Near-resonant two-photon absorption in luminescent CdTe quantum dots

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We report the nonlinear optical absorption studies in two differently sized water-soluble cadmium telluride quantum dot (QD) samples, exhibiting first excitonic absorption peaks at 493 nm and 551 nm, respectively. An optical limiting behavior is observed for near-resonant excitation at 532 nm using nanosecond laser pulses, originating from the effective two-photon absorption (TPA) mechanism. The effective TPA coefficient (β_{eff}) is measured to be in the range of 10^{-12} m/W. This is one order of magnitude higher than the TPA coefficient (β) reported for off-resonant excitation. At this excitation wavelength, the smaller QD shows a relatively weaker photoluminescence and stronger nonlinear absorption. © *2012 American Institute of Physics*. [doi:10.1063/1.3687695]

Semiconducting nanocrystals, also known as quantum dots (QDs), have attracted the attention of the scientific community because of their distinct optical and electronic properties that can be tuned by the quantum size effect and surface chemistry.[1,2] These special properties of QDs make them potential candidates for photonic devices. For photonic applications such as ultrafast optical-switching, optical bistability, and phase conjugation, as well as for other types of signal processing, a large nonlinearity parameter with ultrafast time response is required.[3] Various investigations on nanosized semiconductor materials have been carried out in the past to analyze nonlinear optical properties.[4–11] However, most of them are focused on semiconductor-doped glasses with large size distribution and surface defects. Colloidal synthesis method developed in the last decade has made the studies more precise because of the resulting narrower size distributions and higher luminescence quantum yields (QYs).[12] Nonlinear refractive index for near-resonant excitation[13,14] and nonlinear absorption for off-resonant excitation[8,15] have been previously studied in cadmium telluride (CdTe) QDs. Here, we report near-resonant nonlinear absorption measurements in CdTe QDs using nanosecond laser pulses employing the open-aperture z-scan technique, and show that the two-photon absorption (TPA) coefficient is enhanced by an order of magnitude due to a strong excited state absorption (ESA) process.

Intense radiation can induce substantial changes in the absorption properties of a material resulting in intensity dependent transmittance. This process is known as nonlinear absorption.[16] TPA is a typical nonlinear absorption process occurring in a non-resonant system, in which two photons are simultaneously absorbed to an excited state via a virtual intermediate state. In a resonant system, the intermediate level is real, and the process is a two-step excitation called ESA. For near-resonant excitation, both TPA and ESA will take place, which has been called *effective* TPA in literature.[17,18] In the present work, we have investigated the nonlinear optical absorption of 3-mercaptopropionic acid (MPA) capped CdTe QDs synthesized by hydrothermal methods in the near-resonant excitation (532 nm) region. Measurements reveal that nonlinear absorption occurs due to an effective two-photon absorption process, and the corresponding nonlinearity co-efficient (β_{eff}) is higher by an order of magnitude compared to that for off-resonant excitation (β).

A sample set of colloidal MPA-capped CdTe QDs in water (concentration $\sim 10^{18}$ QDs/L) synthesized by hydrothermal method was used in our experiments. The synthesis procedure is described in detail in our previous report.[19] Optical measurements were performed at room temperature under ambient conditions. Absorption spectra were recorded on an UV–Visible spectrophotometer (Cintra 40), and photoluminescence (PL) spectra were recorded using a Perkin Elmer LS50 B Luminescence spectrometer. The QY values were determined using the formula

$$QY_{(sample)} = \left(\frac{F_{(sample)}}{F_{(ref)}}\right)\left(\frac{A_{(ref)}}{A_{(sample)}}\right)\left(\frac{n^2_{(sample)}}{n^2_{(ref)}}\right)QY_{(ref)}, \quad (1)$$

where F, A, and n are the measured fluorescence (area under the emission peak), the absorbance at the excitation wavelength, and the refractive index, respectively. Quantum yields were determined relative to Rhodamine 6G in ethanol (QY = 95%).[20]

Nonlinear absorption studies were done by the open aperture z-scan technique[21] using 5 ns pulses from a Q-switched, frequency doubled Nd:YAG laser emitting at the wavelength of 532 nm. The z-scan is a single beam experiment where the excitation and probing of the medium are done by the same focused laser beam. In our experiment, laser pulses of approximately 200 μJ energy and Gaussian cross section were used to excite the sample taken in a 1 mm cuvette. The pulse repetition rate is approximately 0.25 Hz. When the sample is translated along the beam axis (z-axis) in small steps, it sees different laser fluences (energy densities) at each position z. The transmittance T, which is a

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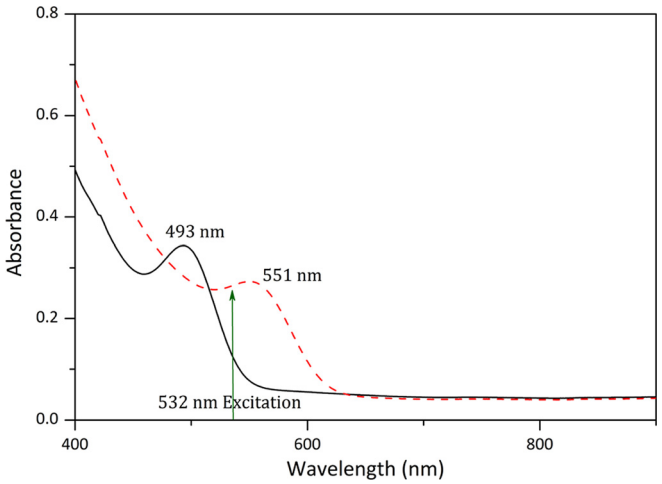

FIG. 1. (Color online) UV-Vis absorption spectra of QD493 (2.4 nm) and QD551 (2.8 nm) used for the z-scan measurements.

function of z for a nonlinear medium, is measured using a pyroelectric detector placed in the far-field, which collects the entire transmitted beam. The measured transmittance is normalized for small fluctuations in the laser energy by means of a reference detector which samples the input laser pulse. The whole experiment is automated using a LabVIEW program.

Figure 1 shows the linear absorption spectra of the two differently sized CdTe QDs used for the measurements. We denote these as QD493 and QD551, respectively, with respect to their first excitonic absorption peak wavelengths. Using the sizing curve given by Rogach *et al.*,[22] the diameter of QD493 is estimated as 2.4 nm, and that of QD551 as 2.8 nm. The quantum yields of the prepared CdTe QDs are obtained in comparison to the fluorescence emission of Rhodamine 6G. These are found to be close to 0.2 for both samples when excited above the bandgap using 365 nm radiation.

The open aperture z-scan results are shown in Figure 2. The valley-shaped curves are the indicative of nonlinear absorption. Symbols denote the experimental data points, while solid lines represent the theoretical fits based on the model discussed below. The data fit well to a two-photon absorption process, given by the equation[16]

$$T = ((1-R)^2 \exp(-\alpha_0 L)/\sqrt{\pi} q_0) \int_{-\infty}^{+\infty} \ln[\sqrt{1+q_0 \exp(-t^2)}]dt, \quad (2)$$

where L and R are the sample length and surface reflectivity, respectively, and α_0 is the linear absorption coefficient. q_0 is given by $\beta(1-R)I_z L_{eff}$, where β is the two-photon absorption coefficient, and I_z is the intensity of the laser beam at position z. L_{eff} is given by $[1-\exp(-\alpha_0 L)]/\alpha_0$. The linear transmissions of the present samples at 532 nm in the 1 mm cuvette are 82% for QD493 and 75% for QD551, respectively, and the residual absorption is a pathway for excited state absorption. Similarly, both samples have a strong absorption at the two-photon wavelength of 266 nm, which promotes the occurrence of TPA. Therefore, the nonlinear absorption observed in these samples has contributions from genuine two-photon absorption as well as excited state absorption, so that the observed nonlinearity is an effective two-photon absorption process. The effective two-photon absorption coefficient β_{eff} is determined from the best numerical fit of the measured data to Eq. (2). The inset of Figure 2 shows normalized transmission plotted against input laser fluence (optical limiting curve), which is derived from the z-scan data. β_{eff} is found to be 5.5×10^{-12} m/W for QD493 and 1.2×10^{-12} m/W for QD551, respectively. These values are about ten times larger than those reported for CdTe QDs for off-resonant excitation.[13]

It may be noted that QD493 shows an enhanced nonlinear absorption compared to QD551. This is rather counter-intuitive, because the QD551 sample we used has less transmission (hence, more absorption) at the irradiation wavelength, which should normally result in an enhanced excited state absorption. However, we note that photoluminescence from QD551 is much stronger compared to that of QD493 when excited at 532 nm (Figure 3). This indicates that in QD551 the first excited state is depleted efficiently

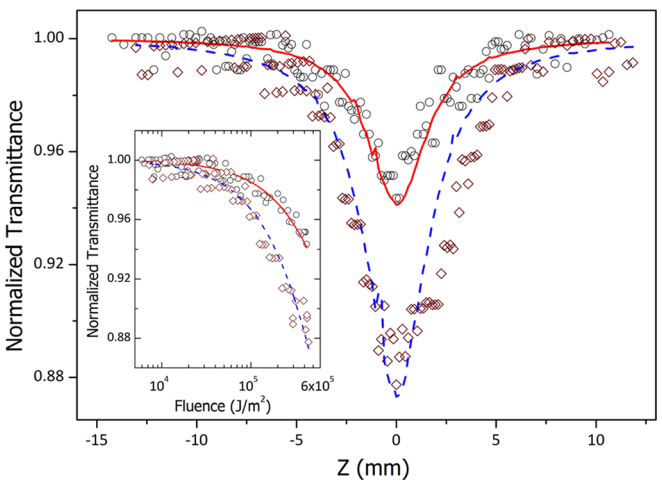

FIG. 2. (Color online) z-scan curves obtained for QD493 and QD551. Symbols represent the experimental data (□-QD493, ○-QD551), and lines represent the best fits obtained using Eq. (2). Inset shows corresponding optical limiting curves, derived from the z-scan data.

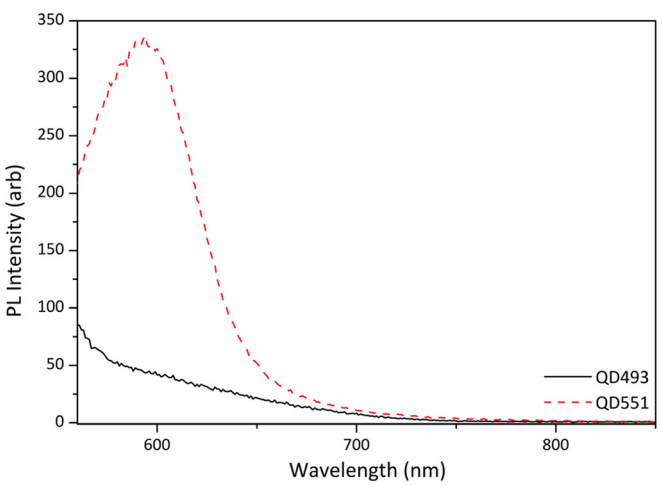

FIG. 3. (Color online) Photoluminescence emission spectra obtained for QD493 and QD551 at 532 nm excitation. The emission is much weaker in the case of QD493 compared to QD551.

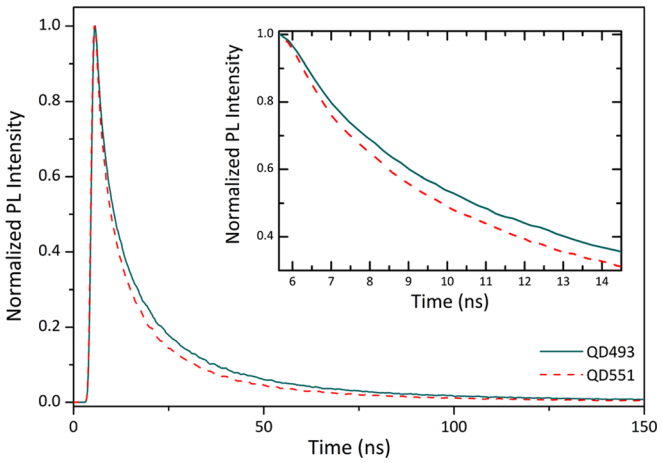

FIG. 4. (Color online) Photoluminescence decay of QD493 and QD551 for excitation at 532 nm. PL lifetimes are 7.1 ns and 8.4 ns, for QD551 and QD493, respectively. Inset shows a zoomed-in view of the decay profile up to 15 ns.

via PL, thereby reducing the cross section for excited state absorption. The measured PL lifetimes are 7.1 ns for QD551 and 8.4 ns for QD493, respectively, as seen from Figure 4. Furthermore, these QDs belong to the strongly confined regime as their radii are close to or smaller than the electron Bohr radius, hole Bohr radius, and exciton Bohr radius of CdTe, which are given by 4.9, 1.5, and 6.4 nm, respectively.[23] In this regime, the nonlinear susceptibility of the QD is inversely proportional to R^3, where R is the radius of the quantum dot.[24] Because of the above reasons, β_{eff} should increase with decrease in the QD diameter in the strong confinement regime, as we have observed.

In conclusion, we have synthesized CdTe quantum dots of two different sizes in the strong confinement regime, excited them at the near-resonant wavelength of 532 nm, and measured their nonlinear transmission response. It is found that near-resonant excitation results in an increased nonlinear absorption compared to off-resonant excitation. The effective two-photon absorption coefficient β_{eff} is lower in QD551 because its photoluminescence is stronger at the excitation wavelength, leading to a more efficient depletion of excited electrons resulting in reduced excited state absorption. The inverse proportionality of the nonlinear susceptibility to the cubic power of the QD radius also contributes to the weaker nonlinear absorption observed in QD551.

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