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Size-dependent optical properties and carriers dynamics in CdSe/ZnS quantum dots*

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Size-dependence of optical properties and energy relaxation in CdSe/ZnS quantum dots (QDs) were investigated by two-colour femtosecond (fs) pump–probe (400/800 nm) and picosecond time-resolved photoluminescence (ps TRPL) experiments. Pump–probe measurement results show that there are two components for the excited carriers relaxation, the fast one with a time constant of several ps arises from the Auger-type recombination, which shows almost particle size-independence. The slow relaxation component with a time constant of several decades of ns can be clearly determined with ps TRPL spectroscopy in which the slow relaxation process shows strong particle size-dependence. The decay time constants increase from 21 to 34 ns with the decrease of particle size from 3.2 to 2.1 nm. The room-temperature decay lifetime is due to the thermal mixing of bright and dark excitons, and the size-dependence of slow relaxation process can be explained very well in terms of simple three-level model.

Keywords: semiconductor quantum dots, Auger-type recombination, time-resolved spectroscopy
PACC: 4265, 4280W

1. Introduction

Semiconductor quantum dots (QDs) whose radii are smaller than the bulk exciton Bohr radius (specifically, 5 nm for CdSe) represent a class of materials intermediate between molecular and bulk forms of matter, in which carrier motion is restricted in all three directions. Due to the three-dimensional (3D) quantum confinement QDs have atomic-like discrete energy spectra that are strongly size-dependent.[1] The spatial confinement for excited carriers can result in size-dependent electronic structure which dominates the optical properties of the semiconductor. Therefore, they can be good candidates for fabrication of QD lasers and diodes,[2] detectors,[3−5] biological labels,[6,7] displays,[8,9] solar cells,[10−12] gas sensors and other applications.[13−15] CdSe is one of the extensively studied semiconductor nanostructure materials because of the well-developed methods for fabricating high-quality samples and the potential realization of green laser diodes. In addition, the quantum confinement can further influence the dynamics of excited carriers in these materials, which provides a possible method to manipulate the excited state relaxation through monitoring the particle size.

Except for the size confinement effect, surface or interface effect also plays an important role in determining the optical properties and carrier dynamics in the semiconductor QDs. Surface states are generally localized in the band gap of the semiconductor, which can result in fast energy relaxation and defect state emission. In order to improve the QDs performance in lasers and diodes application, long chain organic molecules have been used to passivate the surface of the QDs. In addition to passivation with organic molecules, CdSe QDs can be overcoated with a layer of a wide-gap inorganic semiconductor shell such as ZnS, ZnSe etc.[16−20] The capping prevents uncontrolled growth and agglomeration of the QDs. It also allows QDs to be chemically manipulated as if they were large molecules, with solubility and chemical reactivity determined by the identity of the organic molecules. The capping also provides 'electronic' passivation of QDs. As discussed below,

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these capped QDs show narrow absorption and emission bands, such that semiconductor QDs are more applicable.

In this paper, the optical properties and excited carrier dynamics of CdSe/ZnS QDs, with CdSe core diameters of 2.1, 2.4, 2.6 and 3.2 nm, are systematically investigated with time-resolved spectroscopic methods including fs pump–probe and ps TRPL measurement. The excited carriers relaxation consists of two components that can be observed: the fast component with a time constant of several ps that shows almost size-independence, and the slow one that shows strong size-dependence. Combined with the size-dependent absorption and PL spectra, we suggest that the size-independent fast relaxation could be assigned to the Auger-type recombination, and the size-dependent slow relaxation is contributed by the thermal mixing of bright and dark exciton in the QDs. A simple three-level model is employed to explain the experimental results.

2. Experiments

The diameters of the CdSe cores studied were 2.1, 2.4, 2.6, and 3.2 nm with molar concentrations of 93.76, 69.6, 45.3, and 36 nmol/ml, respectively. The PL quantum yields of all samples reached 30%–50% at room temperature. X-ray diffraction measurements showed that the samples had a zinc blende structure. The solution was filled in a 5-mm-thick quartz cell used in steady PL spectra and TRPL characterization. For two-colour fs pump–probe measurement, a 1-mm-thick glass cell was used. All experiments were carried out at room temperature.

The absorption and steady PL spectra were recorded on a UV-vis diode array spectrophotometer and an Edinburgh Instruments FLS290 with an excitation source from Xe lamp in the wavelength range of 350–800 nm.

Measurements of ps TRPL spectra were carried out on a Lifespec-ps picosecond fluorescence lifetime (Edinburgh Instruments, U.K.). The light source is a picosecond pulsed diode laser. The wavelength, pulse width and average power on the sample are 405.2 nm, 64.7 ps and 5 mW respectively.

The ultrafast carrier relaxation was examined via two-colour fs pump–probe experiment. A high peak-power laser beam centred at 800 nm was delivered from a regenerative Ti: sapphire amplifier using chirped pulse amplification technique (RegA 9000, Coherent Inc.). The output pulse with a pulse width of 120 fs and repetition rate of 250 kHz was frequency-doubled in a 0.5 mm long BBO crystal to generate 400 nm pulse beams. A two-colour laser beam was divided into two beams by a dichroic mirror. The transmitted second harmonic generation (SHG) beam (centred at 400 nm) was used as pump beam, which was chopped at a frequency of 1320 Hz and passed through an optical delay driven by a computer-controlled step motor. The reflected fundamental beam was used as probe beam, and the two beams were focused on by a 10 cm-focal-length lens and overlapped on the same spot of the sample with a spot size of 100 μm. After passing through the sample, the pump beam was blocked with a non-transparent aperture, while the probe beam was guided to a photodiode connected to a lock-in amplifier.

3. Results and Analysis

The absorption spectra of CdSe/ZnS core/shell quantum dots with diameters ranging from 2.1 to 3.2 nm are shown in Fig.1, in which the first exciton absorptions peaked at 503, 525, 554, and 570 nm with respective dot diameters of 2.1, 2.4, 2.6 and 3.2 nm are contributed by 1S-1S transitions. It is well known that the blue-shift absorption spectrum with decreasing particle size arises from the quantum confinement; whereas the broadening of optical transitions appearing in the absorption spectra are primarily due to inhomogeneity of particle size distributions. With excitation wavelength at 405 nm, PL spectra of the four QDs are presented in Fig.2(a). The PL spectrum behaves the same evolution as that of absorption spectra, i.e. PL peak shifts to higher energy with decreasing particle size. It is seen that the room-temperature PL spectra of all samples show a narrow band edge emission only, no broad deep trap emission is observed, which indicates that the core (CdSe) was perfectly capped by the ZnS shell structure. The full width at half maximum (FWHM) of all emission spectra is less than 30 nm, indicating that the size variation is less than 5%; hence the high-quality sample shows that the material is good for colour multiplexing applications. Also the Gaussian (solid line) and Lorenz (dotted line) fittings to the PL spectrum of $D = 3.2$ nm

were shown in Fig.2(b). It is seen that the PL spectrum is not completely symmetric, the emission spectrum at longer wavelengths can be well fitted with Lorentz function, and that at shorter wavelengths can be reproduced very well with Gaussian function. The other three samples show very similar PL features to that in the case of $D = 3.2\,\text{nm}$. The origination of the asymmetry PL spectrum can be explained as follows. Firstly, although the CdSe cores were capped by the ZnS shell structure, there are still a few dangling bonds on the surface of CdSe core. The existence of the defect emission can contribute to the PL intensity at the longer wavelengths. Secondly, from the inset of Fig.2(b), it can be seen that there is some overlapping area between the PL and absorption spectra, which results in self-absorption phenomena, i.e. the part of emission was absorbed by itself, thus decreasing the PL intensity at the short wavelengths. Finally, as reported in Refs.[21, 22], there is excitation energy transfer from small QDs to large ones through tunnelling effects, and as a result, the PL intensity at the long wavelengths is higher than that at the shorter wavelengths. In addition, it is seen that the emission peaks show a red-shift with respect to the lowest 1S-1S absorption for all the four samples. This large shift, namely, the so-called Stokes shift, arises from Stokes effect. The maximum shift in our sample can reach 38 nm.

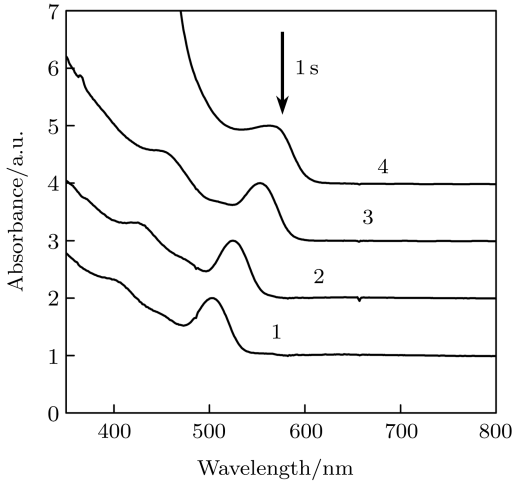


Fig.1. Absorption spectra of CdSe/ZnS core/shell QDs with particle size (1) 2.1, (2) 2.4, (3) 2.6, and (4) 3.2 nm.

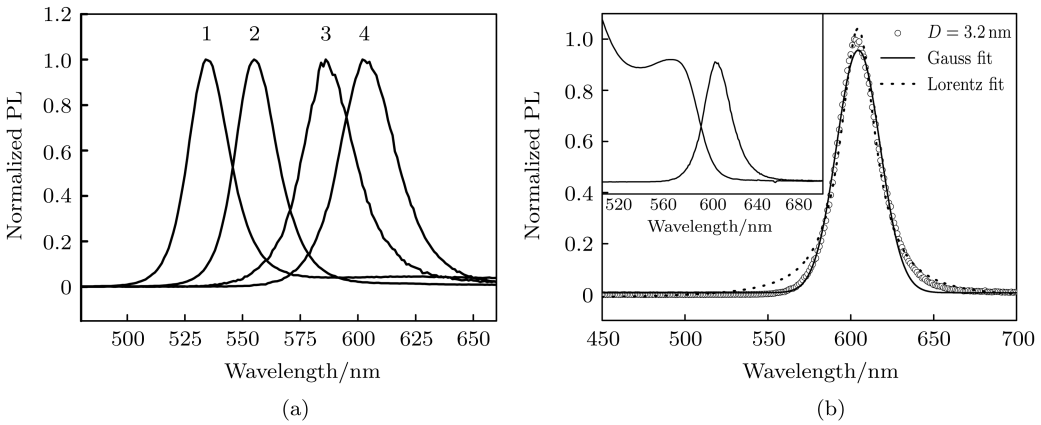


Fig.2. (a) Photoluminescence spectra of CdSe/ZnS QDs with particle size (1) 2.1, (2) 2.4, (3) 2.6, and (4) 3.2 nm; (b) Gaussian (solid) and Lorentz (dotted) fittings to PL spectrum of $D = 3.2\,\text{nm}$. The inset shows the absorption and PL spectra of $D = 3.2\,\text{nm}$ for comparison.

The lowest exciton state ($1S_{3/2(h)}1S_e$) is eightfold degenerate in the spherical band approximation for spherical dots.[23] However, anisotropy in the internal crystal structure and/or shape of the dots raises this degeneracy. The band edge state is split into two fourfold degenerate levels, analogous to the bulk 'A-B' splitting.[24,25] Also the band edge state is further split by the electron–hole exchange interaction. Since this term is proportional to the spatial overlap between the electron and hole wavefunctions, an enhanced exchange effect is expected in low-dimensional structures due to the increased overlap between the hole and electron wavefunctions. Therefore, this shift is thought to be due to a splitting of the lowest hole state as a result of crystal field and electron–hole exchange interactions. The high-energy fine-structure hole states are coupled to the 1S electron state by a strong transition that gives rise to an intense 1S absorption peak. The low-energy fine-structure state is responsible for the PL through a weaker transition.[2]

Time-resolved photoluminescence measurement (Fig.3) was performed to investigate size-dependent excited carrier relaxation. The TRPL spectra monitored at each emission peak for all the four samples are presented in Fig.2(a). It is clearly seen that (i) all TRPL curves show an ultrafast rising followed by two decay processes: the fast decay process with a time constant of tens of ns dominates the relaxation curve (more than 98%), and the slow process with a magnitude less than 2% shows a lifetime of hundreds of ns; (ii) the dominating initial decay shows strong size dependence (Fig.3 inset), i.e. the time constants increase with decreasing particle size.

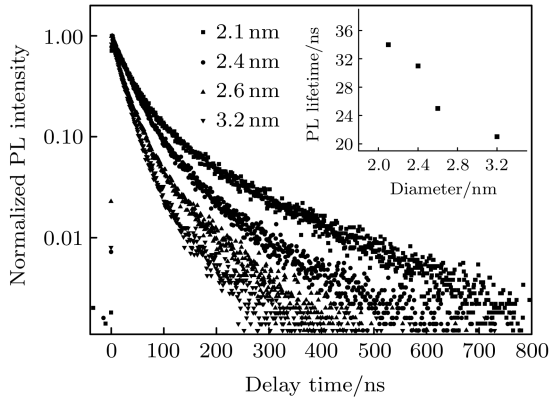


Fig.3. TRPL spectroscopy of CdSe/ZnS QDs monitored at the wavelength of each peak emission (as shown in Fig.2(a)). The inset shows the dominating PL lifetime as a function of particle size.

The size-dependence of lifetimes observed here is consistent with previous experimental data.[26,27] This trend can be explained in terms of band-edge exciton fine structure. In the QDs with zinc blende structure, using a perturbative approach,[28] the lowest exciton is split into a triplet with higher energy (bright exciton) and a quintuplet with a lower energy (dark exciton). The splitting energy is $\Delta E = E_{\rm b} - E_{\rm d} = 4\Delta_X$, where Δ_X is the electron-hole exchange parameter, depending on the particle size. As reported previously,[29] the room-temperature decay lifetime was contributed by the thermal mixing of bright and dark excitons. We have modelled the lifetime $\tau$with a simple three-level scheme as shown in Fig.4. By assuming Boltzmann distribution of excitons between these two levels (states b and d in the inset of Fig.4), the total decay rate can be written as[30]

$$\Gamma = \frac{\Gamma_d + \Gamma_b \exp(-\Delta E/k_{\rm B}T)}{1 + \exp(-\Delta E/k_{\rm B}T)}, \qquad (1)$$

where Γ_b and Γ_d are decay rates of bright and dark states, respectively. The decay lifetime $\tau(\Gamma^{-1})$ was obtained by choosing these parameters $\Gamma_d^{-1} = 1\,\mu$s, $\Gamma_d^{-1} = 8$ ns, $T = 297$ K as reported in Ref.[30]. Reduction in the QD size increases the confinement energies and the electron–hole wave function overlapping, thereby enhancing the electron–hole exchange interaction, and resulting in an increase of the energy gap ΔE. Therefore, we can conclude that the QD lifetime should decrease with increasing QD size according to Eq.(1), which is in agreement with our experimental observations.

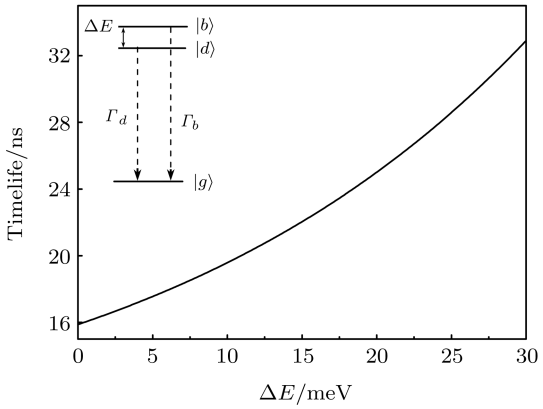


Fig.4. Modelled lifetime by using the simple three-level scheme according to Eq.(1), with $\Gamma_d^{-1} = 1\,\mu$s, $\Gamma_d^{-1} = 8$ ns, $T = 297$ K. The inset shows the three-level model, where $|g\rangle$ is the ground state, $|b\rangle$ and $|d\rangle$ are the triplet and quintuplet states, respectively. Γ_b and Γ_d denote the decay rates of bright and dark states, respectively.

The time resolution of TRPL is less than 10 ps due to the limited instrument response. In order to study the initial relaxation process that follows optical excitation, two-colour fs pump–probe measurement has been performed. The temporal evolution of transmittance change for the four CdSe solutions is shown in Fig.5. An ultrafast photo-induced absorption followed by a slow recovery process can be detected. The photo-induced absorption recovery process has two components, i.e., an initial fast recovery with a time constant of 7–10 ps followed by an extremely slow recovery. It is seen from Fig.5 that the time constant of the fast component almost keeps constant, indicating a particle size independence. While the slow component shows a nanosecond recovery process which is beyond the range of the optical delay line used in the pump–probe setup. In fact, the ns slow recovery process can be well-resolved with ps-TRPL measurement mentioned above.

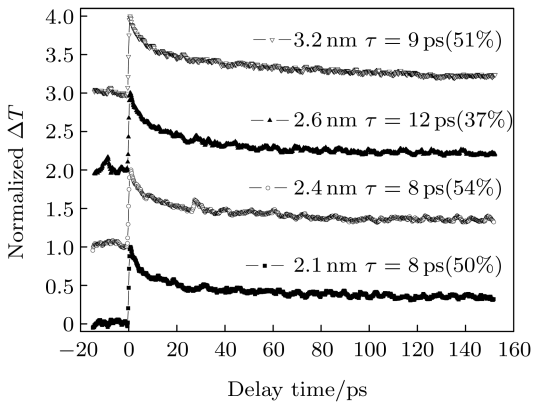


Fig.5. Carriers dynamics of the CdSe/ZnS QDs obtained by two-colour pump–probe measurement. The time constants and the amplitude of the fast component are given in the figure. The fast process is followed by a long slow decay of more than 1000 ps.

Energy relaxation following the optical excitation leads to the establishment of quasi-equilibrium populations of electron and hole quantized states. Depopulation of these states can occur via a variety of radiative and non-radiative mechanisms. The most important processes competing with the radiative one are carrier trapping at surface/interface states or Auger recombination. Most of the ultrafast studies of II-VI quantum dots have concentrated on QD/glass samples which have poorly-controlled surface properties. However, in CdSe samples used in the present studies, the surface-trapping process can be neglected because of almost perfect passivation with ZnS shell, which can be clearly seen from the PL spectra (Fig.2(a)).

The time-dependent spectra in Fig.5 are taken at a high pump fluence. Initial QDs population $< N_0 >$ can be calculated as $< N_0 >= \Phi_{\rm p}\sigma_0$, where $\Phi_{\rm p}$ is the pump fluence (photons/cm^2), σ_0 is the absorption cross section at the pump wavelength (σ_0(cm^2) = $1.6 \times 10^{-16}[R(\mathrm{nm})]^3$ at $\lambda = 400$nm).[31] Therefore, at high pump intensities (more than one e-h pair per QD on average), the carrier energy relaxation occurs mediated by Auger-type e-h energy transfer. Auger recombination which has a relatively low efficiency in bulk semiconductors is greatly enhanced in QDs because the translation symmetry is broken in QDs (the electrons feel the dot's boundaries). This effect is unavoidable in QDs, which is a major factor to hinder the development of QDs laser.

4. Summary

In conclusion, optical properties and excited state dynamics of CdSe nanocrystals with various particle sizes have been investigated with two-colour fs pump–probe and ps-TRPL experiments. The results reveal that the excited state dynamics of CdSe/ZnS core-shell nano-structure shows two relaxation processes, the fast relaxation with a time constant of several ps is likely mediated by Auger-type recombination which is almost size independent. The slow relaxation with a time constant of tens of ns shows a strong particle size dependence, which can be explained qualitatively in term of a simple three-level model. The results indicate that the room temperature lifetime is determined by the populations of bright and dark exciton states. Our calculation is in agreement with the result obtained by Califano *et al*[29] using atomic, semiempirical pseudopotential calculation.

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