

Enhanced two-photon absorption of CdS nanocrystal rods

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In this letter we report that CdS nanocrystals are reshaped into an elongated rod form for increasing two-photon absorption. CdS quantum rods with uniform rod dimensions have been synthesized and their two-photon absorption cross section in solution has been characterized using the z -scan method and the two-photon induced fluorescence study. The absorption cross section was found to be $20.9 \times 10^{-46} \text{ cm}^4/\text{s photon}^{-1}$ under two-photon excitation at wavelength 800 nm, which is an order of magnitude larger than that of CdS quantum dots of similar diameters. The higher two-photon absorption coefficient establishes the potential of this class of quantum rods for various photonic applications. © 2009 American Institute of Physics. [DOI: 10.1063/1.3100196]

Due to their size-controlled spectral tunability, chemical flexibility, and large extinction coefficient,¹ semiconductor colloidal nanocrystals have attracted a broad interest and have been used in a range of single-photon excitation-based applications. However, incorporation of nanocrystals into two-photon (2P) excitation-based photonic applications has emerged only recently.^{2–4} The factor limiting the photonic application of nanocrystals is the moderate 2P absorption cross sections. In particular, the 2P absorption cross section of CdS quantum dots (QDs) is in the order of $\sim 10^{-47} \text{ cm}^4/\text{s photon}^{-1}$,^{5,6} which is comparable to some organic dye molecules with 2P absorption enhanced design.⁷ It is known that the extinction coefficients of nanocrystals are primarily dependent on their volume.⁸ Recent work has demonstrated that elongating CdSe nanocrystals into a rod-shape can dramatically increase the linear absorption cross sections due to an increased volume.⁹ Here, we demonstrate the shape control of CdS nanocrystals as a means to enhance the 2P absorption cross sections.

The 2P absorption cross sections of CdS QDs were measured as a control sample. CdS QDs of different diameters were synthesized by injecting the sulfur (S) precursor at different temperatures.¹⁰ The absorption spectra of three different size QDs are labeled as CdS 430, CdS 437, and CdS 451 corresponding to the diameters of 4.45, 4.7, and 5.32 nm, respectively, determined from the first absorption peak.¹¹ The 2P absorption was measured using open aperture z -scan methods¹² employing a Spitfire amplified-pulsed laser at the wavelength of 800 nm (a pulse width of 100 fs and a repetition rate of 1 kHz). The laser beam was focused by a lens with a focal length of 250 mm, which gives a focal spot radius of 25 μm provided the diameter of the collimated beam is 7.5 mm.¹³ The QDs were well washed and redispersed in chloroform solution in a 1 mm quartz cuvette.

Figure 1(a) shows the open aperture z -scan response of CdS QDs of three different sizes at the incident intensity of 127 GW/cm^2 . The normalized transmittance of the open aperture z -scan is given by¹⁴

$$T(z) = \frac{1}{\sqrt{\pi q_0}} \int_{-\infty}^{\infty} \ln[1 + q_0 \exp(-x^2)] dx, \quad (1)$$

where $q_0 = \beta_2 I_0 L_{\text{eff}}$, $L_{\text{eff}} = [1 - \exp(-al)]/a$, a is the linear absorption coefficient, l is the sample path length, β_2 is the 2P absorption coefficient, and I_0 is the incident intensity within the focus. By fitting the open aperture transmittance using Eq. (1) the 2P absorption coefficient can be obtained. From β_2 2P absorption cross section can be deduced as¹⁴

$$\sigma_2 = \beta_2 hv / N_0, \quad (2)$$

where hv is the photon energy and N_0 is the particle concentration in the solution. At the excitation wavelength of 800 nm, all QDs have no linear absorption. Given the density of $N_0 = 1.2 \times 10^{16} \text{ cm}^{-3}$, the 2P absorption cross sections are determined to be at 4.4×10^{-47} , 5.3×10^{-47} , and $8.4 \times 10^{-47} \text{ cm}^4/\text{s photon}^{-1}$ for CdS QDs with diameters 4.45, 4.7, and 5.3 nm, respectively. This result is comparable with a previous reported value of $7 \times 10^{-47} \text{ cm}^4/\text{s photon}^{-1}$ at the excitation wavelength of 800 nm of CdS QDs of similar diameters.⁵

Figure 1(b) shows a log-log plot of the measured 2P absorption cross sections of CdS QDs versus their diameters. The linear fitting line yields a power-law dependence of 3.6

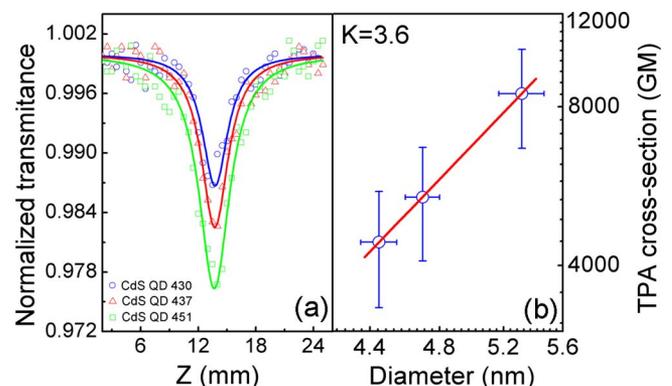


FIG. 1. (Color online) (a) Open aperture z -scan responses of CdS QDs of three different sizes. Blue circles, red triangles, and green squares are data of CdS 430, CdS 437, and CdS 45.1 respectively. The solid lines are the fitting curves from Eq. (1). (b) A log-log plot of 2P absorption cross sections of CdS QDs vs their diameters (1 GM = $10^{-50} \text{ cm}^4/\text{s photon}^{-1}$). The linear fitting line (red) yields a power-law proportionality of 3.6.

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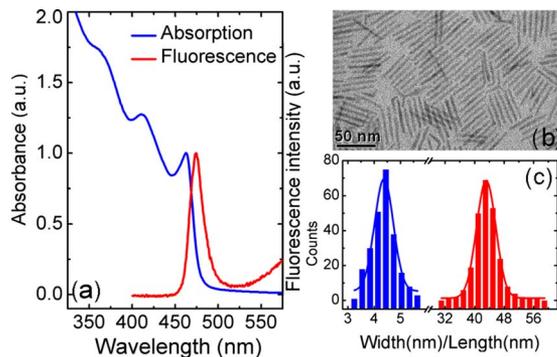


FIG. 2. (Color online) (a) Absorption (blue) and fluorescence (red) spectra of as-prepared CdS QRs. (b) TEM images of well-washed QRs. (c) Counts of statistics of the width (blue) and length (red) of CdS QRs.

in the diameters, in the range of 4.4–5.4 nm. Similarly, 2P absorption cross sections of CdSe QDs showing a power-law dependence of 3.5 ± 0.5 in their diameters, in the range from 2.4 to 4.8 nm, was reported before.¹⁵ Within experimental error and different states involved in the 2P transition,¹⁵ these results imply the correlation of 2P absorption cross sections of CdS QDs with their volumes which are proportional to the cubical diameters. In other words, expanding the volume of CdS nanocrystals may lead to the pronounced increase in 2P absorption coefficient.

CdS quantum rods (QRs) were synthesized by the slight modification of the developed recipe.¹⁶ The S precursor were prepared separately by dissolving S powders into 1-octadecene to a concentration of 0.1 mM and heated to 120 °C. 0.065 g of CdO (0.89 mmol), 0.4 g of n-tetradecylphosphonic acid (0.155 mmol), and 7 g of tri-n-butylphosphine oxide were degassed at 80 °C for 2 h. The mixture was then heated to 340 °C under nitrogen to form the Cd precursor. Then the mixture was then cooled to the desired injection temperature of 300 °C. Rods were synthesized by adding the S precursor dropwise at a rate of 0.25 ml/min. Using this method CdS QRs of uniform size were obtained after 45 min. Figure 2(a) shows the absorption spectra as well as the fluorescence spectra of as-prepared CdS QRs in chloroform. The narrow emission peak with a full width at half maximum of 20 nm is consistent with a narrow particle size distribution. A high resolution TEM image of the as-prepared QRs is shown in Fig. 2(b). The statistics in Fig. 2(c) show that as-prepared QRs have a uniform size distribution with an average width of 4.4 ± 0.4 nm and a length of 43 ± 3.5 nm (aspect ratio of ~ 10). The volume of a single QR is calculated to be approximately 15 times that of a QD with a diameter of 4.45 nm, assuming that the QR and the QD have cylindrical and spherical shapes, respectively.

QRs were washed and then redispersed in the solution for 2P measurement. The concentration of CdS QRs was determined by weighing the mass of the precipitation after centrifugating the washed sample, giving the molar mass of as-prepared QRs, calculated using the dimensions measured in high resolution TEM images. Figure 3 shows the open aperture z-scan response of CdS QRs in chloroform solution at the irradiance of 127 GW/cm². It has been found that under 2P excitation the absorption of QRs is strongly polarization-dependent via $\cos^4(\theta)$, where θ is the angle between the laser polarization and the 2P transition dipole axis

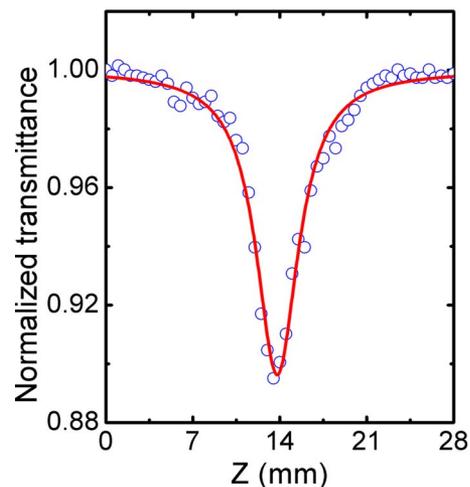


FIG. 3. (Color online) The open aperture z-scan response of CdS QRs in chloroform solution. Blue circles are measured and normalized transmittance and the red line are fitted with Eq. (1).

of QRs.¹⁷ This feature implies that for a linearly polarized excitation source, QRs can absorb the incident energy only when their orientation has a component parallel to the laser polarization. Thus, Eq. (2) is not valid in this case as it assumes that all particles within the focus absorb the excitation. It is safe to assume a random orientation distribution of QRs dispersed in solution. Thus, the 2P absorption cross section of QRs can be corrected by an orientation factor under linearly polarized irradiance given as¹⁸

$$\sigma_2 = 5\beta_2 h\nu / N_0. \quad (3)$$

By fitting the normalized transmittance in Fig. 3 using Eqs. (1) and (3), the 2P absorption cross section of CdS QRs is obtained 20.9×10^{-46} cm⁴/s photon⁻¹ at wavelength of 800 nm. The 2P absorption cross section of QRs is one order of magnitude larger compared to that of QDs. To investigate the 2P absorption cross-section dependence on the excitation wavelength, 2P-induced fluorescence^{6,19,20} measurement was performed. A titanium:sapphire ultrashort pulsed laser with a pulse width of 100 fs and a repetition rate of 80 MHz, operating in the wavelength range of 700–1000 nm, was employed as a 2P excitation source. The laser beam was focused by a high numerical aperture (NA) objective (NA=0.95) and the fluorescence was collected by the same objective and projected onto a charge coupled device (CCD) for fluorescence photon counting. Using the 2P-induced fluorescence data,^{6,19,20} the 2P absorption cross sections can be expressed as

$$F \sim \eta\phi\sigma_2NI^2, \quad (4)$$

where F is the fluorescence counts, η is the fluorescence quantum yield, ϕ is the system collection efficiency, N is the number of particles inside the focus, and I is the incident intensity.

It is plausible to assume that the system collection efficiency and the fluorescence quantum yield are constant for the CdS nanocrystals dispersed solution in the whole investigated spectral window of 720–960 nm. With the given value measured by the z-scan method at wavelength 800 nm the 2P absorption cross sections of CdS QRs at different excitation wavelengths can be obtained using Eq. (4) and are plotted in Fig. 4 (blue circles). CdS QDs of a similar diam-

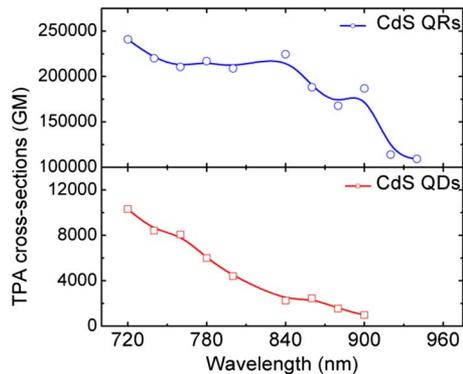


FIG. 4. (Color online) The plot of 2P absorption cross sections of CdS QRs (blue circles) and CdS QDs 430 (red squares) as a function of the excitation wavelength.

eter of 4.45 nm was also measured and the corresponding dependence of 2P absorption cross sections is plotted (red squares). The log-log plot of photoluminescence versus excitation power yields a linear slope close to two in both QD and QR solutions (not shown here), which confirms the 2P-induced emission in both cases. From Fig. 4 it is clear to see that in the investigated spectral range the QRs show a superior 2P sensitivity compared to QDs of similar diameters. Especially in the window of 800–960 nm, which has been widely applied in 2P fluorescence bioimaging,²¹ three-dimensional optical data storage,²² and microfabrication,²³ the 2P absorption cross section of QR is one to two orders of magnitude larger than that of QDs.

The z -scan measurement is confirmed by the 2P induced fluorescence study of single QR. The action cross sections $\eta\sigma_2$ was obtained by averaging the intensity of 10 particles to give $1.15 \times 10^{-48} \text{ cm}^4/\text{s photon}^{-1}$ at wavelength 800 nm. Giving the fluorescence quantum yield of nanocrystals a decrease of 100 fold when the temperature increases from ~ 5 K to room temperature,⁶ the 2P absorption cross sections of CdS QRs is on the order of $10^{-46} \text{ cm}^4/\text{s photon}^{-1}$ and consistent with the z -scan measurement of QRs in solution.

In conclusion, the 2P absorption property of CdS nanocrystals of different sizes and shapes has been investigated by the z -scan method and the 2P-induced fluorescence measurement. It has been found that the 2P absorption cross section of rod-shaped CdS nanocrystals with the dimensions of 4.4 ± 0.4 nm by 43 ± 3.5 nm is 20.9

$\times 10^{-46} \text{ cm}^4/\text{s photon}^{-1}$ at wavelength 800 nm, which is one order of magnitude larger than that of CdS spherical particles of similar diameters. Such a superior performance of the 2P absorption cross section of the QRs holds in the wavelength window from 720 to 960 nm. This enhanced 2P absorption cross section together with the polarization-selective excitation feature¹⁷ promises an attractive potential for multidimensional photonic applications.

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