Saturated near-resonant refractive optical nonlinearity in CdTe quantum dots

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In this work, we report on an experimental investigation of the nonlinear optical properties near the first electronic resonance of thiol-capped CdTe quantum dots (QDs) being in the strong confinement regime. Using a cw laser excitation in a *Z*-scan experimental setup, we show the presence of saturated Kerr-type nonlinear optical properties of the QDs, at low intensity levels. The large optical nonlinearity and the control of the linear and nonlinear optical properties by the size of the QDs are of special interest for applications in integrated nanophotonic devices. © 2010 Optical Society of America

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Quantum dots (QDs) are novel materials extensively investigated at present for their special physical properties associated to discreet energetic levels. Their tuneable linear optical properties with the QDs size and shape are continuously investigated owing to their possible applications in efficient lighting and displays.

Several research groups have studied the nonlinear optical properties of QDs [1–8]. The nonlinear optical properties are in strong correlation with the linear optical properties: the control of the linear optical properties can lead to a useful control of the nonlinear ones. The quantum confinement of the exciton in a QD with much smaller size than the Bohr radius of the material, may also strongly enhance the nonlinear optical properties. The result is that a colloid with a very low concentration of such QDs can produce a much higher nonlinear optical effect than the corresponding bulk material.

Prior to this work, the nonlinear properties of QDs were experimentally studied far from resonance and the results proved an enhancement due to the quantum confinement effect. The values obtained by different authors for the nonlinear refractive index are in the range of -10^{-12} to -10^{-9} cm^2/W [1,4,5]. This spread of values suggested a strong dependence of the nonlinear properties on subtle properties of the QDs as the different surface states, owing to different synthetic procedures.

In this Letter, we study the nonlinear refractive index of thiol-capped CdTe QDs obtained from the same aqueous synthesis by size selective precipitation. We use QDs in the strong quantum confinement regime, which have discrete exciton levels, resonant to the excitation laser wavelength. We observed experimentally saturated Kerr-type nonlinear optical properties at low power levels. We also confirm size-dependent nonlinear optical effects, controllable by the synthesis.

In our experiments, we use a sample set of colloidal thiol-capped CdTe QDs in water (concentration $\sim 10^{18}$ QDs/L). The samples are specially designed to have the absorption and photoluminescence peaks near the wavelength of the laser used for the investigation (Fig. 1) [9]. From the size calibration curve presented in [9], it is deduced that the diameter of CdTe QDs in our set of samples is in the range of 1.8–2.2 nm. Thus, the QDs are much smaller than the Bohr radius of CdTe (R_{Bohr}=7.3 nm [10]), and they reside in the strong quantum confinement regime. As the concentration of the QDs in water is very low, we consider that the refractive index of the colloidal sample is given mainly by the solvent refractive index.

Their absorptions at λ=532 nm, α_{532}, were measured and given in Table 1, confirming that samples with the excitonic peak closer to the laser line (as sample *E*) show larger absorptions. We used the absorption spectra from Fig. 1 to determine the first excitonic absorption peaks ($1s-1s$), located between 471–522 nm and the corresponding transition energies, E_{1s-1s}, from Table 1. A large difference of about 1 eV between the bandgap energy for the CdTe in its quantum-sized form and the bandgap energy for the bulk CdTe (E_g=1.56 eV [10]) is observed.

In the following experiments, we have used the *Z*-scan setup [11] presented in Fig. 2. The laser is a cw frequency-doubled Nd:YAG laser (λ=532 nm, P_m=100 mW), and it is focused with a 5 cm focal length lens. The sample is scanned using a computer controlled motorized stage. The colloidal sample is

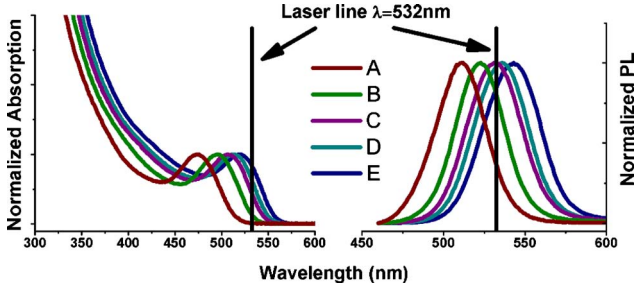

Fig. 1. (Color online) Linear absorption and PL spectra of the thiol-capped CdTe QD samples.

Table 1. Experimentally Measured Linear and Nonlinear Optical Properties for the Thiol-capped CdTe QDs Samples

Name	λ_{1s-1s} (nm)	E_{1s-1s} (eV)	PL max (nm)	Size (nm)	n_2 (10^{-7} cm^2/W)	I_{sat} (W/cm^2)	α_{532} (cm^{-1})	n_2/α_{532} (cm^3/W)	I_{sat}/α_{532} (W/cm)
A	474	2.61	510.4	1.85	−1.36		0.5	−2.7	
B	495	2.505	522.4	2.02	−3.09	3409.9	1.7	−1.8	2005.8
C	507	2.445	531.3	2.14	−7.72	1424.4	4.8	−1.6	296.7
D	511	2.426	535.4	2.18	−9.57	1111.7	6	−1.5	185.3
E	518	2.393	542.1	2.25	−14.65	674.5	11.3	−1.2	59.7

placed in a spectroscopic cell with a thickness of 0.5 mm, much smaller than the Rayleigh distance of the excitation beam (z_0=9.7 mm).

Performing Z-scan experiments for each sample at different excitation intensities, we have derived the corresponding nonlinear change of the induced refractive index. In the Fig. 3, we have plotted these dependences, for all samples. From this figure, one can see that Δn_0 has a saturation-type intensity dependence that can be expressed in the form

$$\Delta n_0(I_0) = \frac{n_2 I_0}{1 + I_0/I_{sat}}, \quad (1)$$

where n_2 is the nonlinear refractive index, I_0 is the intensity at the focus, and I_{sat} is the saturation intensity.

This saturated process may be described by a single nonlinear refractive index as in formula (1) and can easily explain the saturation of the nonlinear refractive index change with excitation intensity. It may also be described by higher-order nonlinearities in the sample,

$$\Delta n_0(I_0) \cong n_2 I_0 + n_4 I_0^2 + n_6 I_0^3 + \ldots, \quad (2)$$

where n_2 is the nonlinear refractive index due to the $\chi^{(3)}$ effects, n_4 is the nonlinear refractive index due to the $\chi^{(5)}$ effects, and so on. Using (1), we have extracted the nonlinear refractive index n_2 and the saturation intensity I_{sat} for all studied samples, which are presented in the Table 1. (Note that I_{sat} for sample A has not been derived, since saturation for this sample has not been reached up to 2000 W/cm^2.) The nonlinear refractive index and the saturation intensity normalized to the absorption coefficient at λ =532 nm, presented in Table 1, are useful for the evaluation of the pure size effects in the observed data.

We have obtained also the dependence of the nonlinear refractive index and the saturation intensity on the size of the QDs as shown in Figs. 4(a) and 4(b).

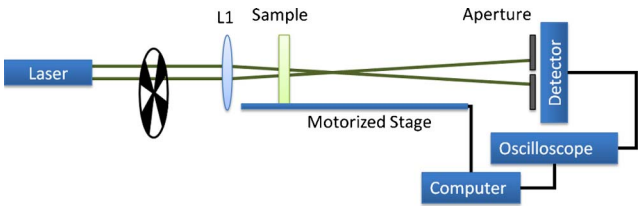

Fig. 2. (Color online) Z-scan experimental setup.

From Fig. 4(a), it is seen that in absolute values the nonlinear refractive index increases exponentially with increasing dot size. This is in accordance with the theory proposed by Cotter *et al.* [12]. In an open-aperture Z-scan setup, we have observed no nonlinear absorptions in any of our samples, which is also in accordance with the results from [12], in the case of very small QDs excited below the excitonic transition energy. In Fig. 4(b), one can observe an exponential decrease of the saturation intensity, which reflects a lower intensity saturation by larger QDs.

The large optical nonlinearity of $n_2 \sim -10^{-7}$ cm^2/W was obtained at low-light intensity (comparable to the photorefractive nonlinearities). It may be attributed to the strong carrier confinement in the very small QDs, in which the first exciton energy levels are resonantly excited by the laser light at λ =532 nm. This interaction can be optimized by the control of the size of the QDs in the synthesis, leading to the possibility of controlling the nonlinear response of the artificial material.

We can compare the large value of the nonlinearity obtained by us with similar values obtained by other authors, with light excitation far from resonance: Pan *et al.* obtained $n_2 \sim -10^{-12}$ cm^2/W [4], Tan *et al.* obtained $n_2 \sim -10^{-11}$ cm^2/W [5], and Seo *et al.* obtained $n_2 \sim -10^{-9}$ cm^2/W [1]. From this comparison, we can deduce that the resonant excitation, which was the target of our experimental work, strongly enhances the optical nonlinearity of this artificial optical material.

We observed experimentally a significant saturation of the nonlinear refractive index at relatively low intensity levels, which could be attributed to the relatively small number of QDs in the volume of excita-

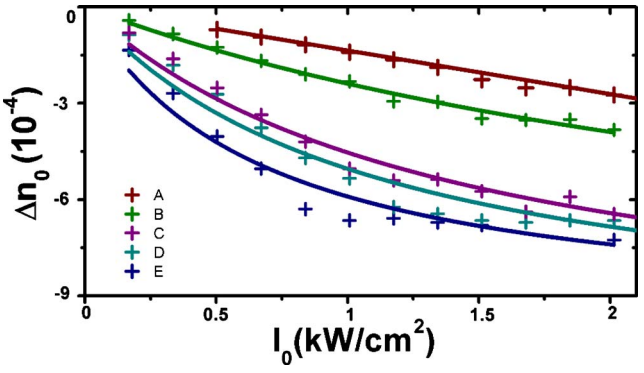

Fig. 3. (Color online) Dependence of the Δn_0 on the intensity in the focus fitted with formula (1), showing the saturation feature of the Δn_0.

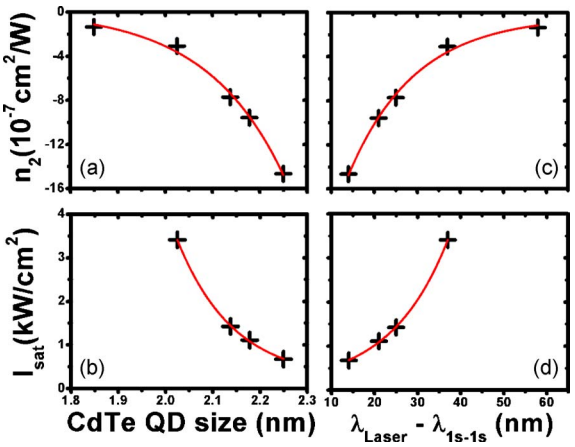

Fig. 4. (Color online) Dependence of the (a) n_2 and (b) I_{sat} versus CdTe QDs size; (c) n_2 and (d) I_{sat} versus the detuning from the resonance.

tion and to the resonant interaction. A strong nonlinear interaction is saturating at lower intensity levels as compared to a weak interaction. This statement is experimentally demonstrated for our samples and it is represented in Fig. 5. The saturation intensity, I_{sat}, decreases exponentially with the nonlinear refractive index n_2 (Fig. 5). In Fig. 5, it is seen that for a higher nonlinearity, the saturation is achieved at lower intensity levels.

The dependence of the nonlinear refractive index on the QD size is in agreement with the results obtained by Pan and can become even more evident if we represent the nonlinear refractive index and the saturation intensity as functions of the detuning from the resonance [Fig. 4(c)]. In this case, it is easily observed that, as we go farther from the resonance and thus at lower absorption levels, the nonlinear refractive index decreases. This is an expected result if we consider absorption in terms of interaction cross-section, as the interaction cross-section decreases, the interaction between the light and the nonlinear material decreases, leading to a decrease of the nonlinear response (of the nonlinear refractive index). In the same way, the nonlinear refractive index saturation is explained. From Fig. 4(d), we deduce that the saturation intensity lowers when the laser excitation is closer to the resonance. Thus, the stronger is the interaction, the lower is the saturation intensity.

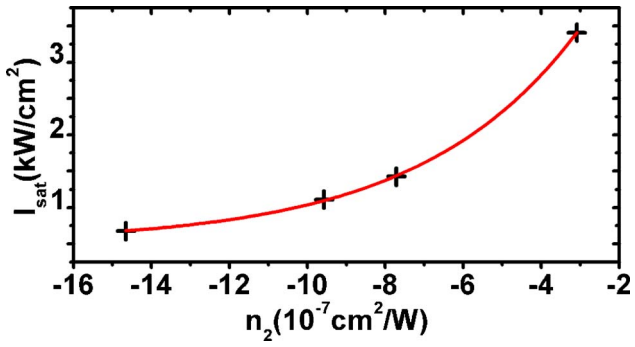

Fig. 5. (Color online) Dependence of the I_{sat} on the n_2 for the thiol-capped CdTe QDs.

In conclusion, in this Letter, we measured remarkably large and size controllable nonlinear optical effects in CdTe colloidal QDs. We have shown the saturation of the nonlinear refractive index change at low-intensity levels (on the order of 10^3 W/cm^2). We demonstrated that by controlling the optical linear properties, one can tune the nonlinear response of the QDs. The spectral range of the response can be further extended by choosing different materials for the QDs. These nonlinear properties have a strong potential in new integrated nanophotonic devices.

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