Quantum size effects on the third order optical nonlinearity of CdS quantum dots in Nafion

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Abstract

Optical nonlinearities of CdS quantum dots in the strongly confined regime are probed through degenerate four-wave-mixing experiments in an attempt to study the size dependence of the third order optical susceptibility $\chi^{(3)}$. The results indicate that $\chi^{(3)}$ is strongly dependent on the diameter of the dots and that there is a large increase in $\chi^{(3)}$ values as the diameter decreases below 2 nm. Polarization discrimination studies point to nonthermal contributions to the mechanism of optical nonlinearity. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Investigation on the nonlinear optical properties of materials with potential applications in photonic devices continues to be an exciting area of optoelectronics. Optical nonlinearities in a variety of systems such as organic and inorganic crystals, polymers and fullerenes are studied extensively [1–4]. Nonlinear optical properties of semiconductor structures in which the carriers are spatially confined have attracted much interest recently. Quantum size effects associated with the low dimensionality and their possible implications on the nonlinearity provides the prime motivation for this. Degenerate four-wave-mixing (DFWM) experiments are carried out on semiconductor quantum dots (SQD) in glass matrices by many groups to study the magnitude and response times of the nonlinearity [5–7]. Jain and Lind [5] observed sub-nano-second response in commercial filter glasses containing CdSSe quantum dots. Oberhauser et al. [6] have studied the intensity and spectral dependence of optical phase conjugate signals resulting from population density grating in bulk CdS and doped glasses. Self-diffraction experiments on quantum dots in a polymer matrix showed higher diffraction efficiency than that in glass matrix [7]. Many reviews which appeared in recent years have focused on the nonlinear mechanisms in quantum dots [7–11].

Even though considerable attention has been given to the study of third order optical susceptibility of SQD in glass [12–18], the current understanding of the nonlinear mechanisms and the magnitude and response time of the nonlinearity in these systems is far from complete. Reported
experimental data on CdS,Se_{1-x}-doped glasses seem to be inconsistent and sometimes contradictory [12,13]. The published values of $\chi^{(3)}$ in these systems vary from $10^{-15}$ to $10^{-19}$ m$^2$ V$^{-2}$. A similar uncertainty exists regarding the response times of the optical phase conjugation (OPC) process, reported grating decay times varying from sub-nano-second to picoseconds. The mechanism of the nonlinearity and its dependence on the quantum dot diameter are still not well understood. Regarding the size dependence of the nonlinearity many groups report an increase in $\chi^{(3)}$ with increasing particle diameter [15] while there are some studies where an increase in $\chi^{(3)}$ with decreasing particle diameter [16] is observed. Still some other groups report that the figure of merit does not depend significantly on the crystallite diameter [17]. Reasons for these apparently contradictory reports could be the difference in the preparation conditions of the samples and the limited understanding of the nature of the clusters and the role of the surrounding matrix. In order to resolve these ambiguities and to get a better understanding of the mechanisms of the nonlinearity and its size dependence it is essential to gather more experimental data on well characterized samples synthesized under controlled conditions.

Only very few reports exist on the third order nonlinearity of SQD in matrices other than glasses [19,20]. The ease of processing and flexibility makes polymeric matrices more suitable for confinement of nanoparticles. Also, the photodarkening effect which is reported to be one of the causes of the contradictory literature [18], is minimal in such systems. Recently we have synthesized and studied quantum confinement effects on the linear optical properties of CdS quantum dots in the polymer Nafion through photoacoustic spectroscopy [21]. In this paper we present the results of our DFWM experiments on these systems at a wavelength of 532 nm in the absorption tail of the samples.

2. Experimental details

The experimental setup used in the present work is that of a self-phase-matched retroreflection geometry and is given in Fig. 1. DFWM experiments are carried out using the second harmonic wavelength of a pulsed Nd:YAG laser (DCR 2(10)), operated at a pulse width of 10 ns. Prism P is used to separate the second harmonic from the fundamental wavelength. The output of the laser is split into three beams, of which the beam marked 1 refers to pump 1 (forward pump) and the beam marked 2 refers to pump 2 (backward pump). Pump 2 is obtained by the transmission of pump 1 through the sample and subsequent normal reflection from mirror M1. The ray marked 3 refers to the probe beam which is relatively lower in intensity. The probe beam is generated from the first pump beam after one reflection each from the beam splitters BS1 and BS2. The angle ($\theta$) between the beams 1 and 3 is $\approx 5^\circ$. To assess the intensity of the beams 1 and 3, the reflection/transmission ratio of BS1 and BS2 are measured. The intensity of the probe beam is kept approximately at 10% of the first pump beam. M1 is a dichroic mirror whose reflectivity
is \approx 95\% at 532 nm. The ray marked 4 indicates the direction of the phase conjugate beam generated in the sample S due to the nonlinear wave mixing. It travels in a direction opposite to that of the probe. Its transmitted part through BS2 is monitored by a photomultiplier tube (PMT) (IP-28). The intensity of the original beam transmitted through BS2 after reflection from BS1 is sensed by photodiode (HP 5082-4207). Indirectly the photodiode provides measures of the intensities of pump and probe since the reflectivities of BS1 and BS2 are known. All components of the experimental setup are kept on a vibration-isolated table. Experiments are carried out at a pulse repetition rate of 2 Hz and the beam diameter on the sample was 2 mm.

In order to deduce the third order optical susceptibility $\chi^{(3)}$ and to understand the nature of the nonlinearity we have conducted three types of experiments. The dependence of the OPC reflectivity on the intensity of the pump beam is studied in the range 0–1.5 mJ. The effect of delaying the backward pump with respect to the other beams is studied by varying the distance between the sample and the back mirror M1. Polarization discrimination studies on the OPC signal are carried out using different polarization combinations of the interacting beams.

3. Results and discussion

3.1. Intensity dependence

CdS quantum dots studied in this work are synthesized in the polymer matrix Nafion through an ion exchange route [21]. Mean size of the dots are determined from a detailed analysis of the X-ray powder diffraction patterns [22]. DFWM experiments are carried out on four samples denoted as S1, S2, S3 and S4 having mean quantum dot diameters 6, 2, 1.8, 1.6 nm. The polymer films containing the CdS quantum dots have a thickness 0.18 mm. The energy of the pump beam is kept below the damage threshold of the samples. Scattering contributions to the signal from the sample and mirrors are subtracted from observed signal intensity. DFWM in the same geometry is also carried out on the undoped polymer Nafion to check whether there is any contribution from the matrix to the OPC signals.

Fig. 2 shows the variation of the OPC energy at 532 nm with pump energy. All beams were vertically polarized. In the figure the continuous lines represent cubic fits to the data. All the samples studied give reasonably strong OPC visible to the unaided eye. The OPC energy increases with increasing pump power in all the samples and shows a cubic dependence on the pump energy as indicated by the fit. Undoped Nafion does not give any significant OPC signal at pump energies used here and the signal in this case shows a linear dependence on the pump power indicating that the signal is purely due to scattering. In sample S1 the OPC energy increases from 0 to 11 lJ as the pump energy is increased to 1.4 mJ. In sample S2 it is less than that of sample S1 at all energies. A maximum energy of 4 lJ is obtained corresponding to the maximum pump energy of 1.3 mJ. In sample S3 the OPC energy is higher than that of S1 and S2 and a maximum OPC energy of 18 lJ was observed at a pump energy of 1.5 mJ. OPC signal from sample S4 containing quantum dots of lower diameter is stronger than that of S1, S2 and S3.

3.2. Polarization discrimination

The effect of different combinations of the input beam polarization on the OPC signal is studied with a view to understanding the types of gratings involved in the process. The polarization of the waves is rotated suitably with the help of half-wave and quarter-wave plates to generate different polarization combinations. OPC experiments are carried out in the samples with the following three combinations of polarization states of the mixing waves. (i) pump 1 and probe parallel; pump 2 orthogonal, (ii) pump 2 and probe parallel; pump 1
orthogonal, (iii) pump 1 and pump 2 parallel; probe orthogonal. The variation of the intensities of the phase conjugate signal as a function of pump energy in these three cases is shown in Fig. 3. The phase conjugate signal shows a nonlinear dependence on the pump energy. However in contrast to Fig. 2 it appears that this dependence is less than cubic in the energy range studied. (In these experiments we were not able to apply higher laser powers due to technical reasons.) The order of OPC signal intensity is (i) > (ii) > (iii).

The third order nonlinear polarization with contributions from each of the above polarization combinations can be written as [23]

\[
P_{NL} = A(E_1 \cdot E_3^*)E_2 + B(E_2 \cdot E_3^*)E_1 + C(E_1 \cdot E_2^*)E_3^*
\]

where \(E_i\) represents the complex electric fields in the pump 1, pump 2 and probe waves. The fields within the parentheses in each term represent the dynamical grating formed and the third field diffracts off this grating. A, B and C give the individual amplitudes. The first two gratings are time independent stationary gratings in space, the first having a coarse grating spacing and the second having a fine grating spacing. The pump beams scattered from these gratings are always counter-propagating to the incident probe beam because of

Fig. 2. Dependence of optical phase conjugate energy on pump energy for quantum dots of different diameters when all beams are vertically polarized. Continuous lines represent cubic fits to the data.
the angular selectivity of the Bragg gratings and the phase matching of the interaction. Fig. 3 shows that the contribution to the phase conjugate signal from these two gratings is nearly the same. The third grating written by the interference of the counter-propagating pump beams is not time independent, but oscillates at a frequency 2 times \( \omega \). In this case the probe wave is not incident at the correct angle for Bragg scattering into \( 180^\circ \) [24]. The phase conjugate beam arising from this polarization combination could be rather due to a scattering of the probe from a two-photon excitation [23].

Thermal gratings, usually characterized by long time constants may easily result in large phase conjugate signal. For thermal contributions to be significant the laser pulse duration \( \tau_p \) should be such that [25],

\[
\frac{A^2}{2\nu_s} \leq \tau_p \leq \frac{A^2}{2\pi^2\xi}
\]

where \( A \) is the grating period, \( \nu_s \) is the sound velocity and \( \xi \) is the thermal diffusivity. In the present experiment where the probe makes a small angle (\( \sim 5^\circ \)) with pump 1, the two gratings considered have a period:

\[
A_{13} \approx \frac{\lambda}{\theta_{13}} = 6096 \text{ nm}
\]

and

\[
A_{23} \approx \frac{\lambda}{2n} = 116 \text{ nm}
\]

where \( \lambda \) is the wavelength (532 nm) and \( n \) (2.32 for CdS) is the refractive index. In CdS (thermal conductivity = 200 mW/cm K; thermal diffusivity = \( 1.3 \times 10^{-5} \) m\(^2\)/s, average sound velocity = 2606 m/s [26]) the large period grating will make a noticeable thermal contribution to the signal only if \( 1.2 \leq \tau_p \leq 74 \) ns. For the small period grating this condition becomes \( 0.02 \leq \tau_p \leq 0.03 \) ns. Thus it appears that the phase conjugate signal resulting from the grating formed by the copolarized pump 2 and probe has a nonthermal origin. According to Eq. (2) the grating formed by the copolarized pump 1 and probe can, in principle produce thermal contribution to the signal. However the fact that the large period grating shows nearly the same amount of phase conjugate signal as the small period grating indicates the possibility of a nonthermal origin of the nonlinearity. A similar observation was made in a previous work on CdS\(_x\)Se\(_{1-x}\) quantum dots in glass matrices in contrast to that of bulk CdS [5].

3.3. Effect of delaying pump 2

For good OPC efficiency the three input waves, the forward pump, the backward pump and the probe should have a good overlap in space and time in the sample volume. We have studied the effect of delay in time of the back pump on the OPC signal. For this purpose, the back mirror M1 is mounted on a translation stage providing for micron level adjustments. When the distance between sample S and mirror M1 increases by \( \Delta z \), the corresponding time delay \( \Delta t \) in back pump with respect to pump 1 (and probe) is \( (2\Delta/c) \) where \( c \) is the speed of light.

Fig. 4 shows the variation in OPC reflectivity as a function of time delay \( \Delta t \) in the range 0.05–0.22
The figure indicates that the phase conjugate reflectivity has a maximum at zero delay. The reflectivity falls monotonously as the delay is increased. The DFWM signal from a thermal grating usually increases with longer delay due to its slow build-up time [19,27]. On the other hand, the signal delay time observed in the present experiment is much shorter than the laser pulse width and hence probably it is the coherence time of the laser that is being monitored here.

3.4. Size dependence of $\chi^{(3)}$

To extract the third order susceptibility of the sample from the experimental data, the phase conjugate reflectivity ($R$) is measured as a function of the pump beam intensity $I$. The data were fitted to the quadratic relation by the least squares technique:

$$R = CI^2$$

Assuming that pump depletion is negligible, third order susceptibility $\chi^{(3)}$ of the samples are calculated using the relation [28]

$$\chi^{(3)} = \frac{2c^2n^2\varepsilon_0\alpha}{3\varepsilon_0e^{2L}(1-e^{-2L})}\frac{R^{1/2}}{I}$$

where $c$ is the speed of light, $n$ is the refractive index, $\varepsilon_0$ is the permittivity of free space, $L$ is the sample thickness and $L'$ is the interaction length in the sample ($L' = L/\cos \theta$). $\alpha$ is the absorption coefficient of the medium and $I$ is the intensity of the pump beam. The slope $C$ of the plot of $R$ vs $I^2$ is used for the determination of $\chi^{(3)}$.

Table 1 gives $\chi^{(3)}$ values deduced using Eq. (3) for quantum dots of different diameters. The data are taken from experiments in which all the four beams are polarized in the vertical direction. It can be seen that $\chi^{(3)}$ is lowest for sample S1 having 6 nm diameter dots, and increases with decreasing quantum dot diameter. It must be noted that sample S1 is having higher absorption at 532 nm than samples S2–S4 due to the quantum confinement induced shift of the absorption edge in them [22]. This explains the lower $\chi^{(3)}$ in sample S1, even though it is having higher phase conjugate energy. In order to make a quantitative comparison of the magnitude of $\chi^{(3)}$ between the different samples, the concentration of CdS inside the polymer has to be taken into account. Our X-ray diffraction studies, reported elsewhere, give relative intensities ($C_{rel}$) of XRD peaks of CdS and the background.

![Fig. 4. Dependence of optical phase conjugate reflectivity on backward pump delay.](image)
polymer [22]. This ratio \((C_{\text{rel}})\) will be a measure of the relative concentration of CdS present in the samples. We have normalized the \(\chi^{(3)}\) values obtained with respect to this factor. It is observed that \(\chi^{(3)}\) as well as the volume normalized \(\chi^{(3)}\) increases with decreasing quantum dot diameter in the size range considered (Table 1). In the case of a predominantly absorptive mechanism of nonlinearity, a more valid quantity for comparison of the nonlinearity will be \(\chi^{(3)}/\alpha\), where \(\alpha\) is the absorption coefficient at 532 nm. The size dependence of this quantity is illustrated in Fig. 5. If we assume that the decay time \(\tau\) does not vary between the samples this quantity gives a measure of the figure of merit. The figure shows that there is a sharp increase in \(\chi^{(3)}/\alpha\) as the size decreases below 2 nm. Finally in the last column of Table 1 we make a rough estimate of the relative values of \(\chi^{(3)}\) per quantum dot by dividing \(\chi^{(3)}\) by the relative number of quantum dots per sample. \(\chi^{(3)}\) per quantum dot is largest for dot diameter of 6 nm. As the diameter changes from 2 to 1.6 nm the relative magnitude of \(\chi^{(3)}\) per quantum dot increases from 5.0 to 10.1.

For bulk semiconductors at room temperature, a mechanism for the resonant nonlinearity can be described by the band-filling model. Nonlinearities in quantum dots of large diameters can be explained in terms of the band-filling model, too, if the defect states can be minimized [29]. However, when the cluster diameter is smaller than the exciton Bohr diameter, as is the case for the samples studied here, the continuous energy bands are replaced by discrete states and the band filling model is no longer appropriate. Excitation of the semiconductor cluster by a short laser pulse results in the generation of an exciton bounded by the cluster surface. The exciton has a very short lifetime and is rapidly trapped by surface defects forming a trapped electron–hole pair. In general it is observed that the nonlinear response of SQDs results from a combination of a fast free carrier contribution and of a slow trapped-carrier component due to particles with traps [18]. The free carrier contribution, which is important only in the early time domains (picoseconds) arises from the saturation of the lowest excitonic band. In the present experiments using nanosecond pulses, the bleaching of the exciton absorption in the presence of trapped carriers could be one of the plausible causes of the nonlinearity.

The trapped carriers can modify the optical properties of the particles through phase-space filling or through the static electric field they create. However, it is seen from the photoluminescence emission studies that the defect luminescence is far red shifted from the absorption edge indicating deep trap states in our samples [22]. Such deeply trapped electrons and holes may not be effective for phase-space filling. Also, the exchange interaction between the trapped carriers and the exciton should be minimal since the wave functions of the electrons and holes are localized and overlap poorly [20]. The bleaching of the exciton absorption could take place because of the reduced overlap of the electron and hole wave functions in the presence of a trapped electron–hole pair. The bleaching efficiency per photon absorbed can be expressed as [9]

![Fig. 5. Figure of merit \((\chi^{(3)}/\alpha)\) of CdS quantum dots plotted against the dot diameter. The continuous line is drawn as an aid to the eye.](image-url)
\[
\frac{\Delta \alpha}{\alpha_0(I/h\omega)} = (\sigma - \sigma_x)\tau(1 - e^{-\tau_p/\tau})
\]  

(5)

where \(\Delta \alpha/\alpha_0\) is the relative absorbance change, \(\tau_p\) is the laser pulse width, \(\tau\) the excited state life time, \(h\omega\) the photon energy and \(I\) the incident laser intensity. \(\sigma\) and \(\sigma_x\) are the values of absorption cross-section in ground and excited state respectively. Thus for a given \(\tau_p\) and \(\tau\) the resonant third order nonlinearity due to trapped carriers is determined by the term \((\sigma - \sigma_x)\). Since the absorption cross-section \(\sigma\) increases with decreasing dot diameter [30], this model predicts an increase in the resonant third order nonlinearity with decreasing quantum dot diameter as is observed in the present experiments.

4. Conclusion

We have studied the third order optical nonlinearity of CdS quantum dots in Nafion in the strong confinement regime, having mean diameters 6, 2, 1.8 and 1.6 nm. DFWM experiments carried out on these samples show that the third order optical nonlinearity, \(\chi^{(3)}(-\omega, \omega, -\omega, -\omega)\) measured at 532 nm is of the order of \(10^{-18} \text{m}^2 \text{V}^{-2}\). \(\chi^{(3)}\) as well as \(\chi^{(3)}/\chi\) increase with decreasing diameter of the quantum dots in the size range studied. Polarization discrimination and pump delay experiments are carried out to probe the mechanism of the nonlinearity. Restrictions imposed on the laser pulse width by heat conduction induced blurring of the grating suggest that OPC signal from the small period grating \((A_{23})\) cannot be thermal. The polarization studies showed that contributions to the phase conjugate signal from large and small spatial period gratings are nearly the same suggesting a nonthermal mechanism. One of the major contributions to the nonlinearity could be due to the bleaching of the exciton absorption in the presence of a trapped electron–hole pair. This picture predicts results consistent with the observation of increased \(\chi^{(3)}\) values in samples containing quantum dots of smaller diameters.

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References