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

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Abstract. We have investigated the optical properties of ZnSe quantum dots (QDs) prepared by a hydrothermal method. The photoluminescence (PL)-decay profiles become slower with an increase in temperature up to 160 K, contrary to an ordinary behaviour due to thermal quenching. The temperature dependence of the PL-decay profile is explained by a three-state model consisting of a ground state and two excited states of the lower-lying bound-exciton and higher-lying dark-exciton states. The analysis of the temperature dependence of the decay time indicates that the dark-exciton state contributes to the PL-decay process in the ZnSe QDs.

1. Introduction

Many studies have been conducted from a scientific viewpoint to understand the intrinsic nature of physical/chemical properties of semiconductor quantum dots (QDs) as well as from an interest in the application to new functional materials. The band-gap energy of ZnSe is 2.7 eV, so that high-quality ZnSe QDs have potentials for applications in photonic devices in the blue and UV regions. Furthermore, ZnSe QDs have an environmental advantage of being Cd-free.

So far, high-quality ZnSe QDs were synthesized in organic solvents [1] and also in aqueous solutions [2, 3], and the PL-wavelength was successfully changed by preparing alloy QDs of ZnCdSe [1, 2] and ZnSeS [4]. For further improvement of PL properties, core/shell QD structures of ZnSe/ZnS [5] and ZnSe/CdSe [6] were also prepared. However, the main concerns of previous studies on ZnSe QDs were the synthesis and PL properties at room temperature. In order to understand the PL mechanism, it is necessary to conduct systematic studies of the temperature dependence of the PL spectra and PL-decay profiles. In the present work, we have investigated the temperature dependence of absorption, PL, and PL-decay profiles in colloidal ZnSe QDs.

2. Experiments

In the synthesis of ZnSe QDs by a hydrothermal method, ZnSe precursor solution was prepared by adding freshly prepared NaHSe aqueous solution to a N$_2$-saturated Zn(ClO$_4$)$_2$·6H$_2$O aqueous solution in the presence of N-acetyl-L-cysteine (NAC) as a ligand [3]. Then, 10 mL of the precursor solution was loaded into an autoclave. The autoclave was maintained at 200 °C for a desired time and then cooled down to room temperature. In order to investigate the temperature dependence of the optical properties, we dispersed colloidal QDs into polymer films as follows. The sample solution was mixed with a polyvinyl alcohol aqueous solution. Then, the mixed solution was spread on a glass, and the excess water was evaporated by heating at 60 °C for 8 hours.
Figure 1. Temperature dependence of absorption and PL spectra for ZnSe QDs.

Absorption spectra were measured using a double-beam spectrometer with a resolution of 0.2 nm. For PL measurements, the 325 nm line of a He-Cd laser was used as the excitation light source, and the emitted PL was analyzed with a single monochromator with a spectral resolution of 0.5 nm. For measurements of PL-decay profiles, third-harmonic-generation (THG) light (355 nm) of a laser-diode pumped yttrium aluminium garnet (YAG) laser with a pulse duration of 20 ns and a repetition of 10 kHz was used as the excitation light. The PL-decay profiles were obtained by a time-correlated single-photon counting method. The sample temperature was controlled using a closed-cycle helium-gas cryostat.

3. Results and discussion

Figure 1 shows the temperature dependence of the absorption and PL spectra of ZnSe QDs with 3.6 nm in diameter. The absorption- and PL-peak energies shift to the higher energy side with a decrease in temperature. Figure 2(a) shows the temperature dependence of the lowest absorption peak (exciton) energy. It is well known that the temperature dependence of the exciton energy in a direct-gap semiconductor can be described by Varshni’s law [7]. The solid curve indicates the calculated result for the temperature dependence of the absorption energy of a ZnSe bulk crystal. This result indicates that the observed temperature dependence results from the intrinsic property of the ZnSe crystal.

Figure 2(b) shows the temperature dependence of the integrated intensity of the band-edge PL band. The intensity of the band-edge PL band at room temperature is almost 50 % of that at 10 K, which

Figure 2. (a) Temperature dependence of the lowest absorption peak energy. (b) Temperature dependence of the integrated intensity of the band-edge PL.
means that the thermal quenching effect is not large. This result demonstrates that the influence of the nonradiative process is remarkably suppressed in the ZnSe QDs.

Figure 3(a) shows the temporal profiles of the band-edge PL at 10, 70, 120, and 200 K. In this temperature range, temporal profiles become slightly slower with an increase in temperature. In the usual case, as the temperature is increased, the nonradiative-decay rate related to the thermal quenching becomes larger, so that the PL intensity and the PL decay time are decreased. In fact, as shown in figure 2(b), the band-edge PL intensity gradually decreases with an increase in temperature. Nevertheless, the observed decay profiles become longer, which is contrary to the above scenario. The temperature dependence of the PL-decay profiles in ZnSe QDs can be quantitatively explained by a three-state model consisting of a ground state and two excited states: a lower-lying bound-exciton state and a higher-lying free-exciton state (“dark-exciton state”) having an optically inactive triplet nature [8]. With an increase in temperature, the thermal population of the higher-lying dark-exciton state is significant, and the decay time becomes longer.

In order to discuss the PL-decay profiles quantitatively, we analyzed them by a Kohlraush-Williams-Watts-type function [8]. The best fits were obtained with a combination of one monoexponential and one stretched exponential functions:

$$A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left[-\left(\frac{t}{\tau_2}\right)^\beta\right]$$

(1)

Here, the parameters $A_1$ and $A_2$ represent the relative weights of the exponential component and stretched exponential decay one. From the stretched-exponential PL-decay component, we can obtain an average decay time $\langle \tau_2 \rangle = (\tau_2/\beta) \Gamma(1/\beta)$ as introduced in reference 9. Figure 3(b) shows the temperature dependence of $\langle \tau_2 \rangle$ and the fast decay time of $\tau_1$. The slow decay time of $\langle \tau_2 \rangle$ becomes slower with an increase in temperature up to 160 K, while the value of $\tau_1$ gradually increases. The intensity ratio of the slow component ($\langle \tau_2 \rangle$) to the fast one ($\tau_1$) is ~0.7 and over at every temperature. Thus, in order to discuss the temperature dependence of the PL decay profiles, we adopt the decay time of $\langle \tau_2 \rangle$ as an intrinsic decay time because the fast component ($\tau_1$) would reflect relaxation processes of excitons and carriers.

Finally, we quantitatively discuss the temperature dependence of $\langle \tau_2 \rangle$ based on the three-state model. The decay time based on the above-mentioned three-state model is given as [8]:

$$\tau = \frac{\tau_1}{1 + \frac{g_1}{g_n} \exp\left(-\frac{\Delta E}{k_b T}\right)}$$

(2)

Figure 3. (a) Temperature dependence of temporal profiles of the band-edge PL. (b) Temperature dependence of the decay time of $\tau_1$ (closed triangles) and $\langle \tau_2 \rangle$ (closed circles).
Here, $1/\tau_T$ ($1/\tau_B$) and $g_T$ ($g_B$) denote the radiative-decay rate and the density of states of the dark-exciton state (the bound exciton state), respectively. The dashed curve in figure 3(b) indicates the calculated result for the temperature dependence of $\tau$ using equation (2) with $\tau_T$=600 ns, $\tau_B$=41 ns, $\Delta E$=15 meV, and $g_T/g_B$=1. The calculated result quantitatively explains the experimental one below 160 K. At temperatures higher than 160 K, the calculated result still increases gradually, while $<\tau_2>$ begins to decrease. The discrepancy between the calculated and the experimental results can be attributed to the influence of the nonradiative recombination process because equation (2) represents only the “radiative” decay rate in the three-state model. Thus, we take into account the temperature dependence of the nonradiative decay rate, $1/\tau_{nr}(T)$, in the form of a well-known thermal-activation type, which is given as:

$$\frac{1}{\tau_{nr}(T)} = \frac{1}{\tau_{nr}(T=0)} \exp \left( -\frac{E_a}{k_B T} \right)$$  \hspace{1cm} (3)

where $E_a$ represents the thermal-activation energy for the nonradiative process. We calculated the temperature dependence of $\tau(T)$, which is defined as:

$$\frac{1}{\tau(T)} = \frac{1}{\tau_T(T)} + \frac{1}{\tau_{nr}(T)}$$  \hspace{1cm} (4)

where $1/\tau_T(T)$ is given by equation (2). The solid curve in figure 3(b) represents the calculated result with use of the fitting parameters of $\tau_{nr}(T=0)=7.5$ ns and $E_a=70$ meV. The calculated result quantitatively explains the temperature dependence of $<\tau_2>$. Thus, a slight decrease in $<\tau_2>$ at temperatures higher than 180 K is consistently explained by taking into account the nonradiative process. Consequently, the semi-quantitative explanation of the temperature dependence of the PL decay time demonstrates the contribution of the dark-exciton state to the PL process in the ZnSe QDs.

4. Conclusion
The optical properties of size-controlled ZnSe QDs prepared by the hydrothermal method were investigated. The temperature dependence of the decay time of the slow component exhibits the following anomalous behaviour: The decay time increases with an increase in temperature up to 160 K, then further increase of temperature leads to a decrease of the decay time. Using the three-state model consisting of the ground state, lower-lying bound-exciton state, and higher-lying dark-exciton state, the increase of the decay time is reasonably explained. This demonstrates that the dark-exciton state is the origin of the anomalous temperature dependence of the decay time.

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