Nonlinear optical properties of CdTe QDs near the resonance regime

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In this paper, we are studying the sign changes of the nonlinear refractive index of CdTe quantum dots (QDs) function of the light wavelength around the resonance. This dependence of the nonlinear refractive index sign is of importance for the control of the nonlinear focusing/defocusing by changing the excitation wavelength only. With the QD samples we also observed a strong enhancement of the nonlinear refractive index with respect to the bulk material which is a consequence of the QD material being in the strong quantum confinement regime and near to the resonance excitation. A Z-Scan experimental setup is used to determine the nonlinear refractive index of the CdTe QDs. A simple method is proposed to avoid thermo-optical effects by using chopped and c.w. lasers as light sourcse for the Z-Scan experiments.

1. Introduction

Semiconductor quantum dots (QDs) or nanocrystals are crystals with sizes smaller than their respective Bohr radius in which the electron and hole energy levels are discrete rather than continuous. Changing the geometry of the surface of the QD or the number of atoms changes the band gap energy and the effects of quantum confinement. Using these capabilities one can tailor the energy levels of the material for achieving an enhanced near resonant nonlinear effect for the specific wavelength of interest.

CdTe is a II-VI semiconductor with a direct band gap in the near IR region at 1.56 eV. In the QD form, CdTe show tuneable band gap in the VIS region producing visible tuneable emission and absorption which is of special interest for solar cells and for white light emitters. Another important application of CdTe is found in nonlinear optical devices.

In order to investigate the nonlinear optical properties of CdTe a number of authors previously used the Z-scan method [1-5]. The Z-scan method is a simple and sensitive method for the characterization of the nonlinear refractive index of optical materials which was introduced by M. Sheik-Bahae et al. [6]. The technique is based on the measurements of the transmitted signal of a sample which is moved along the z-axis of a focused laser beam. Changes in the refractive index due to optical nonlinearities are translated into changes in the laser beam dimension at the detector plane. These changes can be measured using a detector placed behind a small aperture or a CCD camera. The changes of the transmitted signal depend on the sample position, and using an adequate theory one can deduce the nonlinear refractive index. Possible optical nonlinearities in II-VI semiconductors are produced by free carrier excitations, interband transitions [3], thermal effects and discrete level transitions in QDs.

It is important to isolate the thermo-optically induced refractive index which is obtained in almost all Z-scan experiments, especially when c. w. lasers or high repetition rate lasers are used [7-9]. Although the thermo-optically induced refractive index has quite high values due to its long response time, it can not be used for nonlinear devices that require high speed,.

In this paper, we are studying the nonlinear optical properties of CdTe quantum dots in colloidal form with the Z-scan method, isolating electronic effect contributions to the optically induced refractive index from the thermo-optically induced refractive index. We experimentally demonstrate a sign change of the electronic nonlinear refractive index change of CdTe QD samples and the dependence of this effect on the position of the exciting wavelength relative to the resonance wavelength of the QD composite. This change can be formulated as [10]:

$$n_2(\omega) = \frac{K_{mat}}{2n_0(\omega)} \frac{\omega_0 - \omega}{(\omega_0 - \omega)^2 + \Gamma^2} \qquad (1)$$

where K_{mat} is a material coefficient (with real values) and Γ is the spectral with of this transition.

We also experimentally unravel that, in our case, the thermo-optical nonlinear effect near the resonance of the material is extremely small in comparison to the rapid electronic effects and, thus, can be neglected. The thermo-optical effect should be dominant at the resonance where the thermal decay of the excited electrons is predominant and the rapid electronic contribution to the optical nonlinearities should be close to zero.

2. Experimental work

In our experiments, we use a sample of colloidal CdTe QD in water (concentration $\sim 9{,}71 \cdot 10^{-4} mole/l$). The sample is specially designed to have a PL emission peak ($\lambda = 550nm$) near the wavelength of the laser used

for the investigation. The photoluminescence and linear absorption spectra of this sample are presented in Figs. 1 and 2. The description of the syntesis of this sample can be found in ref 11. In this paper, one can find that the measured diameter of CdTe QD used in our sample is $\approx 3nm$. This result, $R_{QD} \approx 1.5nm < R_{Bohr} = 7.5nm$, demonstrates that the nanocrystals are in the strong confinement regime.
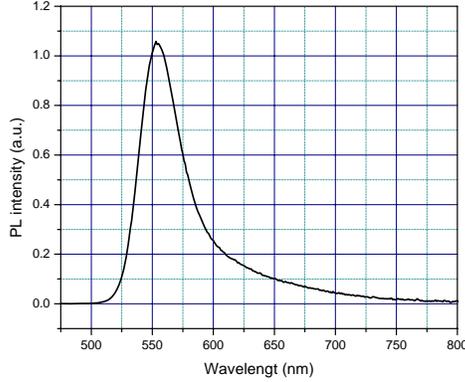

Fig. 1. Photoluminescence spectrum of the QD sample used in our experiments.

As shown in Fig. 2, the first excitonic absorption peak is located around $\lambda = 505nm$ ($h^{-1} \rightarrow e^{+}$) which again indicates the particles being in the strong confinement regime [2].

The study of the third-order optical nonlinearities of these green-emitting CdTe QDs was done by the Z-scan experimental setup shown in Fig. 3. In this setup a c.w. laser with $\lambda = 530nm$ (SHG Nd:YAG) was used. The sample is scanned in the z - direction using a computer controlled motorized stage and the experimental data are acquired from detector 1 using an oscilloscope and an AD converter. The colloidal QD sample is placed in a spectroscopic cell with the thickness $d = 0.2mm$, which is much smaller than the Rayleigh length of the focussed beam used in our setup. Fig. 4 presents our results obtained in this Z-Scan experiment. The nonlinear refractive index was obtained from the Z-scan experimental data by a best fitting with the well known formula given by Sheik-Bahae et al [6]:

$$T(z,\Delta\phi_0) \cong 1 + \frac{4\Delta\phi_0 x}{\left(x^2 + 1\right)\left(x^2 + 9\right)}, \qquad (3)$$

where $x = z/z_0$ is the normalized distance, z_0 - the Rayleigh distance, $\Delta\phi_0 = k\Delta n_0 L_{eff}$, $\Delta n_0 = n_0 - n_2 I$ is the nonlinear induced refractive index change, n_2 - the nonlinear refractive index, $L_{eff} = \left(1 - e^{-\alpha L}\right)/\alpha$ is the

effective length of the medium, α - the linear absorption and L the thickness of the medium.
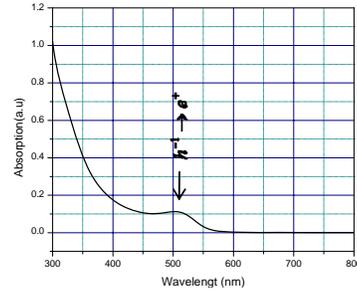

Fig. 2. Linear absorption spectrum of the QD sample used in our experiments.
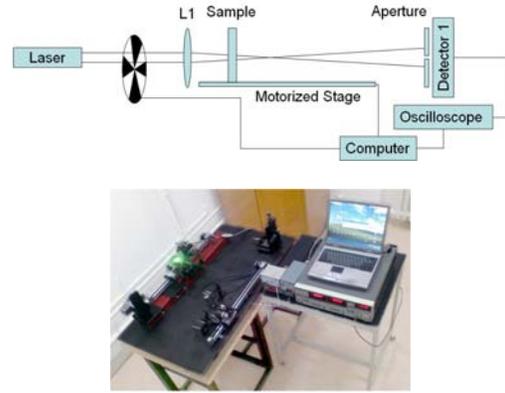

Fig. 3. Experimental setup.

This nonlinear refractive index includes both the thermo-optical contribution and the electronic effect contribution and results as:

$$n_{2,t+e} = -5.2 \times 10^{-8} \frac{cm^2}{W}.$$

In order to avoid the thermo-optical effect development during illumination, we have used, in the same setup, a chopper with a proper frequency. The results obtained in this experiment are presented in Fig. 5. In this case, we obtain a nonlinear refractive index that is produced only by the electronic effect:

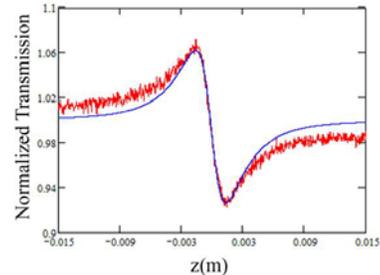$$n_{2e} = -5.3 \times 10^{-8} \frac{cm^2}{W}$$

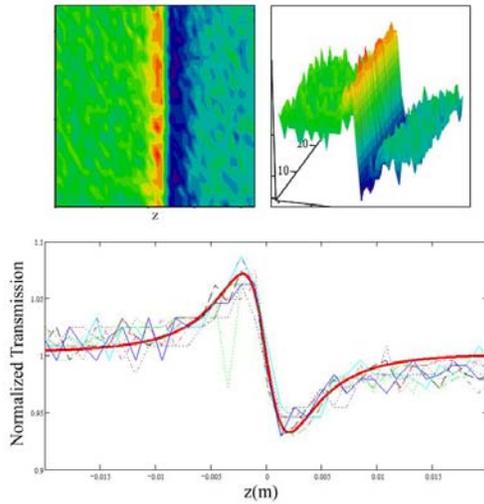Fig. 4. Experimental data obtained in the Z-Scan experiment without chopper.

Fig. 5. Experimental data obtained in a Z-Scan experiment with a chopper.

Fig. 6. Representation of the resonance enhanced nonlinear refractive index change near the resonance corresponding to an optical transition.

The contributions of the thermal and the electronic changes of the refractive index are so small that we consider them as being additive:

$$\Delta n = \Delta n_t + \Delta n_e = n_{2t}I + n_{2e}I = (n_{2t} + n_{2e})I$$

and we can determine the nonlinear refractive index produced by the thermo-optical effect only to be:

$$n_{2t} = n_{2,t+e} - n_{2e} = 1 \times 10^{-9} \frac{cm^2}{W}.$$

3. Remarks and conclusions

Comparing the nonlinear refractive index obtained in our experiments with CdTe quantum dots with the corresponding values obtained by Sheik-Bahae et al. [3] for bulk CdTe, $n_2 = -3 \times 10^{-13} cm^2/W$, (with a Z-Scan setup using a Nd:YAG laser with 40 ps pulses at $\lambda = 1060 nm$), we notice the strong enhancement of n_2 in the QDs. This enhancement may be attributed to the QDs being in the strong confinement regime and to the QD average size, allowing a near resonant interaction with laser light at $\lambda = 530 nm$.

Regarding the negative sign of the nonlinear refractive index obtained in our experiments, we remark that Ma et al. [4] obtained positive values of n_2 in the case of CdTe QDs with resonances around $650 nm$, excited in the NIR at $\lambda = 1032 nm$. This change of sign can be explained if we consider the exciting wavelength to be smaller than the resonance wavelength of the material as can be seen in figure 6. The representation of the nonlinear refractive index versus the light frequency near a resonance of the investigated medium is obtained using formula (1).
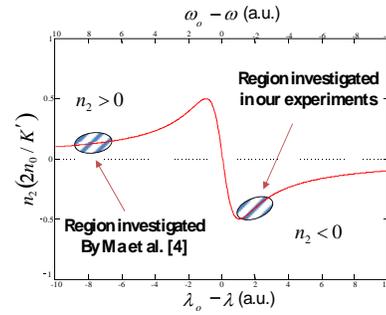
Possible applications of these results are in controlling a nonlinear focusing/defocusing lens by the QD size (for a fixed wavelength) and/or by wavelength tuning (for fixed QD sizes).

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