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Dynamics and Bleaching of Ground State in CdSe/ZnS Quantum Dots

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For resonant excitation of the ground state $1s^e-1S^h_{3/2}$, dynamics of the electron-hole pair in a CdSe quantum dot was investigated by degenerate pump-probe measurement. At low e-h pair densities, the decay of $1s^e-1S^h_{3/2}$ state is dominated by radiative recombination. As the number of the electron-hole pairs increases, new decay features become significant. Theoretical comparison suggests this is attributed to the bi-molecular and Auger-type scattering.

Keywords: Quantum dots, Exciton bleaching, Auger recombination, Exciton Dynamics

OCIS codes : 160.4760, 160.6000, 300.1030, 300.2140, 300.6500

I. INTRODUCTION

Chemically synthesized nanocrystal (NC) quantum dots(QDs) 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 epitaxial QDs [1-3]. In case of bare nanocrystals, the poor surface passivation of NC QDs gives rise to surface trapping, which results in large non-radiative carrier loss and inhomogeneous broadening. Although this problem is somehow suppressed by the core-shell structure, still the intrinsic non-radiative Auger recombination was known to limit stimulated emission despite observation of optical gain [4]. Stimulated emission can be achieved only if its build-up time is faster than the gain relaxation. The gain decay is determined by the Auger recombination. Therefore, unless the Auger-recombination is longer than the build-up time, stimulated emission never occurs.

On the other hand, the Auger-type scattering is also very important to explain the faster carrier relaxation in QDs. Energy relaxation in zero-dimensional QDs is qualitatively different from that in systems of higher dimensionality because the energy spectrum consists of discrete levels. Since the level spacings in QDs are larger than the optical phonon energy, intra-dot relaxation by optical phonon emission is expected to be very slow ($\sim$ 1 ns). This effect is known as the phonon bottleneck effect [5]. On the contrary, much faster relaxation time ($\sim$ 1 ps) has been reported in NCs although the level spacing in a few nm size NC is hundreds of meV. This value corresponds to more than 10 times of longitudinal optic-phonon energy, but sub-ps relaxation time between the 1P to 1S was observed in CdSe NCs [6]. Therefore, the Auger relaxation is a most likely channel to the fast relaxation. At the same time, it also determines the available time limit for stimulated emission. However, most of work has been investigated under the non-resonant excitation [3,7]. Even if the dynamics is monitored at the ground state (the so-called $1s^e-1S^h_{3/2}$) for non-resonant excitation, the higher energy levels are still occupied so the interruption such as carrier-carrier scattering is unavoidable. Only a few works have been reported for resonant excitation [7-8]. In the weak confinement regime, where a quantum dot size (a) is larger than the excitonic Bohr radius (a_B), the onset of the Auger recombination was identified as the Mott-like transition from excitons to electron-hole plasma. Thus, a question may arise in the case of the strong confinement regime under resonant excitation.

In this work, we investigate the dynamics of the ground state under resonant excitation in case of the size being smaller than the excitonic Bohr radius, the so-called strong confinement. While the decay is dominated by radiative recombination at low e-h pair densities, we found that not only the Auger process but also bi-molecular recombination are involved as the density increases.

II. EXPERIMENTS

The CdSe QDs were synthesized with CdO and Se as precursors by the colloidal chemical process. Trio-

ctylphosphine oxide (TOPO), stearic acid, tri-n-butylphosphine (TBP) and ODE (octadecene) were used as solvents. QD 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 QDs was dissolved in toluene as a non-polar solvent. For ZnS shell coating on CdSe QD, a ZnS solution was mixed with hexamethyldislathiane, diethylzinc, and trioctylphosphine.

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 system (OPA). The pump power, which is available upto 100 nJ, was modulated by mechanical chopper with 117 Hz, and the probe beam with the fixed power of 0.3 μW was detected by Si photo-diode combined with a lock-in amplifier. The linear polarization of the pump and probe beams is aligned to be mutually orthogonal, and the pulse duration was estimated 140 fs by autocorrelation. The position of the mechanical delay line was monitored by a feed-back circuit with 0.016 μm resolution accuracy. As a measure of absorption changes $\Delta\alpha = \alpha - \alpha_0$ differential transmission $\Delta T/T_0 = (T_p - T_0)/T_0 \sim -\Delta\alpha d$ was analyzed, where $T_p(T_0)/\alpha(\alpha_0)$ are the transmission/absorption coefficient with (without) the pump, respectively. d is the sample thickness.

III. RESULTS AND DISCUSSION

Preliminarily, an overcoat treatment with ZnS for better surface passivation was assessed by the photoluminescence spectrum. As shown in Figure 1 narrower photoluminescence emission spectra with a significantly reduced Stokes shift (25 meV) was achieved in comparison with the absorption spectrum, otherwise a broad spectral tail below the absorption edge would be seen. The intrinsic 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, and the ground state ($1s^e - 1S^h_{3/2}$) was identified in the absorption spectrum.

The transmission electron microscope image shown in inset of Figure 1 roughly shows the quantum dot size ranges around 3 nm. Regarding the exciton Bohr radius 5.3 nm of CdSe, our sample is likely to belong to the strong confinement regime. This implies that the confined electron and hole have no bound state corresponding to the hydrogen-like exciton, and the zero-point kinetic energy of electron and hole due to confinement is considerably larger than the exciton binding energy (Ry^*). 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 electron-hole pair state (E_{1s1S}) can be expressed as [9]

$$E_{1s1S} = E_g + \pi^2(\frac{a_B}{a})^2 Ry^* - 1.786(\frac{a_B}{a})Ry^* - 0.248Ry^*, \quad (1)$$

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 (578 nm) in the absorption spectrum, the band gap (E_g =1.74 eV), and exciton binding energy (Ry^* = 13.2 meV) in CdSe, the QD size was calculated 2.87 nm. This value is similar to that in the transmission electron microscope image shown in inset of Figure 1.

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 more bound state is allowed. Instead the new phase of the electron-hole plasma occurs. This should lead to a bleaching of the exciton resonance. In a quantum dot, the Mott-like transition is still valid to explain the exciton bleaching only if the QD size is larger than the exciton Bohr radius. However, in strong confinement regime ($a \ll a_B$), the confinement energy becomes much larger than the Coulomb interaction as described in equation (1). In this case, the Pauli exclusion principle governs the state-filling. Therefore, the bleaching (or full occupation) density indicates the maximally-allowed number of e-h pairs in a single dot.

When $<N>$ e-h pairs per dot are generated in average, which is proportional to the excitation photon number, the probability of containing N e-h pairs in a certain dot follows the Poisson distribution; $P(N) = <N>^N e^{-<N>}/N!$. Thus, the average occupation number of the $1s^e - 1S^h_{3/2}$ state is described as [10]

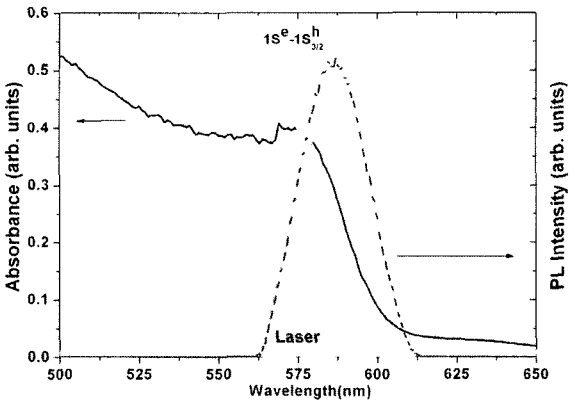

FIG. 1. Absorbance and photoluminescence spectra in core-shell structure CdSe/ZnS nanocrystals at room temperature. Note the laser is tuned resonantly at the ground state ($1s^e - 1S^h_{3/2}$), and inset is the TEM image.

$$< n_{1s1S} > = 1 - e^{-< N >}(1 + < N > /2). \quad (2)$$

For the laser being tuned resonantly at the $1s^e - 1S^h_{3/2}$ state as shown in Figure 1, the absorption saturation of the ground state was measured at the initial maximum population ($\sim$ 1 ps) for increasing the pumping power. The average occupation number ($<n_{1s1S}>$) was measured by the normalized absorption change ($\Delta\alpha/\alpha_0$), and the average number of e-h pairs ($<N>$) was estimated with the injection photon fluence and the absorption cross section as shown in Figure 2 [4]. In the weak confinement regime, the absorption change is expected to have a linear dependence on the exciton density as $\alpha(n) = \alpha_0(1 - n/n_s)$, where n and n_s are the excited and saturation density, respectively. However, the non-linear dependence on the number of e-h pairs was seen in our strongly-confined NC QDs, and the equation (2) describes well. Interestingly, the occupation drop was seen beyond the bleaching e-h pairs. This may be attributed to the Rabi oscillation. In an inhomogeneous broadening system, the similar phenomena have been observed in quantum dots by pump-probe measurements [11]. Unfortunately, higher pumping was limited in our system and the four-wave mixing technique would be more appropriate for this purpose.

Although the bleaching occurs when average 2.7 e-h pairs are occupied, which corresponds to 90 nJ excitation, it is incomplete occupation. Only 82% saturation was observed, and this value is similar to other work of CdSe NC QDs in borosilicate glass [3,8]. As the excitation power increases, it was also known that the biexciton (two e-h pair) states are observed as pronounced induced absorption features on the high energy side of the bleached exciton (single e-h pair) resonances in femtosecond pump-probe experiments of NC QDs [8]. Therefore, the incomplete bleaching could be related to the biexcitonic effect. As the number of the e-h pairs increases in a QD, biexcitons are more likely to be formed. Thus, the decay dynamics of the single e-h pair ($1s^e - 1S^h_{3/2}$) could be also influenced with the biexcitonic effect. Figure 3 shows the decay of the normalized average population $N(t)/N(0)$ at different average numbers of the excited e-h pairs. In the case of the non-resonant excitation, it was known that the long-term decay of the ground state is attributed to the radiative recombination, which is nearly constant for the different numbers of e-h pairs. In our resonant excitation case, long-term decays are also dominated by the radiative recombination with a characteristic life time ($\sim$ 448 ps). However, the initial decay feature changes significantly as the number of the e-h pairs increases.

Various recombination processes in semiconductors can be described in the rate equation model as

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

where the each process with coefficient τ_i is known as radiative, bimolecular, and non-radiative Auger recombination for i = 1, 2, 3, respectively. The each solution is given by

$$\frac{N(t)}{N(0)} = e^{-t/\tau_1}, \; i = 1 \quad (4)$$

$$\frac{N(t)}{N(0)} = (1 + \frac{N(0)^2}{\tau_2} t)^{-1}, \; i = 2 \quad (5)$$

$$\frac{N(t)}{N(0)} = (1 + 2\frac{N(0)^2}{\tau_3} t)^{-0.5}, \; i = 3 \quad (6)$$

At low e-h pair number of $<N(0)>$ = 0.3, the long-

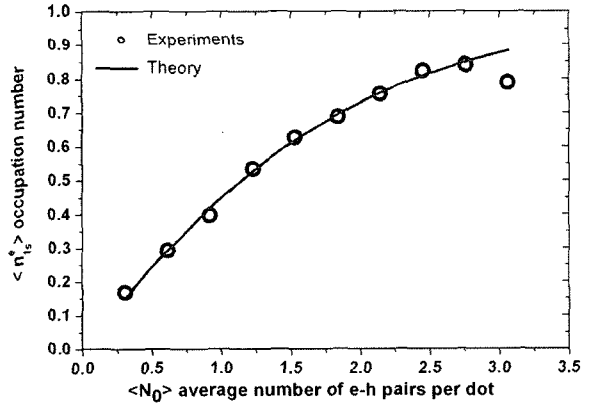

FIG. 2. The pump dependence of the normalized $1s^e - 1S^h_{3/2}$ bleaching.

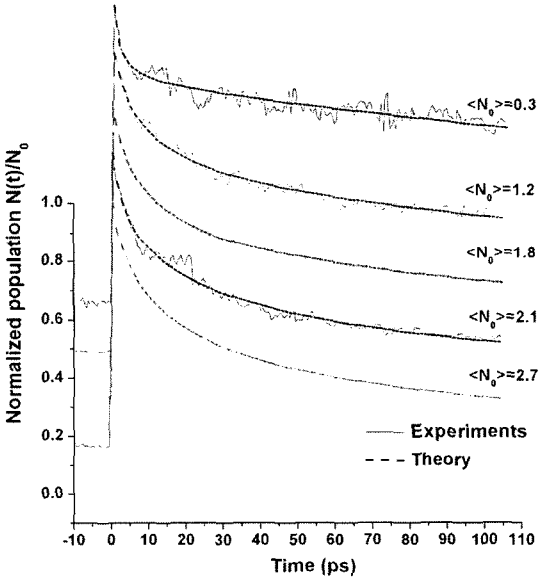

FIG. 3. The pump-dependent dynamics of the normalized average population ($N(t)/N(0)$) in a CdSe/ZnS NC QD. Each graph is shifted vertically for clarity.

term decay is dominated by radiative recombination after the fast initial decay occurs (< 5 ps). Our data was compared with the two-step decay model applying the non-radiative Auger ($i = 3$) and radiative recombination process ($i = 3$). Interestingly, the wiggly feature was seen despite suppressing laser fluctuation. This was also seen for the excitation tuned below the absorption resonance energy as in other recent report, which attributes to coherent LO-phonon oscillation [12]. As the number of initially excited e-h pairs ($N(0)$) increases up to 2, we found only the two processes are necessary for the best fit. However, when the number of e-h pairs exceeds 2 slight deviation becomes significant with the two-step decay model. This was compensated by including the bi-molecular decay model ($i = 2$). This result is consistent with the incomplete bleaching in figure 2, which was suggested to the biexcitonic effect. Consequently, one can conclude that as e-h pairs are increased over 2, the fast initial decay becomes significant due to the non-radiative Auger recombination and the competing the biexciton formation.

IV. CONCLUSIONS

Comparing the size of CdSe/ZnS NCs with the exciton Bohr radius, we confirmed our CdSe QDs is a case of strong confinement. Increasing the excitation power, the bleaching of the ground state was observed with 2.7 e-h pairs. With small e-h pairs ($\ll 1$), The short-term and long-term decay were characterized by the non-radiative Auger recombination and radiative recombination, respectively. As the e-h pairs exceed 2, we found that the biexcitonic effect also begins to contribute.

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