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Subpicosecond spectroscopic studies on the photochemical events of 2-dimethylaminoethanethiol-capped CdS nanoparticles in water

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Abstract

In order to confirm further the charge effect of capping agent on the photochemical events of the surface-capped CdS particles, the colloidal solution of 2-dimethylaminoethanethiol (ET)-capped CdS particles (ET-CdS) was prepared and its subpicosecond time-resolved transient absorption was measured. ET has a positive charge in its protonated form. From the comparison with the data for TG-CdS (TG: 1-thioglycerol), measured under same experimental conditions, the influence of the positive charge of the capping agent on the behavior and decay dynamics of the photo-generated electron and hole was investigated. It was suggested from these results that ET which was used as a capping agent in the present study was protonated and then acted as an electron capturer rather than as a hole scavenger in neutral pH range. As a consequence, disappearance of the photo-generated electrons in the primary photochemical events of ET-CdS colloidal solutions was accelerated, compared with that for TG-CdS colloidal solutions. The result also suggests that the charge of capping agents on the particles significantly affects the behavior of electrons and holes generated by the photo-excitation of the particles. However, pH dependence was not observed for the transient absorption of ET-CdS and its decay dynamics. As the reason, it is considered that the proton-elimination equilibrium of the protonated ET capping on the surface of CdS cores are hardly affected by the change of pH of the solutions in the adjustable pH range, hence, the total electron trapping ability of capping agents on the particles also did not change significantly.

Keywords: Cadmium sulfide; 2-Dimethylaminoethanethiol-capped CdS; Transient absorption; Photocatalyst; Subpicosecond spectroscopy

1. Introduction

When more effective photocatalysts are designed, it is very important to understand the detailed behavior of the electrons and holes generated immediately after the photo-excitation, which influences significantly on the whole efficiency of the semiconductor photocatalysis. To date the large number of mechanistic and kinetic studies on the photochemical events of semiconductor particles have been conducted by transient absorption measurements [1–20]. Since the thiols-capped CdS nanoparticles, which are relatively convenient to deal with and can be prepared easily as optically transparent colloidal solutions, are suitable for the studies of the photocatalytic events of semiconductor particles, preparation and characterization of several kinds of the colloidal solutions containing thiols-capped CdS particles have been done [21–23]. It is considered that the capping agent on the surface of the particles influences significantly for the transfer of the photo-generated electrons and holes to substrates and the approach of the substrates to the surface of the particles. Therefore, the surface-modified semiconductor particles are interesting from the designing of the effective semiconductor photocatalysts with high charge separation efficiency by utilizing actively the capping agents as a mediator for the electron or hole transfer.

We have investigated the influence of the capping agents on the surface of the particles upon the behavior of the photo-generated electrons and holes in the surface-modified CdS nanoparticles by subpicosecond time-resolved transient absorption measurements of the colloidal solutions containing thiols-capped CdS particles [24–29]. From the previous

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results, it was found that the charge of the capping agents influences their electron and hole-trapping abilities and consequently the intensity of the transient absorption (ΔA), which is mainly attributable to the photo-generated electron, in visible wavelength region (500–700 nm). There is no pH dependence on ΔA of the aqueous colloidal solutions containing TG-CdS particles with the surface capped by thioglycerol (TG) which does not have the dissociable proton. However, there is pH dependence on ΔA of the aqueous colloidal solutions containing MA-CdS particles with the surface capped by mercaptoacetate (MA) which exists in the protonated and deprotonated forms, that is, ΔA in high pH range where majority of MA probably exists as a deprotonated form, is higher than that in low pH range. As the reason, it was proposed that the electrons which escaped from the recombination with holes increased in high pH range comparing with in the low pH range because the deprotonated MA with negative charge increased and consequently the hole-trapping ability of the capping agent increased as a whole. Thus, whether the capping agent on the particle surface has charge is an important factor influencing the efficiency and kinetics of the transfer of the photo-generated electrons or holes to substrates in the particle–solution interface. Therefore, it is necessary to consider the pH of the colloidal solutions when the capping agent with the protonated–deprotonated equilibrium is used.

In the present study, the colloidal solution containing 2-dimethylaminoethanethiol (ET)-capped CdS particles (ET-CdS) was prepared and its subpicosecond time-resolved transient absorption was measured in order to confirm further the previous charge effect of capping agent on the photochemical events of the surface-capped CdS particles [29]. ET has a positive charge in its protonated form. From the comparison with the data for TG-CdS (TG: 1-thioglycerol), measured under same experimental conditions, the influence of the positive charge of the capping agent on the behavior and decay dynamics of the photo-generated electron and hole was investigated.

2. Experimental

2.1. Preparation of ET-CdS colloidal solutions

ET-CdS colloidal solution was prepared as follows. A 50 ml of 5 mM ET (adduct with hydrochloride) in water and a 50 ml of 10 mM cadmium acetate in water were well mixed in a 300 ml Erlenmeyer flask in the water bath thermostatted at 23 °C. While stirring the solution, a 100 ml of 5 mM sodium sulfide in water was slowly added into it with a burette. The light yellow turbid solution containing ET-CdS particles was obtained. After the colloidal solution was centrifuged for 1 h, its supernatant portion was allowed to stand overnight in the dark and then used for the transient absorption measurements after the adjustment of the concentration. TG-CdS nanoparticles were synthesized by pyrolysis of thiourea in the presence of cadmium acetate and 1-thioglycerol [23,26]. Aqueous colloidal solutions of TG-CdS were prepared by dispersing the TG-CdS nanoparticles into water. The absorption spectra of aqueous solutions of ET-CdS and TG-CdS prepared are shown in Fig. 1. From the estimation using the absorption spectra in Fig. 1 and the relationship between the particle size and absorption edge for CdS particles [30] the sizes of CdS core parts of ET-CdS and TG-CdS particles used in the present study were ca. 3.0–3.5 nm and ca. 2.5 nm, respectively.

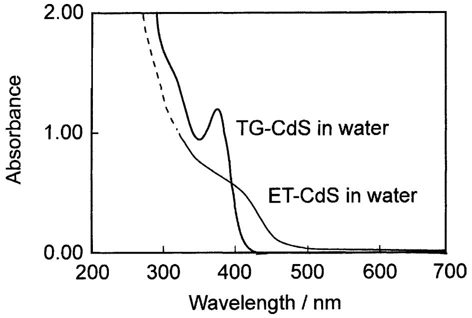

Fig. 1. Absorption spectra of ET-CdS and TG-CdS in water.

In all the measurements, the absorbance of both capped CdS colloidal solutions was adjusted to 0.6 at 396 nm (pumping wavelength) with a 2 mm cell. In the measurements for the pH dependence of the transient absorption of ET-CdS, pH of the colloidal solutions was changed in the pH range of 3.6–8.6. Stable colloidal solutions of ET-CdS could not be prepared in the outside of the pH range because the colloidal solution became turbid.

2.2. The measurements of subpicosecond time-resolved transient absorption spectra

The transient absorption measurements were carried out by a pump-probe technique using a subpicosecond spectroscopy system used in the previous studies [29]. The pump pulse was a 396 nm pulse generated by frequency doubling of the fundamental output (λ_{max} = 792 nm) from a Ti:Sappire regenerative amplifier (10 Hz) using a BBO crystal and the probe pulse was a white light continuum generated by focusing the residual of the fundamental output into a 10 mm quartz cell containing water. The pulse width of both pump and probe pulses, estimated by the cross-correlation between the pump pulse and a fundamental pulse in the probe using the generation of the sum frequency, was less than 1 ps. The pump pulse intensity used was usually 90 μJ per pulse. The quartz flow cell with 2 mm in path length was used usually as a sample cell and the sample solution was circulated using a roller pump during the measurement though a 2 mm quartz cell was used in a part of measurement.

The transient absorption spectra were acquired as follows. At each delay time, 10 shots of signals were accumulated and the calculation of ΔA was carried out by using them. By repeating similar acquisition and calculation, 5–10 sets of ΔA were obtained at each delay time. The average values of them were used as ΔA at each delay time for subsequent data processing. The correction of the chirp for the probe pulse was performed for the transient spectra by utilizing the rise time for the transient absorption of perylene in acetone. However, in the case of that the transient absorption of each sample was discussed at identical wavelength, the uncorrected spectra were used. Other details for the transient absorption and data processing were described elsewhere [27–29].

3. Results and discussions

3.1. Characteristics of subpicosecond time-resolved transient absorption spectra of an aqueous ET-CdS colloidal solution: the comparison with those of aqueous TG-CdS colloidal solutions

The corrected transient absorption spectrum of an aqueous colloidal solution containing. ET-CdS nanoparticles, observed at 1 ps after the 396 nm laser pulse excitation, is shown in Fig. 2, together with that of TG-CdS in water. The spectra of the two different capped CdS nanoparticles grew up within the duration time (ca. 1 ps) of the pump pulse. The transient absorption for ET-CdS is weak compared to that for TG-CdS, especially in a longer wavelength region. Assignment of the spectrum of TG-CdS was performed from the analogy to that of the colloidal solution of usual CdS nanoparticles [10] as follows [27]. The very broad absorption band which spread over a whole visible region is the superposition of three absorption bands. Namely, first one is attributable to the trapped hole which has the absorption maximum around 400–500 nm and extends into the longer wavelength region. Second one is attributable to the trapped electron which has the absorption maximum around 700 nm and extends into the shorter wavelength region of around 500 nm. And third one is attributable to the hydrated electron which exists in the same wavelength region as that for the trapped electron. It is expected that absorption of ET hardly appears in the visible region with a wavelength longer than 500 nm, even if ET with protonated or deprotonated amino group accepted the photo-generated electron. This is because generally the absorption of simple amines without conjugated double bonds and their radical is hardly observed in the region. Therefore, it seems that the absorption of an aqueous ET-CdS colloidal solution is also the superposition of three absorption bands mentioned above. When the transient absorption spectra of ET-CdS were compared in detail with those of TG-CdS, however, the ratio of ΔA around 700 nm to that around 500 nm is different between ET-CdS and TG-CdS. Roughly, the absorption bands around 500 nm and 700 nm are mainly due to holes and electrons, respectively. The difference in the ratio between for TG-CdS and for ET-CdS originates from the difference in the formation and decay dynamics of the holes and the electrons between both aqueous colloidal solutions. Furthermore, it is considered that a large negative absorption in the shorter wavelength region than around 470 nm for both aqueous colloidal solutions is attributable mainly to the stimulated Raman of water because the absorption recovers within the duration time of a pump pulse. The details of the discussion will be described later.

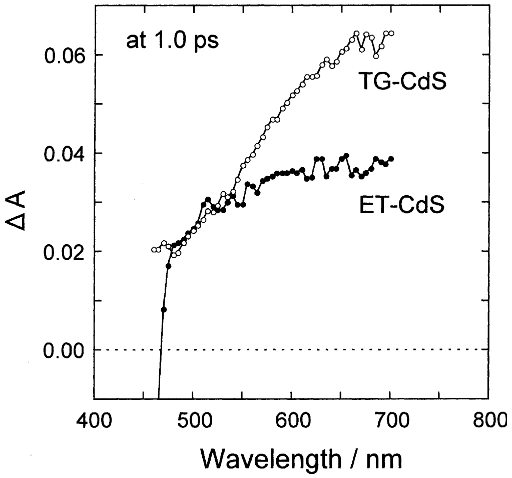

Fig. 2. The transient absorption spectra of ET-CdS and TG-CdS in water at 1 ps after the pump pulse excitation. The spectra are corrected for the chirp of the probe pulse.

3.2. Decay dynamics of the transient absorption of ET-CdS: comparison with that for TG-CdS

For the comparison of the decay dynamics of the transient absorption of ET-CdS and TG-CdS, the time profiles of their ΔA at 700 nm, which were measured under the same excitation intensity (90 μJ/pulse), are shown in Fig. 3. In this figure, the relative intensities normalized to each maximal value were used for their transient absorption in order to facilitate the understanding. The solid lines in the figure are the best fitted curves by using Eq. (1). In general, it is known that the decay of the transient absorption of CdS nanoparticles in

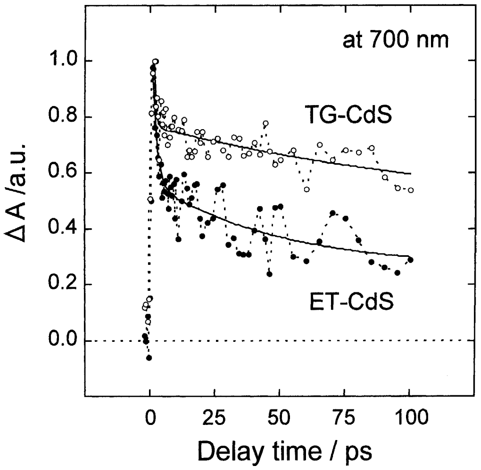

Fig. 3. Time profiles of the transient absorption at 700 nm for ET-CdS and TG-CdS in water.

water consists of the three decay components [27]. Namely, first one is the fast process with the lifetime of several picoseconds, the second one is the slow process with the time constant of several tens to several hundred picoseconds, and third one is the very slow process which decays hardly up to several nanosecond time domain. Therefore, the decay part of their time profiles can be fitted by sum of two exponentials and one constant such as Eq. (1):

$$\Delta A(t) = A_1 \exp(-k_1 t) + A_2 \exp(-k_2 t) + \text{const} \quad (1)$$

where $\Delta A(t)$, A_i and k_i denote the intensity of the transient absorption at t ps after the pump pulse excitation, the pre-exponential factor, and the decay time constant for the fast and slow components, respectively, and further Const denotes the absorption intensity for the very slow component which can be regarded as a constant in several tens of picoseconds. For ET-CdS, the decay dynamics of the transient absorption at a wavelength range longer than ca. 550 nm shows the almost same tendency as that at 700 nm as well as the case of TG-CdS. It was found that the ratio of the fast decay component to the whole decay ones at 700 nm for ET-CdS was evidently larger compared with that for TG-CdS. The decay rate constants (k_1) of the fast component for ET-CdS and TG-CdS, estimated by the best fitted curves in Fig. 3, were 0.59 ps^{-1} and 0.13 ps^{-1}, respectively. The decay constant k_1 for ET-CdS is larger than that for TG-CdS. Evidently the difference of the capping agent also appears in the early stage of the decay kinetics as well as their ΔA.

It is considered that TG and ET also trap the photo-generated holes to some degree since they contain a sulfur atom [7]. Therefore, in the transient absorption immediately after the pump pulse excitation, it is expected that ΔA in a longer wavelength region in which the photo-generated electrons are mainly concerned becomes larger than that in a shorter wavelength range in which the photo-generated holes are mainly concerned. In fact, the expected result was observed in the transient absorption of TG-CdS. However, it was not observed clearly in the transient absorption of ET-CdS compared with the case of TG-CdS. This difference probably originates from the difference in the electron accepting ability between ET and TG as a capping agent. Namely, it is considered that amino group of a part of ET on the surface of CdS particles was protonated and consequently was changed to ammonium ion structure with a positive charge because 2-dimethylaminoethanethiol hydrochloride was used as ET. Therefore, it seems that the decay of the transient absorption of ET-CdS is faster than that of TG-CdS because ET also acts as an electron acceptor and then traps the photo-generated electrons more rapidly, different from TG which does not undergo protonated–deprotonated equilibrium (Fig. 4). It seems that electron transfer occurs more easily with protonated ET than with deprotonated one, when analogized from the reaction of cysteamine and hydrated electron [31]. This is the reason why ΔA for ET-CdS in a longer wavelength is lower and the ratio of the fast decay component in its decay process is higher and further the decay rate is faster than those of TG-CdS. It is known that the particle size does not influence the electron trapping dynamics on the surface of CdS nanoparticles in a size range of 2–4 nm [13]. Therefore, it seems that the difference in the electron transfer dynamics between two type of CdS nanoparticles is not due to the difference in their particle size. The pH effects of the transient absorption of ET-CdS and its decay dynamics will be described later.

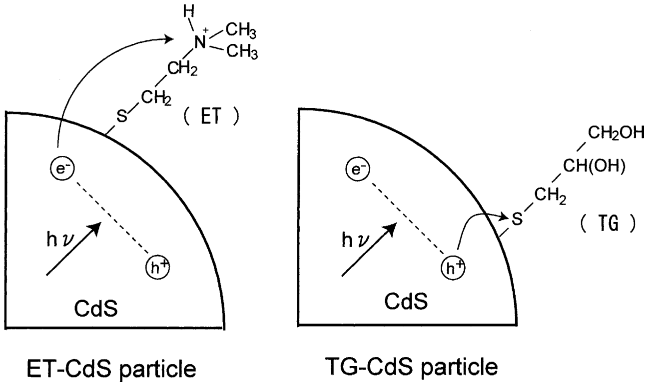

Fig. 4. Schematic representation of the electron and hole transfers to the capping agents on the surface of the particles.

Although there is an influence of the hydrated electron on the transient absorption of aqueous colloidal solutions of ET-CdS and TG-CdS, the influence has not been mentioned here. It is expected that both the influence on the decay dynamics of the transient absorption for the two colloidal solutions and the difference in their influence may be little in the early decay stage in which the fast decay occurs mainly though the influence on the intensity of ΔA may be somewhat different because a hydrated electron is produced within 1 ps and is stable for at least 10 ps. The absorption measurements for both colloidal solutions were carried out under the same conditions including the pump pulse intensity. The details of the influence of the hydrated electron production on their primary photochemical events will be described soon elsewhere.

3.3. The influence of coexisting ions on the transient absorption of ET-CdS in water

In previous section, we concluded that the capped ET with a positive charge on the surface of the CdS particles acts as an electron acceptor, as the reason why the transient absorption of ET-CdS decay more rapidly compared with that of TG-CdS in water. However, it is necessary to evaluate the influence of the difference in the preparation process of their colloidal solutions on their transient absorption because their colloidal solutions were prepared by the different methods as described in the experimental section. Namely, it is considered that non-reacted starting material and counter ions coexist in an aqueous ET-CdS colloidal solution because the colloidal solution was prepared directly as the colloidal solution, though an aqueous TG-CdS colloidal solution contained little contaminants such as starting materials because

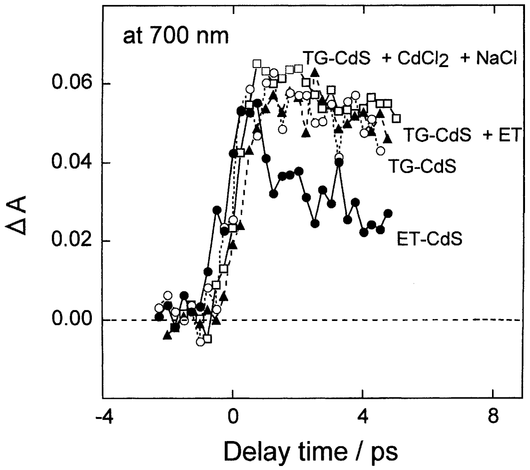

Fig. 5. Time profiles up to 5 ps for the transient absorption (at 700 nm) of TG-CdS in water, in the absence (◯) and the presence of $CdCl_2$ + NaCl (☐) and ET (▲). The time profile for ET-CdS in water (●), measured under the same experimental conditions as TG-CdS (◯), is also shown in the figure.

it was prepared by dispersing TG-CdS particles synthesized as solid powder into water. Since the starting materials with a positive charge such as the protonated ET, Cd^{2+} and Na^{+} may act as an electron scavenger, it is necessary to evaluate their influence on the decay dynamics of the transient absorption. In order to confirm the behavior of these contaminants as an electron scavenger, the solvent environment for TG-CdS was changed to the environment similar to that for ET-CdS by adding such ions and then the influence of the solvent environment on the decay dynamics of the transient absorption of TG-CdS was examined. Both TG-CdS colloidal solutions prepared were the solutions containing 1 mM ET and both 0.5 mM $CdCl_2$ and 5 mM NaCl, respectively. The concentrations of additives were increased more than those of contaminants in ET-CdS which were estimated from the concentration of starting materials in order to enhance the influence of the additives on the decay dynamics. The time profiles (up to 5 ps) of the transient absorption at 700 nm for both TG-CdS colloidal solutions are shown in Fig. 5 together with those of TG-CdS without additives and ET-CdS. As shown in Fig. 5, the decay dynamics for both TG-CdS colloidal solutions containing additives is similar to that for TG-CdS without additives but not that for ET-CdS. This result suggests that additives such as ET, Cd^{2+} and Na^{+} do not affect the fast decay process of the transient absorption of TG-CdS. The similar result was also obtained when methylviologen was used as an additive. The reason may be because additives in a bulk solution can not approach to the CdS core of TG-CdS particles due to steric hindrance of TG covering the surface. Furthermore, taking into account that time constant for the diffusion of additives in the aqueous solutions is in the nanosecond time domain, it is not considered that the additives in a bulk solution affect significantly the decay of the transient absorption within the time domain of several picoseconds. It can be inferred from this discussion that coexisting ions in aqueous ET-CdS colloidal solutions do not also influence the fast decay process of the transient absorption of ET-CdS. Therefore, it is considered that the fast decay of the transient absorption of ET-CdS is due to the capturing of the photo-generated electrons by ET capping the CdS core of the particles.

3.4. Influences of pH of the colloidal solutions of ET-CdS on their transient absorption and its decay dynamics

Recently, we reported that the transient absorption of mercaptoacetate-capped CdS particles (MA-CdS) in water enhanced at a longer wavelength region concerning the photo-generated electrons when pH of the colloidal solution was increased over about 7 [29]. This is because most of MA with a dissociable proton in the carboxyl group except for a thiol proton exists as the deprotonated form in this pH range and its hole-trapping ability is enhanced due to its negative charge and consequently the electrons which escaped from the recombination with holes increases. On the other hands, since TG-CdS does not have a dissociable proton except for a thiol proton, pH dependence was not observed.

As ET used as a capping agent in the present study was supplied as the adduct with hydrochloride, it was considered that its amino group was protonated and there was the protonation equilibrium in an aqueous colloidal solution of ET-CdS. Therefore, it is expected that the transient absorption of ET-CdS colloidal solutions and its decay dynamics are affected by the pH of the solutions different from the case of TG-CdS because the hole-trapping ability of ET is influenced significantly by whether ET is protonated or not. The transient absorption spectra of ET-CdS colloidal solutions with various pHs which were measured at 0.5 ps after the pump pulse excitation are shown in Fig. 6. The inset in the figure is a plot of the absorption intensity (Δ*A*) at 700 nm versus pH of the colloidal solutions. In the pH range we adjusted

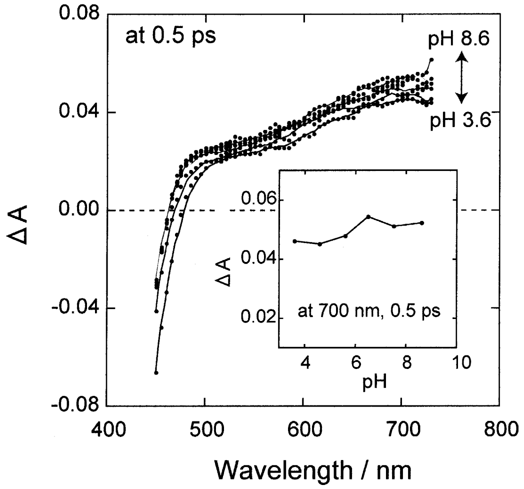

Fig. 6. The pH dependence of the transient absorption spectrum of ET-CdS in water. The spectra at various values of pH were measured at 0.5 ps after the pump pulse excitation and corrected for the chirp of the probe pulse. The inset is the pH dependence of Δ*A* at 700 nm at 0.5 ps.

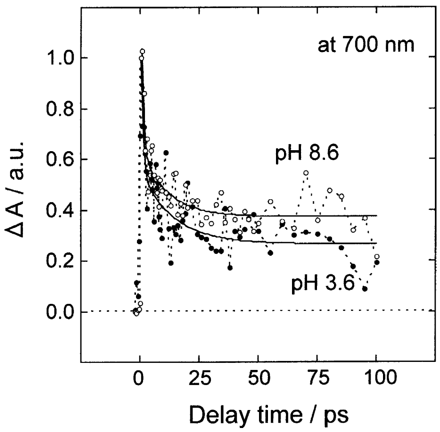

Fig. 7. Time profiles up to 100 ps for the transient absorption (at 700 nm) of ET-CdS in water at pH 3.6 and 8.6. The solid lines in the figure are the best fitted curves by using Eq. (1) in the text.

in the present study, there was hardly pH dependence in the transient absorption of ET-CdS colloidal solutions. The time profiles of the transient absorption at 700 nm for both ET-CdS colloidal solutions with pH 3.6 and 8.6 are shown in Fig. 7. Curves in the figure are the best fitted curves by using Eq. (1) for the decay part of the transient absorption. It seems that the rate constant k_1 for the fast decay component is somewhat larger and overall decay is also faster at the low pH than those at the high pH. However, it seems that the difference between the two results can not be regarded as a significant difference because there is large dispersion in these spectra. A similar tendency was also observed at 600 nm and 650 nm. As generally judged from the transient absorption intensity and its decay dynamics, it seems that pH of the solutions does not influence the behavior of the transient absorption of ET-CdS at least in the pH region (pH 3.6–8.6) we investigated. It may be appropriate that the transient absorption of ET-CdS colloidal solutions is hardly dependent on pH of the solutions, as well as the colloidal solutions of TG-CdS which does not have the dissociable proton except for a thiol proton, provided that most of ET exists as a protonated form and deprotonation occurs hardly by the change of pH in this pH range we could adjust, because pK_a of aliphatic amines is more than 10 [32]. As described in the experimental section, stable colloidal solutions of ET-CdS could not be prepared in high pH range because the colloidal solution became turbid.

In conclusion, it was found that ET which was used as a capping agent in the present study was protonated and then acted as an electron capturer rather than as a hole scavenger in neutral pH range. As a consequence, disappearance of the photo-generated electrons in the primary photochemical events of ET-CdS colloidal solutions was accelerated, compared with that for TG-CdS colloidal solutions. The result suggests that the charge of capping agents on the particles significantly affects the behavior of electrons and holes generated by the photo-excitation of the particles. However, pH dependence was not observed for the transient absorption of ET-CdS and its decay dynamics. As the reason, it is considered that the proton-elimination equilibrium of the protonated ET capping on the surface of CdS cores are hardly affected by the change of pH of the solutions in the adjustable pH range, hence, the total electron trapping ability of capping agents on the particles also did not change significantly.

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