

Effects of surface modification on photoluminescence properties of self-assembled monolayer of CdSe quantum dots

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Abstract. We have investigated surface-modification effects on photoluminescence (PL) properties of the self-assembled monolayer of CdSe quantum dots from the viewpoint of the temperature dependence of PL properties. The band-edge PL band is strongly activated by the surface modification and is observed as the main PL band, contrary to the fact that the defect-related PL band is dominant in the as-grown sample. From the analysis of PL decay dynamics, it is demonstrated that the contribution of a bound exciton state to PL processes would suppress a trapping process to defects.

1. Introduction

Semiconductor quantum dots (QDs) have been intensively investigated from the viewpoint of the fundamental physics and from the interest in the application to functional materials [1, 2]. CdSe QDs have been a model material for QD studies since the synthesis of size-controlled QDs with high photoluminescence (PL) yield has been well established [3, 4]. It is important to extract QDs from the solution and to disperse them into polymer films from the view point of application for optoelectronic devices. A typical method for preparing film samples is spin-coating and/or drop-casting of QD solutions. Compared to these popular methods, the formation of a self-assembled monolayer (SAM) of QDs is a simple and convenient method for preparing highly-homogeneous QD films [5, 6]. Although the thiol group, which is a constituent of the reagent for formation of the SAM, degrades the PL properties during the SAM formation process, we demonstrated that the band-edge PL intensity is increased remarkably with an additional dipping treatment in $\text{Cd}(\text{ClO}_4)_2$ aqueous solution with pH=10 [7]. The improvement of PL properties is due to surface modification with a $\text{Cd}(\text{OH})_2$ layer.

In the present work, we have investigated the surface-modification effects on PL properties of the SAM of CdSe QDs from the viewpoint of the temperature dependence of PL dynamics. Although a defect-related PL band is dominant at low temperatures in the as-grown sample, the band-edge PL is observed as a main PL band after the surface modification of the SAM. The temperature dependence of the PL-decay time is explained using a four-state model which introduces a bound-exciton state into a conventional three-state model consisting of a ground state and two excited states; a lower lying dark-exciton state and a higher-lying bright-exciton state.

2. Experimental details

CdSe QDs with 3.3 nm in diameter were purchased from Sigma-Aldrich. The substrates of quartz were cleaned by immersion in fresh piranha solution [1/3 (v/v) mixture of 30% H_2O_2 and 98% H_2SO_4]



for 20 min. Then the substrates were rinsed with water. SAM of (3-mercaptopropyl) trimethoxysilane (MPTMS) molecule was deposited to link CdSe QDs to SiO₂ substrates. Next, the substrate was rinsed thoroughly with toluene. The SAM of the QDs linked by thiol group of a MPTMS was prepared in a QD/toluene solution. The samples were thoroughly rinsed with toluene and dried with a stream of nitrogen gas. An additional dipping treatment of the SAM of the CdSe QDs was performed in a 0.6 mM Cd(ClO₄)₂ aqueous solution with pH 10 according to the method in ref. [7] in order to improve PL properties. This process corresponds to the surface-modification treatment of the CdSe QDs with a Cd(OH)₂ layer.

The absorption spectra were measured with 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 light (355 nm) of a laser-diode pumped yttrium aluminum garnet laser with a repetition of 10 kHz was used as the excitation light. The pump fluence was 3 $\mu\text{J}/\text{cm}^2$. 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 1a shows absorption and PL spectra at 10 K of the SAM of the CdSe QDs. It is obvious that a defect-related PL band with a large Stokes-shift of ~ 0.5 eV is dominant at 10 K. This is because that the thiol group degrades the PL properties of the SAM of the CdSe QDs [8, 9]. Figure 1b shows absorption and PL spectra at 10 K of the SAM after the surface-modification treatment of the CdSe QDs with a Cd(OH)₂ layer. The PL spectrum is drastically changed by the surface modification. The band-edge PL band is strongly activated and is observed as the main PL band, contrary to the fact that the defect-related PL band is dominant in the as-grown sample. In order to understand the surface-modification effects on PL properties of the SAM of the CdSe QDs, we measured the temperature dependence of the absorption and PL spectra, and PL-decay profiles.

Figure 2 shows the temperature dependence of the absorption and PL spectra of the SAM after the

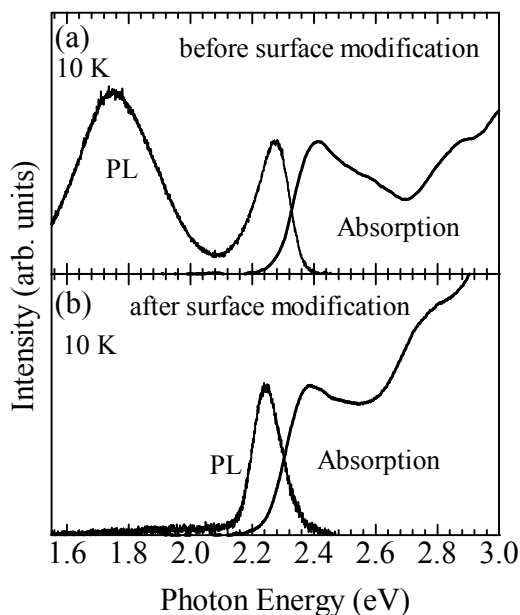


Figure 1 Absorption and PL spectra at 10 K of the SAM of the CdSe QDs before ((a)) and after ((b)) the surface modification.

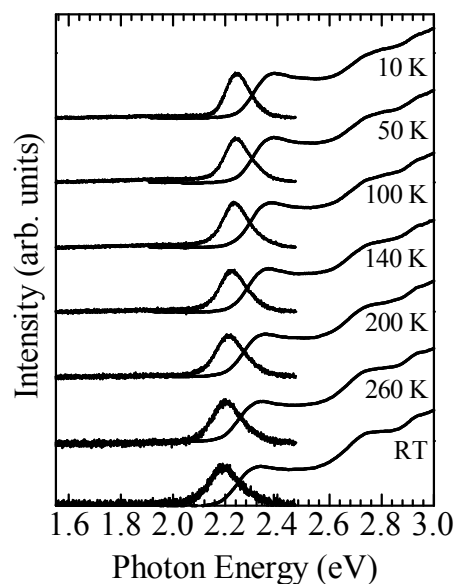


Figure 2 Temperature dependence of absorption and PL spectra of the SAM after the surface modification.

surface-modification treatment. The absorption- and PL-peak energies shift to the lower energy side with an increase in temperature. The intensity of the band-edge PL band at room temperature is almost 10 % of that at 10 K. Figure 3(a) shows the temperature dependence of the lowest absorption- and PL-peak energies. It is well known that the temperature dependence of the exciton energy in direct-gap semiconductors can be described by Varshni's law [10];

$$E(T) = E(0) - \alpha T^2 / (T + \beta), \quad (1)$$

where $E(0)$ is the exciton energy at $T=0$ K, α is the temperature coefficient, and β is a parameter related to the Debye temperature of the crystal. The solid curve indicates the calculated result for the temperature dependence of the absorption and PL energies, where the parameter values of $\alpha=3.7 \times 10^{-4}$ eV/K and $\beta=150$ K in a CdSe bulk crystal were used. The calculated result using the parameters in bulk crystal quantitatively explains the temperature dependence of the absorption energy, which indicates that the observed temperature dependence is an intrinsic optical property of the CdSe crystal. For the PL energy, the calculated result quantitatively explains the experimental one at the higher temperature than 140 K. In the low temperature region, the PL energy becomes lower than the calculated result. Thus, the Stokes-shift becomes larger in the lower temperatures. There is a possibility that "bound-exciton state" caused by the Cd(OH)₂ layer is formed on the low energy side of the free-exciton state as discussed in ref. [11]. The bound-exciton state would suppress a trapping process to defects, and the band-edge PL is observed as a main PL band. Thus, the temperature dependence of the PL dynamics was measured in order to clarify the contribution of the bound-exciton state to PL processes.

Figure 4 shows the temperature dependence of the decay time of the band-edge PL. In the temperature range lower than 180 K, the decay time becomes larger 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. Although the band-edge PL intensity gradually decreases with an increase in temperature, the decay time becomes larger. The characteristic temperature dependence of the decay time in the SAM of the CdSe QDs was explained by a four-state model consisting of a ground state, a bound-exciton state, and two free-exciton states of a lower-lying dark-exciton state and a higher-lying bright-exciton state [11]. The decay time based on the four-state model is given as [11]

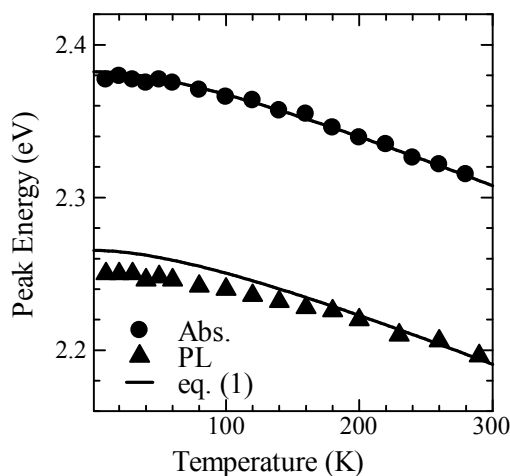


Figure 3 Temperature dependence absorption- and PL-peak energies. The solid curve indicates the calculated result using Varshni's law.

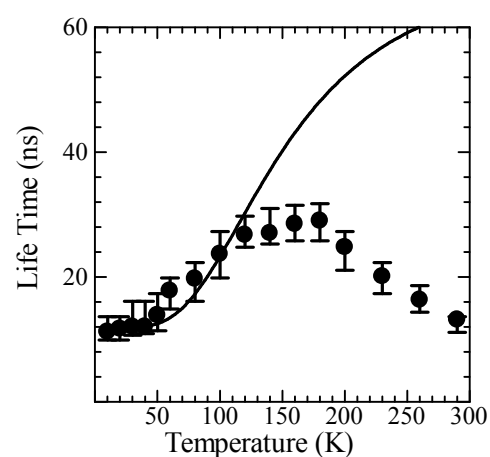


Figure 4 Temperature dependence of the decay time of the band-edge PL (●). The solid curve indicates the calculated result using eq. (2).

$$\frac{1}{\tau} = \frac{\frac{1}{\tau_{\text{Bx}}} + d \frac{1}{\tau_{\text{Dx}}} \exp\left(-\frac{\Delta E}{k_B T}\right) + d \frac{1}{\tau_{\text{Brx}}} \exp\left(-\frac{\Delta E + \Delta_{\text{ST}}}{k_B T}\right)}{1 + d \exp\left(-\frac{\Delta E}{k_B T}\right) + d \exp\left(-\frac{\Delta E + \Delta_{\text{ST}}}{k_B T}\right)}. \quad (2)$$

Here, τ_i denotes the radiative-decay time of bound-exciton ($|Bx\rangle$) and “free”-exciton states ($|Brx\rangle$ and $|Dx\rangle$), respectively. d represents the ratio of the density of state of $|Bx\rangle$ and “free”-exciton states ($|Brx\rangle$ and $|Dx\rangle$). Δ_{ST} is the splitting energy between the bright- and dark-exciton states, and the bound-exciton state $|Bx\rangle$ lies below the dark-exciton state by an energy spacing of ΔE . The solid curve in Fig. 4 indicates the calculated result for the temperature dependence of τ using eq. (2) with $\tau_{\text{Brx}}=42$ ns, $\tau_{\text{Dx}}=1000$ ns, $\tau_{\text{Bx}}=12$ ns, $\Delta_{\text{ST}}=14$ meV, $\Delta E=26$ meV, and $d=18$. The calculated result quantitatively explains the experimental one below 140 K. At higher temperatures, the calculated result still increases gradually, while the observed decay time begins to decrease. The discrepancy between the calculated and the experimental results can be attributed to the influence of the nonradiative recombination process because eq. (2) represents only the “radiative” decay rate in the four-state model. The magnitude of the energy difference between $|Dx\rangle$ and $|Bx\rangle$, ΔE , in the as-grown SAM is ~ 17 meV [11]. Thus, ΔE becomes larger by the surface modification of the SAM. It is considered that an increase in the localization energy of the bound-exciton state would suppress a trapping process to defects and result in the activation of the band-edge PL.

4. Conclusions

The surface modification effects on PL properties of the SAM of CdSe QDs were investigated by measuring the temperature dependence of absorption and PL spectra, and PL dynamics. After the surface modification of the CdSe QDs with the Cd(OH)₂ layer, the band-edge PL is observed as a main PL band at every temperature between 10 K and RT. The decay time of the band-edge PL becomes larger slightly with an increase in temperature. The temperature dependence of the PL-decay time is explained using a four-state model including the bound-exciton state. The contribution of the bound exciton state to PL processes suppresses a trapping process to defects, and the band-edge PL is observed as a main PL band.

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References

- [1] Woggon U 1996 “Optical Properties of Semiconductor Quantum Dots (Springer)”.
- [2] Klimov V I 2004 “Semiconductor and Metal Nanocrystals (Marcel Dekker Inc)”.
- [3] Efros A L, Rosen M, Kuno M, Nirmal M, Norris D J and Bawendi M 1996 *Phys. Rev. B* 54, 4843.
- [4] Donegá C M, Bode M and Meijerink A 2006 *Phys. Rev. B* 74, 085320.
- [5] Bakkers E P A M, Roest A L, Marsman A W, Jenneskens L W, Steensel L I J, Kelly J J and Vanmaekelbergh D 2000 *J. Phys. Chem. B* 104, 7266.
- [6] Marx E, Ginger D S, Walzer K, Stokbro K and Greenham N C 2002 *Nano Lett.* 2, 911.
- [7] Yokota H, Okazaki K, Shimura K, Nakayama M and Kim D G, 2012 *J. Phys. Chem. C* 116, 5456.
- [8] Aldana J, Wang Y A and Peng X 2001 *J. Am. Chem. Soc.* 123, 8844.
- [9] Pradhan N, Battaglia D M, Liu Y and Peng X 2007 *Nano Lett.* 7, 312.
- [10] Varshni Y 1967 *Physica* 34, 149.
- [11] Kim D G, Yokota H, Shimura K and Nakayama M 2013 *Phys. Chem. Chem. Phys.* 15, 21051.