

Influences of Initial Particle Size on Preparation of Monodisperse CdS Nanoparticles with Size-Selective Photoetching

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It was found that the size-selective photoetching of CdS particles prepared in Nafion films could be achieved only for particles having the particle sizes smaller than about 12 nm in the diameter. The particles greater than this threshold size were photocorroded until complete dissolution was attained.

Size-quantized semiconductor nanoparticles change the bandgaps with changing their size, and by this reason preparation of monodisperse nanoparticles is essential in studies on their chemical and physical properties.¹⁻⁶ We previously reported the utility of size-selective photoetching as the means of preparation of monodisperse CdS nanoparticles,⁴⁻⁶ where large CdS particles are selectively photoetched to smaller ones by monochromatic light irradiation until irradiated photons are not absorbed anymore in the particles. In this communication, we report the size-selective photoetching of CdS particles immobilized in Nafion matrices with focusing to the influence of the initial size of CdS particles on their photocorrosion. Nafion has been used to stabilize semiconductor nanoparticles such as CdS^{7,8} and PbS⁹ in its matrices.

Nafion films were prepared by casting of a 10 mm³ cm⁻² 5 wt% Nafion solution (Aldrich Nafion 117 solution) on a Pyrex glass plate, followed by drying and then heating at 150 °C for 1 h. The prepared film was immersed for 15 h in Cd(ClO₄)₂ aqueous solutions of various concentrations which ranged from 1.0 to 500 mmol dm⁻³. After rinsing with water and then drying, the film was exposed to hydrogen sulfide gas for 1 h, resulting in the formation of CdS particles stabilized in Nafion film (CdS/Nafion). The amount of CdS formed in Nafion film increased from 0.13 to 0.27 μmol cm⁻² with a concentration increase of Cd(ClO₄)₂ from 1.0 to 500 mmol dm⁻³, as determined by X-ray microanalyses. The CdS particles prepared had absorption onset at 520 nm which agreed with that expected for the bulk material, regardless of the concentration of Cd(ClO₄)₂ used in the immersion. With observations of CdS/Nafion by a transmission electron microscope (TEM), however, it was found that the average diameter (d_{av}) of the CdS particles increased from 8.9 to 24 nm with an increase of the concentration of Cd(ClO₄)₂ from 1.0 to 500 mmol dm⁻³.

Irradiation to CdS/Nafion were performed in air-saturated water using an argon ion laser. With irradiation of monochromatic light at 488.0 nm, CdS particles were photocorroded, but behaviors of the photocorrosion were largely different depending on the size of CdS particles immobilized in the Nafion matrices as shown in Figure 1a. When CdS particles having d_{av} of 8.9 nm were used, the size selective photoetching was successfully achieved with irradiation for 4 h, as recognized both from blue-shifts of the absorption onset to 488.0 nm and from appearance of clear exciton peak at 450 nm, and further irradiation did not bring any change in absorption spectra. On the other hand, if much bigger CdS particles with d_{av} of 24 nm were used, the absorbance monotonously decreased with irradiation of any monochromatic light whose

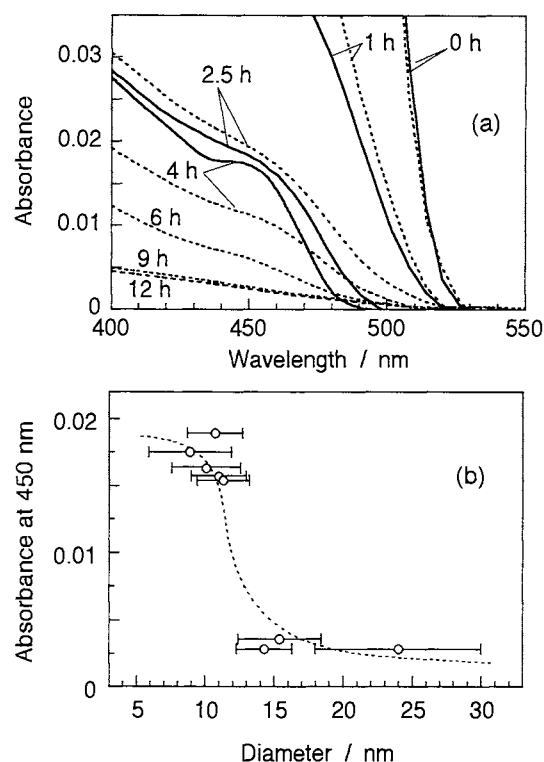


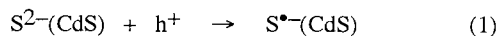
Figure 1. (a) Change in absorption spectra of CdS/Nafion caused by argon ion laser irradiation at 488.0 nm. The average diameter of CdS/Nafion used were 8.9 (—) and 24 nm (---). (b) Absorbance at 450 nm after 12 h irradiation as a function of the average diameter of CdS particles used for photoetching. The error bar indicated the size distribution. Irradiation intensity was 12 mW cm⁻².

wavelength was shorter less than the original absorption threshold as shown in the figure. Irradiation beyond 9 h caused little change of absorption spectra, indicating that the complete photocorrosion of CdS was attained. After irradiation for 12 h, the CdS/Nafion film contained elemental sulfur of 0.4 % of the total amount of sulfide ions contained in the original CdS particles, and then the null absorbance was not obtained due to the light scattering of the formed sulfur colloid.

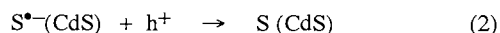
The same experiments were carried out for CdS/Nafion of different particle sizes. Figure 1b shows the relationship between the absorbance at 450 nm obtained after irradiation of 488.0 nm laser light for 12 h and the initial particle size of CdS/Nafion. It was found that CdS/Nafion whose diameter was smaller than about 12 nm was successfully photoetched to the monodisperse nanoparticles whose size were straightforwardly determined by

the wavelength of monochromatic light used, whereas CdS particles greater than about 12 nm were completely photocorroded. Similar size dependence of photocorrosion behaviors was obtained for CdS particle colloids stabilized by hexametaphosphate (HMP), CdS/HMP. As reported in our previous papers,⁶ CdS/HMP having d_{av} smaller than 6.5 nm were successfully monodispersed to desired sizes with irradiation of monochromatic light of various wavelengths. However we found that if the irradiation was performed with monochromatic light at 488.0 nm to aqueous suspensions of commercially available bulk CdS particles (Mitsuiwa Chemicals, d_{av} : ca. 50 nm) with various concentrations ranging from 1.0×10^{-3} to 1.0 mol dm^{-3} in the presence of the same concentration of HMP, no absorption spectra assignable to CdS nanoparticles were obtained for any cases. The concentration of CdS nanoparticles to be expected after the photoetching at 488.0 nm of 1.0 mol dm^{-3} bulk CdS particle is $0.34 \text{ mmol dm}^{-3}$ which is high enough to obtain its absorption spectrum, if the size selective photoetching occurs.

We found that elemental sulfur was produced in addition to the formation of SO_4^{2-} when CdS particles were completely dissolved out by photocorrosion, but no formation of sulfur was observed when CdS nanoparticles were able to be photoetched to the size determined by the monochromatic light used. If this finding is stressed, the following discussion may be postulated on the capability of CdS particles for being photoetched. As already reported,^{5,10} a stoichiometric amount of SO_4^{2-} is produced via the formation of $\text{S}_2\text{O}_3^{2-}$ together with Cd^{2+} when the photoetching occurs at the CdS nanoparticles. Further detailed mechanisms of SO_4^{2-} formation is not known, but it may not be unreasonable to assume that the first step of oxidation of S^{2-} of CdS is the formation of sulfur radical $\text{S}^{\bullet-}$, as given by eq. 1.¹¹



The rate of photogeneration of positive holes (h^+) in the unit volume of CdS must be the same between the big particles and small ones as long as the irradiation intensity is equal to each other. However, the number of photogenerated h^+ in a particle for a given time must be different between the two, that is, the larger particle had the greater amount of h^+ . If h^+ is generated within the lifetime of $\text{S}^{\bullet-}$, then the production of elemental sulfur given by eq. 2¹² may be increased, as experimentally observed for the bigger particles.



Anyway if elemental sulfur was formed on CdS particle surfaces, adsorption of stabilizing agents such as Nafion and HMP on the particle surfaces would be weakened, resulting in an increasing in aggregation into bigger particles which are further photocorroded.

CdS/Nafion which was successfully photoetched by irradiation at 488.0 nm allowed further photoetching with irradiation by monochromatic light shorter than 488.0 nm. As shown in Figure 2, the absorption threshold was blue-shifted to the wavelength of monochromatic light used for irradiation and an exciton peak appeared in absorption spectrum, as already reported.⁴⁻⁶ TEM observations of CdS/Nafion film revealed that the original CdS particles had the average diameter of 8.9 nm and its standard deviation was 3.6 nm. The average diameter of CdS nanoparticles obtained by irradiation at 488.0, 476.5, and 457.9 nm were 3.5, 3.3, and 2.9 nm, respectively, and its standard deviation was 0.11, 0.17, and 0.14 nm, respectively. The obtained standard deviation

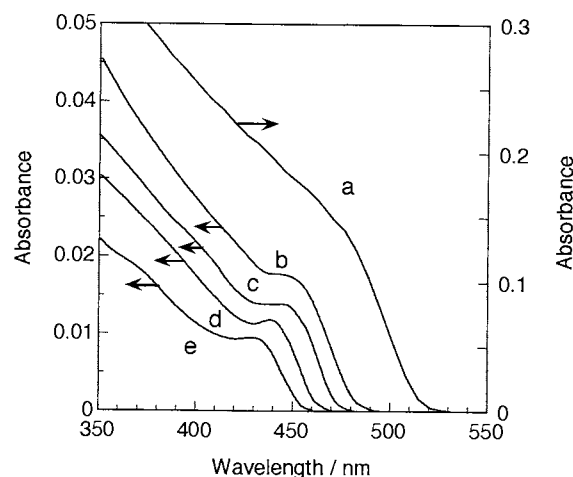


Figure 2. Steady-state absorption spectra of CdS nanoparticles stabilized in Nafion matrices obtained after Ar ion laser irradiation with various wavelengths. Before irradiation (a), and after irradiation at 488.0 (b), 476.5 (c), 465.8 (d) and 457.9 nm (e). Initial average diameter of CdS particles was 8.9 nm.

of photoetched nanoparticles were less than about 5% of the average diameter, which is comparable to our previous results of CdS nanoparticles dispersed in aqueous solution.⁶ It is then concluded that the highly monodisperse CdS nanoparticles immobilized in Nafion films can be prepared by the size-selective photoetching.

The immobilization of CdS in Nafion films before photoetching is of practical significance in the point that if monodisperse particles are prepared in colloid particles, the immobilization in appropriate matrices is required on their use. However, if the particles are immobilized before photoetching we need not to immobilize CdS nanoparticles after photoetching.

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