Temperature dependence of photoluminescence properties of water-soluble CdS quantum dots

Kunio Shimura, TaeGi Lee, and DaeGwi Kim*
Department of Applied Physics, Graduate School of Engineering, Osaka City University, 3-3-138, Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan
*tegi@a-phys.eng.osaka-cu.ac.jp

Abstract. We investigated the size dependence of band-edge photoluminescence (PL) dynamics for CdS quantum dots (QDs). The temperature dependence of the PL-decay profiles of CdS QDs with an average diameter of 3.7–6.0 nm was measured. The PL-decay profiles became longer as the temperature increased. Further, it was found that the temperature dependence of the PL-decay profiles depends greatly on the QD size. These experimental results can be understood by considering that the magnitude of the splitting energy between the bright- and dark-exciton states depends on the QD size and becomes larger as the QD size becomes smaller.

1. Introduction
The observation of an optically passive state, the so-called dark-exciton state, is a characteristic photoluminescence (PL) property of semiconductor quantum dots (QDs) [1,2]. Theoretical and experimental studies indicate that the splitting energy ($\Delta_{ST}$) between optically active bright- and dark-exciton states, which is less than 1 meV in the bulk crystal, increases from several meV to several tens of meV owing to the quantum confinement effect in QDs [3, 4]. CdSe QDs have been extensively studied as a model material for QD studies [5, 6]. Crooker et al. quantitatively explained the temperature dependence of the PL dynamics using a three-state model comprising a ground state and two excited bright- and dark-exciton states [7]. Compared to CdSe QDs, it is theoretically predicted that CdS QDs have a larger $\Delta_{ST}$ value [8, 9], and the contribution of dark excitons to the PL processes is considered to be large.

Previously, we prepared water-soluble CdS QDs in which the band-edge PL is observed as the main PL band [9]. In addition, film samples containing CdS QDs with an average grain size of 4.2 nm were prepared, and the temperature dependence of the PL dynamics was measured. We found that the dark-exciton state has a large influence on the PL processes, even at room temperature (RT), because $\Delta_{ST}$ has a value of 40 meV for CdS QDs with a diameter of 4.2 nm [9]. Since the value of $\Delta_{ST}$ largely depends on the QD size, it is important to investigate the size dependence of the PL dynamics. In this study, we investigate the size dependence of the band-edge PL dynamics in CdS QDs.

2. Experiments
CdS QDs were prepared by injecting H$_2$S gas into aqueous solutions containing Cd(ClO$_4$)$_2$ and sodium hexametaphosphate (HMP). The sizes of the CdS QDs were controlled using a size-selective photoetching technique [9]. The QD surface was modified by the addition of Cd(ClO$_4$)$_2$ after adjusting the pH of the solutions to the alkaline region. The sample solution was mixed with polyvinyl alcohol (PVA)
aqueous solutions, and the final solution was spread on glass. The excess water was evaporated by heating the glass to 80 °C for 2 h to obtain film samples, i.e., CdS QDs dispersed in PVA films.

For PL measurements, the 325-nm line of a He-Cd laser was used as the excitation-light source. Third-harmonic-generation light (355 nm) from a laser-diode-pumped yttrium aluminum garnet laser with a pulse duration of 20 ns and a repetition of 10 kHz was used as the excitation light for measuring the PL-decay profiles.

3. Results and discussion

Figure 1 shows the absorption and PL spectra of CdS QD solution samples with mean diameters of 3.7, 4.9, and 6.0 nm. Note that band-edge PL is clearly observed in all the samples. This makes it possible to study the PL dynamics in detail. QD-dispersed PVA film samples were prepared to investigate the PL characteristics at low temperatures as well as their temperature dependence.

The temperature dependence of the PL spectra was measured. Band-edge PL was observed as the main PL band at all temperatures ranging from 10 K to RT (not shown). The PL intensity at RT is ~60% of that at 20 K. Therefore, the influence of thermal quenching is small. These results suggest that the prepared CdS QDs are suitable for detailed studies of the temperature dependence of PL dynamics.

Figure 2 shows the decay profiles of band-edge PL at 10, 100, and 200 K for CdS QDs with mean diameters of 3.7, 4.9, and 6.0 nm, respectively. In this temperature range, the PL-decay profiles become longer as the temperature increases; the temperature dependence of the 3.7-nm QDs is smaller than that of the other two larger QDs. The decay profile at 200 K has a slow decay time of the order of hundreds of nanoseconds. This long decay-time component suggests a contribution by the optically passive dark-exciton state to the PL processes [9]. Usually, as the temperature increases, the non-radiative-decay rate increases, and the PL intensity and PL decay time decrease; however, the observed PL-decay profiles became longer with increasing temperature. In Ref. [9], we proposed a three-state model consisting of a ground state and two excited states (a lower-lying bound-exciton state and a higher-lying dark-exciton state), to explain the anomalous temperature dependence of PL dynamics. With increasing temperature, the thermal population of the higher-lying dark-exciton state becomes larger, and the PL-decay time becomes longer.

The observed PL-decay profiles exhibit multi-exponential decay. To quantitatively discuss the PL-decay profiles, we used a combination of monoexponential function and stretched-exponential function [9]: 

\[ A_1 \exp(-t/t_1) + A_2 \exp\left(-\left(t/t_2\right)^\beta\right). \]

As discussed in Ref. [9], the decay components, \( t_1 \) and \( t_2 \), correspond to the decay times of the bright-exciton state and that characterized by the three-state model, respectively. As an example, the fitting results of the PL-decay profiles in 4.9-nm CdS QDs are shown.
by the open circles in figure 2(b). The fitting results and the experimental results demonstrate agreement.

The temperature dependence of the decay times of $\tau_1$ and $\tau_2$ obtained from the analysis of the PL-decay profiles in each sample are shown in figures 3(a)-3(c). In CdS QDs with diameters of 4.9 and 6.0 nm, $\tau_2$ becomes longer with increasing temperatures up to ~180 K and becomes shorter in the temperature region higher than 200 K. The temperature dependence of $\tau_2$ in the temperature range up to 180 K qualitatively corresponds to the temperature dependence of the decay time characterized by the three-state model [9]. The decay time of $\tau_1$ becomes longer with increasing temperature in the higher-temperature region. Conversely, for smaller CdS QDs with diameter of 3.7 nm, both $\tau_1$ and $\tau_2$ are nearly independent of temperature.

The value of $\Delta_{ST}$ in 6.0-nm CdS QDs is ~9 meV [10], which is smaller than the thermal energy at RT. As a result, $\tau_1$, which reflects the decay time of the bright-exciton state, becomes longer with increasing temperature in the high-temperature region owing to the thermal-energy-assisted mixing of bright- and dark-exciton states, which was not considered in smaller-sized CdS QDs having a large $\Delta_{ST}$ [9]. Because $\Delta_{ST}$ in 3.7-nm CdS QDs is ~50 meV [10], there is no influence of the mixing of bright- and dark-exciton states on them. Therefore, $\tau_1$ and $\tau_2$ are considered to be constant regardless of the temperature.

Finally, we quantitatively discuss the temperature dependence of the PL-decay time. In Ref. [11], a simple approach to evaluate the distribution of the decay time and the statistical average PL-decay time $\langle \tau \rangle$ from experimentally observed stretched-exponential PL decays was presented. Figure 3(d) shows the temperature dependence of $\langle \tau_2 \rangle$ in 4.9-nm CdS QDs. Based on the three-state model, the temperature dependence of the decay time is expressed by the following equation [9]:

$$\tau = \frac{1}{\tau_{1n}} \left( \frac{1}{g_{Dx}} + \frac{1}{g_{Bx}} \right) \exp \left( -\frac{\Delta E}{k_B T} \right) \left( 1 + \frac{1}{g_{Dx}} \exp \left( -\frac{\Delta E}{k_B T} \right) \right).$$  (1)

Here, $1/\tau_{1n}$ ($1/\tau_{2n}$) denotes the radiative-decay rate, $g_{Dx}$ ($g_{Bx}$) denotes the density of states of the dark-exciton (bound-exciton) state, and $\Delta E$ corresponds to the energy difference between the dark- and bound-exciton states.

The broken curve in figure 3(d) represents the result calculated using equation (1) with $\tau_{Dx} = 1600$ ns, $\tau_{Bx} = 25$ ns, $\Delta E = 8$ meV, and $g_{Dx}/g_{Bx} = 90$. This result demonstrates agreement with $\langle \tau_2 \rangle$ becoming longer as the temperature increases up to ~180 K. Conversely, at temperatures higher than 180 K, the experimental result shows a decreasing behavior, while the calculated result continues to increase gradually. This discrepancy appears to be due to the influence of the non-radiative recombination process, i.e., thermal-quenching at temperatures higher than 180K. To consider the influence of the non-radiative recombination process, we assumed the following thermally active non-radiative process:
\[ \frac{1}{\tau_n(T)} = \frac{1}{\tau_n(0)} \cdot \exp\left(\frac{-E_a}{k_B T}\right), \]

where \( E_a \) represents the thermal-activation energy for the non-radiative process. The solid curve in the figure shows the result calculated using the parameters of \( \tau_n(0) = 8 \text{ ns} \) and \( E_a = 120 \text{ meV} \). This result quantitatively explains the temperature dependence of \( \langle \tau_2 \rangle \). Therefore, we can explain the PL-decay time becoming shorter in the high-temperature region (higher than 180 K) by considering the thermally activated non-radiative recombination process.

4. Conclusions

The size dependence of the PL dynamics in CdS QDs prepared by the colloid method was investigated. In all the samples, band-edge PL was clearly observed. The PL intensity at RT is \( \sim60\% \) of that at 10 K, demonstrating that the non-radiative recombination process is remarkably suppressed. The PL-decay profiles show a peculiar behavior different from ordinary semiconductors, in which the decay time increases with temperature. The temperature dependence of the PL-decay time can be quantitatively explained using a three-state model assuming dark- and bound-exciton states.

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