

Surface Modification Effects on Luminescence Properties of CdS Quantum Dots Prepared by Chemical Synthetic Methods

D. Kim, N. Teratani, K. Mizoguchi, and M. Nakayama

Department of Applied Physics, Faculty of Engineering, Osaka City University

3-3-138, Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan

Fax: 81-6-6605-2739, e-mail: tegi@a-phys.eng.osaka-cu.ac.jp

We have investigated surface-modification effects on luminescence properties of CdS quantum dots (QDs) prepared by chemical synthetic methods. The size-distribution width of QDs was successfully reduced by a size-selective photoetching treatment. The size of CdS QDs with the narrow distribution was controlled by changing the initial condition of the sample preparation and the irradiation-light energy. The band-edge-emission intensity was remarkably increased by the surface modification. Decay profiles of the band-edge emission were also drastically changed before and after the surface modification: The fast decay component (≤ 50 ps) due to the nonradiative recombination at surface defects, which was observed before the modification, became extinct after the modification. These results indicate that the surface modification improves the luminescence properties of CdS QDs.

Key words: surface modification, CdS, quantum dot, size-selective photoetching, colloidal method, reverse-micelle method

1. INTRODUCTION

Semiconductor quantum dots (QDs) have been intensively investigated to understand the size dependence of their electronic states and interactions between elementary excitations in them [1]. Since optical properties of QDs depend on the size, the preparation of QDs with a narrow size distribution is essential. Furthermore, surface structures of QDs strongly affect the relaxation process of photo-generated carriers because of a high value of the surface to volume ratio. Thus, the control of the surface structure is important to control luminescence properties of QDs.

Matsumoto *et al.* reported the preparation of CdS colloidal QDs with a narrow size distribution by using a size-selective photoetching [2]. The photoetching effect is based on the fact that many semiconductors are photoetched in aqueous solutions when electrons and holes are excited under the band-gap excitation. In studies on the photoetching of CdS QDs, only sodium hexametaphosphate (HMP) has been used as a disperse agent so far [2, 3]. Furthermore, the details of luminescence properties were not reported.

Spanhel *et al.* reported that the surface modification of CdS QDs with $\text{Cd}(\text{OH})_2$ enhanced the band-edge emission intensity [4]. However, the problem about the inhomogeneity of the QD size was not cleared since their samples have a wide size distribution. It is noted that no report about the luminescence properties for CdS QDs whose size distribution and surface structures are controlled.

In the present work, we have investigated the surface-modification effect on the enhancement of the band-edge-emission intensity in CdS QDs prepared by chemical synthetic methods such as a colloidal method

and a reverse-micelle one. The size distribution of QDs was reduced by using a photoetching treatment. We controlled the size of CdS QDs with the narrow distribution by changing the initial condition of the sample preparation and the irradiation-light energy. By the surface modification of QDs, the band-edge emission was clearly observed in all of the samples. We also observed the drastic change of decay profiles of the band-edge emission before and after the surface modification. The profile before the modification has a fast decay component (≤ 50 ps), while the fast component is not observed after the modification. The fast component is due to the strong nonradiative recombination at the surface of QDs. By the surface modification, the nonradiative process is remarkably reduced, and the intensity of the band-edge emission is drastically increased.

2. EXPERIMENTAL

2.1 Sample preparation

The colloidal QDs of CdS were prepared by injecting H_2S gas into aqueous solutions containing $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and disperse agents such as HMP, polyvinylpyrrolidone (PVP), and polyvinyl alcohol (PVA). For the preparation of CdS QDs by the reverse-micelle method, two heptane solutions of sodium bis (2-ethylhexyl) sulfosuccinate, Na(AOT) (AOT: Aerosol OT), were prepared separately. An aqueous solution of $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ was added to one heptane solution of AOT, while an aqueous solution of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ was added to the other solution, to give a molar ratio $W = [\text{H}_2\text{O}]/[\text{AOT}]$ of 4.0 for both the solutions. The micellar solution containing $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ was added slowly to the micellar

solution containing $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$. This process yields CdS QDs in reverse micelles.

The surface modification of CdS colloidal QDs was performed by the addition of $\text{Cd}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$ after adjusting pH of the solution to the alkaline region [4]. For the surface modification of QDs grown by the reverse-micelle method, pyridine was added to the micellar solution. This process causes the precipitation of QDs coated by pyridine. The particles were washed with ethanol for several times to remove AOT. The pyridine-modified CdS QDs were dispersed in ethanol.

2.2 Size-selective photoetching and optical measurements

A 150-W Xe lamp was used as a light source for the photoetching of QDs. Monochromatic light was obtained by using interference filters: The full-width at half of the intensity maximum of the light was ~ 10 nm. We performed absorption measurements during the photoetching process. For luminescence measurements, a 325-nm line of a He-Cd laser was used as the excitation-light source. The spectral resolution was 0.2 nm in absorption and luminescence measurements.

For the measurements of luminescence-temporal profiles for the longer time region than ~ 10 ns, the excitation source was a pulsed nitrogen laser with the pulse width of ~ 300 ps. The decay curves were observed by a 500-MHz digitizing oscilloscope. For the measurement of temporal profiles in a few nanosecond time region, a mode-locked Ti:sapphire pulse laser (400 nm center wavelength, 150 fs pulse duration, and 82 MHz repetition rate) was used as the excitation light source. The decay curves were detected and analyzed with a streak camera with the time resolution of ~ 50 ps. All the spectra were measured at room temperature.

3. RESULTS AND DISCUSSION

Figure 1 shows absorption and luminescence spectra for the surface-modified CdS QDs grown in HMP solutions during the photoetching process. The spectra at the top were measured before the photoetching. The broken curve indicates a luminescence spectrum before the surface modification. First, we discuss the photoetching effect on the size-distribution reduction of CdS QDs. The absorption structure corresponding to the lowest optical transition energy is observed in the higher energy side than the band-gap energy of ~ 2.5 eV in a CdS bulk crystal. This result clearly indicates the formation of CdS QDs. According to the theory for the quantum size effect in QDs [5], the average radius of the CdS QDs before the photoetching is estimated to be 2.9 nm. Before the photoetching, no excitonic absorption peak is observed because of a wide size distribution of the QDs.

Down arrows in Fig. 1 indicate the energy positions of the irradiated monochromatic light for the photoetching treatment. The energy positions of the absorption onset and the absorption structure are shifted to the higher energy side and the spectral width is decreased with the increase of the irradiation-light energy. After the photoetching process, the clear absorption peak is observed. These results indicate that the average radius and the size-distribution width of QDs become smaller by a sequential irradiation of the monochromatic light.

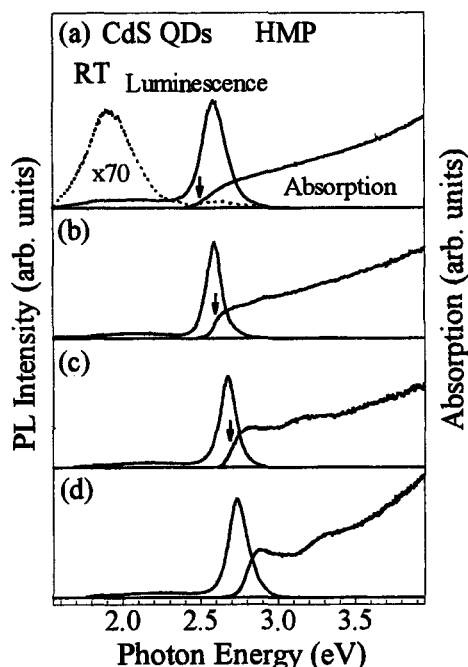


Fig. 1. Absorption and luminescence spectra for the surface-modified CdS QDs in HMP solutions during a photoetching process. Down arrows indicate the energy positions of the irradiated light. The broken curve at the top indicates a luminescence spectrum before the surface modification.

The mechanism of the size-distribution reduction due to the photoetching is explained as follows [2, 6]. Among the QDs with different sizes, the QDs whose exciton energies are resonant with the irradiation-light energy are photoetched. The QDs to be photoetched become smaller by increasing the irradiation-light energy because the exciton energy of the QD increases with the decrease of the QD size, and the QDs with the narrow size distribution are finally obtained. The average radius and the size-distribution width can be estimated from the line-shape analysis [6]: The estimated values of the average radius R_0 and the size-distribution width σ are $(R_0, \sigma) = (2.9 \text{ nm}, 40 \%)$ and $(2.2 \text{ nm}, 7 \%)$ before and after the size-selective photoetching treatment, respectively.

Next, we discuss the surface-modification effect on luminescence properties of CdS QDs. The broken curve at the top in Fig. 1 indicates a luminescence spectrum before the surface modification. The broad luminescence band originated from defects is dominant before the modification. Comparing the two luminescence spectra at the top, it is evident that the band-edge emission is strongly activated by the surface modification: The intensity is increased 460 times by the modification. These results demonstrate that the surface modification improves the luminescence properties of QDs, which is similar to the results in ref. 4. We note that the photoetching effect was not combined with the surface

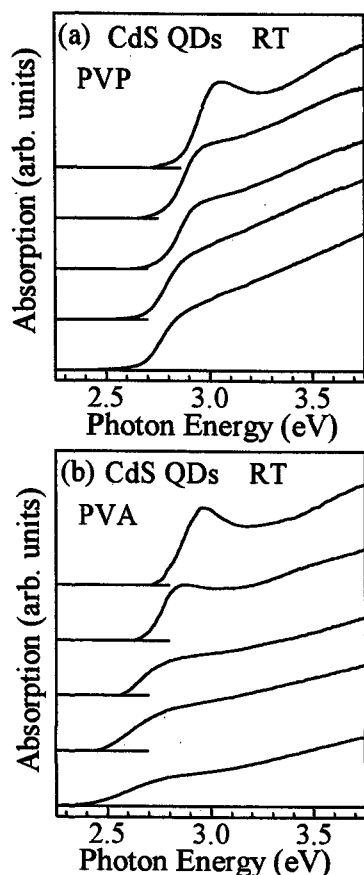


Fig. 2. Absorption spectra for CdS QDs in PVP ((a)) and PVA ((b)) aqueous solutions during a size-selective photoetching process.

modification in ref. 4. By performing the photoetching treatment, the luminescence-peak energy as well as the absorption energy is shifted to the higher energy side with the increase of the irradiation-light energy.

Figure 2 (a) and (b) shows absorption spectra for CdS QDs grown in 5 wt% PVP and PVA aqueous solutions during the photoetching process, respectively. We note that the photoetching treatment was applied only to CdS QDs in HMP solutions so far. The absorption spectra in the bottom were measured before the photoetching. The clear absorption peaks are also observed for CdS QDs in PVP and PVA solutions after the photoetching treatment. These results demonstrate the success of narrowing the size distribution of CdS QDs in PVP and PVA solutions.

Figure 3 shows absorption spectra after the photoetching for CdS QDs prepared with different concentrations of CdS and disperse agents (PVP, PVA, and HMP). It is obvious that the absorption spectra after the photoetching exhibit clear peak structures, reflecting that the size distribution of QDs is narrow. These results indicate that we can control the size of CdS QDs with the narrow size distribution by changing the initial condition of the sample preparation and the irradiation-light energy for the photoetching treatment.

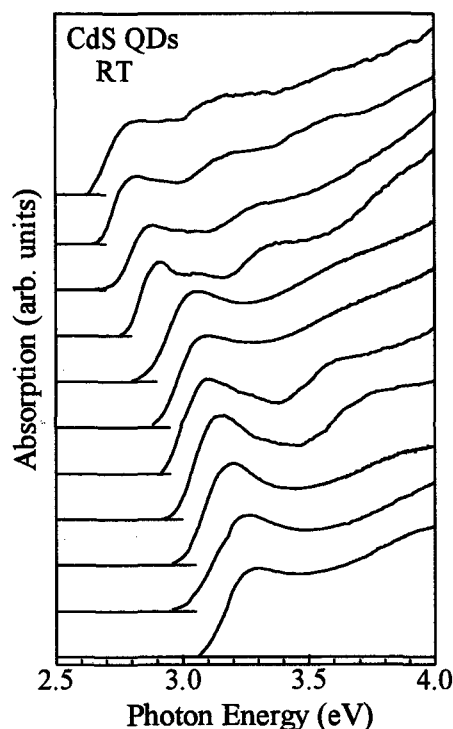


Fig. 3. Absorption spectra after the photoetching for CdS QDs prepared with different concentrations of CdS and disperse agents (PVP, PVA, and HMP).

Next, we discuss the surface modification effect from the viewpoint of luminescence-decay profiles. Figure 4 (a) shows the temporal profile of the band-edge emission before the surface modification of CdS QDs with the mean radius of 2.1 nm and the size-distribution width of 5 %. The cross indicates the temporal profile of the Ti:sapphire laser pulse used as the excitation source: The response time of the measurement system is ~ 50 ps. The luminescence-decay profile before the modification has a fast decay component (≤ 50 ps). Figure 4 (b) shows the temporal profile of the band-edge emission after the surface modification. The nitrogen laser was used as the excitation light source. The profile after the surface modification is drastically changed: The fast component is not observed after the modification. We also measured the temporal profile in a few nanosecond time region with the combination of the Ti:sapphire laser and the streak camera. However, the fast decay component, which is observed before the modification, is not observed at all. The remarkable increase of the band-edge emission intensity due to the surface modification indicates that most of nonradiative-recombination sites exist at the QD surface. The fast component before the modification is considered to be due to the high nonradiative-recombination rate at the surface of QDs. By the surface modification, the nonradiative process is remarkably reduced and the intensity of the band-edge emission is drastically increased.

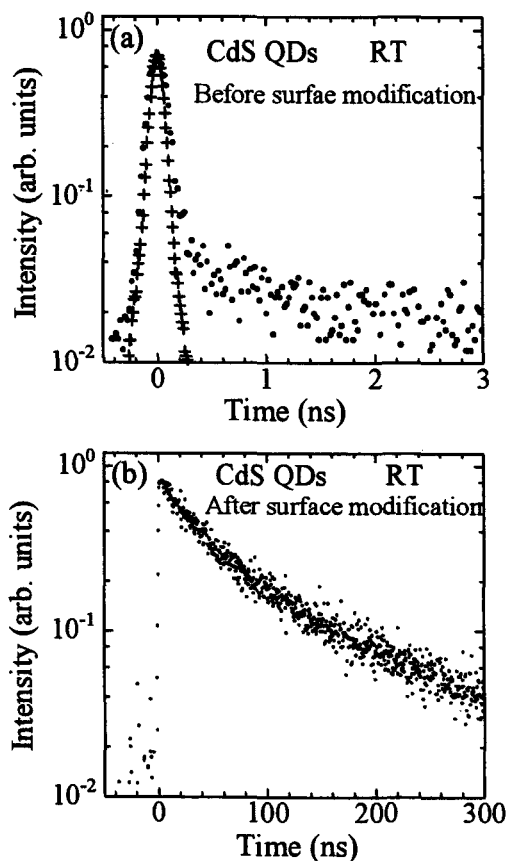


Fig. 4. (a) Temporal profile of the band-edge emission before the surface modification of CdS QDs with the mean radius of 2.1 nm and the size distribution of 5%. The cross indicates a temporal profile of the excitation laser pulse (Ti:sapphire laser). (b) Temporal profile of the band-edge emission with the excitation of the nitrogen laser after the surface modification.

Finally, we discuss the photoetching effect and the surface modification of CdS QDs grown by the reverse-micelle method. Figure 5 shows absorption spectra for CdS QDs before (broken curve) and after (solid curve) the photoetching treatment and the luminescence spectrum for pyridine-modified CdS QDs. By the photoetching treatment, the absorption onset and the absorption peak shift to the higher energy side accompanied with the decrease of the spectral width, which indicates that the average radius and the width of the size distribution of QDs become smaller. Thus, we can also reduce the size distribution of CdS QDs in reverse micelles by the photoetching treatment. In luminescence spectra for CdS QDs grown by the reverse-micelle method, the defect-origin luminescence has been dominant so far. By the surface modification

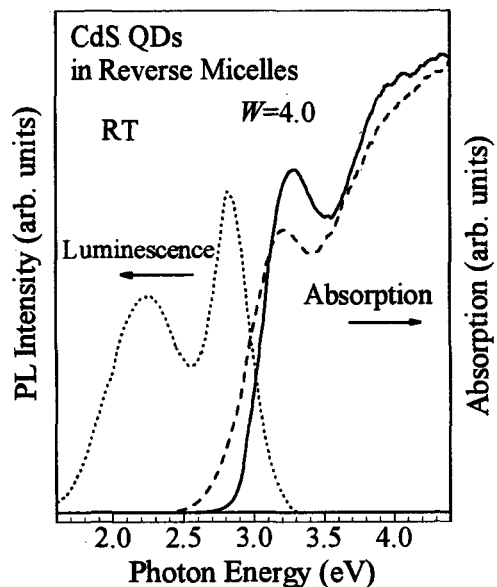


Fig. 5. Absorption spectra for CdS QDs in reverse micelles before (broken line) and after (solid line) the photoetching treatment and luminescence spectra for pyridine-modified CdS QDs.

with pyridine, the band-edge emission is clearly observed as a main luminescence band.

In conclusion, we have investigated surface-modification effects on luminescence properties of CdS QDs prepared by the chemical synthetic method. The QDs with the narrow size-distribution were successfully prepared by the size-selective photoetching treatment. The drastic changes of the band-edge-emission intensity and of the decay profiles were observed by the surface modification. From the results, we conclude that the surface modification improves the luminescence properties of CdS QDs.

References

- [1] For a review, *J. Lumin.* **70** (1996), edited by L. E. Brus, A. L. Efros, and T. Itoh.
- [2] H. Matsumoto, T. Sakata, H. Mori, and H. Yoneyama, *J. Phys. Chem.* **100**, 13781 (1996).
- [3] A. Dijken, D. Vanmaekelbergh, and A. Meijerink, *Chem. Phys. Lett.* **269**, 494 (1997).
- [4] L. Spanhel, M. Haase, H. Weller, and A. Henglein, *J. Am. Chem. Soc.* **109**, 5649 (1987).
- [5] L. E. Brus, *J. Chem. Phys.* **80**, 4403 (1984).
- [6] D. Kim, N. Teratani, K. Mizoguchi, H. Nishimura, and M. Nakayama, to be published in *International Journal of Material Science B*.

(Received December 20, 2001; Accepted January 31, 2002)