Auger recombination and state filling of resonantly excited ground state in CdSe quantum dots

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Dynamics and state filling of the resonantly excited ground state ($1s^{e}$-$1S^{h}_{3/2}$) in a strongly confined CdSe quantum dot were investigated by degenerate pump-probe measurements. With increasing the electron-hole (e-h) pairs per dot the state filling and bleaching were observed with ~2.7 e-h pairs. While radiative recombination was dominant with a small number of the e-h pairs ($\ll 1$), the Auger-type recombination became significant near the bleaching number of e-h pairs (~2.7). This result suggests that, for resonant excitation, either cold electron or hole of the ground state is scattered into the higher-energy states of a ZnS shell via Auger recombination process (~28 ps).
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INTRODUCTION

Chemically synthesized nanocrystal quantum dots (NQDs) were proposed as a prospective gain medium for their size tunability, temperature insensitivity, narrow emission linewidth, low threshold power, and low cost in comparison with epitaxially grown QDs.[1,2] In the case of bare NQDs, the poor surface passivation gives rise to surface trapping which results in large nonradiative carrier loss. Although this problem is somehow suppressed by core-shell structure, still the intrinsic nonradiative Auger recombination was known to inhibit stimulated emission by limiting the gain lifetime.[2]

On the other hand, the Auger-type scattering is also very important to explain the fast carrier relaxation in a QD.[3–5] Energy relaxation in a zero dimensional QD is qualitatively different from that in bulk due to discrete energy levels. Since the level spacing is hundreds of meV in a few nanometer size NQD, more than ten LO phonons are necessary for the interlevel relaxation. Therefore, the intradot relaxation is expected to be very slow (~1 ns) in NQDs. This theoretical prediction was known as phonon bottleneck effect.[6] On the contrary, significantly faster relaxation time (~1 ps) has been observed in QDs,[5] and this result was attributed to the Auger-type e-h scattering; a rapid transfer of the electron energy to a hole in the valence band could occur via their Auger-type Coulomb scattering, and the hole could then relax very rapidly through its dense spectrum of states. A drastic decrease of the interlevel relaxation time for reducing the excitation density also supports the Auger-type e-h scattering.[7] As hot e-h pairs are generated for nonresonant excitation, the Auger effect is greatly enhanced by high energy carrier-carrier scatterings. But only few results have been reported for dynamics of resonantly excited cold e-h pairs[8,9] concerned with Auger recombination. When a quantum dot size (a) is larger than the excitonic Bohr radius (a_B), the so-called weak confinement regime, the onset of the Auger recombination for resonant excitation was verified over the exciton bleaching density, which implies that the Auger recombination becomes more efficient in e-h plasma than bound e-h pair states (exciton) for resonant excitation as in bulk materials.[9] However, in strong confinement regime ($a < a_B$), the confinement energy is much larger than the Coulomb binding energy between an e-h pair, so bleaching, in fact, originates from the state filling rather than the screening effect.

In this work, with increasing the number of e-h pairs, we investigate the dynamics of the resonantly excited ground state ($1s^{e}$-$1S^{h}_{3/2}$) in a strongly confined NQD. While the decay was characterized by radiative recombination with a small number of e-h pairs ($\ll 1$), we found that the initial fast decay becomes significant due to Auger recombination as the state is fully occupied.

EXPERIMENTS

The CdSe NQDs were synthesized with CdO and Se as precursors by the colloidal chemical process. Trioctylphosphine oxide (TOPO), stearic acid, tri-*n*-butylphosphine (TBP), and octadecine (ODE) were used as solvents. NQD size was controlled by varying reaction time. The unreached Cd and Se were extracted at the last step of the QD preparation. The final product of NQDs was dissolved in toluence as a nonpolar solvent. For ZnS shell coating on CdSe core, a ZnS solution was mixed with hexamethyldislathiane, dieth-

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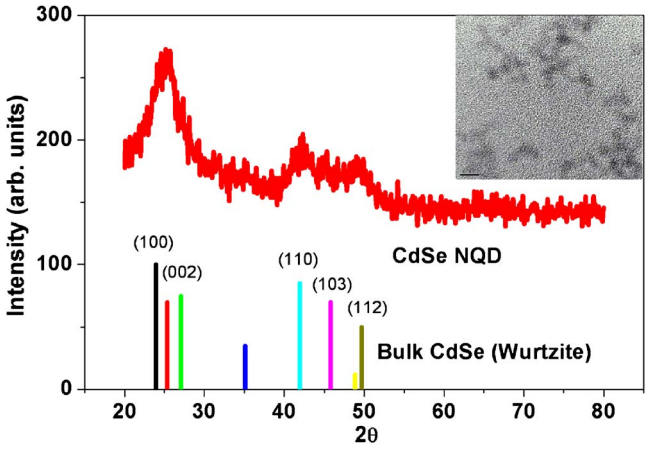

FIG. 1. (Color online) XRD pattern in CdSe NQDs is compared with that in bulk CdSe (bar), and the inset shows TEM image.

ylzine, and trioctylphosphine. The crystal structure and size of CdSe NQDs are determined by analyzing the the x-ray diffraction (XRD) pattern and the transmission electron microscope (TEM) image.

The degenerate pump-probe technique was performed at central wavelength of 578 nm. The 800 nm femtosecond seeding pulse was amplified in regenerative amplifier at a 1 kHz repetition rate (Spectra-Physics, Hurricane), and the wavelength was tuned at homemade optical parametric amplifier (OPA) system. The pump power, which is available up to 100 nJ, was modulated by mechanical chopper with 200 Hz. The probe beam with the fixed weak energy of 0.3 nJ was detected by Si photodiode combined with a lock-in amplifier. The linear polarization of the pump and probe beams is aligned mutually orthogonal and the pulse duration was estimated 140 fs by autocorrelation. As a measure of absorption change ($\Delta\alpha=\alpha-\alpha_0$) with the sample thickness d differential transmission $\Delta T/T_0=[T_p(t)-T_0]/T_0 \approx -\Delta\alpha d$ was analyzed, where $\Delta T/T_0$ and $\Delta\alpha/\alpha_0$ are the transmittance and absorption coefficients with/without the pump, respectively.

RESULTS AND DISCUSSION

Figure 1 shows the XRD pattern of CdSe NQD powder prepared with colloidal form. The bars at the bottom of Fig. 1 represent the XRD peaks of bulk CdSe in a wurtzite structure, the pattern of which has the (100), (110), and (112) peaks. Comparing the XRD pattern of the NQDs with that of bulk CdSe, we concluded that CdSe NQDs are crystallized in wurtzite structure. The dot size can be calculated with the full width of half maximum (FWHM) of the XRD peaks. The relationship between dot size and FWHM is given by the Scherrer equation $L=0.9\lambda/R_\theta \cos\theta$. Assuming dot to be a sphere, the dot size $L=2.90\pm0.25$ nm was estimated at the maximum XRD peak, where the x-ray wavelength ($\lambda=1.5405$ Å), FWHM of a XRD peak ($R_{2\theta}=5.06\times10^{-2}$ rad), and the Bragg angle of the peak ($2\theta=25°$) are given. The TEM image of the CdSe QD powder in Fig. 1 also reveals that the size of CdSe NQDs is close to 2.9 nm.

An overcoat treatment with ZnS for better surface passivation was assessed by Stokes shift of the photoluminescence spectrum. As shown in Fig. 2(a), narrower photoluminescence emission spectra with a significantly reduced Stokes shift (25 meV) were achieved in comparison with the absorption spectrum, otherwise broad spectral tail below the absorption edge would be seen due to the trap states of a NQD core. The instrinsic small Stokes shift in core-shell structures was attributed to a splitting of the lowest hole state due to crystal field and electron-hole exchange interactions. The ground state ($1s^e$-$1S^h_{3/2}$) was identified in the absorption spectrum.

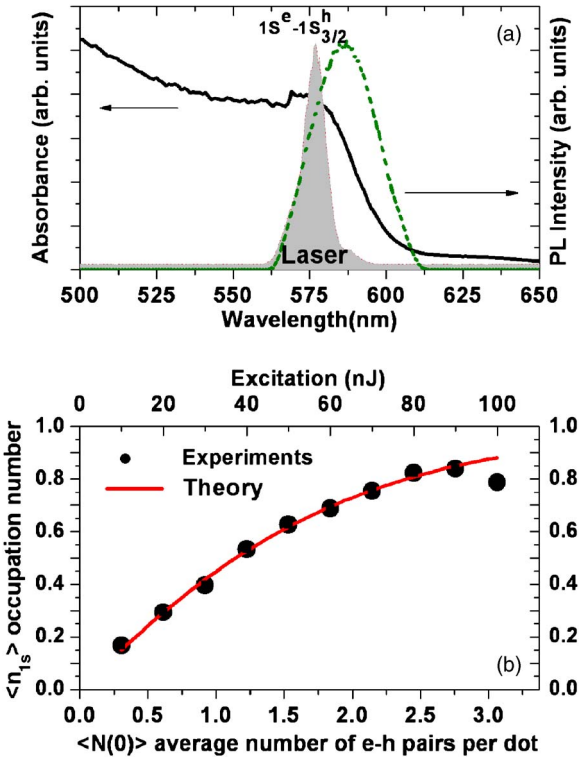

FIG. 2. (Color online) (a) Absorbance and photoluminescence spectra in core-shell structure CdSe/ZnS NQDs at room temperature. Note the laser is tuned resonantly at the ground state ($1s^e$-$1S^h_{3/2}$). (b) Pump dependence of the $1s^e$-$1S^h_{3/2}$ bleaching.

Regarding the excitonic Bohr radius of 5.3 nm in bulk CdSe, our sample belongs to the strong confinement regime. In fact, we obtained that the zero-point kinetic energy of electron and hole due to confinement (402 meV) is considerably larger than the excitonic binding energy ($R_y^*=13.2$ meV). In this case, the uncorrelated motion of an electron and hole may be considered as the first approximation, and the Coulomb interaction gives a small correction. Theoretically, the energy of the ground state (E_{1s1S}) (Ref. 10) can be expressed as

$$E_{1s1S}=E_g+\pi^2\left(\frac{a_B}{a}\right)^2R_y^*-1.76\left(\frac{a_B}{a}\right)R_y^*-0.248\left(\frac{a_B}{a}\right)R_y^*, \quad (1)$$

where the second term is attributed to the confinement effect and the other terms to the effective Coulomb interaction, respectively. For a given $E_{1s1S}=2.14$ eV in the absorption spectrum, the band gap ($E_g=1.74$ eV) and exciton binding energy (R_y^*) in bulk CdSe, the QD size of 2.87 nm was ob-

tained. This value is similar to that of the XRD result (2.90 +0.25 nm).

In bulk system, the Coulomb interaction between electron and hole is expected to become screened with increasing density. As the electron and hole become dissociated, no bound state is allowed. Instead the new phase of the electron-hole plasma occurs. This should lead to a bleaching of the exciton resonance. However, in a quantum dot, the Mott-like transition is no more valid to explain the exciton bleaching unless QD size is larger than the excitonic Bohr radius. Rather the Pauli exclusion principle governs the state filling in the strong confinement regimes. Therefore, the maximally allowed number of e-h pairs in a single dot can be estimated via resonance bleaching.

When $\langle N\rangle$ e-h pairs per dot are generated in average, the probability of containing m e-h pairs in a certain dot follows the Poisson distribution $P(m)=\langle N\rangle^m \exp(-\langle N\rangle)/m!$. The average occupation number of the $1s^e$-$1S^h_{3/2}$ state is described as[11]

$$\langle n_{1s1S}\rangle = 1 - \exp(-\langle N\rangle)(1 + \langle N\rangle/2). \tag{2}$$

As the laser was tuned at the $1s^e$-$1S^h_{3/2}$ state as shown in Fig. 2(a), the absorption saturation of the ground state was measured at the initial rising time (~1 ps) for increasing the excitation power. The average occupation number $\langle n_{1s1S}\rangle$ was measured by the normalized absorption change $(\Delta\alpha/\alpha_0)$. The average number of e-h pairs per NQD $\langle N\rangle$ is calculated from $\langle N\rangle=\sigma_A J_p$,[12] where J_p and σ_A are the excitation photon flux and NQD absorption cross section, respectively. J_p was estimated from the excitation power with the spot size (78 μm), which was obtained by high resolution scaled image. The correction of glass sample container loss and effective absorption volume were also considered. The absorption cross section of the ground state ($1s^e$-$1S^h_{3/2}$) was also obtained $\sigma_A=5.17\times10^{-15}$ cm^2.[12] Figure 2(b) shows the filling of $1s^e$-$1S^h_{3/2}$ state as increasing the average e-h pairs per dot. The absorption change is expected to have a linear dependence on the excitation density in the weak confinement regimes, but nonlinear dependence of the excited e-h pairs was observed in strongly confined NQDs, as shown in Fig. 2(b). The state filling of $1s^e$-$1S^h_{3/2}$ was well described with Eq. (2).

Although bleaching occurs when average 2.7 e-h pairs are occupied only 82% saturation was observed. This value is quite similar to other work of CdSe NQDs embedded in borosilicate glass.[8] As the excitation power increases it was known that the biexciton (or two e-h pair) states are observed as pronounced induced absorption features on the high energy side of the bleached single e-h pair resonances. Therefore, the incomplete bleaching could be related to the biexcitonic effect. Interestingly, the occupation number drop was seen beyond the bleaching e-h pairs. This is possibly attributed to the coherent Rabi oscillation in an inhomogeneous broadening system.[13]

Figure 3(a) shows the decay of the normalized average population $N(t)/N(0)$ for different numbers of the excited e-h pairs. With a small number of e-h pairs ($\ll$1) the radiative recombination dominates the monoexponential decay with the characteristic time (~448 ps). However, as the number of e-h pairs increases the initial decay feature becomes faster. Various recombination processes in semiconductors are described in the rate equation model as

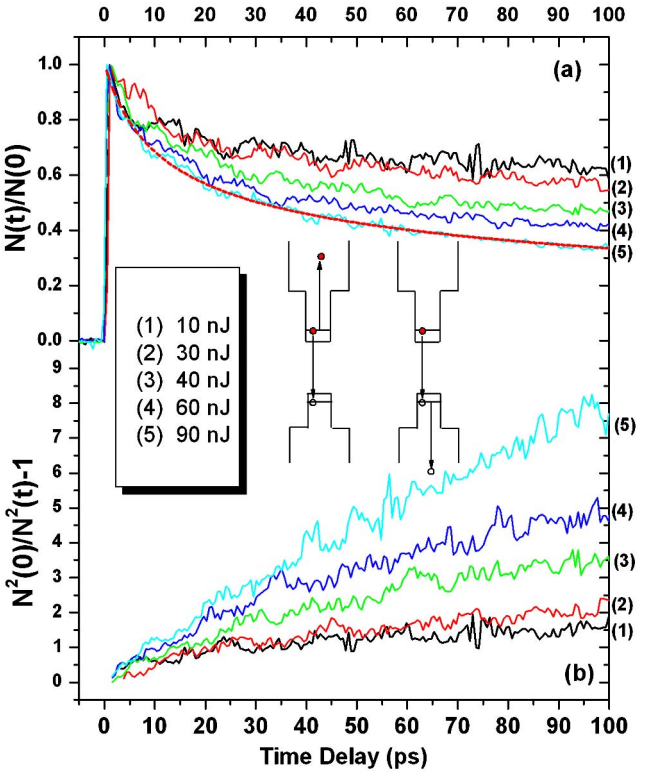

FIG. 3. (Color online) (a) Pump-dependent dynamics of the normalized $1s^e$-$1S^h_{3/2}$ population $N(t)/N(0)$. (b) The Auger-type recombination at bleaching power is verified with linear time dependence from Eq. (4). As pictorially described either electron or hole of the ground state is scattered into the higher-energy level of a ZnS shell via Auger recombination.

$$\frac{dN(t)}{dt} = -\frac{N^i}{\tau_i}, \tag{3}$$

where each process with characteristic time constant τ_i is known as radiative, bimolecular, and Auger recombination for i=1, 2, and 3, respectively. As our NQD is a case of the strong confinement the bimolecular decay due to e-h plasma can be ruled out. In order to identify enhancement of the fast initial decay, the solutions of Eq. (3) for i=3 are given as

$$\frac{N(t)}{N(0)} = \left[1 + 2\frac{N(0)^2}{\tau_i}t\right]^{-1/2}. \tag{4}$$

Hence $[N(0)/N(t)]^2$ shows a linear dependence on time in the Auger recombination. $[N(0)/N(t)]^2$-1 shows a significant linear dependence within ~100 ps with the bleaching number of 2.7 e-h pairs, as shown in Fig. 3(b). This result suggests that the fast short-term decay is enhanced due to the Auger recombination as e-h pairs are increased. The Auger recombination is a three-particle process so at least 1.5 e-h pairs are required, and the decay becomes faster as increasing the excited e-h pairs $N(0)$. The characteristic time constant τ_3~28 ps was also obtained by comparing the normalized population decay $N(t)/N(0)$ with a two-step decay model, where the Auger and radiative recombination dominates in short- and long-term decay, relatively. This theoret-

ical model describes data well as shown in Fig. 3(a) (dotted line). As momentum conservation vanishes in strong confinement regimes it was proposed that Auger recombination is characterized by quantized decays of the multiparticles.[4] This model was applied to the case of nonresonant excitation, but it was not successful to fit our resonant excitation case. Nevertheless, the characteristic time constant of Auger recombination $\tau_3 \sim 28$ ps with 2.7 e-h pairs is comparable with the quantized Auger recombination time of 3 e-h pairs ($\tau_3 \sim 21$ ps) in 2.3 nm size CdSe NQD for nonresonant excitation.[4] Assuming the band offset ratio of ~ 5.67,[14] the potential well of conduction (1.63 eV) and valence (0.29 eV) band in core CdSe/ZnS NQD were estimated with ZnS band gap of 3.66 eV. Considering the ground state electron energy (2.08 eV), the excitation energy involved with the Auger process exceeds the NQD potential well. Consequently, as the ground state is being filled by resonant excitation Auger recombination becomes activated. Either the cold electron or hole of the ground state is scattered into the higher-energy state of a ZnS shell via the Auger recombination process, as pictorially shown in Fig. 3.

SUMMARY

Size of core-shell CdSe/ZnS NQDs ($\sim$2.9 nm) was measured by XRD, TEM, and absorption spectrum. In comparison with a given excitonic Bohr radius of 5.3 nm in bulk CdSe, we confirmed that our NQD is case of the strong confinement where bleaching is governed by state filling. The bleaching of the resonantly excited ground state ($1s^e$-$1S^h_{3/2}$) was observed with 2.7 e-h pairs, and enhancement of the fast initial decay was attributed to Auger recombination. As a result, either cold electron or hole of the ground state is scattered into the higher-energy state of ZnS shell.

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