

The Influence of Surface Trapping and Dark States on the Fluorescence Emission Efficiency and Lifetime of CdSe and CdSe/ZnS Quantum Dots

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Abstract To investigate the influence of surface trapping and dark states on CdSe and CdSe/ZnS quantum dots (QDs), we studied the absorption, fluorescence intensity and lifetime by using one- and two-photon excitation, respectively. Experimental results show that both one- and two-photon fluorescence emission efficiencies of the QDs enhance greatly and the lifetime increase after capping CdSe with ZnS due to the effective surface passivation. The lifetime of one-photon fluorescence of CdSe and CdSe/ZnS QDs increase with increasing emission wavelength in a supralinear way, which is attributed to the energy transfer of dark excitons. On the contrary, the lifetime of two-photon fluorescence of bare and core-shell QDs decrease with increasing emission wavelength, and this indicates that the surface trapping is the dominant decay mechanism in this case.

Keywords Quantum dots · Fluorescence · One-photon excitation · Two-photon excitation · Lifetime

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Introduction

Semiconductor quantum dots (QDs) have been the research topic of growing interest in recent years for their particular optical properties of size-dependent tuning, high quantum yields, narrow fluorescence emission bands, etc [1–4]. The high surface-to-volume ratio of small nanocrystals suggests that the surface properties should have significant effects on their structural and optical properties [5, 6]. For higher quantum yield, the core-shell structure has been synthesized and confirmed that it could lead to the QDs with improved luminescence, higher stability [7, 8]. CdSe/ZnS colloidal nanocrystals are the typical QDs of this core-shell structure. Capping CdSe core with a shell of higher-band-gap material such as ZnS was found to increase the luminescence quantum yield significantly by passivating the CdSe surface traps [8]. Many studies have been carried out on the fluorescence emission efficiency of such core-shell structure, most of which are mainly focused on the syntheses of the core-shell structure and the method of improving the quantum yields, and in such studies the photoluminescence are considered under the linear absorption and the one-photon process (OPF) process [8–15]. For the potential applications of the QDs in many fields such as luminescence probes for bio-system, the research on the two-photon absorption (TPA) and two-photon fluorescence (TPF) properties of the QDs becomes important [15–17].

The research on the fluorescence lifetime is helpful to reveal the energy decay mechanisms. Two important factors which influence the excitons' decay rate are dark excitons and the surface states. It is reported that due to the effect of the dark excitons, the OPF lifetime of the QDs would increase largely [18–25]. And the surface states could reduce the OPF lifetime of QDs [26–33]. But the research

on the frequency dependent lifetime of two-photon fluorescence lifetime is seldom reported. In this paper, we investigate the effects of dark excitons and the surface traps on CdSe and CdSe/ZnS QDs by studying the absorption, fluorescence intensity and lifetime with one- and two-photon excitation, respectively.

Experimental

The bare CdSe QDs and CdSe/ZnS core-shell QDs were synthesized according to the procedure reported in the previous literature [34]. The average sizes of CdSe and CdSe/ZnS core-shell QDs are about 2.98 nm and 3.75 nm, respectively. In the preparation of the samples, the size of the CdSe core in CdSe/ZnS QDs is controlled to be the same with the bare CdSe QDs, and the molarities of the two solutions are also the same. The concentration of CdSe QDs is about 0.8 mg/ml, and CdSe/ZnS QDs is about 2 mg/ml. The linear absorption spectra of CdSe and CdSe/ZnS core-shell QDs are recorded by UV-VIS-NIR spectrophotometer (Cary 5000, Varian). The path length of the sample cell containing QDs is 1 mm. The two-photon absorption properties of the samples were measured by open-aperture Z-scan technique at 800 nm. The decay curves were obtained by time-correlated single photon counting (Time-Harp 200, PicoQuant GmbH). The sample was excited with a femtosecond (fs) pulsed laser and detected with a CCD detector (SPEC-10, Princeton) through a monochromator (Spectrapro 2500i, Acton). The pulsed laser is provided by a Ti:Sapphire laser (Mira 900, Coherent) with pulse width of 130 fs and repetition rate of 76 MHz.

Results and discussion

Linear absorption and emission efficiency of one-photon fluorescence

Figure 1 is the absorption spectra of CdSe and CdSe/ZnS QDs with the same molarity. The absorption peaks of CdSe and CdSe/ZnS QDs center at 547 nm and 580 nm, respectively. At the excitation wavelength 400 nm, the linear absorption coefficient of CdSe/ZnS QDs is $\alpha_{C-S} = 8.53 \text{ cm}^{-1}$, and that of CdSe QDs is $\alpha_C = 4.38 \text{ cm}^{-1}$, which give the value of ratio $\alpha_{C-S}/\alpha_C = 1.95$.

The OPF spectra of CdSe and CdSe/ZnS QDs under the same excitation intensity at 400 nm are presented in Fig. 2. The peak for CdSe QDs centers at 560 nm, and for CdSe/ZnS QDs is 590 nm. The full widths at half-maximum (FWHM) of the fluorescence spectra for CdSe and CdSe/ZnS are almost the same, about 28 nm. The ratio of the OPF peak intensity of CdSe/ZnS to that of CdSe with the

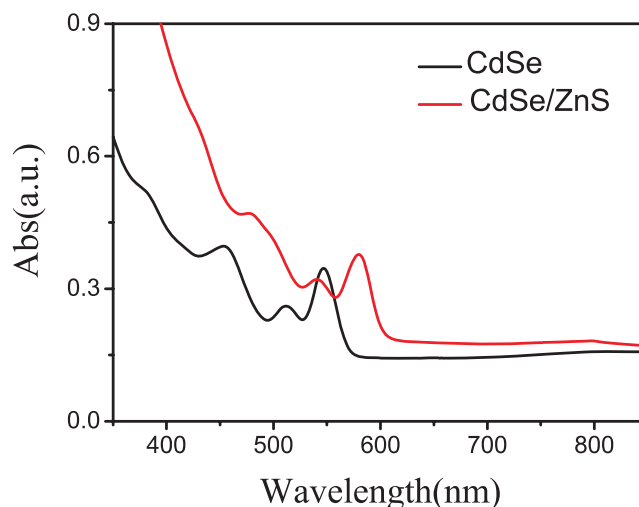


Fig. 1 Linear absorption spectra of CdSe and CdSe/ZnS core-shell QDs in *n*-hexane

same molarity is $I_{C-S}^{OPF}/I_C^{OPF} = 7.7 : 1$, which indicates that the ratio of the emission efficiency of the core-shell QDs to that of bare QDs is $\eta_{C-S}^{OPF}/\eta_C^{OPF} = (I_{C-S}^{OPF}/I_C^{OPF})/(\alpha_{C-S}/\alpha_C) = 3.9$. The results above demonstrate that the surface traps are effectively depressed after capping the ZnS shell. We conclude that the surface properties have significant effects on the emission properties of the QDs. There are lots of surface unsaturated bonds on the surface of CdSe forming the gap surface states. Part of the electrons excited to the conduction band would first transfer to the surface states lying in the mid band gap, and then recombine nonradiatively with the holes in the valance band, correspondingly reducing the emission intensity. Capping the CdSe core with a shell of higher-band-gap material ZnS could passivate the surface traps of CdSe, so that the possibility of the nonradiative recombination of the surface states would decrease.

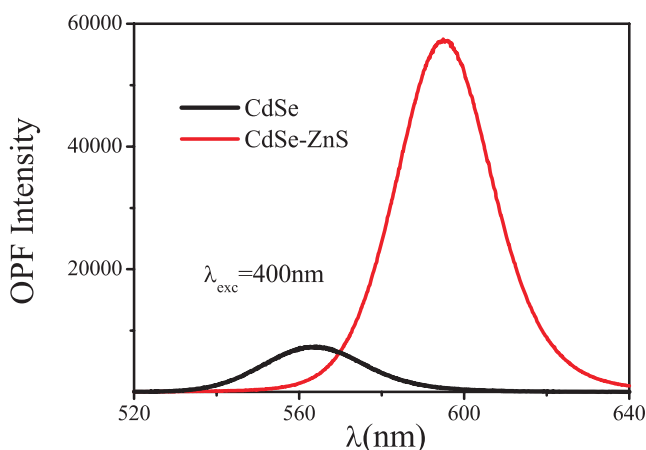


Fig. 2 OPF spectra of CdSe and CdSe/ZnS QDs. The excitation intensity is $70 \mu\text{W}$ and the ratio of the emission peak intensities of CdSe/ZnS to CdSe is 7.7:1

Frequency dependent lifetime of one-photon fluorescence

The frequency-dependence of OPF lifetime of CdSe/ZnS QDs is shown in Fig. 3a with solid line. A large increase of lifetime (from ~18 to 65 ns) is observed in this core-shell system. The OPF decay curve of CdSe/ZnS core-shell QDs at the emission peak 590 nm is shown in the inset. It is indicated that the fluorescence decay curves, at a given frequency, are very close to single exponential. One-component decay model fits the measurements very well. The extracted radiative lifetime τ_{rad} of OPF is 19 ns. The frequency-dependence of OPF lifetime of CdSe QDs is

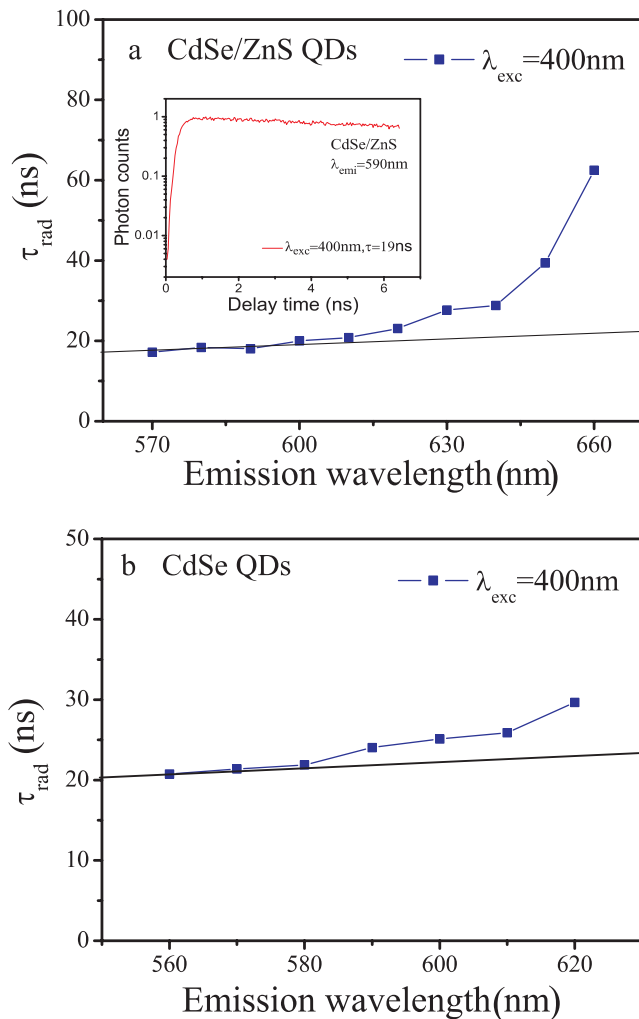


Fig. 3 **a** Frequency-dependent lifetime of one-photon fluorescence of CdSe/ZnS core-shell QDs. The OPF decay curve of CdSe/ZnS core-shell QDs at the emission peak 590 nm is shown in the inset. **b** Frequency-dependent lifetime of one-photon fluorescence of CdSe QDs. For the OPF, the lifetime increases with increasing emission wavelength. For the TPF, the lifetime decreases with increasing emission wavelength. The *dash lines* in **a** and **b** is a guide line of linear dependence through zero which show the frequency-dependence of fluorescence lifetime without the effect of dark excitons

shown in Fig. 3b with solid line. The dash lines in Fig. 3a and b are guide lines of linear dependence through zero which show the frequency-dependence of fluorescence lifetime without the effect of dark excitons. It is reported that the thermal occupation of dark excitons at room temperature leads to a supralinear increasing of fluorescence lifetime with the emission wavelength [21],

$$\tau_{rad} = A\lambda \left[1 + \frac{R^3}{6\sqrt{\pi}} \left(\frac{2m^*kT}{\eta^2} \right)^{3/2} \right] \quad (1)$$

where $\hbar = h/2\pi$, A is a constant, λ is the emission wavelength, m^* is the hole effective mass, k is the Boltzmann constant, T is the temperature, h is the Planck constant and R is the crystal radius, which determines the emission frequency. The theoretical calculated frequency-dependent of the OPF decay rate with the tide-binding model in Driel’s literature excellently fits the measured results of CdTe QDs [21]. Its OPF lifetime increases from 18 to 50 ns when the emission wavelength increases from 520 to 720 nm. In our experiment the frequency-dependent OPF lifetimes of both CdSe QDs and CdSe/ZnS QDs increase with the emission wavelength. However, the variations of the OPF lifetimes with emission wavelength of the core-shell structure are more obvious than those of the bare QDs. The reason is that not only the dark states could affect the fluorescence lifetime of the QDs, but also the surface traps play an important role on the lifetime. The thermal occupation of dark excitons leads to an increased fluorescence lifetime while the surface states reduce the radiative lifetime of the fluorescence. Since there are more surface defects on the bare CdSe QDs than the core-shell structure, the effect of the surface states of CdSe comes more obvious, and therefore, the OPF lifetime of CdSe is shorter than that of CdSe/ZnS.

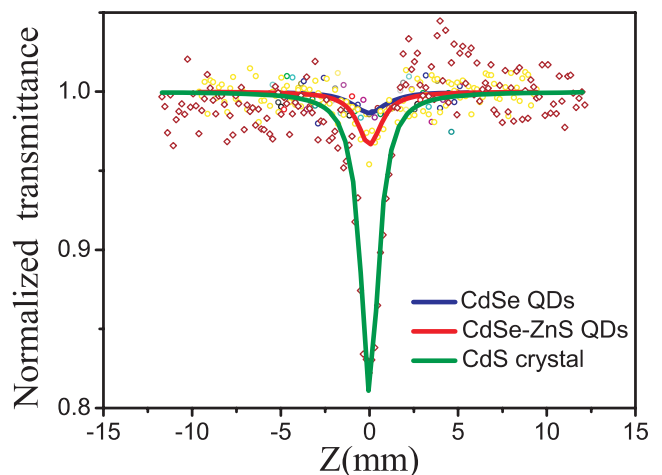


Fig. 4 Normalized open-aperture transmittance T_{OP} of CdSe, CdSe/ZnS core-shell QDs

Nonlinear absorption and emission efficiency of two-photon fluorescence

The two-photon absorption coefficients are measured by the open-aperture Z-scan method. The normalized transmittance of the open-aperture Z-scans of the thin film sample can be described by the relationship [35],

$$T_{OP}(z) = \sum_{m=0}^{\infty} \frac{(-q_0)^m}{(1 + z^2/z_0^2)^m (1 + m)^{3/2}} \quad (2)$$

where, $q_0 = \beta I_0 L_{eff}$ and $L_{eff} = [1 - \exp(-\alpha L)]/\alpha$, β is the two-photon absorption coefficients, α is the linear absorption coefficients, I_0 is the peak irradiance at the focus ($z=0$), L is the thickness of the sample, L_{eff} is the effective length of the sample, z is the displacement of the sample away

from the beam waist and z_0 is the Rayleigh length of the Gaussian incident beam.

The open-aperture Z-scans of CdSe, CdSe/ZnS QDs in n-Hexane and CdS crystal are shown in Fig. 4, which are obtained under the excitation wavelength 800 nm. The CdS crystal is a reference sample. The ratio of the two-photon absorption coefficient of CdSe/ZnS QDs to that of CdSe QDs with the same molarity is $\beta_{C-S}/\beta_C=2.33$.

Figure 5a is the TPF spectra of CdSe and CdSe/ZnS QDs under the same excitation intensity at 800 nm. For both structures, the peaks of TPF shift to shorter wavelength for about 0.5 nm comparing to the peaks of OPF. The power-dependence of the fluorescence intensity for CdSe and CdSe/ZnS QDs with the same molarity is shown in Fig. 5b. The slopes are 1.92 and 1.84 for CdSe and CdSe/ZnS QDs, respectively. This result indicates that the up-converted

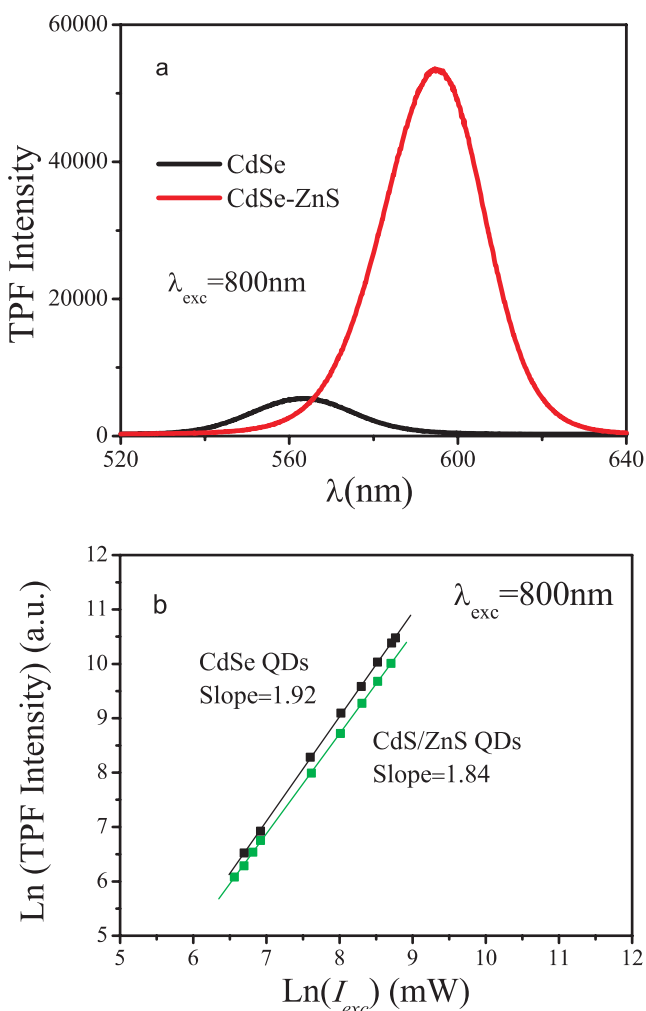


Fig. 5 **a** TPF spectra of CdSe and CdSe/ZnS QDs. The excitation intensity is 400 mW and the ratio of the emission peak intensities of CdSe/ZnS to CdSe is 9.7:1. **b** Power dependence of the PL intensity on the excitation intensity for TPF

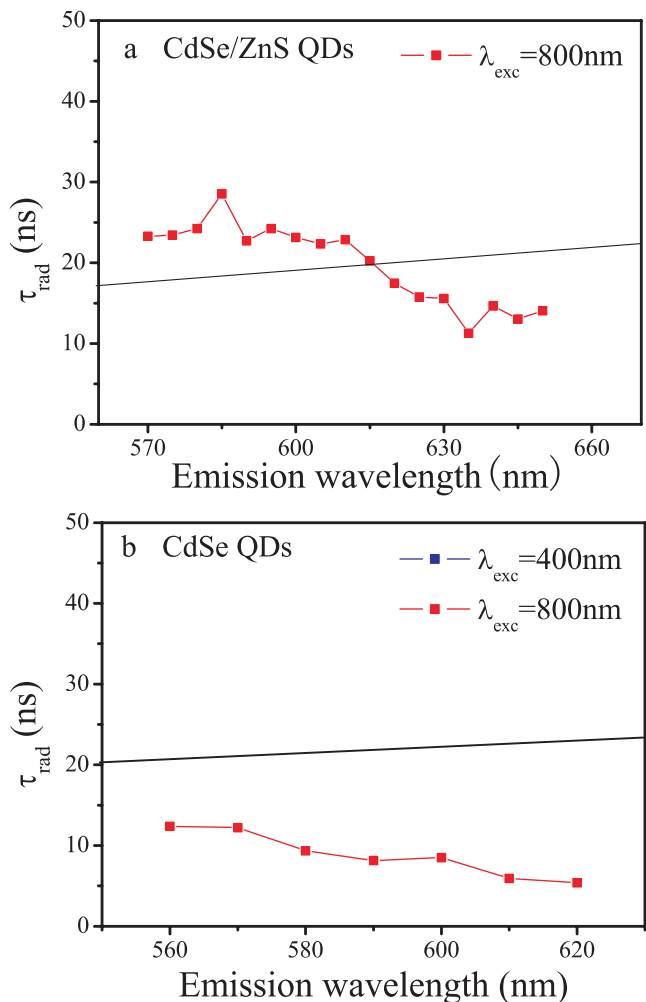


Fig. 6 **a** Frequency-dependent lifetime of two-photon fluorescence of CdSe/ZnS core-shell QDs. **b** Frequency-dependent lifetime of two-photon fluorescence of CdSe QDs. For the OPF, the lifetime increases with increasing emission wavelength. For the TPF, the lifetime decreases with increasing emission wavelength. The *dash lines* in **a** and **b** is same with those in Fig. 3a and b

fluorescence is induced by a two-photon excitation process. The ratio of the TPF peak intensity of CdSe/ZnS to that of CdSe is $I_{C-S}^{TPF}/I_C^{TPF} = 9.7 : 1$, so the ratio of the emission efficiency of CdSe/ZnS with core-shell structure to that of the bare CdSe QDs is $\eta_{C-S}^{TPF}/\eta_C^{TPF} = (I_{C-S}^{TPF}/I_C^{TPF})/(\beta_{C-S}/\beta_C) = 4.2$.

Frequency dependent lifetime of two-photon fluorescence

A quite different frequency-dependent lifetime of TPF of CdSe/ZnS QDs is shown in Fig. 6a with dot line. The dash lines in Fig. 6a and b are the same with those in Fig. 3a and b. The TPF lifetime decreases from 24 to 12 ns when the emission wavelength increases from 570 to 660 nm. This frequency dependence of lifetime can not be explained by the occupation of dark states, which implies another channel of excitonic energy transfer. The most possible mechanism of the decreased lifetime is the traps of surface hole, which is created by the two-photon excitations with the frequency below the absorption band of the QDs. It is reported that when the principal laser excitation is complemented with an infrared laser, the extra holes would appear in the QDs [27]. In our experiments when the QDs were excited by 800 nm, there would be the TPF as well as the surface holes. The surface holes could induce the mixing of dark and bright excitons, which leads to a large decrease in the radiative lifetime of the dark exciton [32]. Consequently, the corresponding fluorescence lifetime would decrease. The frequency-dependent lifetime of the bare QDs shown in Fig. 6b decreases from 12 ns to 5 ns when the emission wavelength increases from 560 nm to 620 nm. Comparing with the bare QDs, the TPF lifetime of the core-shell structure is always longer at the corresponding emission wavelength and the decreasing rate is relatively smaller, which is attributed to the depressing of surface traps. More precise explanation for the TPF lifetimes of CdSe/ZnS and CdSe decreasing with the emission wavelength remains to be further investigated.

Conclusions

The emission efficiency and the lifetime of fluorescence of CdSe and CdSe/ZnS core-shell QDs with the same molarity in n-hexane were investigated by using fs laser of 400 and 800 nm, respectively. At the excitation wavelength 400 nm, the linear absorption coefficient, peak intensity and the emission efficiency of one-photon fluorescence of CdSe/ZnS QDs is measured to be about 1.9, 7.7 and 3.9 times of those of CdSe QDs, and the lifetime of one-photon fluorescence increases with increasing emission wavelength in a supralinear way due to the energy transfer of dark excitons. At the excitation wavelength 800 nm, the two-

photon absorption coefficient, peak intensity and the emission efficiency of two-photon fluorescence of CdSe/ZnS QDs is measured to be about 2.3, 9.7 and 4.2 times of those of CdSe QDs, and the lifetime of two-photon fluorescence decrease with increasing emission wavelength, which is caused by the traps of surface holes.

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