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Size-Selective Photoetching Effects on Preparation of Semiconductor Quantum Dots with a Uniform Size

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We have investigated size-selective photoetching effects on the size-distribution reduction of CdS and ZnS-CdS ($Zn_{1-x}Cd_xS$) alloy quantum dots (QDs). The QDs of CdS, ZnS, and $Zn_{1-x}Cd_xS$ were prepared in polyvinylpyrrolidone solutions by a standard colloid-chemical synthetic method. The reduction of the size-distribution width was achieved by the size-selective photoetching treatment for the QDs of CdS and $Zn_{1-x}Cd_xS$ with x=0.4, 0.6, and 0.8. The photoetching treatment was also applied to CdS QDs grown by a reverse-micelle technique.

Key words: size-selective photoetching, CdS, ZnS-CdS alloy, quantum dot

1. INTRODUCTION

Semiconductor quantum dots (QDs) have been extensively investigated from the viewpoint of the fundamental physics and from the interest in the application to functional materials [1]. Since the physical and/or chemical properties of the QDs depend on the size, the preparation of the QDs with a narrow size distribution that is with a uniform size is essential.

Colloidal technique is one of the most popular methods of preparing various QDs, such as CdS [2, 3], ZnS [4], and ZnO [5], with nanometer sizes. However, they have a wide size distribution of about 20-40 %.

Matsumoto *et al.* reported that a size-selective photoetching makes it possible to prepare CdS QDs with a narrow size distribution [6]. It is based on the fact that many semiconductors are photoetched in aqueous solution if electrons and holes are excited under band-gap excitation. However, in studies of the photoetching of CdS QDs, only sodium hexametaphosphate has been used as a disperse agent so far [6-8]. Moreover, there has been no report on the photoetching effects on preparation of alloy QDs.

In the present work, we have investigated size-selective photoetching effects on preparation of CdS and ZnS-CdS ($Zn_{1-x}Cd_xS$) alloy QDs. We prepared CdS, ZnS, and $Zn_{1-x}Cd_xS$ QDs in polyvinylpyrrolidone (PVP) aqueous solutions by a colloidal technique. Initially grown QDs have a wide size distribution whose standard deviation is ~35 %. We succeeded narrowing the size distribution of the QDs by the size-selective photoetching treatment: The size distribution was reduced to ~6 %. The CdS QDs were also prepared by using a reverse-micelle technique. This technique is considered to be an advantageous method of preparing QDs with a relatively narrow size distribution because the size of a reaction field for QD synthesis is restricted. We achieved the further reduction of the size distribution of CdS QDs grown in reverse micelles by the size-selective photoetching.

2. EXPERIMENTAL

2-1. Sample Preparation

The colloidal QDs of CdS were prepared by adding $Na_2S{\cdot}9H_2O$ to PVP aqueous solutions containing $Cd(ClO_4)_2{\cdot}6H_2O$. The $Zn_{1-x}Cd_xS$ QDs were grown by injecting $Zn(ClO_4)_2{\cdot}6H_2O$, $Cd(ClO_4)_2{\cdot}6H_2O$, and $Na_2S{\cdot}9H_2O$ with a fixed molar ratio into PVP solutions, where $x=[Cd^{2+}]/([Cd^{2+}]+[Zn^{2+}])$. The molar ratio of $[Cd^{2+}]+[Zn^{2+}]$ to $[S^{2-}]$ was 1 for all values of x.

For preparation of CdS QDs in reverse micelles, two heptane solutions of sodium bis (2-ethylhexyl) sulfosuccinate (Aerosol OT: AOT) were prepared separately. An aqueous solution of $Cd(ClO_4)_2{\cdot}6H_2O$was added to one heptane solution of AOT, while an aqueous solution of $Na_2S{\cdot}9H_2O$ was added to the other solution. The micellar solution containing $Na_2S{\cdot}9H_2O$ was added slowly to the micellar solution containing $Cd(ClO_4)_2{\cdot}6H_2O$. This process yields CdS QDs in reverse micelles. The water content W (=$[H_2O]/[AOT]$) was varied in the range of 2.0-7.0. Changing the W-value can control the mean radius of the QDs.

2-2. Size-Selective Photoetching and Absorption Measurements

For the photoetching of the QDs, a 150-W Xe lamp was used as a light source. 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 at room temperature during the photoetching process.

3. RESULTS AND DISCUSSION

3-1. CdS QDs in PVP Solutions

In order to study the size-selective photoetching effect on narrowing the size distribution, absorption spectra were measured during the photoetching process. Figure 1 shows absorption spectra for CdS QDs grown in 5 wt% PVP solutions during the photoetching process. The absorption spectrum in the bottom was measured

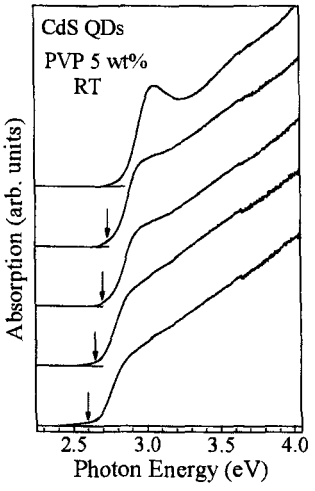


Fig. 1. Absorption spectra for CdS QDs in PVP solutions during a size-selective photoetching process. Down arrows indicate the energy positions of the irradiated monochromatic light.

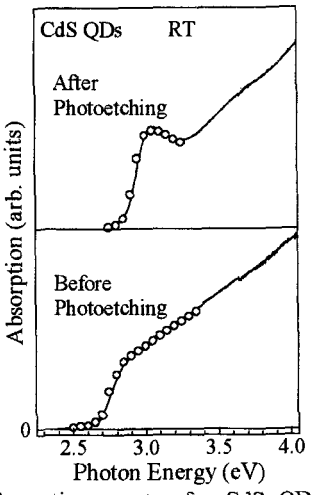


Fig. 2. Absorption spectra for CdS QDs in PVP solutions before and after the size-selective photoetching process. Open circles indicate results of the line-shape analysis.

before the photoetching. The absorption structure which corresponds 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, indicating the formation of CdS QDs. According to the theory for the quantum size effect in QDs [9], the average radius of the CdS QDs before the photoetching is estimated to be 2.0 nm. The absorption spectrum is broad because of the wide size distribution of the QDs. We determined the absorption energy from the minimum point of the second derivative spectrum.

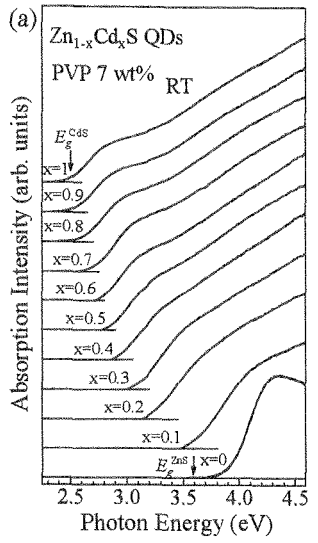
The down arrows in Fig. 1 indicate the energy positions of the irradiated monochromatic light. With the increase of the light energy, the energy position of the absorption structure is shifted to the higher energy side and the width is decreased. After the photoetching process, the sharp absorption peak is observed. This result indicates that the average radius and the width of the size distribution of the QDs become smaller by a sequential irradiation of the monochromatic light. The mechanism of the size-distribution reduction is explained as follows. Among the QDs of different sizes, the QDs whose exciton energies are resonant with the irradiation-light energy are photoetched [6]. Since the exciton energy of the QD increases with the decrease of the QD size, the QDs to be photoetched become smaller by increasing the irradiation-light energy. This process results in narrowing the size distribution. Such a photoetching treatment was applied only to CdS QDs in sodium hexametaphosphate solutions [6-8]. Our results demonstrate the success of narrowing the size distribution of the CdS QDs in PVP solutions. We could prepare CdS QDs with the narrow size distribution as well as those in sodium hexametaphosphate solutions.

We performed the line-shape analysis in order to estimate the magnitude of the size-distribution width σ. Figure 2 shows absorption spectra (solid lines) before and after the photoetching treatment and results of the analysis (open circles). The total absorption spectrum is given as a superposition of each absorption spectrum of QDs with different sizes, where we assume the line shape of each spectrum to be a Gaussian shape. From the absorption energy, the average radius R_0 is first determined. We calculated the absorption spectra with a fitting parameter σ. The values of R_0 and σ estimated from the analysis are (R_0, σ)=(2.0 nm, 35 %) and (1.8 nm, 6 %) before and after the size-selective photoetching process, respectively. The size of the CdS QDs with the narrow size distribution can be controlled by changing the initial condition of the sample preparation, such as concentrations of CdS and PVP, and the irradiation-light energy [10].

3-2. $Zn_{1-x}Cd_xS$ Alloy QDs in PVP Solutions

Figure 3 shows absorption spectra for $Zn_{1-x}Cd_xS$ QDs grown in 7 wt% PVP solutions. For x=0 and 1, the absorption structures corresponding to the lowest optical transition energies are observed in the higher energy side than the band gap energies (↓) in ZnS (E_g^{ZnS}) and CdS (E_g^{CdS}) bulk crystals, respectively, which demonstrates the formation of ZnS and CdS QDs. From the shift energies due to the quantum size effect, the radii of ZnS and CdS QDs are estimated to be 1.4 and 1.9 nm, respectively. We note that the absorption-edge energy successively shifts to the lower energy side from the absorption energy in ZnS QDs with the increase of the CdS composition. Thus, it is considered that the preparation of the alloy QDs of $Zn_{1-x}Cd_xS$ is successful.

Figure 3 (b) shows an alloy-composition dependence of the absorption energies (•), which are obtained from the minimum point of the second derivative of the absorption spectra shown in Fig. 3 (a). The broken line indicates the calculated result for the x-dependence of the lowest optical transition energies in $Zn_{1-x}Cd_xS$ QDs with a radius of 1.9 nm. The experimental results are well fit to the calculated one between x=0.2 and 1. This result indicates that the mean size of $Zn_{1-x}Cd_xS$ QDs is constant to be 1.9 nm from x=0.2 to 1. For x=0 and 0.1, the mean radius is estimated to 1.4 and 1.5 nm, respectively.



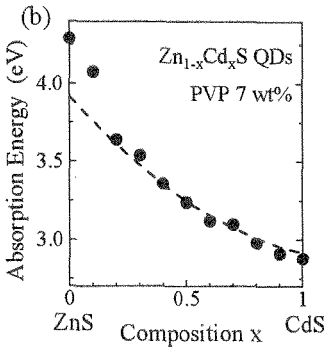


Fig. 3. (a) Absorption spectra for $Zn_{1-x}Cd_xS$ QDs grown in PVP aqueous solutions. Down arrows indicate band-gap energies E_g^{ZnS} (E_g^{CdS}) in ZnS (CdS) bulk crystals. (b) Alloy-composition dependence of absorption energies (●) for $Zn_{1-x}Cd_xS$ QDs in PVP solutions. Broken line indicates the calculated result for the lowest optical transition energies in $Zn_{1-x}Cd_xS$ QDs with a radius of 1.9 nm.

We investigated the possibility of the size-selective photoetching in alloy QDs of $Zn_{1-x}Cd_xS$. Figure 4 shows absorption spectra before (broken lines) and after (solid ones) a sequential irradiation of the monochromatic light for x=0.4, 0.6, 0.8, and 1. Before the photoetching, each absorption spectrum is broad because of a wide size distribution of the QDs. After the photoetching, clear absorption peaks are observed. These results clearly indicate that we can also reduce the size distribution of alloy QDs by the size-selective photoetching treatment: The size-distribution width estimated from the line-shape analysis is reduced to 10, 7, 6, and 6 % for x=0.4, 0.6, 0.8, and 1, respectively.

3-3. CdS QDs in AOT/Heptane Reverse Micelles

Figure 5 (a) shows absorption spectra for CdS QDs grown in reverse micelles with W ($[H_2O]/[AOT]$)=7.0, 5.4, 4.0, 3.0, and 2.0. Absorption peaks were observed at 2.87, 2.97, 3.22, 3.31, and 3.61 eV, which indicates the formation of CdS QDs with the mean radii of 2.0, 1.9,

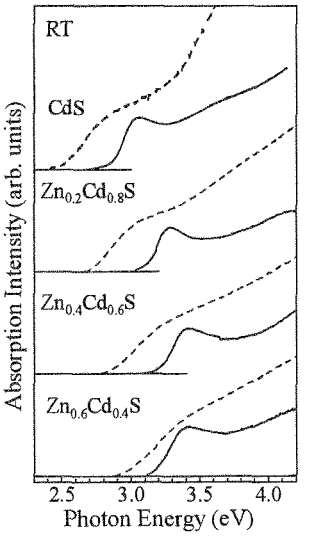


Fig. 4. Absorption spectra for $Zn_{1-x}Cd_xS$ QDs (x=0.4, 0.6, 0.8, and 1) in PVP solutions before (broken lines) and after (solid lines) the size-selective photoetching treatment.

1.6, 1.5, and 1.2 nm for W=7.0, 5.4, 4.0, 3.0, and 2.0, respectively. This result demonstrates that the size of QDs can be controlled by changing the W-value. From the line-shape analysis, the size-distribution widths were estimated to be 8-11 %, which is relatively small compared to that of the colloidal QDs grown in PVP solutions before the photoetching.

For the further reduction of the size distribution of the QDs, we attempt the size-selective photoetching treatment for CdS QDs in reverse micelles. Figure 5 (b) shows absorption spectra before (broken line) and after (solid one) the photoetching for CdS QDs in AOT/heptane reverse micelles with W=3.0. 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 the QDs become smaller during the size-selective photoetching process. Thus, we can also reduce the size distribution of CdS QDs in reverse micelles by the photoetching.

Figure 6 (a) shows the absorption spectrum for CdS QDs in the reverse micelle with W=5.4 after the photoetching. Open circles indicate the result of the line-shape analysis: The estimated R_0 and σ are 1.9 nm and 6 %, respectively. An image of transmission electron microscopy (TEM) of the QD is shown in Fig. 6 (b): The TEM image indicates good crystallinity and spherical shape of QDs. From TEM images, the size distribution of the QD was obtained as shown in Fig. 6 (c): The mean radius and the distribution width are 1.8 nm and 5 %, respectively. These values well correspond to those of R_0 and σ estimated from the line-shape analysis. Thus, the line-shape analysis is considered to be a convenient method of estimating the magnitude of the size-distribution width.

In conclusion, we have demonstrated the success of

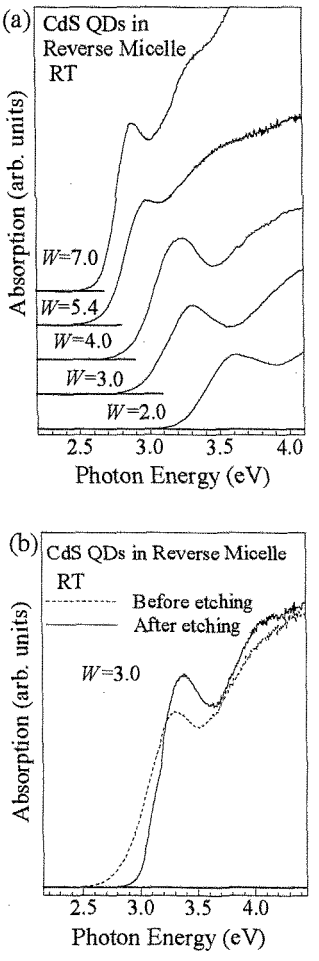


Fig. 5. (a) Absorption spectra for CdS QDs grown in reverse micelles with various values of water contents (W=2.0, 3.0, 4.0, 5.4, and 7.0). (b) Absorption spectra for CdS QDs with W=3.0 before (broken line) and after (solid line) the photoetching treatment.

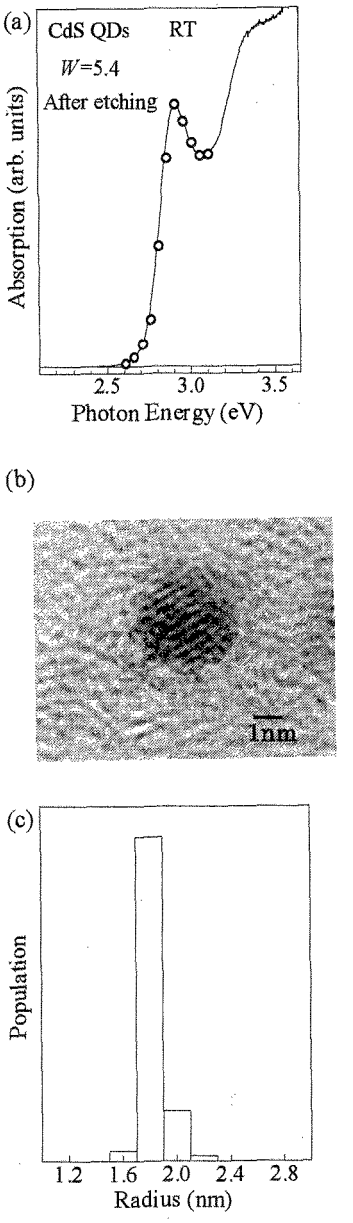


Fig. 6. (a) Absorption spectrum for CdS QDs in the reverse micelle with W=5.4 (b) TEM image of the CdS QD. (c) Size distribution of CdS QDs obtained from TEM images.

narrowing the size distribution of CdS and $Zn_{1-x}Cd_xS$ alloy QDs grown in PVP aqueous solutions and in AOT/heptane reverse micelles by the size-selective photoetching treatment.

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