 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 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 improves the limiting performance of ZnO.

## II. EXPERIMENT

Colloids of ZnO are synthesized by a modified polyol precipitation method.<sup>12</sup> The monodisperse ZnO colloidal spheres are produced by a two-stage reaction process. The method of preparation involves the hydrolysis of zinc acetate dihydrate in diethylene glycol medium and is explained in detail in Ref. 12. The copper nanocolloids are prepared by a hydrolysis method.<sup>13</sup> The method of preparation involves the hydrolysis of copper sulphate in H<sub>2</sub>O near boiling temperature. The solution is kept boiling for 1 h to get a monodisperse stable colloid. The molar concentration of the precursor solution is 0.025 M.

The ZnO–Cu nanocomposites are prepared by colloidal chemical synthesis by mixing a certain amount of Cu colloid to ZnO colloid at 120 °C during its preparation stage and stirred for 1 h at that temperature. The volume fraction of Cu is changed keeping the volume of ZnO constant. The samples having ZnO–*x*Cu composition with (*x* = ) 0.1%, 0.5%, 1%, 1.5%, 2%, and 5% are named as ZnO–0.1Cu, ZnO–0.5Cu, ZnO–1Cu, ZnO–1.5Cu, ZnO–2Cu, and ZnO–5Cu, respectively.

The ZnO-Cu nanocomposites are characterized by optical-absorption measurements recorded using a spectrophotometer (JascoV-570 UV/VIS/IR, Hachioji, Japan), and the fluorescence emission measurements are recorded using a Cary Eclipse fluorescence spectrophotometer (Varian, Mulgrave, Australia). In the present investigation, we have used the single beam z-scan technique with nanosecond laser pulses to measure nonlinear optical absorptive and refractive properties of ZnO-Cu nanocomposites. The z-scan technique developed by Sheik Bahae and 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.<sup>14,15</sup> A Q-switched Nd:YAG laser (Spectra Physics LAB-1760, 532 nm, 7 ns, 10 Hz) is used as the light source, and the wavelength dependence of the samples are studied using a tunable laser (Quanta Ray MOPO, 5 ns, 10 Hz). The experimental set up is explained in detail in Ref. 15.

### III. RESULTS AND DISCUSSION

Optical-absorption measurement is an initial step to observe the single colloid and metal-semiconductor nanocomposite behavior. Figure 1 gives the room temperature absorption spectra of the ZnO-Cu 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.<sup>16</sup> For copper nanocolloid, the surface plasmon absorption band (SPA) lies in the 560-nm region. Although the conduction and valence bands of semiconductors are separated by a well-defined band gap, metal nanoclusters have close-lying bands and electrons move freely. The free

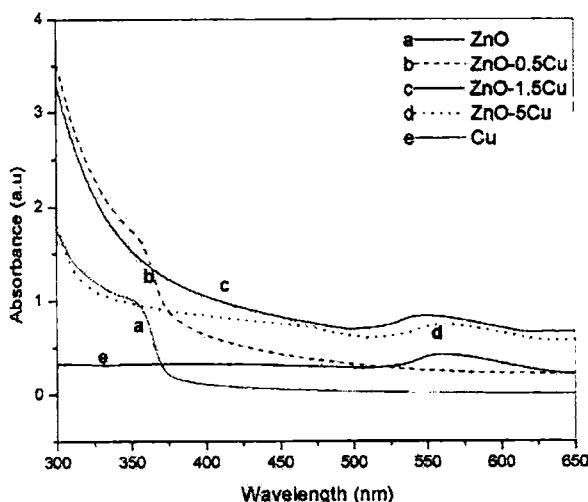


FIG. 1. Absorption spectra of ZnO-Cu nanocomposites.

electrons give rise to a SPA band in metal clusters, which depends on both the cluster size and chemical surroundings.<sup>3</sup> The plasmon band of metal particles, as explained on the basis of the Mie theory, involves dipolar oscillations of the free electrons in the conduction band that occupy energy states near the Fermi level.<sup>3</sup> For small-volume fraction of Cu, the composite exhibits the characteristics of ZnO with a red shift in the excitonic peak. However, the ZnO-1.5Cu nanocomposite exhibits both the semiconductor and metallic behavior. Optical-absorption spectra indicate the presence of a well-defined ZnO excitonic feature along with the Cu SPA feature at 545 nm.<sup>17</sup> The optical-absorption spectra of the clusters show a gradual shift in absorbance toward the UV region, over which an extremely weak surface plasmon resonance is superposed. The band of metal nanoclusters is very sensitive to the surface-adsorbed species and SPA dielectric of the medium. For example,  $I^-$  and  $C_6H_5S^-$  ions result in damping of the surface plasmon band of colloidal silver particles.<sup>18</sup> Alternately, one can also observe bleaching of the surface plasmon band with electrons deposited from radiolytically produced radicals, which cause a blue shift and narrowing of the plasmon band. A more detailed discussion on the damping effects caused by surrounding material can be found elsewhere.<sup>3</sup> When the volume fraction of Cu increases beyond 1.5%, the surface plasmon peak is shifted towards 560 nm, and it has been established that the shift of the plasma band of Cu observed is a result of the accumulation of excess electrons on the ZnO/Cu particles, which leads to equalization of the potentials of the conduction zones of the semiconductor and the metallic components of the nanocomposite.<sup>19</sup>

The pronounced dependence of the absorption band edge on the size of semiconductor nanocrystals and SPA band on the size of metal nanocrystals is used to determine the particle size. An order of magnitude estimate of the grain size is possible from the absorption spectra. The size of ZnO and Cu nanocolloids are in the range of 10–30 nm. The presence of excitonic peak and SPA band itself indicates that the composites are of nanometer size. The size evolution of nanocomposites may also have some relation with optical characteristics in addition to the composition, and the study is in progress.

PL spectra of all samples measured at room temperature are shown in Fig. 2. The intensities of the emission peaks depend on the volume fraction of Cu in the samples. ZnO and ZnO-0.5Cu have only emissions at 385 nm, but the intensity of the peak of ZnO-0.5Cu is much stronger than that of ZnO. ZnO-0.5Cu has the strongest UV emission, which is over three times stronger than that of ZnO. It is clear that the intensity of this peak increases with the increasing amount of the Cu and Zn acceptors. At small-volume fractions, Cu acts as a

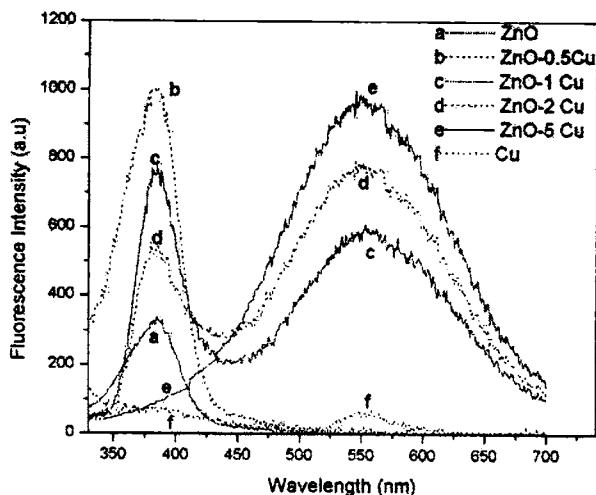


FIG. 2. Fluorescence spectra of ZnO–Cu nanocomposites.

sensitizer in the nanocomposites. ZnO–1Cu has UV and visible emissions. As the volume fraction of Cu increases beyond 0.5%, intensity of UV peak decreases and visible peak increases. When the ZnO colloid is overdoped by Cu the CuO nanoclusters appear, which will introduce defect states due to anion vacancies, and hence, there is reduction in PL intensity and increase in visible intensity.<sup>20</sup> ZnO–5Cu and Cu have only visible peak centered at 550 nm. It is obvious that the intensity of 550-nm peak agrees with the content of Cu nanocolloids. The emission of ZnO at 385 nm can be attributed to exciton transition. An undoped ZnO colloid has insufficient holes and therefore restricted exciton concentration. After Cu doping, Cu acceptors bring more holes to make the concentration of the excitons increase, 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 material.<sup>21</sup> Therefore, there are many holes existing in the interface between Cu nanoclusters and ZnO grains. The electrons in ZnO arrive at the interface easily because of their short mean free paths and the Coulomb forces. On the basis of the quantum confinement effects, plenty of excitons can be formed, and then the UV emission due to exciton transition is enhanced.

At larger volume fractions of Cu in the nanocomposites, i.e., when ZnO is overdoped by Cu, defect states due to anion vacancies are introduced and hence there is ten times enhancement in visible emission compared to that of Cu. As the volume fraction of Cu increases beyond 0.5%, the intensity of UV luminescence decreases, but the intensity of green luminescence increases.<sup>22</sup> The intensity of green emission becomes stronger than that of UV emission in the composite after a certain volume fraction of Cu, and dominant peak position is changed

from UV emission to green emission. The intensity variation of green luminescence is systematically observed depending on the volume fraction of Cu to investigate the emission mechanism. This difference could be mainly because UV luminescence is degraded by excessively oxidized layer formed on the surface and the grain boundary of ZnO and Cu.

Copper-doped ZnO is a strong luminescent material, and the green emission is due to copper induced levels. The transition mechanism for copper-doped ZnS has been thoroughly discussed by Suzuki and Shionoya.<sup>23</sup> They attributed it to donor–acceptor transitions. The donor level is due to  $\text{Al}^{3+}$  used as the coactivator, and acceptor levels are due to  $\text{Cu}^{2+}$  in the excited state under the UV radiation. When excited, the levels of  $\text{Cu}^{2+}(3d^9)$  configuration are split into  ${}^2t_2$  and  ${}^2e$  states with  ${}^2t_2$  lying in the higher position. In our experiments, no coactivator is used so that one can rule out the presence of donor levels due to  $\text{Al}^{3+}$ . We do not observe any other impurities that would introduce donor levels. Another model to explain the green luminescence due to copper in zinc sulphide was recently proposed by Peka and Schulz.<sup>24</sup> Green copper luminescence in their model is due to a transition from the conduction band of ZnS to the “ $t_2$ ” level of excited  $\text{Cu}^{2+}$  in the ZnS band gap. Figure 3 shows the luminescence mechanism in ZnO–Cu nanocomposites, in which the doping introduces defect levels due to anion vacancies. Impurities, such as sodium, copper, lead, potassium, nickel, cadmium, iron, etc., can lead to impurity levels in the band gap and lead to luminescence.<sup>25</sup> Without doping, radiative transition occurs from near conduction band to the valence band. In the case of Cu-doped ZnO nanocomposites, enhancement of visible luminescence is due to transition from defect level to the copper induced  $t_2$  level.

The optical-absorption spectroscopy and PL studies reveal the reaction mechanism at the junction. A twofold enhancement of steady-state luminescence of Rhodamine

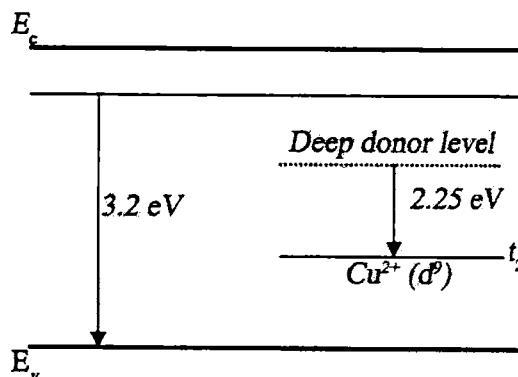


FIG. 3. UV and visible PL mechanism of ZnO–Cu nanocomposites: (a) transition from near conduction band edge to valence band and (b) transition from deep donor level to  $t_2$  induced level.

Ag has been observed when it is doped with metal nanoparticles.<sup>26</sup> The presence of silver aggregates causes substantial depolarization of the luminescence and the electromagnetic interaction between Ag surface plasmons and dye molecules can result, under certain conditions, in an enhanced fluorescence quantum efficiency and photostability of the dye. The strongest UV emission of a certain ZnO–Ag film is reported to be over ten times stronger than that of a pure ZnO film, and the enhancement of UV emission is caused by excitons formed at the interface between Ag nanoclusters and ZnO grains.<sup>20</sup>

Figure 4 shows the nonlinear absorption of ZnO–Cu nanocomposites at a typical fluence of 300 MW/cm<sup>2</sup> 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 by<sup>14</sup>

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

where

$$q_0(z, r, t) = \beta I_0(t) L_{\text{eff}} \quad . \quad (1)$$

Here,  $L_{\text{eff}} = 1 - e^{-\alpha l} / \alpha$  is the effective thickness with linear absorption coefficient  $\alpha$ , nonlinear absorption coefficient  $\beta$ , 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  $\beta$  at an intensity of 300 MW/cm<sup>2</sup> are shown in Table I.

Interestingly, ZnO and Cu colloids show a minimum

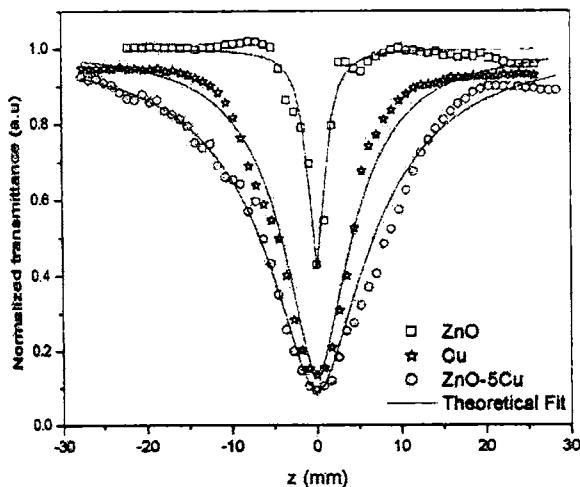


FIG. 4. Open aperture z-scan traces of ZnO–Cu nanocomposites at an intensity of 300 MW/cm<sup>2</sup> for an irradiation wavelength of 532 nm.

nonlinearity, while the ZnO–Cu 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 increases substantially in the nanocomposites, as compared to pure ZnO and Cu colloids. It is reported that the nonlinear absorption coefficient increases in the bimetallic and core-shell nanocomposites, as compared to pure metals.<sup>27</sup>

Different processes, such as two-photon absorption, free-carrier absorption (FCA), 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 and infers that TPA is the basic mechanism. There is the possibility of higher order nonlinear processes such as FCA contributing to induced absorption. The free carrier lifetime of ZnO is reported to be 2.8 ns.<sup>28</sup> 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 FCA is weak compared to TPA and hence the corresponding contribution in the z-scan curves is relatively less. Copper nanoparticles are well-known materials for nonlinear optical applications because of their subpicosecond time response of third-order optical nonlinearity. Transient absorption and nonlinear absorptive mechanisms are reported to lead to optical limiting in the case of metal nanoparticles.<sup>29</sup>

A laser pulse can cause an intraband or interband absorption in the metal nanoparticle system, depending on the excitation wavelength and incident intensity. The electrons thus excited are free carriers possessing a whole spectrum of energies, both kinetic and potential, immediately after the absorption leading to the bleaching of the ground state plasmon band. This process is accompanied by the nascent excited state showing a transient absorption due to the FCA.<sup>30</sup> The possibility of photoejection of electrons, which is an ultrafast phenomena occurring by a two photon or multiphoton absorption process, should also be considered as a contributing factor leading to nonlinear absorption, since the excitation photons in the visible region are usually not energetic enough for monophotonic electronic ejection. In our case, the excitation energy (532 nm or 2.3 eV) is higher than the interband threshold of copper from *d*-level to *p*-level (571 nm  $E_{dp} = 2.17$  eV), and hence interband absorption accompanied by the absorption of free carriers generated in the conduction band is possible. Strong optical limiting properties because of interband absorption are reported in different nanoparticle systems.<sup>31</sup> Thus, we propose that the observed nonlinearity is caused by two-photon absorption and weak FCA with a contribution from interband absorption occurring in the nanocomposites.



TABLE I. Measured values of nonlinear absorption coefficient, saturation intensity, and nonlinear refractive index of ZnO–Cu nanocomposites at an intensity of 300 MW/cm<sup>2</sup> for different irradiation wavelengths.

ZnO–Cu nanocomposites	Nonlinear absorption coefficient				Nonlinear refractive index
	532 nm	570 nm		650 nm	532 nm
	$\beta$ cm/GW	$\beta$ cm/GW	$I_s$ GW/cm <sup>2</sup>	$\beta$ cm/GW	$n_2$ 10 <sup>-17</sup> m <sup>2</sup> /W
ZnO	20.7	17.3		6.7	1.5
Cu	145.2		0.04	76.0	5.9
ZnO–0.1Cu	172.8	131.3		103.7	6.6
ZnO–0.5Cu	190.1	179.7		121.0	7.3
ZnO–1.5Cu	248.8	138.2		145.2	9.5
ZnO–2Cu	276.5	29.4		190.1	11.0
ZnO–5Cu	293.8	5.4		241.9	12.3

Figure 5 shows the nonlinearity observed at 570 nm at a fluence of 300 MW/cm<sup>2</sup>. An absorption saturation behavior is found in Cu colloid. However, the saturation changes over to induced absorption in all other ZnO colloids and ZnO–Cu nanocomposites. Such a changeover in the sign of the nonlinearity is related to the interplay of plasmon band bleach and optical limiting mechanisms, as found from earlier studies of metal nanoparticles in liquid and glass media.<sup>30,32</sup> Such behavior can generally be modeled by defining a nonlinear absorption coefficient  $\alpha(I)$ , which is a sum of independent positive and negative transmission coefficients<sup>33</sup>

$$\alpha(I) = \frac{\alpha}{1 + (I/I_s)} + \beta I \quad (2)$$

where  $I_s$  is the saturation intensity. The obtained values of nonlinear absorption coefficient,  $\beta$ , and saturation intensity,  $I_s$ , at an intensity of 300 MW/cm<sup>2</sup> are shown in Table I.

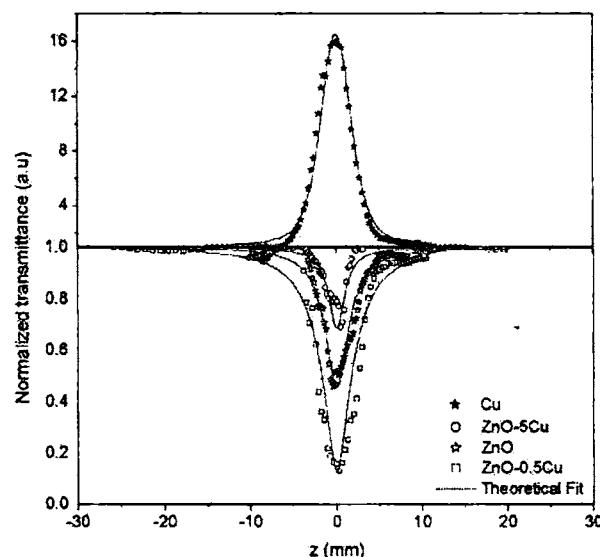


FIG. 5. Open aperture z-scan traces of ZnO–Cu nanocomposites at an intensity of 300 MW/cm<sup>2</sup> for an irradiation wavelength of 570 nm.

The surface plasmon band is sensitive to laser excitation. The plasmon band of metal particles, as explained on the basis of the Mie theory, involves dipolar oscillations of the free electrons in the conduction band that occupy energy states near the Fermi level.<sup>3</sup> Once these electrons are excited by a laser pulse, they do not oscillate at the same frequency as that of the unexcited electrons, thus causing the plasmon absorption band to bleach. These aspects have been addressed in several recent spectroscopic investigations.<sup>34</sup> Plasmon bleach effects are seen when the Cu nanocolloids are excited at its SPR with nanosecond laser pulses of 570 nm. Therefore, increased transmission behavior is observed for Cu nanocolloids, which fits to a saturable absorption mechanism. The saturation changes over to induced absorption in all the other ZnO colloids and ZnO–Cu nanocomposites. For small-volume fraction of Cu, the nonlinear absorption coefficient increases substantially in the nanocomposites, as compared to pure ZnO. ZnO–0.5Cu exhibits maximum nonlinear absorption at 570 nm since ZnO features dominate until that composition is clearly exhibited in absorption spectra. When the volume fraction of Cu increases beyond 0.5%, the nonlinear absorption coefficient decreases with an increase in Cu composition due to the affect of plasmon bleach. Thus, the nonlinearity of the ZnO–Cu nanocomposites is related to the interplay of plasmon band bleach and optical limiting mechanisms at 570 nm.

Figure 6 shows the nonlinear absorption at 650 nm. At this off-resonant excitation wavelength, there is no local field enhancement within the particles and hence the nonlinearity is less at 300 MW/cm<sup>2</sup>. Interestingly, colloids containing only Cu or ZnO nanoparticles show a minimum nonlinearity at this wavelength, while the composites clearly exhibit a larger induced absorption behavior. The obtained values of nonlinear absorption coefficient  $\beta$  at an intensity of 300 MW/cm<sup>2</sup> are shown in Table I.

Figure 7 gives the closed aperture z-scan traces of ZnO–Cu nanocomposites at a fluence of 300 MW/cm<sup>2</sup>. The closed-aperture curve exhibits a peak–valley shape,

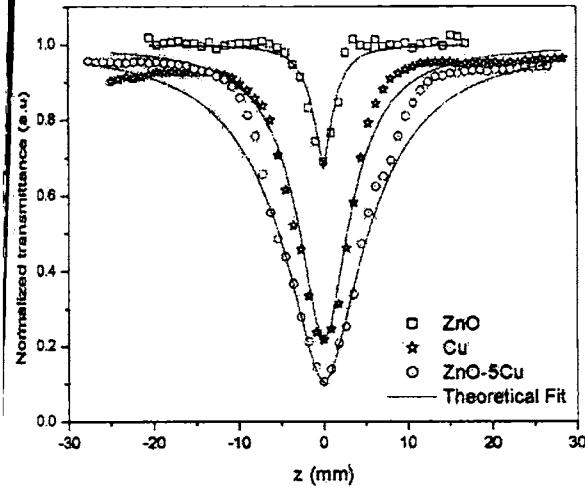


FIG. 6. Open aperture z-scan traces of ZnO–Cu nanocomposites at an intensity of 300 MW/cm<sup>2</sup> for an irradiation wavelength of 650 nm.

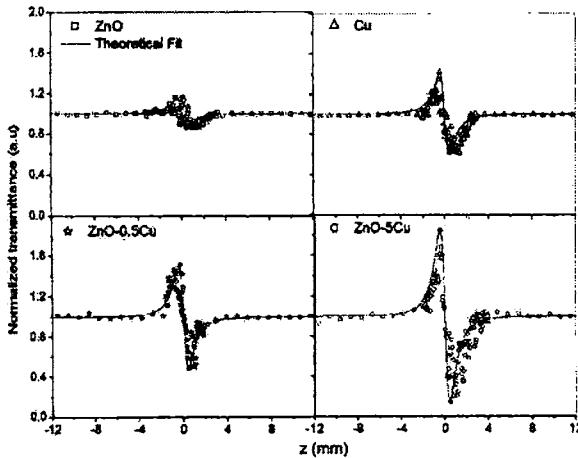


FIG. 7. Closed aperture z-scan traces of ZnO–Cu nanocomposites at an intensity of 300 MW/cm<sup>2</sup> for an irradiation wavelength of 532 nm.

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.<sup>14</sup> 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.<sup>14</sup> The value of the difference between the normalized 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. (3) and is tabulated in Table I

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

where

$$|\Delta\Phi_0| = \frac{2\pi}{\lambda} n_2 I_0 L_{\text{eff}} \quad . \quad (3)$$

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 picosecond pulsed lasers have shown positive nonlinearity for individual Cu nanoclusters.<sup>35</sup> The nonlinear refractive index increases substantially in the nanocomposites, as compared to pure ZnO and Cu colloids. The dramatically enhanced nonlinear refractive response is due to the enhanced electromagnetic field existing in the interface between Cu nanoclusters and ZnO grains.<sup>36</sup> 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 increase in  $n_2$  with increase of absorption.<sup>37</sup> The figure of merit for the third-order nonlinearity measured using a two-beam degenerate four-wave mixing configuration by Uchida et al. shows an increase with the particle size of Cu as well as Ag.<sup>7</sup> We therefore attribute the steady increase in the  $n_2$  values to the increase of third-order susceptibility as a function of particle size from ZnO–0.1Cu to ZnO–5Cu.

The significant optical nonlinearities of the pure metal nanocolloid at 532 nm are reported to have the nonlinear refractive index of the order of  $10^{-16}$  to  $10^{-17}$  m<sup>2</sup>/W. The nonlinear coefficients of metallic films are about one order of magnitude larger than that of metal nanocolloids.<sup>38</sup> It is worth noting that certain representative third-order nonlinear optical materials, such as CuO chain compounds, Ag<sub>2</sub>S/CdS nanocomposites, organic coated quantum dots, metal clusters, etc., yielded values of order of  $10^{-9}$  to  $10^{-14}$  m/W for nonlinear absorption coefficient at a wavelength of 532 nm.<sup>39,40</sup> These values are comparable to the value of  $\beta$  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–Cu 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.<sup>6</sup> Furthermore, the nonlinear optical properties of nanomaterials are of great interest for optical switching, pulse power shaping of optical parametric oscillator

(OPO)/optical parametric generator (OPG), 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 ZnO–Cu 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 because of absorptive nonlinearity, which corresponds to the imaginary part of third-order susceptibility.<sup>41</sup> 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 8 illustrates the influence of volume fraction of copper in ZnO–Cu 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 MW/cm<sup>2</sup>) in comparison to the Cu colloids (10 MW/cm<sup>2</sup>). These values are of the order of the reported optical limiting threshold for CdS nanocolloids.<sup>42</sup> ZnO–Cu nanocomposites are found to be good optical limiters compared to ZnO and Cu, and the optical limiting threshold of ZnO–5Cu nanocomposites is observed to be 3 MW/cm<sup>2</sup>. 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 Cu reduces the limiting threshold and enhances the optical limiting performance.

#### IV. CONCLUSION

The spectral and nonlinear optical properties of ZnO–Cu nanocomposites prepared by a colloidal chemical synthesis are investigated. Strong UV and visible emissions at room temperature are observed from ZnO–Cu nanocomposites. Compared to the regular ZnO colloid, ZnO–Cu nanocomposite has a stronger UV and visible emission. The strongest UV emission is observed to be over three times stronger than that of pure ZnO. Cu acts as a sensitizer and the enhancement of UV emission are caused by excitons formed at the interface between Cu and ZnO. The intensity of green emission becomes stronger than that of UV emission in the composite after a certain volume fraction of Cu and dominant peak emission shifts to green. This difference could be mainly because UV luminescence is degraded by excessively oxidized layer formed on the surface and the grain boundary of ZnO and Cu. The strongest visible emission of a typical ZnO–Cu nanocomposite is over ten times stronger than that of pure Cu due to transition from defect level to the copper induced  $t_2$  level. The emission mechanism is discussed. Nonlinear optical response is studied using nanosecond laser pulses from a tunable laser in the wavelength range of 450–650 nm, which includes the SPA band. The nonlinear response is wavelength dependent and switching from RSA to SA has been observed for Cu nanocolloids as the excitation wavelength changes from the low absorption window region to higher absorption regime near the SPA band. However, ZnO colloids and ZnO–Cu nanocomposites exhibit induced absorption at this wavelength. Such a changeover in the sign of the nonlinearity of ZnO–Cu nanocomposites, with respect to Cu nanocolloids, is related to the interplay of plasmon band bleach and optical limiting mechanisms. The SA again changes back to RSA when we further move over to the infrared region. The ZnO–Cu nanocomposites show self-defocusing nonlinearity and good nonlinear absorption behavior. The nonlinear refractive index and the nonlinear absorption increases with increasing Cu volume fraction at 532 nm. The observed nonlinear absorption is explained through two-photon absorption followed by weak FCA and interband absorption mechanisms. This study is important in identifying the spectral range and composition over which the nonlinear material acts as a RSA-based optical limiter. ZnO–Cu is a potential nanocomposite material for the light emission and for

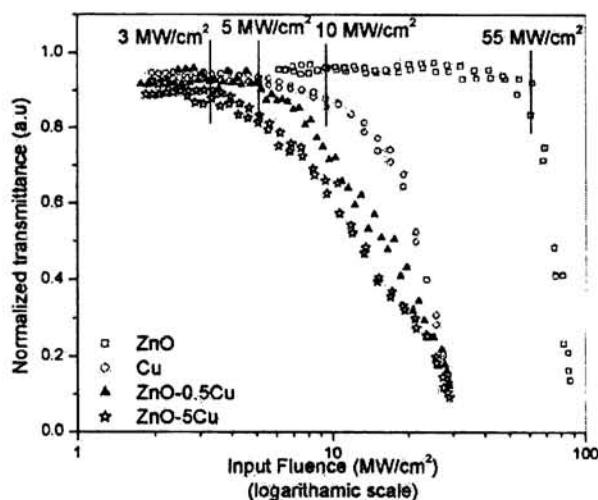


FIG. 8. Optical limiting response of ZnO–Cu nanocomposites generated from the open aperture z-scan traces at 532 nm.

the development of nonlinear optical devices with a relatively small limiting threshold.

## ACKNOWLEDGMENT

L. Irirpan acknowledges University Grants Commission (UGC) for research fellowship.

## REFERENCES

1. Y. Kayanuma: Quantum-size effects of interacting electrons and holes in semiconductor microcrystals with spherical shape. *Phys. Rev. B: Condens. Matter* **38**, 9797 (1988).
2. L. Irirpan, B. Krishnan, V.P.N. Nampoore, and P. Radhakrishnan: Luminescence tuning and enhanced nonlinear optical properties of nanocomposites of ZnO-TiO<sub>2</sub>. *J. Colloids Interface Sci.* **324**, 99 (2008).
3. U. Kreibitz and M. Vollmer: *Optical Properties of Metal Clusters* (Springer, Berlin, 1995).
4. B. Kraeutler and A.J. Bard: Heterogeneous photocatalytic preparation of supported catalysts. Photodeposition of platinum on TiO<sub>2</sub> powder and other substrates. *J. Am. Chem. Soc.* **100**, 4317 (1978).
5. T. Sekino, T. Nakajima, S. Ueda, and K. Niihara: Reduction and sintering of a nickel-dispersed-alumina composite and its properties. *J. Am. Ceram. Soc.* **80**(5), 1139 (1997).
6. Y. Sun, J.E. Riggs, K.B. Henbest, and R.B. Martin: Nanomaterials as optical limiters. *J. Nonlinear Opt. Phys. Mater.* **9**, 481 (2000).
7. K. Uchida, S. Kaneko, S. Omi, C. Hata, H. Tanji, Y. Asahara, A.J. Ikushima, T. Tokizaki, and A. Nakamura: Optical nonlinearities of a high concentration of small metal particles dispersed in glass, copper and silver particles. *J. Opt. Soc. Am.* **11**(7), 1236 (1994).
8. L. Irirpan, A. Deepthy, B. Krishnan, V.P.N. Nampoore, and P. Radhakrishnan: Size dependent fluorescence spectroscopy of nanocolloids of ZnO. *J. Appl. Phys.* **102**, 063524 (2007).
9. D.M. Bagnall, Y.F. Chen, Z. Zhu, T. Yao, S. Koyama, M.Y. Shen, and T. Goto: Optically pumped lasing of ZnO at room temperature. *Appl. Phys. Lett.* **70**, 2230 (1997).
10. Ü. Özgür, Ya.I. Alivov, C. Liu, A. Teke, M.A. Reshchikov, S. Doğan, V. Avrutin, S.-J. Cho, and H. Morkoç: A comprehensive review of ZnO materials and devices. *J. Appl. Phys.* **98**, 041301 (2005).
11. A. Tsukazaki, A. Ohtomo, T. Onuma, M. Ohtani, T. Makino, M. Sumiya, K. Ohtani, S.F. Chichibu, S. Fuke, Y. Segawa, H. Ohno, H. Koinuma, and M. Kawasaki: Repeated temperature modulation epitaxy for p-type doping and light-emitting diode based on ZnO. *Nat. Mater.* **4**, 42 (2005).
12. L. Irirpan, A. Deepthy, B. Krishnan, V.P.N. Nampoore, and P. Radhakrishnan: Nonlinear optical characteristics of self assembled films of ZnO. *Appl. Phys. B* **90**, 547 (2008).
13. A.A. Khosravi, M. Kundu, L. Jatwa, S.K. Deshpande, U.A. Bhagwat, M. Sastry, and S.K. Kulkarni: Green luminescence from copper doped zinc sulphide quantum particles. *Appl. Phys. Lett.* **67**, 18 (1995).
14. M.S. Bahae, A.A. Said, and E.W. van Stryland: High-sensitivity, single-beam  $n_2$  measurements. *Opt. Lett.* **14**, 955 (1989).
15. L. Irirpan, B. Krishnan, A. Deepthy, V.P.N. Nampoore, and P. Radhakrishnan: Size dependent enhancement of nonlinear optical properties in nano colloids of ZnO. *J. Appl. Phys.* **103**, 033105 (2008).
16. D.L. Moreno, E.D. Rosa-Cruz, F.J. Cuevas, L.E. Regalado, P. Salas, R. Rodriguez, and V.M. Castano: Refractive index measurement of pure and Er<sup>3+</sup>-doped ZrO<sub>2</sub>-SiO<sub>2</sub> sol-gel film by using the Brewster angle technique. *Opt. Mater.* **19**, 275 (2002).
17. L. Irirpan, V.P.N. Nampoore, and P. Radhakrishnan: Spectral and nonlinear optical characteristics of nanocomposites of ZnO-Ag. *Chem. Phys. Lett.* **455**, 265 (2008).
18. T. Linnert, P. Mulvaney, and A. Henglein: Surface chemistry of colloidal silver: Surface plasmon damping by chemisorbed iodide, hydrosulfide (SH<sup>-</sup>), and phenylthiolate. *J. Phys. Chem.* **97**, 679 (1993).
19. A.L. Stroyuk, V.V. Shvalagin, and S.Ya. Kuchmii: Photochemical synthesis, spectral-optical and electrophysical properties of composite nanoparticles of ZnO/Ag. *Theor. Exp. Chem.* **40**(2), 98 (2004).
20. L. Duan, B. Lin, W. Zhang, S. Zhong, and Z. Fua: Enhancement of ultraviolet emissions from ZnO films by Ag doping. *Appl. Phys. Lett.* **88**, 232110 (2006).
21. L. Irirpan, B. Krishnan, V.P.N. Nampoore, and P. Radhakrishnan: Linear and nonlinear optical characteristics of ZnO-SiO<sub>2</sub> nanocomposites. *Appl. Opt.* **47**, 4345 (2008).
22. L. Irirpan, D. Ambika, V. Kumar, V.P.N. Nampoore, and P. Radhakrishnan: Effect of annealing on the spectral and nonlinear optical characteristics of thin films of nano ZnO. *J. Appl. Phys.* **104**, 033118 (2008).
23. A. Suzuki and S. Shionoya: Mechanism of the green-copper luminescence in ZnS crystals. I. Direct evidence for the pair emission mechanism. *J. Phys. Soc. Jpn.* **31**, 1455 (1971).
24. P. Peka and H.J. Schulz: Empirical one-electron model of optical transitions in Cu-doped ZnS and CdS. *Physica B (Amsterdam)* **193**, 57 (1994).
25. A.A. Khosravi, M. Kundu, L. Jatwa, S.K. Deshpande, U.A. Bhagwat, M. Sastry and S.K. Kulkarni: Green luminescence from copper doped zinc sulphide quantum particles. *Appl. Phys. Lett.* **67**, 18 (1995).
26. R. Reisfeld, M. Eyal, and D. Brusilovsky: Luminescence enhancement of rhodamine 6G in sol-gel films containing silver aggregates. *Chem. Phys. Lett.* **153**, 210 (1988).
27. B. Karthikeyan, M. Anija, and R. Philip: In situ synthesis and nonlinear optical properties of Au:Ag nanocomposite polymer films. *Appl. Phys. Lett.* **88**, 053104 (2006).
28. X.J. Zhang, W. Ji, and S.H. Tang: Determination of optical nonlinearities and carrier lifetime in ZnO. *J. Opt. Soc. Am. B* **14**, 1951 (1997).
29. P.V. Kamat, M. Flumiani, and G.V. Hartland: Picosecond dynamics of silver nanoclusters. Photoejection of electrons and fragmentation. *J. Phys. Chem. B* **102**(7), 3123 (1998).
30. R. Philip, G. Ravindra Kumar, N. Sandhyarani, and T. Pradeep: Picosecond optical nonlinearity in monolayer-protected gold, silver, and gold-silver alloy nanoclusters. *Phys. Rev. B: Condens. Matter* **62**(19), 13160 (2000).
31. S. Qu, Y. Song, H. Liu, Y. Wang, Y. Gao, S. Liu, X. Zhang, Y. Li, and D. Zhu: A theoretical and experimental study on optical limiting in platinum nanoparticles. *Opt. Commun.* **20**, 3283 (2002).
32. B. Karthikeyan, J. Thomas, and R. Philip: Optical nonlinearity in glass-embedded silver nanoclusters under ultrafast laser excitation. *Chem. Phys. Lett.* **414**, 346 (2005).
33. L. Irirpan, V.P.N. Nampoore, and P. Radhakrishnan: Spectral and nonlinear optical characteristics of nanocomposites of ZnO-CdS. *J. Appl. Phys.* **103**, 094914 (2008).
34. T.S. Ahmadi, S.L. Logunov, and M.A. El Sayed: Picosecond dynamics of colloidal gold nano particles. *J. Phys. Chem.* **100**, 8053 (1996).
35. Y. Hamanaka, A. Nakamura, S. Omi, N. Del Fatti, F. Vallee, and C. Flytzanis: Ultrafast response of nonlinear refractive index of

- silver nanocrystals embedded in glass. *Appl. Phys. Lett.* **75**(12), 1712 (1999).
36. W. Gang, Z. Yu, C. Yiping, D. Muyun, and L. Mi: Study on the non-linear refraction of silver nanoparticles with aggregation effect. *Opt. Commun.* **249**, 311 (2005).
37. P. Prem Kiran, G. De, and D. Narayana Rao: Nonlinear optical properties of copper and silver nanoclusters in SiO<sub>2</sub> sol-gel films. *IEEE Proc. Circuits Devices Syst.* **150**(6), 559 (2003).
38. G. Yang, D. Guan, W. Wang, W. Wu and Z. Chen: The inherent optical nonlinearities of thin silver films. *Opt. Mater.* **25**(4), 439 (2004).
39. M.Y. Han, W. Huang, C.H. Chew, L.M. Gan, X.J. Zhang, and W. Ji: Large nonlinear absorption in coated Ag<sub>2</sub>S/CdS nanoparticles by inverse microemulsion. *J. Phys. Chem. B* **102**, 1884 (1998).
40. L. Irimpan, A. Deepthy, B. Krishnan, L.M. Kukreja, V.P.N. Nampoon, and P. Radhakrishnan: Effect of self assembly on the nonlinear optical characteristics of ZnO thin films. *Opt. Commun.* **281**, 2938 (2008).
41. F.M. Quereshi, S.J. Martin, X. Long, D.D.C. Bradley, F.Z. Heneri, W.J. Balu, E.C. Smith, C.H. Wang, A.K. Kar, and H.L. Anderson: Optical limiting properties of a zinc porphyrin polymer and its dimer and monomer model compounds. *Chem. Phys.* **231**, 87 (1998).
42. E.P.W. Jia, D.F. Guo, and W. Suna: Optical limiting of semiconductor nanoparticles for nanosecond laser pulses. *Appl. Phys. Lett.* **85**(26), 6326 (2004).