Narrowing Size Distribution of CdS Nanocrystals by Size Selective Photocorrosion

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Sequential irradiation with monochromatic light of 500, 480, 460, 430 nm of CdS nanocrystals (Q-CdS), whose average diameter was 4.9 nm with the standard deviation of 2.0 nm, steadily narrowed the size distribution to finally give a Q-CdS colloid having an absorption spectrum characteristic of highly monodispersed Q-CdS and an absorption onset of 430 nm.

In the past decade, fairly intensive studies have been done on semiconductor nanocrystals (Q-particles) for their unique properties arising from the size quantization effects.[1-3] Since chemical and physical properties of Q-particles depend on their size, the preparation of monodispersed Q-particles of various sizes has been attempted using various techniques such as use of inverse micelles,[4] size selective precipitation method,[5,6] fractionation by gel-chromatography of the prepared Q-particle colloids,[7] and rigid control of preparation baths.[8] However, the size of the prepared particles using these methods does not necessarily give narrow size distribution. In this communication, we report a novel and easy preparation of Q-CdS of a very narrow size distribution using selective photocorrosion of as-prepared Q-CdS colloidal particles.

Irradiation of Q-CdS particles in aerated solutions with light of wavelengths shorter than the absorption onset results in photocorrosion of the particles. The reaction schemes are given by Eqs. (1)~(3).[9,10]

anodic reaction

$$CdS + 4h^+ + 2H_2O + O_2 \longrightarrow Cd^{2+} + SO_4^{2-} + 4H^+ \quad (1)$$

cathodic reaction

$$O_2 + 4e^- + 2H^+ \longrightarrow 2OH^- \quad (2)$$

overall stoichiometry for the photoprocess

$$CdS + 2O_2 \longrightarrow Cd^{2+} + SO_4^{2-} \quad (3)$$

The absorption onset of a Q-particle colloid consisting of the particles of various sizes is determined by the largest particle in the colloid. If such colloids are irradiated with monochromatic light with the wavelength a little shorter than the absorption onset, the largest particles are photocorroded, and the particles would become smaller until they do not absorb the irradiated photons any more. By changing the monochromatic light for irradiation to that of the shorter wavelength step by step, the absorption onset of Q-CdS colloids must be accordingly shifted to the shorter wavelengths, and simultaneously the size distribution of Q-particles must become narrower. In the present study, this idea has been successfully utilized for preparation of Q-CdS of very narrow size distribution.

A stoichiometric amount of H_2S gas (1.2 mL) was injected into a nitrogen-bubbled aqueous solution containing 2×10^{-4} mol dm^{-3} of $Cd(ClO_4)_2$ and 2×10^{-4} mol dm^{-3} of sodium hexametaphosphate (HMP) at pH 10.0. After vigorous mixing for 1 min, the resulting colloid was stirred for 10 min at 0°C and concentrated by a factor of 10 under reduced pressure at 35°C. A 1.2 cm^3 portion of the colloid prepared in this way was placed into a 1 cm x 1 cm x 4 cm quartz cell and the absorbance at 300 nm of the solution was adjusted to 1.2 by the addition of water. A 500 W Xe lamp was used as a light source and monochromatic light of various wavelengths was obtained by using interference filters.

When photoirradiation was initiated using monochromatic light of 500 nm for original Q-CdS colloid, its absorption spectrum was gradually changed and after a few hours of irradiation, a stable absorption spectrum (b) of Figure 1 was obtained. Subsequent irradiation at 480 nm gave a steady spectrum (c), and finally a spectrum (e) was obtained by irradiation at 430 nm. The results obtained here suggest that Q-CdS particles are photocorroded to the extent that gives the absorption onset equal to the wavelength of the irradiated photons. However, judging from the absorbance shown in Figure 1, the number of Q-CdS nanocrystals seems to have decreased with decreasing the wavelength for irradiation.[6] Presumably, HMP working as a stabilizing agent desorbs from Q-CdS surfaces in the photocorrosion, resulting in aggregation of Q-CdS particles to be further photocorroded. Qualitative analysis of the solution after a series of irradiations by ion-chromatography revealed that SO_4^{2-} ions were produced during the course of the irradiation and the solution pH was not changed at that time, supporting the photocorrosion process given by Eqs. (1)~(3).

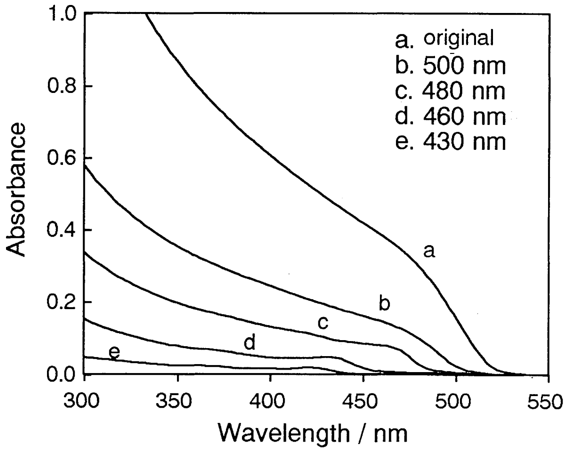

Figure 1. Absorption spectra of Q-CdS before and after irradiation with monochromatic light. (a) before irradiation, (b) 500 nm, (c) 480 nm, (d) 460 nm, (e) 430 nm.

Figure 2 shows normalized absorption spectra for the data in Figure 1, obtained by dividing the absorbance at each wavelength by that at the first exciton peak or shoulder. Structured absorption spectra are emerged with decreasing wavelength of monochromatic light used. This is especially prominent for the case of 430 nm, for which three exciton peaks are seen. The development of clear exciton peaks is indicative of monodispersive distribution of Q-CdS prepared.[5,6]

Figure 3 shows the size distributions of Q-CdS obtained from the results of transmission electron micrography (TEM) at three different stages of the irradiation. The electron diffraction patterns

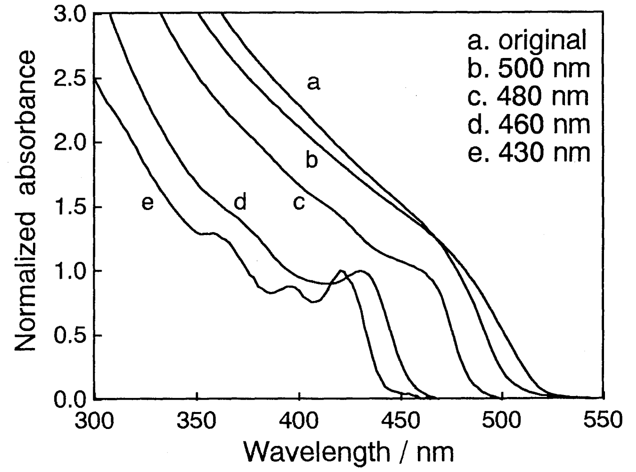

Figure 2. Normalized absorption spectra of Figure 1, obtained by dividing the absorbance of each wavelength by that of the first exciton peak or shoulder.

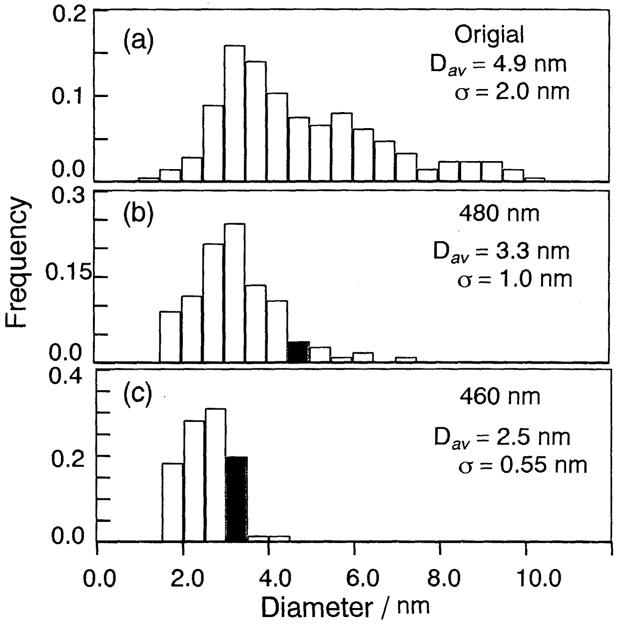

Figure 3. Size distribution of Q-CdS particles obtained by TEM pictures. The average diameter and its standard deviation are denoted by D_{av} and σ, respectively. (a) before irradiation, (b) and (c) after irradiation with monochromatic light of 480 nm and 460 nm, respectively. The diameter theoretically derived from the absorption onset is given by filled bars.

simultaneously obtained with TEM revealed that Q-CdS had a zinc-blende structure. It is seen that the larger particles of Q-CdS colloids were removed by the irradiation with the monochromatic light, and the standard deviation of the size distribution decreased with decreasing wavelength of monochromatic light used. As shown in Table 1, the average diameters obtained by TEM observation (D_{TEM}) are in good accordance with the theoretically estimated diameters (D_{calc}) which were obtained by applying the exciton peak or shoulder of Q-CdS spectra to the reported energy gap *vs.* particle diameter relation.[11] The particle diameters evaluated from the absorption onset instead of the exciton peak or the shoulder are given in Table 1 as D_{onset} and also in Figure 3 with filled bars. Since the absorption onset of Q-CdS is determined by the largest particles present in the colloid with an amount not to be negligible, the evaluated D_{onset} seem to be reasonable.

The standard deviation and the average diameter for the 430 nm irradiation were not determined because the amount of Q-CdS particles obtained in that case was too small to be applied to TEM observations. However, considering the fact that the difference between D_{onset} and D_{calc} was nearly equal to the standard deviation (σ) for the cases of irradiation at 480 and 460 nm, CdS particles prepared with irradiation at 430 nm may have a distribution of their size roughly equal to the difference between D_{onset} and D_{calc}, which is 0.2 nm (= 2.8 - 2.6). Since the value of 0.2 nm is smaller than the lattice distance of CdS (0.25 nm), it is then concluded that a highly monodispersed distribution must have been achieved by irradiation at 430 nm as suggested by the appearance of clear exciton peaks, as already described. The discussion based on the difference between D_{onset} and D_{calc} made here is not useful for cases where bulk particles are contained in Q-particles as in the original colloids. Details will be discussed in a paper to be published in future.

Table 1. Size parameters of the photoetched Q-CdS obtained by TEM observations and using the theoretically derived relationship by Lippens *et al.*[11]

sample	E_g[a] /eV	D_{calc}[b] /nm	D_{TEM}[c] /nm	σ[d] /nm	λ_{onset}[e] /nm	E_{onset}[f] /eV	D_{onset}[g] /nm
original	2.57	4.5	4.9	2.0	520	2.38	>8
500 nm	2.59	4.2	n.d.[h]	n.d.[h]	503	2.47	5.8
480 nm	2.65	3.8	3.3	1.0	486	2.55	4.7
460 nm	2.84	2.8	2.5	0.55	454	2.73	3.3
430 nm	2.92	2.6	-	-	438	2.83	2.8

[a] Exciton energy estimated from the first exciton peak or shoulder given in Figure 1. [b] Particle diameter determined by applying E_g to the reported energy gap *vs.* particle diameter relation.[11] [c] Average diameter determined from TEM pictures. [d] Standard deviation. [e] Absorption onset. [f] Photon energy at λ_{onset}. [g] Particle diameter determined by applying E_{onset} to reported energy gap *vs.* particle diameter relation.[11] [h] not determined.

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