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Nonlinear Absorption, Scattering and Optical Limiting Studies of CdS Nanoparticles

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Abstract: The nonlinear optical absorption, scattering and optical limiting properties of CdS nanoparticles dispersed in dimethylformamide (DMF) are investigated. The nanoparticles are synthesized using the standard chemical synthesis method with thioglycerol as the capping agent. The investigations are carried out at 532 nm in the ns regime. Strong two-photon absorption and nonlinear scattering are found to be responsible for good optical limiting characteristics in these nanoparticles.

OCIS codes: (190.5890) Scattering, stimulated; (190.5970) Semiconductor nonlinear optics including MQW; (190.3970) Micro particle nonlinear optics.

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1. Introduction

The development of modern optical technology demands the ability to control the intensity of light in a pre-determined and predictable manner. In this aspect optical limiters have received significant attention. An ideal optical limiter exhibits a linear transmission below a threshold and clamps the output to a constant above it. This phenomenon can be achieved by one or more of the nonlinear optical mechanisms such as excited state absorption (ESA), free-carrier absorption (FCA), two photon absorption (TPA), thermal defocusing/scattering, photo refraction, nonlinear refraction, and induced scattering [1]. Optical limiting performance is enhanced by coupling two or more of the nonlinear optical mechanisms like self-defocusing in conjunction with TPA in semiconductors [2] or TPA of one molecule with ESA in another molecule [3]. Cascaded optical limiter using a reverse saturable absorption (RSA) material along with CS_2 has also been reported for achieving better limiting performance [4]. Wide range of materials with various nonlinear optical mechanisms contributing for the optical limiting and nonlinear absorption have been investigated [5]. In this perspective, semiconductor nanoparticles have attracted much attention recently. The optical nonlinearities of these and their potential applications are being extensively investigated [6, 7]. One of the current challenges is the preparation and characterization of well-defined nanoparticles for nonlinear optical (NLO) applications including optical limiting. Synthesis and characterization of nearly mono disperse cadmium sulphide (CdS) nanocrystallites have been undertaken by several investigators [8, 9]. However, little literature is available on its application to optical limiting. Han *et al.* [10] observed strong nonlinear absorption in Ag_2S/CdS particles by inverse micro emulsion technique. They observed poor optical limiting performance of CdS. In the present work we have synthesized the nanoparticles of CdS using the procedure suggested by Vossmeyer *et al.* [8] and presented the results on their optical limiting characteristics. Our investigations showed a strong nonlinear absorption and nonlinear scattering leading to good limiting characteristics.

2. Synthesis and characterization

CdS nanoparticles have been synthesized using thioglycerol as a capping agent. 2.35 g (8.82 mmol) of cadmium acetate dihydrate, 0.473 g (12.48 mmol) of thiourea and 0.95 mL (10.95 mmol) of thioglycerol in about 5 mL of DMF are heated at 110^{o}C for 1 hour under nitrogen atmosphere. Subsequently about 20% (v/v) water is added to the cooled solution followed by refluxing the mixture for 12-14 hours. The solution is then condensed to about 1/10th of its original volume using rotary evaporator. The condensed mixture is subjected to size selective treatment. Then acetone is added drop-wise until large size nanoparticles begin to precipitate. This solution is stirred for about 3 hours at room temperature and the contents are centrifuged to separate the precipitate of larger size particles. The supernatant liquid is again treated with acetone and the same procedure is repeated to get different sized nanoparticles, ranging from 70 nm to 4.5 nm. Studies in the present work however are confined to 4.5 nm size particles and one particular concentration of CdS: DMF = 1:100.

The nanoparticles are characterized using three techniques: 1) UV-Vis absorption studies, 2) X-ray diffraction (XRD) data and 3) TEM studies. UV-VIS spectra are recorded using Shimatzu 3101PC UV-VIS spectrometer in the wavelength range of 250nm to 550nm. The XRD data is recorded with INEL X-ray powder diffractometer. The Scanning Electron Microscope (SEM) pictures are taken with XL30 unit and the Transmission Electron Microscope (TEM) pictures are taken on copper grid with JEOL 100cx unit.

Nonlinear absorption studies are done using the standard Z-scan technique [11]. Briefly, in a typical Z-scan experimental set up, a laser beam with a transverse gaussian profile is focused using a lens. The sample is then moved along the propagation direction of the

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focused beam. At the focal point, the sample experiences maximum pump intensity, which will gradually decrease in either direction from the focus. An f/24 configuration is used for the present studies. The thickness of the sample is chosen in such a way that it is smaller than the Rayleigh range of the focused beam, which is nearly 3 mm. A frequency doubled Nd: YAG Laser (Spectra-Physics, INDI 40, 532 nm, 6 ns, 10Hz) is used as the excitation source. Apertures are introduced in the path for beam shaping and calibrated neutral density filters are used to vary the laser intensity. A 50-50 beam splitter introduced immediately after the sample collects the transmitted light that includes scattered light. This reflected beam is focused on to the detector 1 by using a large area lens. Detector 1 therefore, sees only the losses due to linear and nonlinear absorption of the sample. The transmitted beam is collected with a small area lens at far field to reduce the scattered light falling on the detector 2. Hence, detector 2 accounts for the absorptive as well as scattering losses. Fig. 1 shows the experimental set up for the Z-scan experiment. The sample cell and the beam splitter are mounted on a translation stage and the detector 1 along with the collection lens L3 are positioned accordingly. The data is recorded by scanning the cell across the focus and collecting the data through a SRS boxcar averager (model SR250), the output of which is given to a PC with an ADC card.

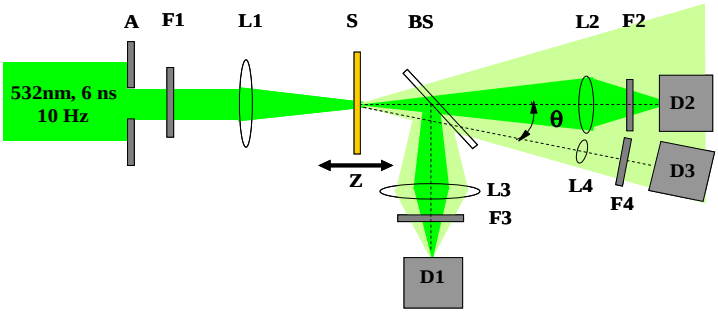

Fig. 1. Schematic of the Z scan set up for recording the nonlinear absorption and scattering. A - aperture, S – sample, F1, F2, F3, F4 – Neutral Density Filters, D1, D2, D3 – Detectors, BS – Beam splitter, L1, L2, L3, L4 – lens.

3. Results and discussion

UV-Vis absorption spectra of 4.5 nm CdS nanoparticles in DMF are shown in Fig. 2. With increasing particle size, the absorption peak shifts towards red as a consequence of the size effect. The absorption peak of the bulk CdS was reported [8] to be around 520 nm. Typical XRD plot of thioglycerol capped CdS nanoparticles is shown in the Fig. 3. Size of the CdS nanoparticles is calculated from the XRD peaks using Scherer formula and the calculated particle size is ~ 4 nm. The TEM picture as in Fig. 4 shows mono dispersed particles having an average size of 4.5 nm.

The open aperture Z-scan studies revealed RSA behavior at low as well as high intensities as can be seen in Fig. 5. Nonlinear scattering was observed at high intensities and at intensities lower than 100 $MWcm^{-2}$, no scattering was observed. One can observe an enhanced depletion in the transmitted beam collected with detector 2, which is reflected in the Z-Scan curve as seen in Fig. 5, where the transmittance goes to < 0.1. Scattering is a fundamental manifestation of the interaction between matter and radiation, resulting from the inhomogeneities in the refractive index [12].

The Z-scan curves are recorded by placing the detectors at two positions as explained in the experimental section in order to estimate the contribution from the pure nonlinear absorption and that from both nonlinear absorption as well as the scattering. The detector 1 looking at the 'whole transmitted light' is taken as that due to the nonlinear two-photon absorption alone. The detector 2 kept at the far field and looking at the transmitted beam minus the scattered beam is taken as that due to both two photon absorption and the nonlinear

#5971 - $15.00 US Received 6 December 2004; revised 23 January 2005; accepted 24 January 2005

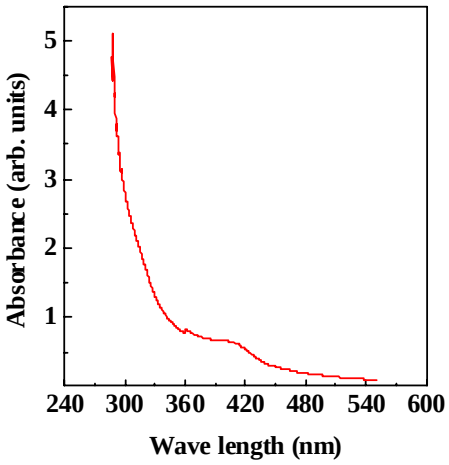

Fig. 2. UV-Vis absorption of 4.5 nm size of CdS nanoparticles in DMF.

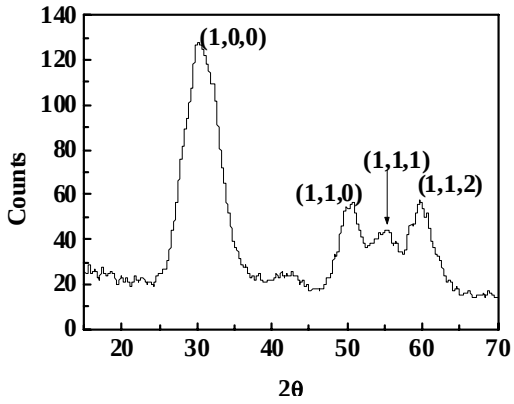

Fig. 3. XRD of 4.5 nm CdS nanoparticles powder on glass plate.

scattering. We have also collected scattering at different forward scattering angles with beam propagation direction using detector 3 and this data is shown in Fig. 6. The values of beam waist at focus are ~ 20-30μm and the corresponding peak intensities are ~ 10^8 to 10^9 Wcm^{-2}.

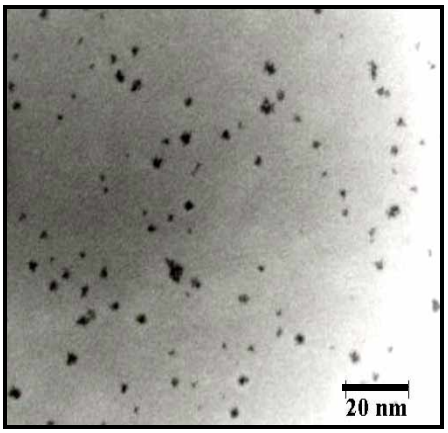

Fig. 4. TEM image of 4.5 nm CdS nanoparticles.

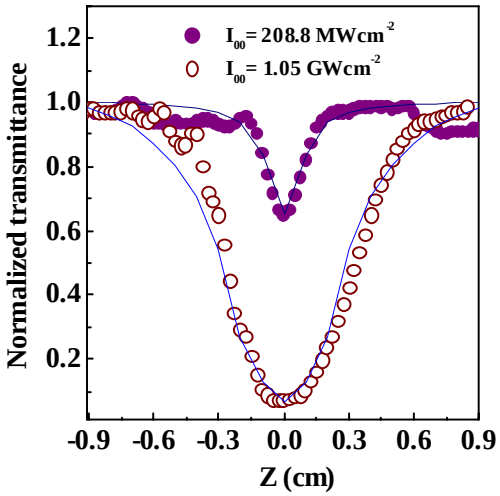

Fig. 5. Open aperture Z-Scan (Detector 2) of 4.5 nm CdS nanoparticles in DMF and its theoretical fits (solid line) at two different intensities and at a concentration of CdS: DMF = 1:100

The Rayleigh ranges are calculated to be ~ 3 mm. To account for the losses as seen in the detector 2, we have introduced the scattering losses α_s, as derived by Joudrier *et al.* [13]. From Fig. 2, we clearly see that the linear absorption coefficient is very small at the excitation

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wavelength 532 nm. Thus in our analysis we have neglected the contribution of the linear absorption cross section.

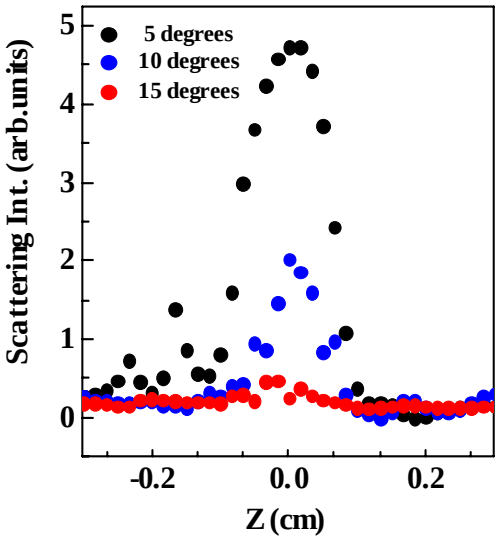

Fig. 6. Scattering of 4.5 nm CdS nanoparticles at three different angles with intensity (Z- position).

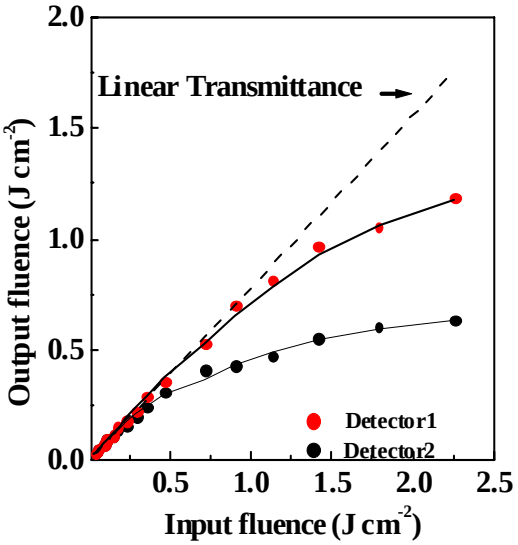

Fig. 7. Transmitted light and scattering (Detector1), transmitted light minus scattering (Detector2) of 4.5 nm CdS nanoparticles with respect to input fluence. Dashed line represents linear transmittance of 0.76 at 532 nm and the solid line is the curve obtained by integrating the equation 3.

The rate equations for transitions between the valence band and the conduction band can be written as:

$$\frac{dN_0}{dt} = -\frac{\beta I^2}{2\hbar\omega} + \frac{N_1}{\tau_1} \tag{1}$$

$$\frac{dN_1}{dt} = \frac{\beta I^2}{2\hbar\omega} - \frac{N_1}{\tau_1} \tag{2}$$

Where N_0, N_1 are populations of valance and conduction bands respectively, the transmitted intensity through the sample is given by:

$$\frac{dI}{dz} = -\alpha_s I - \beta I^2 \tag{3}$$

Where $\alpha_s = g_s [\Delta\tilde{n}]^2$, $\Delta\tilde{n} = \Delta n_l + \Delta n_{nl}$, $\omega(z) = \omega_0 \left[1 + \left(\frac{z}{z_0}\right)^2\right]^{\frac{1}{2}}$, $z_0 = \frac{\pi\omega_0^2}{\lambda}$

and $I = I_{00} \left(\frac{\omega_0^2}{\omega^2(z)}\right) . \exp\left(\frac{-t^2}{\tau_p^2}\right) . \exp\left(\frac{-2r^2}{\omega^2(z)}\right)$.

#5971 - $15.00 US Received 6 December 2004; revised 23 January 2005; accepted 24 January 2005

α_s is the effective scattering coefficient, β is the two photon absorption cross-section, g_s is a parameter which is independent of intensities but depends only on the size, shape, concentration of particles and wavelength of light, $\Delta\tilde{n}$ is the difference in the effective refractive indices of both linear and nonlinear components, Δn_l is the difference in the linear refractive indices of CdS and DMF, Δn_{nl} is the difference in nonlinear refractive indices of CdS and DMF, which is a function of intensity, τ_1 is the lifetime of the excited state and is taken as 114 ps [14], z_0 is the Rayleigh range, ω_0 is the beam waist at focus, I is intensity as a function of r, t, and z, I_{00} is peak intensity at the focus of the gaussian beam and τ_p is the input pulse width used. The differential equations are solved numerically using Runge-Kutta fourth order method. The differential equations are first de-coupled and then integrated over time, length, and along the radial direction. Assuming the input beam to be a gaussian, the limits of integration for r, t, and z are varied from 0 to ∞, $-\infty$ to ∞, and 0 to L (length of the sample) respectively. Typical number of slices used for r, t, and z are 60, 30, and 5 respectively. $g_s\Delta n_l$, $g_s\Delta n_{nl}$, β and α_s are then estimated through least square fit of the experimental data.

As the absorption starts increasing for shorter wavelengths from around 415 nm and since the pump is at 532 nm, we see a strong two-photon absorption. The nonlinear scattering behavior of the CdS nanoparticles as a function of the input intensity (Z-position) is as shown in Fig. 6, in which the curves shown are of those obtained for three different forward scattering angles with respect to the beam propagation direction. The observed scattering behavior is quite interesting in the sense that no scattering was observed below 100 $MWcm^{-2}$ and at higher intensities the scattering losses help achieve better limiting thresholds. Thus CdS nanoparticles serve as a good scatterer at high intensities, without getting damaged due to nonlinear absorption alone. By using the two-level model, we first estimated the two-photon absorption cross-section β (3.15×10^{-8} cmW^{-1}) and used this value to estimate α_S, the nonlinear scattering coefficient. The refractive index of the solvent (DMF) and the CdS nanoparticles are taken as 1.42 and 2.5 respectively to estimate the value of g_s (0.034 cm^{-1}). The calculated value of the n_{nl} of the CdS particles is $6.9 \times 10^{-8} cm^2W^{-1}$, which agrees very well with the literature values [15, 16]. The estimated value of α_S is 8.218 cm^{-1}. Solid line in Fig. 7 represents a theoretical fit using equation 3. Limiting threshold and the threshold for nonlinear scattering are found to be dependent on the concentration and particle size, which would be discussed in a later communication.

4. Conclusions

CdS nanoparticles are synthesized with thioglycerol as a capping agent. TEM pictures indicate that the size of the nanoparticles is 4.5 nm. The nanoparticle mix was quite stable even at high laser powers. The CdS nanoparticles showed a transmittance of < 0.1 at 1.05 $GWcm^{-2}$ intensity and the limiting threshold value, $I_{1/2}$ is 0.5 Jcm^{-2}. The scattering at high intensities was comparable to the two-photon absorption contribution to the Z-scan curves. Because of the strong two-photon absorption coefficient and the nonlinear scattering coefficient, we expect that the CdS nanoparticles would exhibit better nonlinear losses if the size and the solution were optimized, leading to a good optical limiter.

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