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Nonlinear optical properties of free standing films of PbS quantum dots in the nonresonant femtosecond regime

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Abstract

Devices based on optical technology for high speed communication networks require materials with large nonlinear optical response in the ultrafast regime. Nonlinear optical materials have also attracted wide attention as potential candidates for the protection of optical sensors and eyes while handling lasers. Optical limiters have a constant transmittance at low input influence and a decrease in transmittance at higher fluences and are based on a variety of mechanisms such as nonlinear refraction, nonlinear scattering, multiphoton absorption and free carrier absorption. As we go from bulk to nanosized materials especially in the strong quantum confinement regime where radius of the nanoparticle is less than the bulk exciton Bohr radius, the optical nonlinearity is enhanced due to quantum confinement effect. This paper is on the ultrafast nonresonant nonlinearity in free standing films of PbS quantum dots stabilized in a synthetic glue matrix by a simple chemical route which provides flexibility of processing in a variety of physical forms. Optical absorption spectrum shows significant blue shift from the bulk absorption onset indicating strong quantum confinement. PbS quantumdots of mean size 3.3nm are characterized by X-ray diffraction and transmission electron microscopy. The mechanism of nonlinear absorption giving rise to optical limiting is probed using open z-scan technique with laser pulses of 150 fs pulse duration at 780 nm and the results are presented in the nonresonant femtosecond regime. Irradiance dependence on nonlinear absorption are discussed.

Keywords

PbS quantum dots; femtosecond z-scan; non resonant optical nonlinearity; optical limiting

1.INTRODUCTION

Both the linear and nonlinear optical properties of semiconductor nanocrystals are known to differ appreciably from those of the bulk semiconductor [1,2], particularly in the regime of strong quantum confinement, when the cluster sizes are below a critical size called bulk exciton Bohr radius. In this regime, the bulk semiconductor energy bands are split into discrete energy levels with an increase in the effective bandgap. Materials with large optical nonlinearities have immense potential in various photonics device applications like optical switching and optical limiting. This has led to a lot of interest in exploring the linear as well as nonlinear optical processes and mechanisms in these materials. PbS is a direct band gap material with bulk bandgap of 0.41eV and exciton bohr radius of 9nm.

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Most of the studies on the third order nonlinearity have been on semiconductor quantum dots in inorganic materials such as glasses [3,4] . A few papers have appeared on other nanoclusters stabilized in matrices like organic materials such as polymers [5,6]. Eventhough several studies have been done on the nonlinear optical properties of semiconductor nanostructures, the mechanisms for the origin of nonlinearity and the size dependence on the nonlinearity are not well understood. Earlier work from our laboratory based on the polymer based CdS nanostructures showed an increase in third order susceptibility $\chi^{(3)}$ with the decrease in particle size [7].

In this work we use a single beam femtosecond z scan technique to investigate nonlinear absorption in the non-resonant regime $E_g > \hbar\omega > E_g/2$, where E_g is the first excitonic transition of PbS nanocrystals and $\hbar\omega$ is the incident photon energy and probe the nonlinear absorption mechanisms in the samples. In addition to the simplicity and sensitivity of this technique, this provides us information regarding the nonlinear refraction arising from real part of $\chi^{(3)}$ and nonlinear absorption arising from imaginary part of $\chi^{(3)}$ separately compared to other techniques used for third order nonlinear optical characterization. Materials with large optical nonlinearity and ultrafast response are required for nonlinear optical device applications. Optical limiters are nonlinear optical devices which have a constant transmittance at low input influence and a decrease in transmittance at higher fluences. The origin of the optical limiting can be due to a variety of mechanisms. The aperture limited optical limiting can be due to self focusing or self defocusing effects. Optical limiters based on nonlinear absorption processes are more efficient limiters and origin of this optical limiting can be due to two photon absorption or free carrier absorption arising from third order nonlinearity ($\chi^{(3)}$ process), three photon absorption arising from fifth order nonlinearity ($\chi^{(5)}$ process), two photon assisted excited state absorption arising from fifth order nonlinearity ($\chi^{(3)} : \chi^{(1)}$) etc. In this paper we present our results on the large nonlinear absorption of PbS quantum dots of mean size 3.3 nm due to two photon absorption in the non resonant regime enabling them as candidates for efficient optical limiting.

2.EXPERIMENTAL

Free standing films of PbS quantum dots are prepared in a synthetic glue matrix using a colloidal chemistry method followed by air drying. Details of synthesis and characterization are available elsewhere[8]. The precursors used are lead acetate and sodium sulphide. The concentrations of lead acetate used is 2 mM and an appropriate concentration of sodium sulphide is used to obtain an equimolar ratio of Pb^{2+}:S^{2-} in all cases. The composite film is found to be very stable and they retain their physical properties for long periods of time. The composite film is of 150 μ m thickness.

The morphological characterization is done using a Jeol 3010 high resolution transmission electron microscope with an accelerating voltage of 300 kV. Optical absorption spectra are recorded on a Jasco V-570 spectrometer in the wavelength region 300nm-800nm in which the host matrix is transparent.The photoacoustic spectroscopic studies are done by the gas microphone technique[9]. The spectrum is recorded using an automated home-built photoacoustic spectrometer. A xenon arc lamp of 500W is used as the excitation source. The light beam selected using a monochromator (Jobin Yvon) is modulated using a mechanical

chopper (SR540, Stanford research systems) and focused to an airtight photoacoustic (PA) cell. The modulation frequency is 10Hz. The PA cell consists of an aluminium cylinder with an option for inserting a microphone in its periphery. The periodically chopped beam is allowed to fall on the sample kept inside the PA cell through the transparent cell window. The nonradiative transitions within the sample heat up the boundary layer of air in contact with the sample. The periodic heating effect causes the layer to function as a vibrating piston. This results in periodic pressure fluctuations inside the cell which are detected by the sensitive microphone(G.R.A.S). The amplitude and phase angle of the PA signal are finally detected by a lock in amplifier (SR830, Stanford research systems) whose reference channel is connected from the chopper. The spectral measurements are carried out at room temperature in the wavelength range of 360 to 720 nm in steps of 2 nm resolution. The PA spectrum is corrected for variations in source intensity as function of wavelength using carbon black absorber for normalization.

The nonlinear absorption studies are done by the z-scan technique [10] using 120 fs pulses at 780 nm with 76 MHz repetition rate from a mode locked tunable Coherent Mira titanium: sapphire laser (model 900) which is pumped by a Coherent Verdi frequency-doubled Nd:vanadate laser. From beam profile measurements using the knife edge method, the spatial intensity profile of the laser is found to be near Gaussian. An automated open aperture z-scan set up is used to measure intensity dependent transmission. The laser beam is focused using a lens of focal length 200 mm and the transmittance is measured using a pyroelectric energy probe as a function of sample position z by translating the sample along the beam axis (z-axis). The sample sees a different fluence at each position of z. The small fluctuations in the pulse energy are accounted for by using a reference energy probe. The pulse to pulse energy stability is found to be approximately ± 5%. Depending on the absorption mechanism involved, we get a Lorentzian or inverted Lorentzian with its maximum or minimum at the focal point, z=0 where the fluence is a maximum.

3.RESULTS AND DISCUSSION

Fig. 1 shows the HRTEM picture of a single PbS nanocrystal embedded in the host matrix. The mean size of the nanoparticles are determined to be 3.3 nm after evaluating 290 particles.

The optical absorption spectrum of the PbS nanocomposite in Fig-2 shows large blue shift from the bulk PbS bandgap of 0.41eV. The host matrix is transparent in the spectral range considered here. The excitonic transitions are investigated by photoacoustic spectroscopy. Fig-3 shows the photoacoustic spectrum of the nanocomposite film of PbS nanocrystals. The photoacoustic signal of host matrix is very weak and featureless in the spectral range studied here. PAS spectrum of the sample shows two peaks, one at 2.15eV (corresponding to the peak at 578nm) and another one at 3.04 eV(corresponding to the peak at 408 nm). The peaks are analysed by a curve fitting program assuming Gaussian lineshape as shown in our earlier work [8]. The peak at 2.15eV corresponds to the first exciton transition and the peak at 3.04eV corresponds to the second exciton transition. The experimentally observed transitions agree well with the theoretically calculated first and second exciton energies for PbS quantum dots using the four band envelope formalism [11]. This theoretical calculation is based on the

nonparabolic and anisotropic bandstructure of this material and is the first theoretical calculation using envelope function approach in the case of a narrow gap material.

Open aperture z-scan studies on the PbS nanocrytalline sample indicates a reverse saturable absorption behaviour. The excitation energy 1.55 eV used for the present studies lies in the transparency region of the sample as the first excitonic transition determined from PAS studies is at 2.15eV, indicating a two photon absorption (2PA) mechanism. The experiment is done at three excitation intensities, 7.71 TW/m^2 , 9.09 TW/m^2 and 11.98 TW/m^2.

Fig-4 shows the open aperture z-scans obtained for PbS nanocrystals. The symbols denote experimental data points and the solid line is a theoretical fit .The theoretical model is based on saturable absorption followed by two photon absorption. We consider a nonlinear absorption coefficient of the form [12]

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

where α_o is the linear absorption coefficient, β is the two photon absorption coefficient, I is the laser intensity and I_s is the saturation intensity.

Therefore the modified normalized transmittance using eqn. (1) can be written as

$$T(z) = \frac{Q(z)}{\sqrt{\pi} q(z)} \int_{-\infty}^{\infty} ln\left[1+q(z)\, exp\left(-\tau^2\right)\right] d\tau \quad (2)$$

where $Q(z)=\exp(\alpha_o LI/(I+I_s))$, $q(z)=\alpha_o I_o L_{eff}/1+(z/z_o)^2$ with I_o being the peak intensity at the focal point and $L_{eff}=[1-\exp(-\alpha_o L)]/\alpha_o$ where L is the sample length and $z_o=\pi\omega_o^2/\lambda$, where ω_o is the beam waist and λ is the light wavelength. The fitting is good and indicates that the mechanism here is saturable absorption followed by 2PA. The values of β and I_s for different intensities are given in Table-1.

The 2PA coefficient increases with the increase in intensity. Several mechanisms of optical nonlinearity are known to operate in semiconductor nanocrystalline systems depending on the wavelength and pulse duration of the laser used. The excitation is in the non resonant regime in the present case. Free carrier absorption is not expected at the short pulse duration used here. The agreement of the experimental data with the theoretical model suggests that the mechanism of nonlinearity in the present case is predominantly two photon absorption.

4.CONCLUSION

PbS quantum dots of mean size 3.3 nm shows significant blue shift in both optical and photoacoustic spectrum indicating strong quantum confinement. Nonlinear transmission of free standing films of PbS quantum dots is studied using a femtosecond z-scan technique in the non resonant regime. The origin of the large nonlinear absorption is predominantly due to two photon absorption. The experimental data are theoretically fitted using a model envisaging saturable absorption followed by two photon absorption. The theoretical fit is found to agree well with the experiment data. Irradiance dependent studies on nonlinear absorption shows that the two photon absorption coefficient increases with the increase in

intensity. The strong nonlinear absorption of these systems and the ultrafast response in the nonresonant regime renders them as potential candidates for optical limiting application.

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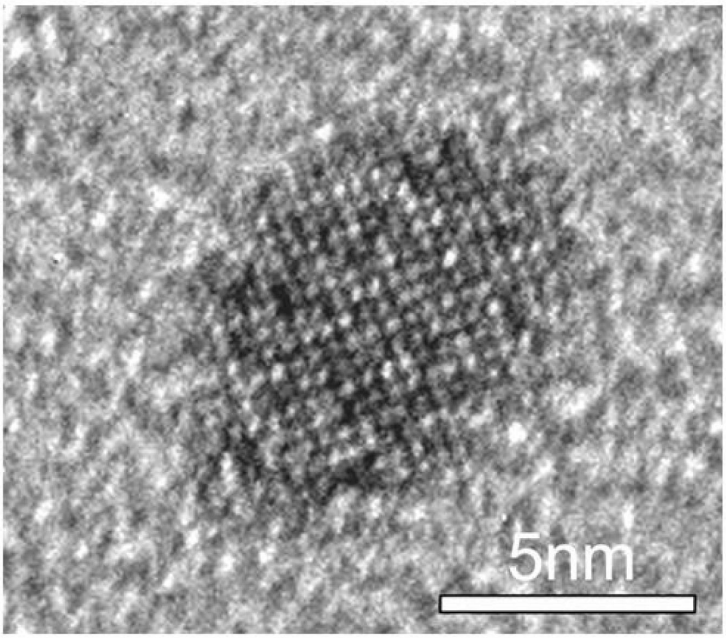

Figure-1.
HRTEM image of a single PbS nanocrystal

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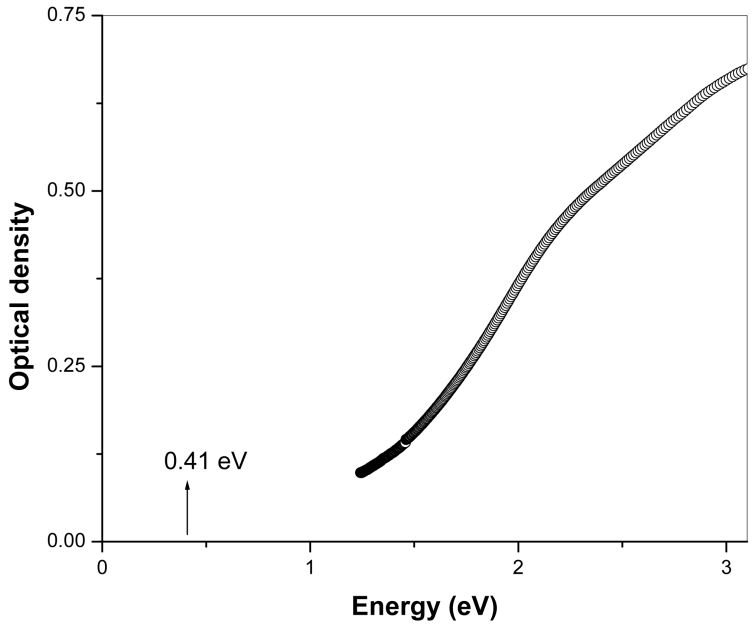

Figure-2.
Optical absorption spectrum of PbS nanocrystals

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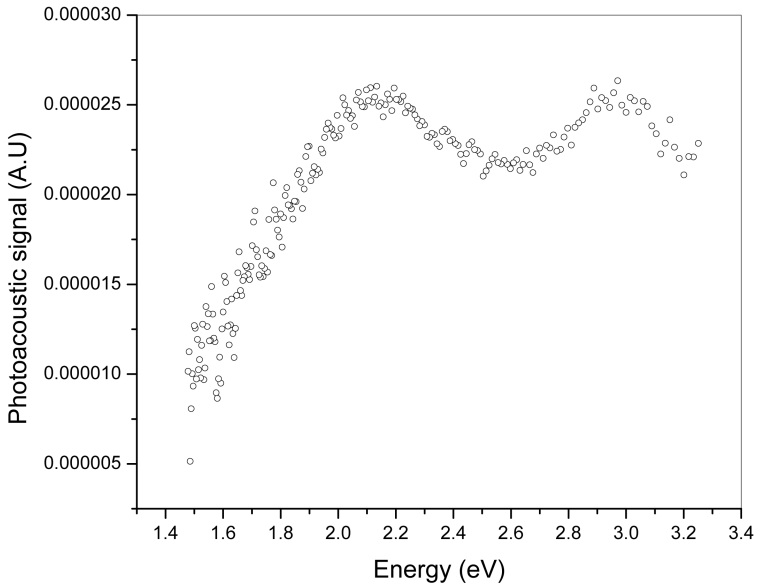

Figure-3.
Photoacoustic spectrum of PbS nanocrystals

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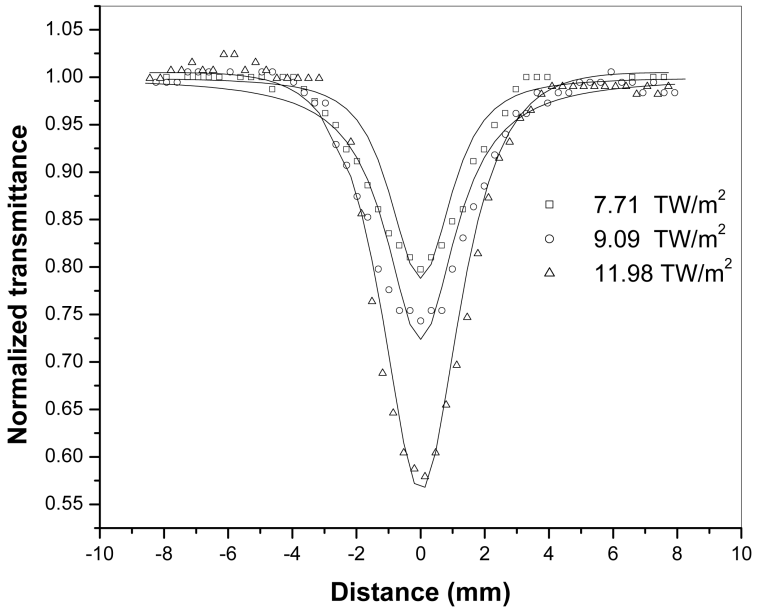

Figure-4.

Open z-scan traces of PbS nanocrystals for different irradiances. The experimental points are shown by symbols and solid lines are numerical fits using two photon absorption model

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Table-1

Input intensity (TW/m^2)	$\beta (mW^{-1})$	I_s (Wm^{-2})
7.71	14×10^{-10}	3.1×10^{12}
9.09	15×10^{-10}	6×10^{12}
11.98	28×10^{-10}	1×10^{12}