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Optical Nonlinear Properties of CdSeS/ZnS Core/Shell Quantum Dots

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The optical nonlinear properties of CdSeS/ZnS quantum dots (QDs) are investigated by Z-scan technique using fundamental harmonic generation (1064 nm) of mode-locked Nd:YAG laser for the first time. The experimental results show that two photon absorptions (TPA) occur at input intensity up to 12.5 GW/cm^2. CdSeS/ZnS QDs have an average TPA cross section of 13710 GM and large nonlinear refractive index on order of 10^{-7} esu. The large optical nonlinearities perhaps allow the CdSeS/ZnS QDs to be one kind of candidate material for bioimaging and fluorescence label, optical limiting and all-optical switching.

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Quantum dots (QDs) whose radii are smaller than the bulk exciton Bohr radius constitute a class of materials intermediate between molecular and bulk forms of matter. Confinement effects make QDs become promising materials possessing unique optical properties such as tunable photoluminescence spectra with narrow bandwidth, high quantum yield, large multiphoton absorption cross section and fast-response nonlinear refractive index. These predominant properties of QDs lead to potential applications in many fields. For instance, QDs with large multiphoton absorption cross section can be favourable to the development of the deep image and fluorescence label in biological samples and QDs exhibiting large nonlinear refractive index may be a candidate material for all-optical switching.[1−5] Therefore, research for the optical nonlinearities in various types of semiconductor QDs are fast-growing subject of much interest due to their uses in such fields.

The two photon absorption (TPA) and intensity-dependent nonlinear refractive indices arise from the third-order nonlinear optical effect. In the last years, the nonlinear refractive index and TPA in various QDs were found to be several orders of magnitude larger than those in bulk counterparts.[6−9] QDs obtained by chemical route are inevitably coated with an organic capping agent. Inorganic passivating agents are usually superior to that of organic passivating agent and very often exhibit an enhancement in quantum efficiency. Recent experimental investigations have demonstrated that the surface passivation can improve the optical properties by formation of a core/shell structure.[10−12] As a result, numerous experiments as well as calculations were carried out to investigate the nonlinearity properties of core/shell QDs, including CdSe/ZnS, ZnSe/ZnS, and etc.[13−16] In comparison with the above-mentioned QDs, the optical nonlinear properties of CdSeS/ZnS QDs can be easily tailored by means of the composition variation, which makes extending of their applications in many fields. However, the optical nonlinearities of CdSeS/ZnS QDs have not yet been determined. In this Letter, we synthesize the CdSeS/ZnS QDs and investigate the nonlinear absorption from two-photon absorption process and nonlinear refractive index by the Z-scan technique with picosecond laser pulse, to our knowledge, for the first time. For their large TPA cross section and nonlinear refractive index, they can be one type of the promising materials for bioimaging and fluorescence label, optical limiting and all optical switching.

CdSeS/ZnS QDs were prepared by injection of trioctylphosphine (TOP) selenide and TOP sulfide mixture into the Cd-containing and Zn-containing precursor reaction medium. The preparation method was similar to the description in Ref. [17]. The resulting yellow precipitate was separated by centrifugation and washed several times with ethanol. After drying in vacuum, the solid was dissolved in some amount of chloroform with the concentration of CdSeS/ZnS QDs of 5×10^{-3} mol/L. The CdSeS/ZnS QDs solution was kept in the room temperature.

The size and morphology were inspected by the transmission electron microscope (TEM, Philip TZOST) operating at 190 kV. The linear absorption spectra were recorded on the UV-Vis spectrometer (TU-1901). The emission spectrum was measured by the fibre spectrofluorometer (HR2000, ocean optics). The All the measurements were performed at room temperature.

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The Z-scan was employed to determine TPA coefficients and nonlinear refractive index at the different input intensity. The incident light source was the fundamental harmonic radiation of a Nd:YAG laser (YG901C, Quantel Co.) operating at 1064 nm wavelength, 35 ps pulse width and 10 Hz repetition rate. The output light was split into two beams using a beam splitter. One beam was used as a reference beam and detected by a photodiode (J3-09, Molectron Co.) to monitor the pulse-to-pulse fluctuations. The other beam was focused with a lens ($f = 18$ cm) and used as excitation beam. The transmittances were measured through a close aperture and an open aperture, as a function of sample position z, using an identical calibrated photodiode D_2 (J3S-10, Molectron Co.) and D_3 (J3S-10, Molectron Co.), respectively. The detailed description of the Z-scan setup was presented in Ref. [18]. The pulse intensities incident on the sample were maintained between 6.8 and 22.6 GW/cm^2, to avoid the damage. Thermal effect could be ignored since the low repetition rate of 10 Hz was used. Pure solvent was also examined under the same experimental condition and its nonlinear response was found to be insignificant.

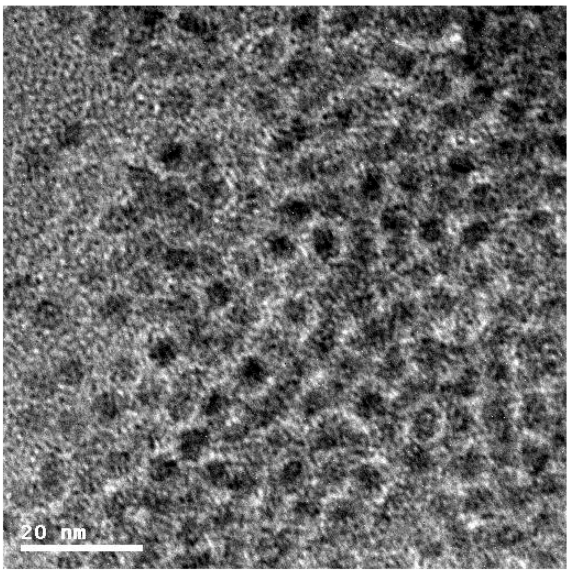

Fig. 1. TEM image of CdSeS/ZnS QDs.

Figure 1 presents a TEM image of the CdSeS/ZnS QDs. The dark spheres represent CdSeS/ZnS QDs. It is seen from Fig. 1 that the average diameter is found to be about 4 nm. In this nanoscale, the quantum confinements can occur as the theoretical calculation predicted.[19] The UV-visible absorption spectrum of CdSeS/ZnS QDs is shown in Fig. 2. There appears an absorption band almost covering the range from 250 nm to 550 nm. The inset in Fig. 2 shows the excitonic absorption peak is localized at 530 nm. It is ascribed to the $1s-1s$ transition from CdSeS core,[20] of which the forbidden gap is estimated to be 2.34 eV. The fluorescence spectra of CdSeS/ZnS QDs is given in Fig. 3. It is noted that the CdSeS/ZnS QDs exhibit a very high photostability upon laser irradiation. Curve A is the fluorescence spectrum under 532 nm laser pulse excitation, wherein the very narrow band at 532 is contributed by the scattering of excitation light. Curve B is the fluorescence spectrum under 1064 nm laser pulse excitation. They have identical peak wavelengths. The former is assigned to near-band-edge emission, the latter is assigned to the two-photon-induced fluorescence.

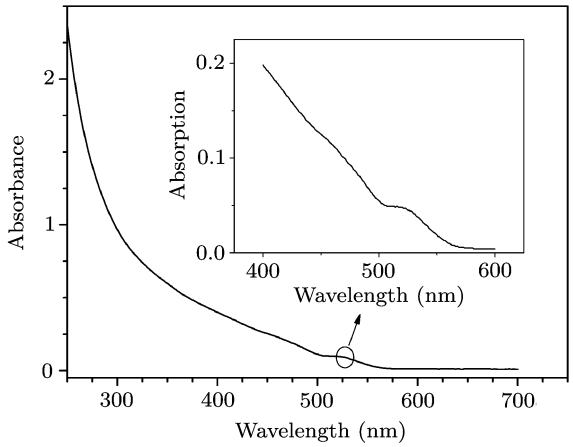

Fig. 2. Linear absorption spectrum of CdSeS/ZnS QDs.

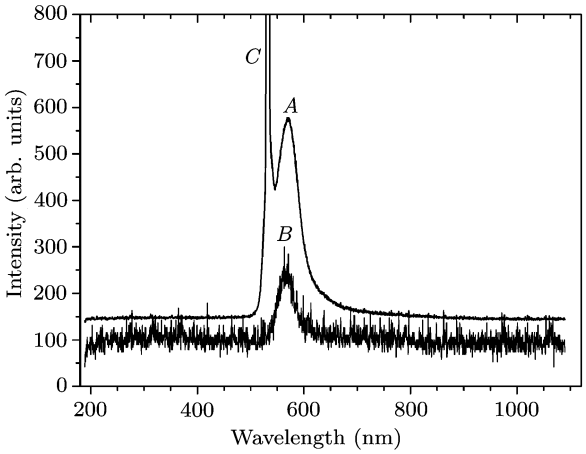

Fig. 3. Fluorescence spectra of CdSeS/ZnS QDs (A) $\lambda_{ex} = 532$ nm (B) $\lambda_{ex} = 1064$ nm.

Table 1. TPA coefficient, TPA cross section and nonlinear refractive index of CdSeS/ZnS core-shell for different pulse irradiances.

I_0 (GW/cm^2)	6.8	12.5	14.7	22.6
β (cm/GW)	0	3.0	1.7	1.9
δ_2 (GM)	0	18700	10590	11840
n_2 ($\times 10^{-11}$ esu)	3.7	2.7	1.8	1.8
n_{2qd} ($\times 10^{-7}$ esu)	1.8	1.4	0.8	0.8

The Z-scan curves for the samples are shown in

Figs. 4 and 5. The circles represent the experimental data obtained in Z-scan measurements while the solid curves are theoretical fits of the experimental data. Each data point corresponds to an average of 20 independent measurements. The relevant results are summarized in the following. First, the normalized transmittance curve of close aperture Z-scan in Fig. 4(a) exhibits symmetric valley-peak configuration and it means no nonlinear absorption at input laser pulse intensity of 6.8 GW/cm^2, which is supported by open-aperture Z-scan curve in Fig. 4(b). Second, the enhanced valley precedes the suppressed peak in Fig. 5(a), which not only indicates self-focused effect but also infers the presence of the nonlinear absorption at input intensity of 12.5 GW/cm^2. Third, the open-aperture Z-scan curve in Fig. 5(b) exhibits a symmetric valley with respect to the beam focus, which further confirms the presence of nonlinear absorption under excitation wavelength of 1064 nm. Since there is no obvious linear absorption beyond 550 nm and incident photon energy (1064 nm) almost amounts to half of forbidden gap, it is reasonable for us to infer that this nonlinear absorption effect originates from the TPA of CdSeS/ZnS QDs. This is further supported by the direct observation of two-photon induced fluorescence. The Z-scan curves at higher input intensity are similar to those at input intensity of 12.5 GW/cm^2, which are not presented in this study.

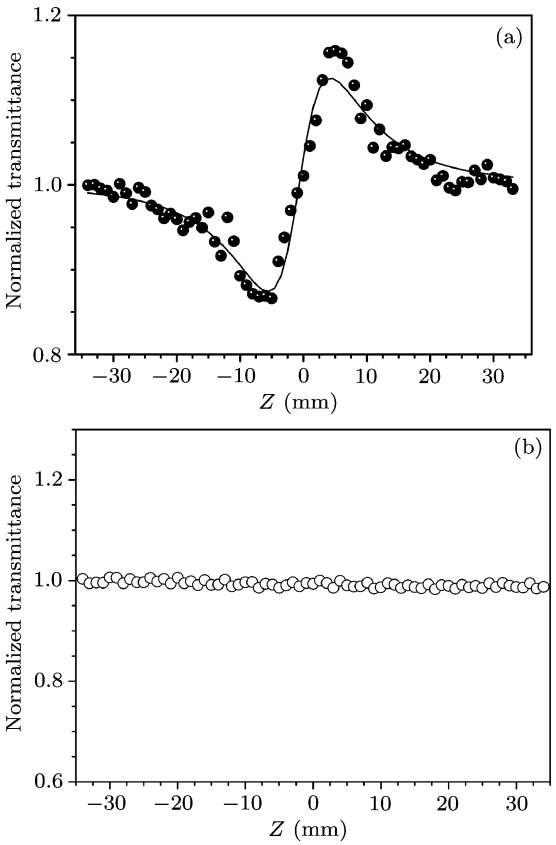

Fig. 4. Z-scan curves of the CdSeS/ZnS core/shell QDs at pulse intensity 6.8 GW/cm^2: (a) closed aperture, (b) open aperture.

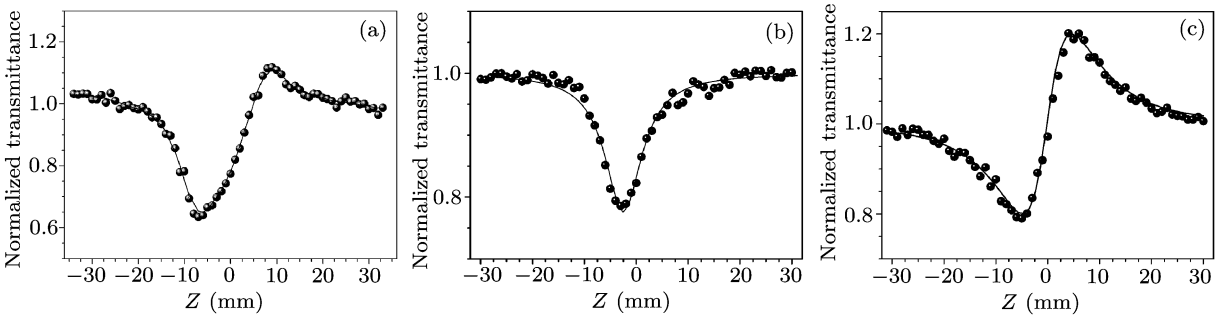

Fig. 5. Z-scan curves of the CdSeS/ZnS core/shell QDs at pulse intensity of 12.5 GW/cm^2: (a) closed-aperture, (b) open-aperture, and (c) closed-aperture divided by open-aperture Z-scan data.

Z-scan data induced by purely nonlinear refraction are obtained by dividing the closed-aperture data with the corresponding open-aperture data as shown in Fig. 5(c). The nonlinear refractive can be determined using the following relationship:[21]

$$T(z) = 1 + \frac{4x}{(x^2+9)(x^2+9)}\Delta\Phi_0, \qquad (1)$$

where $T(z)$ is the normalized transmittance of the sample with $x = z/z_0$, $z_0 = k\omega_0^2/2$ is the diffraction length with ω_0 the radius of the beam waist, $\Delta\Phi_0 = k\gamma I_0 L_{\text{eff}}$ is the phase changes induced by nonlinear refraction with the wave vector $k = 2\pi/\lambda$. Here γ is the nonlinear coefficient (measured in SI units), I_0 the laser radiation intensity in the focal plane, $L_{\text{eff}} = [1 - \exp(-\alpha_0 L)]/\alpha_0$ the effective length of the sample with α_0 being the linear absorption coefficient and L being the sample length. The nonlinear refractive index n_2 (measured in units of esu) and γ are connected by the relation γ (m^2 W^{-1}) = $40\pi n_2(\text{esu})/c(\text{m}\cdot\text{s}^{-1})n_0$, where c is the velocity of light and n_0 the linear refractive index. Considering the volume fraction of about 2×10^{-4}, we can assume an additive rule for nonlinear refractive index of the solution n_2:

$$n_2 = g n_{2\,qd} + (1-g) n_{2\,\text{solvent}}, \qquad (2)$$

where g is the volume fraction of the CdSeS/ZnS QDs relative to chloroform, n_{2qd} is the nonlinear refractive index of CdSeS/ZnS QDs, and $n_{2\text{solvent}}$ is the nonlinear refractive index of chloroform. As a result, the nonlinear refractive index n_2 is 2.7×10^{-11} esu in the case of pulse peak intensity at focus ($I_0 = 12.5\,\text{GW/cm}^2$). Based on Eq. (2) and $n_{2\text{solvent}} = 0$, we can easily obtain $n_{2\text{qd}} = 1.4 \times 10^{-7}$ esu.

For the open aperture Z-scan, the normalized transmittance $|q_0(z,0)| < 1$, $T(z)$ can be written as a simple series[21]

$$T(z) = \sum_{m=0}^{\infty} \frac{[-q_0(z,0)]^m}{(m+1)^{3/2}}, \tag{3}$$

$$q_0(z,t) = \frac{\beta I_0 L_{\text{eff}}}{1+x^2}, \tag{4}$$

where β is the TPA coefficient and other parameters are defined previously. We can easily extract the TPA coefficient β from Z-scan data by fitting the open aperture data using Eqs. (3) and (4). The TPA cross section δ_2 can be estimated using $\delta_2 = h\nu\beta/N$, where N is the number of molecules per cm^3 and $h\nu$ is the photon energy; β and δ_2 are 2.7 cm/GW and 18700 GM ($1\,\text{GM} = 10^{-50}\,\text{cm}^4\,\text{s photon}^{-1}$), respectively, at input intensity of $12.5\,\text{GW/cm}^2$.

We perform a set of Z-scans at different input intensities. The values of n_2, $n_{2\,qd}$, β and δ_2 are listed in Table 1. As shown in Table 1, the nonlinear refractive indices of CdSeS/ZnS QDs are in the range from 0.8×10^{-7} esu to 1.8×10^{-7} esu, which exceeds CdSe/ZnS QDs reported in Ref. [14] by several orders of magnitude. For β and δ_2, no TPA occurs at the input irradiance of $6.8\,\text{GW/cm}^2$, but TPA process appears at higher intensity, which may imply that the threshold for TPA occurrence is about $12.5\,\text{GW/cm}^2$. The average TPA cross section within the range from 12.5–22.6 GW/cm^2 is 13710 GM, which is higher than the ZnS QDs and several orders of magnitude larger than those of conventional fluorescent probes.[22]

In conclusion, we have investigated the two-photon absorption and nonlinear refractive index of CdSeS/ZnS QDs using Z-scan technique with 1064 nm picosecond laser pulse. The CdSeS/ZnS QDs possess a large TPA cross section, which can be applicable to the deep image and fluorescence label in biological samples. Moreover, the large nonlinear refractive indices allow them to be used in photoelectronic devices.

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