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Studies on Reaction Conditions for Size-selective Photoetching of Cadmium Telluride Nanocrystals

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Effects of reaction conditions on size-selective photoetching of CdTe nanocrystals were presented focusing on electron mediator and wavelength of irradiating light. Methyl viologen, which was expected to work as an electron mediator of photo-induced oxygen reduction accelerating the photoetching, decreased significantly the rate of the reaction. The results are compared with the photoetching of CdS nanocrystals in terms of overpotential for oxygen reduction and adsorption of electron mediators on nanocrystals. Under optimized conditions, the photoetching can produce highly monodispersed nanocrystals having fluorescence peak of fwhm value as small as 23.5 nm around the wavelength region where CdTe nanocrystals are stably produced by the conventional synthesis. However, further blue shifts of irradiating light gradually increased the fluorescence fwhm value, and the exciton peaks became unclear as well. The results were considered by comparing with recently reported magic-sized nanoclusters.

Key Words : Size-selective Photoetching, Electron Mediator, CdTe Nanocrystals, Magic-sized Nanoclusters

1 Introduction

Semiconductor nanocrystals (NCs) are attracting intense attention because of their many desirable properties, such as large absorption coefficient, intense emission and durability when exposed to light irradiation.¹⁻⁷ Their properties as semiconductors make them absorb wide wavelength range of light that is shorter than the bandgap, enabling multicolored emission by exposing to a single light source. In fact, their energy bands are slightly discrete compared to those of bulk semiconductors due to the spatially confined electron-hole pairs called excitons. The absorption maxima concerning excitons, exciton peaks, are the indicator of good surface modification of nanocrystals. The quantum size effect, which increases bandgap as the size of the NC decreases, are one of the most remarkable properties of semiconductor NCs.⁸⁻¹² Therefore, the size of the NCs is very important factor determining their optical properties; i.e., absorption and emission spectra blue-shifts as the size of the NCs decrease.

In the conventional synthetic procedures, the size of NCs is controlled by heating the NC colloidal solution. A mean NCs diameter increases as they are heated in the solution, at the expense of smaller particles or excess monomer.¹³⁻¹⁵ The former is called Ostwald ripening process where size distribution becomes wider as the reaction time elapse, while the latter to some extent narrows the size distribution during the reaction. In any cases, conventional synthetic methods cannot generate highly monodispersed NCs due to the inhomogeneity of the reactions. As far as we know, there is only a method

to obtain monodispersed NCs solution by the post-treatment so-called size-selective precipitation, which utilizes the differences in solubility between different-sized particles.^{4,16,17} However, if one will to obtain monodispersed NCs having a certain emission wavelength, the product yield end up with very low, i.e., the inverse of the number of separated fractions.

Recently we developed methods to obtain highly monodispersed NCs of CdS,¹⁸⁻²² CdSe²³ and CdTe²⁴ by using photocorrosion. The photocorrosion occurs by positive holes after removing electrons from excited semiconductor NCs. Then, the quantum size effect increases the bandgap of NCs with the blue shifts of the optical properties. When the monochromatic light is used, photoetching proceeds until the bandgap becomes equal to the irradiating energy, giving highly monodispersed NCs with their bandgap corresponding to irradiating energy.

In the present study, factors determining efficiency of the photoetching of CdTe NCs were studied. Effects of solution composition, especially, the role of electron mediator were investigated, and they were compared with the photoetching of CdS NCs. Under the optimized reaction conditions the photoetching produced highly-monodispersed CdTe NCs having PL corresponding to irradiating wavelength with fwhm of PL peak as small as 23.5 nm. When the wavelength of the irradiating light was further blue shifted, the resulting CdTe NCs emitted nearly white light with their exciton peak became unclear. The results were compared with the recently developed fluorescent magic-sized nanoclusters of cadmium chalcogenide NCs.²⁵⁻³⁷

2 Experimental

2.1 Chemicals

We purchased cadmium chloride, sodium borohydride, thioglycolic acid (TGA), and sodium hydroxide from Wako Pure Chemicals Industries and used them without further purification. Methyl viologen dichloride was purchased from TCI. Te powder (99.8%, 200 mesh) was purchased from Aldrich. Water used in this study was purified by Milli-Q gradient A10 (Millipore, 18.2 M Ω cm).

2.2 Synthesis of CdTe nanocrystals

CdTe nanocrystals were synthesized following Weller *et al.* with some modification. Briefly, tellurium powder was reacted with sodium borohydride in aqueous solution at 0°C; after 8 h a pale red colored NaHTe solution was obtained. In another flask, cadmium chloride and TGA were dissolved in 125 mL water, and the solution's pH was adjusted to 9 by the addition of 1M NaOH. After de-aeration, the prepared NaHTe solution was added with agitation to obtain the precursor of the nanocrystals. The molecular ratio of Cd : TGA : Te was 1 : 1.8 : 0.25. The solution was refluxed for several hours until the nanocrystals grew to the desired particle size. The quality of nanocrystals was checked with UV-Vis and fluorescence spectra using a photodiode array spectrometer (Shimadzu, MultiSpec-1500) and a fluorospectrometer (Hitachi, F-4500). We measured quantum yield using a diode-array spectrometer equipped with an integrating sphere (Hamamatsu, PMA-12).

2.3 Size-selective photoetching

The CdTe NC colloidal solution was diluted by a factor of 20 with NaOH or KOH aqueous solution of different concentrations and pH values. Some of the samples contained 1 mM of methyl viologen as an electron mediator. An aliquot of 3 mL was put into a quartz cell (1 × 1 × 4 cm) and oxygen was bubbled into the solution for 10 min prior to photoetching. The solution was irradiated with monochromatic light from an Hg lamp through a monochromator (Bunkoh-Keiki, KX-025). The power of the light was ~ 10 mW/cm² in the wavelength region used for the photoetching (500–600 nm), and the area of irradiation was fixed to ~ 2 cm². The solution was stirred continuously during the photoetching process. Absorption and fluorescence spectra were measured intermittently during the course of photoetching. Irradiation was continued until a constant absorption spectrum was obtained.

3 Results and Discussion

3.1 Effects of electron mediators

Figure 1(a) shows changes in the absorption spectra as a function of duration time of photoetching without methyl viologen. The photoetching is a photo-oxidation of NC itself by the positive holes, after removing electrons from the photo-excited NC. Optimization of reaction conditions revealed that the photoetching of CdTe proceeded under strong alkaline conditions (pH > 13.5), in which photo-oxidized species become soluble in the forms of TeO₄²⁻, TeO₃²⁻ and HCdO₂⁻.²⁴⁾

The photoetching of CdS NCs in the presence of methyl viologen was three orders of magnitude faster

Fig. 1 Absorption spectra during the photoetching in the absence (a) and in the presence (b) of methyl viologen (1 mM), and plots for absorbance at the exciton peak as a function of duration time of the photoetching; without (I) and with (II) electron mediator (c). The pH of the solution was 13.5, and the irradiation wavelength was 580 nm.

than that without methyl viologen.¹⁹⁾ Therefore, we expected the addition of methyl viologen promotes the rate of the photoetching of CdTe. Figure 1(b) shows spectra of the same reaction as Fig. 1(a) but in the presence of 1 mM methyl viologen. Unexpectedly, such effect was not observed; on the contrary, the reaction rate was slowed down by the addition of methyl viologen. Changes in the absorption at the wavelength of the original exciton peak were displayed in Fig. 1(c). Apparently, the reaction rate was lower by a factor of 10 in the pres-

ence of methyl viologen. The large difference in the effects of electron mediator was discussed from two points: the difference in absolute band-edge potentials between CdS and CdTe, and the specific adsorption of methyl viologen on the surface of TGA-CdTe NCs.

Photoetching rate are considered to rely on the efficient removal of the electrons from photo-excited NCs. In the cases of hexametaphosphate-capped CdS (HMP-CdS) NC, the edge of conduction band was expected to be -1.0 to -1.2 volts vs NHE dependent on its size, which was estimated from flatband potential of bulk CdS and size-quantization effects.³⁸⁾ However, taking account of the fact that oxygen reduction on metal and semiconducting electrodes generally needs large overpotentials, these potentials are not negative enough for the sufficient removal of electrons from NCs by dissolved oxygen. On the other hand, in the case of CdTe NCs, the lower edge of the conduction band of the thiol-stabilized CdTe NCs was investigated by the pulse radiolysis experiment to be -2.0 to -2.4 volts dependent on the particle size.³⁹⁾ Thus, the oxygen reduction, which is for instance -0.12 V for two electron reduction at pH = 13.5, occurred effectively without mediators, giving relatively faster photoetching rate compared with CdS NCs that inevitably need electron mediators.¹⁹⁾

The above mentioned largeness of overpotential cannot explain the decrease in the photoetching rate in the presence of methyl viologen. Here, we considered the possibility of adsorption of methyl viologen onto the NCs' surface. Figure 2 shows the quenching of photoluminescence from TGA-CdTe by the addition of methyl viologen. The inset shows the Stern-Volmer plots, giving coefficients (K_{SV}) of $5.4 \times 10^6 \text{ M}^{-1}$. This value is two to three orders of magnitude larger than K_{SV} that reported for organic fluorophores and quenchers under diffusion mediated photoinduced electron transfer. Therefore, it is natural to consider that methyl viologen is adsorbed on the NCs, although they are not covalently bonded. Considering large potential gap between the lower conduction band edge of TGA-CdTe NC and methyl viologen, the electron transfer rate is expected to be much

Fig. 2 Emission quench of CdTe NCs by methyl viologen. The inset is the corresponding Stern-Volmer plots (Ex = 460 nm).

faster than diffusion rate; and the quenching occurred through methyl viologen that is adsorbed on the NCs. Although quenching of HMP-CdS NCs were also reported to be caused by adsorbed methyl viologen, its K_{SV} value ($2.1 \times 10^5 \text{ M}^{-1}$) was *ca.* 25 times smaller than that obtained in the present study for TGA-CdTe, indicating that the adsorption coefficient of methyl viologen on TGA-CdTe is much larger than that on HMP-CdS.⁴⁰⁾

3. 2 Blue limit of photoetching

One of the interests concerning size-selective photoetching is how small we can prepare the CdTe NCs.²⁰⁾ While the photoetching produced highly-monodispersed CdTe NCs with emission fwhm value as small as 23.5 nm, the fwhm became larger by the irradiation less than 560 nm.²⁴⁾ Figure 3 shows the UV-Vis (a) and PL (b) spectra of TGA-CdTe NCs photoetched with various wavelengths, from 540 to 500 nm. The exciton peak, which was clearly observed when irradiated with 540 nm light, became unclear as the further blue shifts of the irradiating light, while it shifted steadily from 499 nm (irradiation at 540 nm) to 440 nm (500 nm). The PL also decreased significantly as the extinction of the exciton peaks, leaving longer wavelength component. The QY decreased from 45% to 5.8%, when the irradiation wavelength was changed from 580 nm to 500 nm. Figure 4 shows the PL spectrum of TGA-CdTe photoetched with 500 nm light. It had a peak at 503 nm, but the color of

Fig. 3 Absorption (a) and PL (b) spectra (Ex = 460 nm) after the photoetching with irradiating wavelength less than 540 nm.

Fig. 4 PL spectrum of TGA-CdTe NCs photoetched with 500 nm irradiation. Excitation wavelength is 420 nm.

emission when exposed to UV-light was almost white, as it can be expected from large fwhm of the PL (84 nm).

Although the quantum size effect steadily blue-shift the optical properties of semiconductor NCs, small limit until which particles can exist stably is known to exist. Some representative studies were done on very small particles called magic-sized clusters^{20,25-37} which are thermodynamically stable small clusters having electronic closed-shell structures. They are considered to be generated in the early stage of the synthetic reactions of semiconductor NCs, and in some cases were preferentially synthesized and isolated under very strictly controlled reaction conditions. Some of the studies about magic-sized clusters reported white-light emission originating from the increase in the surface trap sites.³⁰⁻³² We also observed broad-band emission from the CdTe NCs photoetched with 500 nm light, and the wavelength of the exciton peak (440 nm) was comparable with magic-sized CdTe clusters synthesized by Chikan *et al.*^{28,31} However, the exciton peak was not as clear as their reports, indicating that the resulting NCs are imperfect having many trap sites that recombine excitons. We speculated that the instability of these particles was due to the continuous reaction of photoetching, which lower significantly the stability of NCs deviated from magic-sizes, resulting in the increase in the surface traps and/or instant decomposition of particles themselves. The result that the photoetching of CdTe NCs to the diameter close to the magic-size is unfavorable coincided with our previous report of preparation of ultrasmall CdS NCs by the photoetching.²⁰

4 Conclusion

We investigated the reaction conditions for the photoetching of CdTe. In terms of solution composition, effects of electron mediator on size-selective photoetching were studied for CdTe NCs and they were compared with the previous results for CdS NCs. Addition of methyl viologen to the CdTe NCs solution during the photoetching significantly slowed down the reaction rate, while it accelerated about 3 orders of magnitude the pho-

toetching rate of CdS NCs. These differences were due to the strong adsorption of methyl viologen on the CdTe NCs surface originating from large valency of TGA molecules densely bound to CdTe. Thus, methyl viologen served as a trap site of electrons, rather than the electron mediator. Under the optimized reaction conditions, blue limit of irradiating light for the photoetching was investigated. Although the photoetching of CdTe NCs produced highly-monodispersed particles with the fwhm of the PL peak as small as 23.5 nm, further blue shifts of irradiating light lowered the monochromaticity. Furthermore, the exciton peak became unclear when its wavelength reached to that of magic-sized clusters which were recently reported by the precise control of the reaction conditions. This is due to the mismatch between the photoetching that is intrinsically the continuous reaction and the nature of magic-sized clusters that need preferential sizes to be stabilized.

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