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Subpicosecond studies of primary photochemical events of CdS particles with surface modified by various capping agents

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Abstract

Q-CdS particles with surface modified by thiophenol (PhS) or 2-mercaptobenzoxazole (MBO) were prepared and their time-resolved transient absorption spectra were measured in acetonitrile in subpicosecond to picosecond time domain in order to investigate the influences of capping agents on primary photochemical events such as electron and hole trapping processes and decay kinetics of the trapped charge carriers on capped semiconductor Q-particles. In addition, time-resolved transient absorption spectra of aqueous CdS colloidal solutions containing sodium hexametaphosphate (HMP) as a stabilizer against flocculation were also measured in the same time domain and compared to obtain knowledge about the trap sites for electrons photo-produced on capped CdS particles in acetonitrile. The shape and the decay profile of transient absorption spectra obtained by subpicosecond laser flash photolysis of PhS-CdS and MBO-CdS in acetonitrile are markedly different from those of non-capped CdS particles in acetonitrile obtained previously using picosecond laser flash photolysis by Kamat et al. The results suggest that capping agents such as PhS and MBO influence significantly hole trapping process and decay dynamics of the trapped charge carriers on the capped CdS. Furthermore, it seems that the trap site of the electrons generated by laser excitation of PhS-CdS or MBO-CdS in acetonitrile is mainly at the interface of particle-solution and the possibility for the production of solvated electrons is low because the shapes and decay kinetics of the transient absorption spectra of PhS-CdS or MBO-CdS in acetonitrile are clearly different from those HMP-CdS in water in which the photo-production of the hydrated electrons is known. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Capped CdS; Q-particle; Subpicosecond; Trapped holes; Trapped electrons

1. Introduction

The synthesis of Q-cadmium sulfide particles with narrow size distribution has been carried out by various methods [1–15] in order to elucidate the characteristic photochemical and photocatalytic properties of nanometer-size semiconductor particles (Q-particles) with quantum size effects. Among them, Q-CdS particles with the surface modified chemically by capping agents such as organic sulfur compounds are noted to be advantageous for mechanistic and kinetic investigations of primary photochemical events of semiconductor particles using fast kinetic spectroscopy because they have more narrow size distribution and are available as bottlable solids which can be redispersed in organic solvents without stabilizer against flocculation [8,12,16]. However, there are few studies of the measurements of transient absorption spectra to investigate the effects of the capping agents on the primary photochemical events of the particles such as hole

and electron trapping and decay kinetics of the trapped charge carriers [16].

In addition, there are still some arguments about the trap site of photo-induced electron, that is, whether the electron is trapped at the solid-solution interface or becomes solvated electron, despite a number of studies on the primary photochemical events of Q-CdS particles by the measurements of the transient absorption including the recent studies by femtosecond laser systems have been reported so far [17–29]. And further, while the rise and decay processes of transient absorption were followed in detail at a few wavelengths in the time region of subpico- to picoseconds, the time-resolved transient absorption spectra in the whole visible region (> 460 nm) attributed to trapped electrons and holes are not shown [27–29]. Therefore, it is important to obtain the shape of the transient absorption spectra for the Q-particles in subpico- to picoseconds time domain from the standpoint to consider the trapping and decay processes of photo-generated electrons and holes in more details.

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In this study, Q-CdS particles (PhS-CdS, MBO-CdS) capped by organic sulfur compounds were prepared and the time-resolved transient absorption spectra of these particles dispersed in acetonitrile were measured in visible wavelength region mainly at subpico- to several picoseconds time domain. To obtain knowledge about trap sites for electrons which are photo-produced on capped CdS particles in acetonitrile, the time-resolved transient absorption spectra of aqueous CdS colloidal solutions containing sodium hexametaphosphate (HMP) as a stabilizer against flocculation were also measured in the same time domain. The hole and electron trapping processes on semiconductor Q-particles that occur in ultrafast time region and their trap sites were discussed on the basis of the effects of the capping agent and solvent on the shape and decay dynamics of the transient absorption spectra.

2. Experimental details

2.1. Materials

Cadmium acetate dihydrate (Kanto Chem.), cadmium nitrate tetrahydrate (Kanto), sodium sulfide (Wako Chem.), thiophenol (PhS) (anhydrous, Kanto), 2-mercaptobenzoxazole (MBO, Tokyo Kasei), sodium hexametaphosphate (Kanto) and acetonitrile (spectro grade, Kanto) were used as received. Triply distilled water was used for the preparation of aqueous colloidal solutions.

2.2. Synthesis of capped CdS particles and preparation of their colloidal solutions for absorption measurements

PhS-CdS particles were prepared with an initial ratio of sodium sulfide to thiophenol of 2.0 in the following way [8,16]. Sodium sulfide (80 ml, 0.1 M) in water/methanol (1:1) was stirred for 10 min together with thiophenol (20 ml, 0.2 M) in acetonitrile in a three-neck flask under the nitrogen atmosphere. Cadmium acetate (100 ml, 0.105 M) in methanol/acetonitrile (8:2) purged with nitrogen was then added, producing a bright yellow cloudy suspension. And further, thiophenol (30 ml, 0.2 M) in acetonitrile was added to insure the capping of the particles. The solution was stirred for an additional 1 h before being evaporated to dryness. Extraction of the residue with 200 ml of acetonitrile by stirring overnight, followed by centrifugation and filtration, gave a yellow solid and a bright yellow filtrate from which a bright yellow solid was obtained by evaporative removal of acetonitrile. MBO-CdS particles were synthesized almost in the same way using 2-mercaptobenzoxazole instead of thiophenol as capping agent.

The colloidal solutions of the capped CdS particles for transient absorption measurements were prepared as follows. PhS-CdS colloidal solutions were prepared by dispersing the prescribed amounts of PhS-CdS powder in acetonitrile by sonication and then allowing to stand overnight before final

adjustment to desirable concentration by additional dilution with acetonitrile solvent. MBO-CdS colloidal solutions were prepared by dispersing the excess amounts of MBO-CdS powder in acetonitrile by sonication and then removing the insoluble solid from them by centrifugation after standing overnight.

The preparation of aqueous CdS colloidal solutions (HMP-CdS) containing HMP as stabilizer against flocculation was carried out as follows [30]. A 400-ml aqueous solution containing 2.5 mM sodium sulfide and 10 mM of HMP was stirred for 10 min in an Erlenmeyer flask. Cadmium nitrate aqueous solution (2 ml, 0.5 M) was then injected rapidly, producing a bright yellow transparent solution. The solution was prepared at the day before the measurements and used after diluting to desirable concentration. Typically, all colloidal solutions were prepared as their absorbance at 396 nm, maximum wavelength of pump pulse for pump and probe system, becomes ca. 0.3 using a quartz cell of 2 mm path length.

2.3. Measurements of subpicosecond transient absorption spectra

2.3.1. Laser system

The measurements of time-resolved transient absorption spectra presented here were performed with a subpicosecond laser flash photolysis system. Its schematic diagram is shown in Fig. 1. The light source of the system is a fundamental output (792 nm, ~ 1 mJ/pulse, ca. 250 fs FWHM, 10 Hz) from a Ti:sapphire regenerative amplifier system (TR 70, Continuum) with a Q-switched Nd:YAG laser (Surelite,

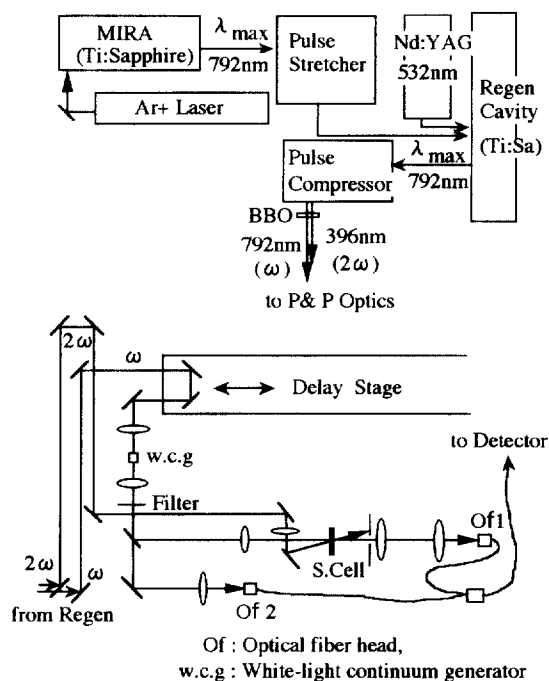


Fig. 1. Schematic diagram of the subpicosecond laser flash photolysis system.

Continuum), where the fundamental pulse (792 nm, ca. 170 fs FWHM, 76 MHz) from a cw self mode-locked Ti:sapphire laser (MIRA 900 Basic, Coherent) pumped by an argon ion laser (Innova 310, Coherent) is introduced as a seed beam.

A 396-nm pulse (ca. 250 $\mu\text{J}/\text{pulse}$) generated by frequency doubling of the fundamental output from the regenerative amplifier using a BBO crystal was used as a pump pulse for pump and probe measurements. The residual of the fundamental output was focused into a quartz cell of 1 cm path length containing water to generate a white-light continuum. The continuum pulse was divided into two, one being used as a probe pulse and the other as a reference pulse to correct shot-to-shot fluctuation of the spectra shapes and intensity of the probe pulse. The probe pulse that passed through a flow quartz cell of 2 mm path length containing a sample solution was focused at a head of an optical fiber cable by lenses and then introduced into an upper part of a dual diode array multichannel analyzer equipped a monochromator (DDA detector, Princeton Instrument). The reference pulse was introduced similarly into a lower part of the DDA detector by another optical fiber cable. The configurational angle between probe pulse and pump pulse at the sample cell was ca. 5° . The time delay between the pump and the probe pulses was controlled by changing the path length of the residual fundamental output by a translation stage (Sigma Koki, LTS-1000WLB) with a computer-controlled stepping motor before it was focused into the quartz cell for the generation of white-light continuum.

The controls of the shutters for pulses and a translation stage controller in the system, the selection for the data acquisition, and the processing of data obtained were performed using the software (supplied by Tokyo Instruments) and a personal computer.

2.3.2. Absorption measurements and chirp correction of the absorption spectra

At each delay time, 10 sets of the data that accumulated 10 shots of signals corresponding to I_0 , I , Dark (D), and Emission (E) in 400–700 nm wavelength region were acquired and then transient absorption spectra were obtained by calculating Δ absorbance by Eq. (1) for each set and averaging for 10 sets:

$$\Delta A = \log \left\{ \frac{[(I_0 - D)_S / (I_0 - D)_R]}{[(I - E)_S / (I - E)_R]} \right\} \quad (1)$$

where I_0 and I are the intensity of probe pulse in the absence and the presence of pump pulse, respectively, and the subscripts S and R denote the signals attained into the upper and lower parts of the dual diode array detector, respectively. Some transient spectra were calculated from a set of the data accumulated 50 shots of the signals. Sample solutions were circulated between the flow cell and a sample reservoir by a peristaltic pump (RP-N2, Furue Sci.) during the measurements to avoid the damage from the pump pulse. Typically, the pump pulse was adjusted to 250 $\mu\text{J}/\text{pulse}$ of energy by varying the configuration angle of the BBO crystal for frequency doubling and focused by a lens so as to be ca. 2.5 mm

in a spot size at the position of the sample cell. In every measurement of the transient absorption, the cross-correlation of a pump pulse (396 nm) and a residual fundamental (792 nm) one in the probe beam was taken by detecting sum frequency (264 nm) generated by a BBO crystal replaced the sample cell and used it as a standard of delay time (time = 0).

The determination of the temporal dispersion (chirp) with wavelength of the probe pulse was carried out by utilizing optical Kerr effect of carbon tetrachloride and acetonitrile. Both solvents showed same results. In the present laser system, the chirp between 450 nm and 700 nm of the probe pulse was ca. 2.0 ps. For all the transient absorption spectra at early time stage within a few picosecond after laser excitation, in which the chirp of the probe pulse influences seriously the shape and the intensity of the spectra, the correction of the chirp were performed for the spectra.

3. Results and discussion

3.1. Sizes of the capped CdS particles

The absorption spectra of PhS-CdS and MBO-CdS particles in acetonitrile and an aqueous HMP-CdS solution used in the present study are presented together with those of capping agents in Fig. 2. From the relationship between particle size and its absorption edge for CdS particles [31], the particle size of the capped CdS particles used in the present study was estimated to be about 30, 35, and 35–40 Å for PhS-CdS, MBO-CdS, and HMP-CdS, respectively.

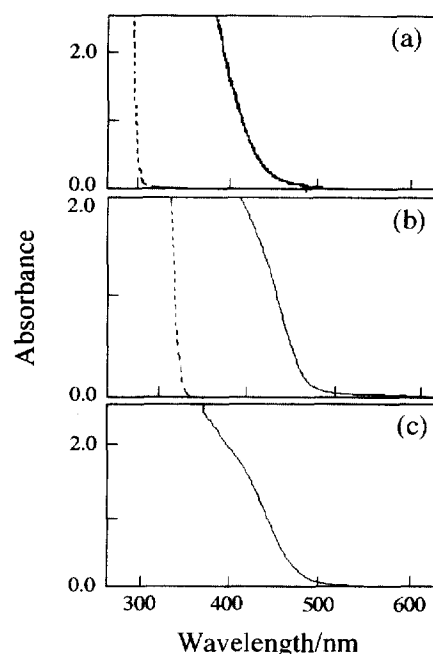


Fig. 2. The absorption spectra of PhS-CdS (a) and MBO-CdS (b) in acetonitrile and HMP-CdS (c) in water, measured using a quartz cell with 1 cm path length. Absorption spectra of capping agents used are also shown with dotted curves in the figure.

3.2. Transient absorption spectra of PhS–CdS

The corrected time-resolved transient absorption spectra of PhS–CdS particles in acetonitrile at various delay times of subpicosecond to picosecond after laser excitation are shown in Fig. 3. The upper part of the figure is the growth stage of the transient absorption and the lower part the decay stage. The transient absorption grows up thoroughly within ~ 1 ps after laser excitation, then decays rapidly until a few ps, and further decays slowly though it remains somewhat at 1 ns, except for the shorter wavelength region ($< \sim 460$ nm) influenced seriously by the stimulated Raman emission of solvent due to the pump pulse and the negative absorption of PhS–CdS particles owing to characteristic photo-bleaching of Q-particles [32–34]. The intensity of the transient absorption in longer wavelength region ($> \text{ca. } 600$ nm) observed immediately after laser excitation is larger than that in shorter wavelength region (around 480 nm) due to the trapped holes (S^- radical and/or PhS radical) [16,19,20,23]. The transient absorption in longer wavelength region observed in the present study is mainly assigned to the trapped electrons at the interface of particle–solution as will be described later, though it is known that hydrated electrons and the electrons ejected to organic solvent also have absorption at same longer wavelength region [25,27–29,35].

The results observed in the present study are different from those of nanosecond laser flash photolysis for PhS–CdS [16] and picosecond laser flash photolysis of naked CdS particles in acetonitrile [24]. Especially, the difference with results of naked CdS particles reported by Kamat et al. [24] is remarkable. They observed that there was scarcely any absorption in the longer wavelength region (> 600 nm) up to several hundreds picoseconds after laser excitation, but then the growth of the absorption continued in whole wavelength region including longer wavelength region up to over several nanoseconds with keeping the absorption maximum around 500 nm. Therefore, the pronounced difference suggests that thiophenol capped on the surface of the particles influences significantly the hole trapping process and decay kinetics of the trapped charge carriers at the surface of the particles. Namely, sulfur of thiophenol capped on the surface of the particles traps the photogenerated holes and consequently absorption in longer wavelength region due to trapped electrons is enhanced as the trapped electrons escaped from the recombination with the photogenerated holes increase in a very fast stage immediately after laser excitation. It is known that thiophenol as capping agent coordinates to cadmium atom on the surface of PhS–CdS particles with sulfur atom of thiol group [8] and that organic thiols (RSH) effectively suppress photoanodic decomposition of n -CdS in aqueous solutions and undergo photoelectrochemical oxidation to form the corresponding disulfides ($RSSR_2$) [36].

Furthermore, the difference from the results of nanosecond laser photolysis for PhS–CdS in acetonitrile seems to be attributable to the difference of the time region observed. In the present study using subpicosecond laser pulses, the

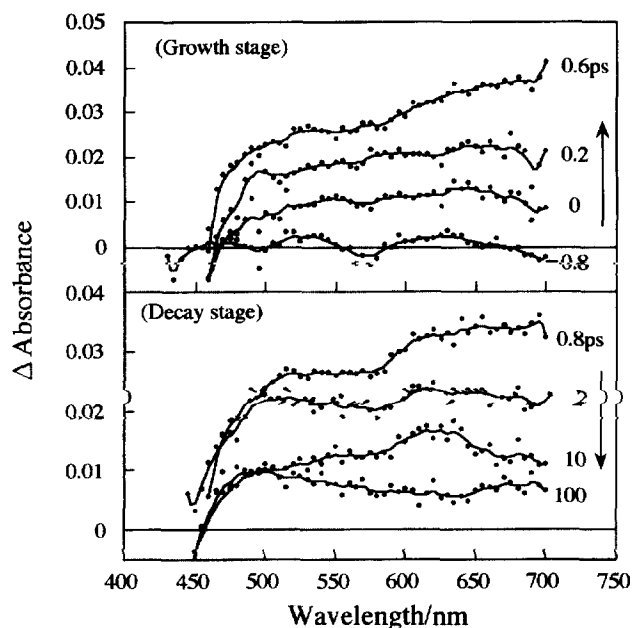


Fig. 3. The time-resolved transient absorption spectra of PhS–CdS in acetonitrile at various delay times. The spectra are corrected for temporal dispersion (chirp) of probe pulse.

absorption of the short-lived trapped electrons which was not observed in nanosecond time domain, was observed in longer wavelength region in subpicosecond to picosecond time domain in addition to the absorption due to trapped holes in shorter wavelength region. As a result, the spectra with relatively large absorption in a longer wavelength region were observed. Actually, the shape of the spectra recorded later than 100 ps after laser excitation in the present study is similar to that obtained immediately after laser excitation in nanosecond laser flash photolysis of PhS–CdS in acetonitrile reported previously [16]. In the nanosecond laser flash photolysis of PhS–CdS in acetonitrile, only the absorption with λ_{max} at 480–500 nm due to trapped holes (S^- radical and/or PhS radical) has been observed.

In order to investigate the temporal behavior for the growth and decay stages of the transient absorption of PhS–CdS, the time profiles of the transient absorption at 500 nm and 680 nm are shown up to 10 ps after laser excitation in Fig. 4. The transient absorption at 680 nm due to electrons trapped on the surface of the particles grow up completely within ~ 1 ps though the growth of the transient absorption at 500 nm mainly owing to trapped holes seems to be somewhat slower presumably because of the interference from the negative absorption in shorter wavelength region due to stimulated Raman emission and characteristic photo-bleaching of Q-particles. The decay of these transient absorption consists of a fast component which decays within a few picoseconds and a slow one which does not decay even in 10 ps time region.

Skinner et al. [29] have reported that the decay process of the transient absorption at 620 nm of probe wavelength obtained by subpicosecond laser flash photolysis of PhS–CdS in acetonitrile fits well to first order kinetics and therefore the

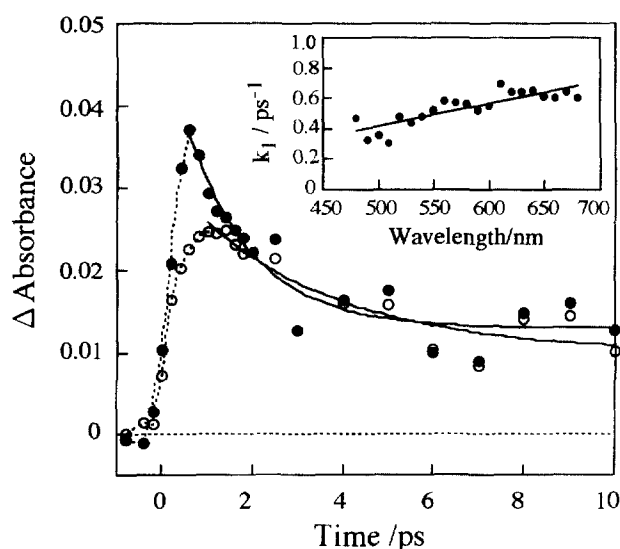


Fig. 4. The time profiles of transient absorption spectra of PhS-CdS in acetonitrile up to 10 ps at 500 nm (○) and 680 nm (●). The solid lines in the figure are best curves fitted with sum of an exponential function and base line for decay parts of the transient absorption. The inset is wavelength dependency of the first-order rate constant (k_1) obtained by the curve fitting.

growth and the decay processes of the transient absorption within ca. 2 ps can be fitted with the sum of an exponential growth (time constant: 90 fs) incorporated the convolution of a pump pulse, an exponential decay (time constant: 0.33 ps) corresponding to a fast decay component, and the base line corresponding to a long-lived decay one which decays hardly in this time region. Furthermore, it was reported by Zhang et al. [27,28] that the time profile of the transient absorption at longer wavelengths than ca. 600 nm for an aqueous mercaptoacetate-stabilized CdS colloidal solution can be well fitted with the sum of an exponential growth incorporated the convolution of a pump pulse, two exponential decays with time constants of 2–3 ps (attribute to non-geminate electron-hole recombination) and ~50 ps (attribute to geminate electron-hole recombination), and the offset corresponding to a more slower decay component which do not decay in this time region. Taking these reports into account, the curve fitting for only the decay part of the transient absorption of the present study was carried out with the sum of an exponential function (corresponding to a fast electron-hole recombination) and a base line (corresponding to a more slower decay component which do not decay in this time region) to obtain the rate constant k_1 for the fast decay component. The results were shown with solid lines in the figure. The first-order rate constants obtained from the curve fitting are $0.36 \times 10^{12} \text{ s}^{-1}$ (time constant $\tau_1 = 2.8 \text{ ps}$) and $0.60 \times 10^{12} \text{ s}^{-1}$ ($\tau_1 = 1.7 \text{ ps}$) for 500 nm and 680 nm, respectively.

The values of the first-order rate constant for a fast decay component of the transient absorption determined at various wavelengths are shown in the inset in Fig. 4. Although the inset shows some scatter, it appears that the first-order rate constants at longer wavelength mainly due to the trapped

electrons are somewhat larger than those at shorter wavelength mainly owing to the trapped holes. The present result seems to suggest that the process other than the recombination with the trapped holes participates partly in the decay of the trapped electrons (for example, the reaction with excess Cd^{2+} ion at the surface of the particles). However, since the molar ratio of Cd^{2+} ion to the sum of S^{2-} and PhS used at the preparation of PhS-CdS is smaller than unity, the excess Cd^{2+} ions adsorbed onto the surface, which can react with the trapped electrons, are probably absent. Furthermore, the wavelength dependency is not due to the reaction of the trapped electrons with adsorbed oxygen because there is no such tendency for the decay constant for MBO-CdS measured under the same experimental conditions. Therefore, the wavelength dependency seems to be mainly due to the influence from the recovery of photo-bleaching of PhS-CdS particles because, as seen from the figure, the rise of the absorption immediately after laser excitation at shorter wavelength (500 nm) is somewhat slower than that at longer wavelength, different from the case of MBO-CdS (as will be shown later in Fig. 6). Accordingly, it seems that the fast decay of the transient absorption occurs exclusively by the recombination of the trapped electrons and trapped holes.

3.3. Transient absorption spectra of MBO-CdS

The chirp-corrected time-resolved transient absorption spectra of MBO-CdS in acetonitrile, measured under the same experimental condition as PhS-CdS, are shown in Fig. 5. In addition to the negative absorption below 460 nm, as well as the case of PhS-CdS, the positive absorption which grows up fully within 1 ps after laser pulse excitation and

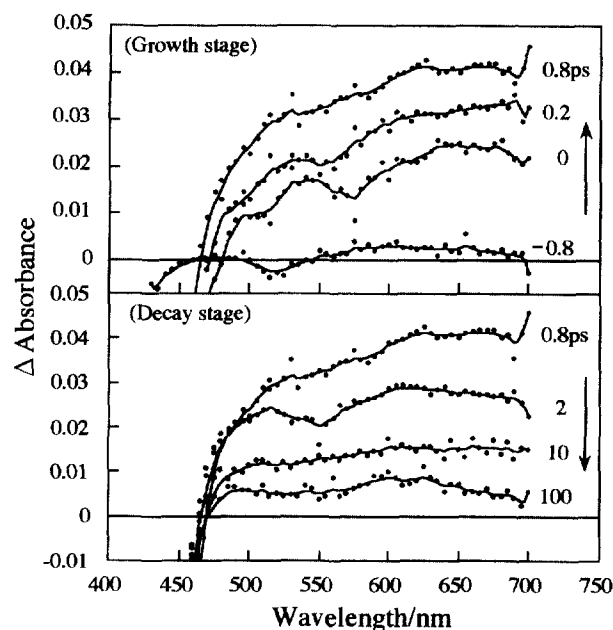


Fig. 5. The time-resolved transient absorption spectra of MBO-CdS in acetonitrile at various delay times. The spectra are corrected for the chirp of probe pulse. The experimental conditions are the same as those of Fig. 3.

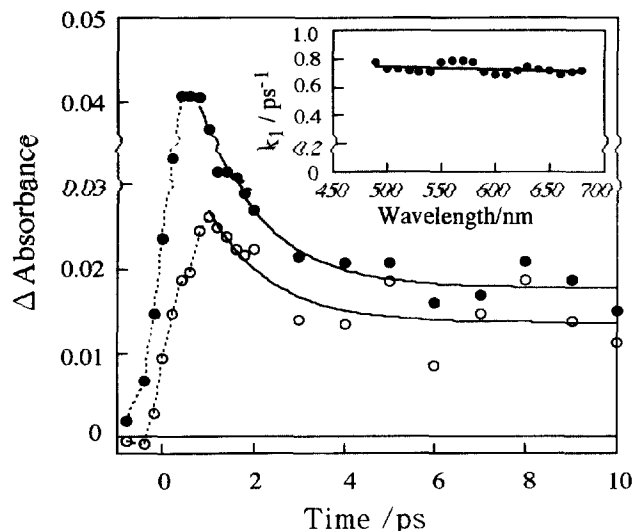


Fig. 6. Time profiles of transient absorption spectra of MBO-CdS in acetonitrile up to 10 ps at 588 nm (\circ) and 688 nm (\bullet). The solid lines in the figure are best curves fitted with sum of an exponential function and base line for decay parts of the transient absorption. The inset is wavelength dependency of the first-order rate constant (k_1) obtained by the curve fitting.

then decays is observed at the wavelengths longer than 460 nm. In the transient absorption spectrum after having grown up fully, the absorption at the longer wavelength region (< 600 nm) due to the trapped electrons is clearly larger than that at around 500 nm which seems to be mainly attributable to the trapped holes. The tendency is remarkable than in the case of PhS-CdS. It is considered that MBO as a capping agent exhibits analogous behavior as PhS.

The time profiles of the transient absorption at 500 nm and 680 nm are shown in Fig. 6. The time profiles at both wavelengths have a fast and a slow decay components as well as the case of PhS-CdS. The solid lines in the figure are the best curves consisting of the sum of an exponential function and a base line fitted to the decay part in these time profiles. The values of the first-order rate constant k_1 for the fast decay component at various wavelengths are also plotted as a function of wavelength in the inset in Fig. 6. The time constant for a fast decay component of the transient absorption is ca. 1.3–1.4 ps at all wavelengths measured. There is no wavelength dependency of the rate constant for a fast decay component in the case of MBO-CdS. Namely, it is clear that the fast decay of the transient absorption occurs exclusively by the recombination of the trapped electrons and trapped holes. And further, the rate constants are almost same as those at longer wavelength region for PhS-CdS and then there is hardly the difference in the effects of capping agents on the decay dynamics of the trapped charge carriers between MBO and PhS.

3.4. Transient absorption spectra of HMP-CdS

The transient absorption of CdS aqueous colloidal solutions containing HMP as colloid-stabilizer (HMP-CdS) was measured under similar experimental conditions with PhS-

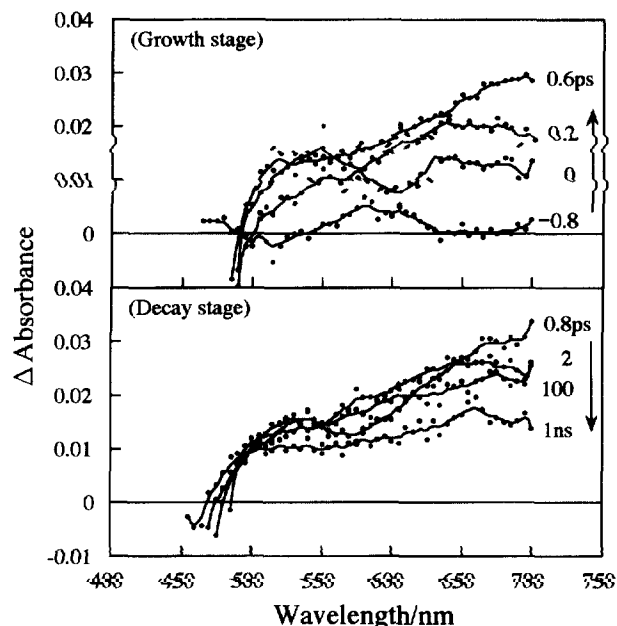


Fig. 7. The time-resolved transient absorption spectra of HMP-CdS in water at various delay times. The spectra are corrected for the chirp of probe pulse. The experimental conditions are the same as those of Fig. 3.

CdS and MBO-CdS in acetonitrile in order to obtain the information in connection with the effects of capping agents and solvents on the transient absorption of the capped CdS in acetonitrile at the longer wavelengths region. It is known that the hydrated electrons are generated by subpicosecond laser pulse excitation of aqueous HMP-CdS colloidal solutions [25].

The time-resolved transient absorption spectra of HMP-CdS, corrected for the chirp of probe pulse, are shown in Fig. 7. Although the large negative absorption below 480 nm is mainly attributable to the stimulated Raman emission due to OH stretching vibration of water as a solvent, it is considered that the photo-bleaching of HMP-CdS itself also participates in the negative absorption because the negative absorption did not disappear even at 500 ps after laser excitation. As mentioned above, since the particle size of 35–40 Å estimated for HMP-CdS from its absorption spectrum is slightly larger than those of PhS-CdS and MBO-CdS, it is supposed that the transient photo-bleaching shifts to longer wavelengths compared to the cases of PhS-CdS and MBO-CdS. Although the intensity of the transient absorption of HMP-CdS after having grown up fully is almost same as those of PhS-CdS and MBO-CdS in acetonitrile at longer wavelength region, the absorption intensity at shorter wavelength region mainly due to the trapped holes is considerably smaller compared to the latter two. Namely, the ratio of the absorption intensity of HMP-CdS at longer wavelengths (> 650 nm) to that at shorter wavelengths (around 500 nm) is clearly larger than those of PhS-CdS and MBO-CdS. On the other hand, the decay of its transient absorption at whole wavelength region measured is evidently slower than those of PhS-CdS and MBO-CdS as shown in Fig. 8. The results may

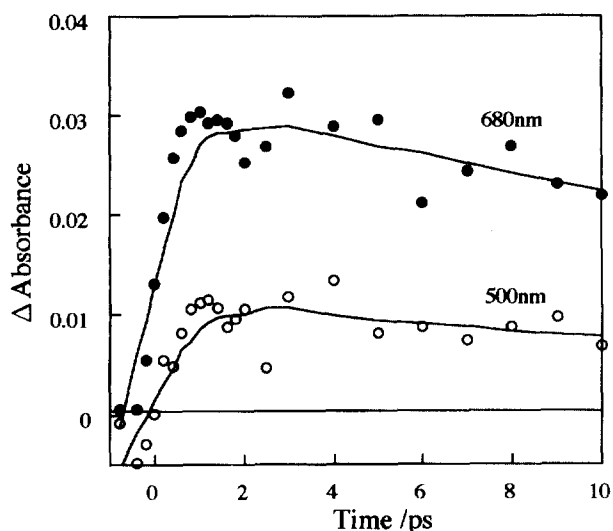


Fig. 8. The time profiles of transient absorption spectra of HMP-CdS in water up to 10 ps at 500 (○) and 680 nm (●).

suggest that the recombination between hydrated electrons which presumably exist in the vicinity of the interface of the particle–solution and the holes trapped at the surface of particles is slower and consequently the decay of the transient absorption becomes slower in aqueous HMP-CdS solutions at whole wavelength region where the transient absorption of both hydrated electrons and trapped holes appears. Such differences between PhS-CdS or MBO-CdS in acetonitrile and HMP-CdS in water seem to suggest that the trap site of electrons photo-generated in CdS particles in organic solvents such as acetonitrile is different from that of HMP-CdS in water where the production of hydrated electron is known.

4. Conclusions

The shape and decay profiles of the transient absorption spectra of PhS-CdS and MBO-CdS in acetonitrile obtained by subpicosecond laser flash photolysis are significantly different from the results of picosecond laser flash photolysis of ordinary non-capped CdS particles in acetonitrile previously reported by Kamat et al. It seems to suggest that thiophenol and 2-mercaptobenzoxazole as capping agents influence strongly the trapping processes of photo-generated holes and decay kinetics of trapped charge carriers at the surface of capped CdS particles. Furthermore, the shapes and decay kinetics of the transient absorption spectra of PhS-CdS or MBO-CdS in acetonitrile is clearly different from those of HMP-CdS in water, in which the photo-production of the hydrated electrons is known. These results seem to suggest that the trap site of the electrons generated by laser excitation of PhS-CdS or MBO-CdS in acetonitrile is mainly at the interface of particle–solution and the possibility for the production of solvated electrons is low unlike the case of HMP-CdS in water.

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