Preparation of Monodisperse ZnS Nanoparticles by Size Selective Photocorrosion

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The size-distribution of ZnS nanoparticles (Q-ZnS) of 4.2 ± 0.6 nm was narrowed to 2.6 ± 0.2 nm by sequential irradiation with monochromatic light of 313 nm, 303 nm, and 297 nm to an air-saturated ZnS colloidal solution in the presence of sodium hexametaphosphate as a stabilizer and methylviologen as an electron acceptor.

Quantized semiconductor nanoparticles (Q-Sc) exhibit unique properties which are different from those of bulk crystals due to quantum size effects.[1-3] Since the bandgap of Q-Sc is significantly influenced by the size of Q-Sc in such a way that it increases with a decrease of the size, it is desired to prepare a monodisperse Q-Sc for both fundamental and application studies. Recently, we reported that the size-selective photocorrosion of Q-CdS provides easy way for the preparation of monodisperse Q-CdS.[4] Here, we report the utility of the same technique in the preparation of monodisperse Q-ZnS.

Referring to our previous works, it seems that the preparation of monodisperse Q-Sc can be achieved with the use of the size selective photocorrosion only when all the photocorrosion products are soluble in aqueous solutions in which the Q-Sc particles are present. For example, the preparation of monodisperse Q-CdS particles were unsuccessful for big CdS particles due to the formation of elemental sulfur as a side reaction of the photocorrosion, as already reported.[5] Failure of the preparation of monodisperse Q-PbS resulted from the same reason.[6] Though ZnS was reported to be photocorroded in air-saturated aqueous solutions with the reaction given by eq (1),[7,8] no quantitative data to confirm this equation have been presented;

$$\mathrm{ZnS} + \mathrm{O_2} \rightarrow \mathrm{Zn^{2+}} + \mathrm{SO_4^{2-}} \qquad (1)$$

If any side reaction such as elemental sulfur formation is included in the photocorrosion reaction of Q-ZnS, the utility of the photocorrosion is questioned. If one thinks of these problems, the success of the preparation of monodisperse Q-ZnS particles with the use of the photocorrosion reaction is not straightforwardly anticipated.

A Q-ZnS colloidal solution was prepared using an ice bath under N_2 atmosphere. A 50 mL aqueous solution of Na_2S (4×10^{-3} mol dm^{-3}) was added slowly into a 50 mL aqueous solution containing a stoichiometric amount of $Zn(ClO_4)_2$ and sodium hexametaphosphate (HMP) under vigorous stirring, followed by agitation for 3 h. The resulting Q-ZnS colloid was transparent and colorless, and its pH value was 7.0. When the photocorrosion experiments were carried out, the Q-ZnS colloid was diluted to 1×10^{-3} mol dm^{-3}, and a 2.0 cm^3 portion of it was put into a 1 cm × 1 cm × 4 cm quartz cell. A 500 W Hg lamp was used as a light source and monochromatic light of various wavelength was obtained by using a monochromator with a full width at half maximum (FWHM) of 6 nm. Hg emission lines of 313 nm, 303 nm, and 297 nm were used, and light intensities of these monochromatic lights were 1.4 mW cm^{-2}, 1.1 mW cm^{-2}, and 1.2 mW cm^{-2}, respectively. Before irradiation, methylviologen (MV^{2+}) was added as an electron acceptor whose concentration was adjusted to 0.01 mol dm^{-3} and the solution was bubbled with O_2 gas for 1 h. It is well-established that MV^{2+} picks up electrons more easily than dissolved oxygen, and it was confirmed in preliminary experiments that the rate of photocorrosion of Q-ZnS particles was highly enhanced with the use of MV^{2+}. The absorption of MV^{2+} was found not to seriously disturb the photocorrosion experiments as suggested from its absorption spectrum given by curve e in Figure 1. All the absorption spectra of Q-ZnS colloids in this paper are given by subtracting the absorption by MV^{2+}.

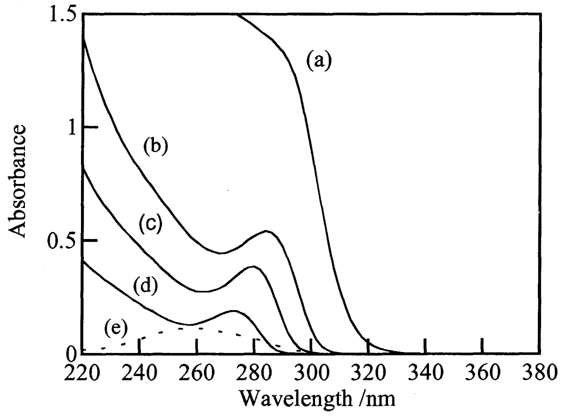

Figure 1. Steady-state absorption spectra of Q-ZnS colloids obtained (a) before irradiation, and after sequentially irradiation with monochromatic light of (b) 313 nm, (c) 303 nm, and (d) 297 nm. (e) is the absorption spectrum of 0.01 mol dm^{-3} MV^{2+}.

Absorption spectra of the Q-ZnS colloid were measured intermittently during irradiation, and the irradiation was continued until no change in the absorption spectra was observed. Figure 1 shows the steady-state absorption spectra of the Q-ZnS colloid after the sequential irradiation of monochromatic light of 313, 303, and 297 nm. When the original Q-ZnS colloid whose absorption spectrum is given by curve a in Figure 1, was irradiated by 313 nm monochromatic light, its absorption spectrum was gradually changed, and a steady state absorption spectrum given by curve b was obtained after 20 h. An exciton peak was developed at 300 nm, suggesting that the Q-ZnS colloid was changed to monodisperse. The steady state spectra obtained by monochromatic light of 303 and 297 nm are given by curves c and d, respectively. Recently, Dijken et al. reported the photocorrosion of Q-ZnS,[6] but absorption spectra which they obtained were not so sharp as those given in Fig. 1.

It is recognized that the onset wavelength was blue-shifted depending on the wavelengths of monochromatic light used. With promotion of the photocorrosion, the absorbance of the spectra decreased over the whole range, and then a decrease of the number of Q-ZnS was suggested, as already reported for the photocorrosion of Q-CdS.

The absorption spectrum of MV^{2+} was not changed at all during the course of photocorrosion of Q-ZnS, suggesting that MV^{2+} was regenerated with the scheme given by,

$$MV^{2+} + e^- \rightarrow MV^+ \qquad (2)$$

$$O_2 + 4MV^+ + 2H^+ \rightarrow 2OH^- + 4MV^{2+} \qquad (3)$$

$$ZnS + 4h^+ + 2\,H_2O + O_2 \rightarrow Zn^{2+} + SO_4^{2-} \qquad (4)$$

In the preliminary experiments, it was confirmed that SO_4^{2-} ions were produced during the photocorrosion and the pH value of the solution was not changed. Then the photocorrosion reaction of Q-ZnS is formulated by eq (1).

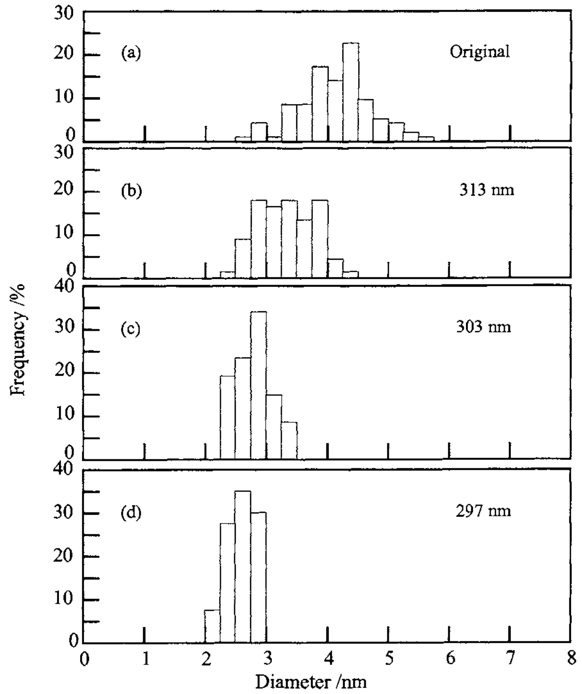

Figure 2. Size distribution of Q-ZnS nanoparticles: 1) before photoirradiation, 2) after 313 nm irradiation, 3) after 303 nm irradiation, 4) after 297 nm irradiation.

Figure 2 shows the size distributions of Q-ZnS obtained by high resolution transmission electron microscopy (TEM). The electron diffraction patterns simultaneously obtained revealed that Q-ZnS particles had a cubic structure. As shown in the figure, the sequential irradiation with the monochromatic light narrowed the size distribution of Q-ZnS by selectively dissolving the larger Q-ZnS particles to the smaller ones. The Q-ZnS obtained after 297 nm photoirradiation had a size-distribution of 2.6 ± 0.2 nm. Table 1 shows the average diameter of Q-ZnS particles determined by TEM observations (D_{TEM}), its standard deviation (σ), and the wavelength at the absorption threshold (λ_{onset}). The particle diameters (D_{exiton}) evaluated from the exciton peaks ($\lambda_{exciton}$) using the reported particle diameter vs. energy gap relation derived from an effective mass approximation[9] are also given in Table 1. So far, several theoretical approaches have been published concerning the bandgap vs. particle size relations, for example, an effective mass approximation,[9] a tight-binding approximation[10] and a finite depth well model.[2] Among them, the $D_{exciton}$ evaluated from an effective mass approximation[9] was found to be in good accordance with the average D_{TEM} of Q-ZnS.

Table 1. Size parameters of the photocorroded Q-ZnS obtained by TEM observations and the particle size predicted by a published bandgap vs particle size[9]

sample	D_{TEM}[a] /nm	σ[b] /nm	λ_{onset}[c] /nm	$\lambda_{exciton}$[d] /nm	D_{exiton}[e] /nm
original	4.2	0.6	333	290	3.6
313 nm	3.4	0.5	312	285	3.2
303 nm	2.9	0.3	303	280	3.0
297 nm	2.6	0.2	295	275	2.8

[a]Average diameter determined by TEM observation. [b]Standard deviation. [c]Absorption onset. [d]Exciton peak position. [e]Particle diameter evaluated from exciton peaks by using the reported energy gap vs. particle diameter relation derived from an effective mass approximation.[9]

Considering that the standard deviation of 0.2 nm obtained after 297 nm photoirradiation is smaller than the distance of ZnS interlattice (0.31 nm), it may be concluded that highly monodisperse ZnS nanoparticles was easily and successfully prepared by the size selective photocorrosion. The achievement reported here may open a new gate to further study on chemistry and physics of Q-ZnS.

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