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Subpicosecond spectroscopic studies of photochemical events involving thioglycerol-capped cadmium sulfide particles

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Abstract

In order to elucidate the dynamics of electrons and holes photoproduced on the surface-modified semiconductor Q-particles, subpicosecond laser flash photolysis of thioglycerol-capped cadmium sulfide (TG-CdS) particles was carried out in various solvents. The transient absorption due to electrons and holes photoproduced on TG-CdS particles was observed immediately after subpicosecond laser pulse excitation. The transient absorption is larger in water than in water + acetonitrile (4 : 1) and dimethylformamide (DMF). The difference among them may be attributable to the production of hydrated electrons. The decay process of the transient absorption can be classified roughly into three groups as follows; (1) the fast one decaying within a few picoseconds due to electron–hole recombination in which plural electron–hole pairs participate, (2) the second one with life time of several tens to several hundred picoseconds due to normal electron–hole recombination and (3) the third component concerning with hydrated electrons which does not decay up to several nanoseconds. In DMF, however, the third component was not observed. The relative ratio among three decay components depends on solvents.

Keywords: Cadmium sulfide; Thioglycerol-capped CdS; Q-particles; Subpicosecond spectroscopy; Hydrated electrons

1. Introduction

The photocatalytic reaction utilizing powerful redox forces of electrons and holes photogenerated in semiconductor particles is attracting the attention of a large number of chemists because of the potential usefulness for hydrogen production from water by use of solar energy, novel organic syntheses, the treatment of industrial wastes, etc. [1–3]. However, when the semiconductor photocatalyst is utilized for them, it becomes a significant disadvantage that its quantum efficiency is generally very low owing to the very fast recombination of electrons and holes photogenerated in the particle [1,2]. Therefore, the improvement in the quantum efficiency is needed for applications.

On the other hand, it is known that semiconductor nanoparticles (Q-particles) show characteristic photophysical and photochemical properties due to the quantum size effect [4–8]. However, Q-particles with narrower size distribution are necessary to elucidate their photophysical and photochemical properties in detail and then their syntheses are attempted with various synthetic methods [9–25]. Among them, Q-CdS particles with the surface modified by capping agents such as thiols have relatively narrow size distribution and are available as bottlable solids which can be dispersed in the solvents without stabilizer against flocculation [15,19]. And further, these capped Q-particles are advantageous to study their photophysical and photochemical properties, especially the primary photochemical events using ultrafast kinetic spectroscopy. In addition, it is considered that the capping agents on the surface of Q-particles act not only as trap and recombination sites for the charge carriers photogenerated in the particles but also as the mediator for the charge carrier transfer at the particle–solvent interface. Therefore, there are the possibilities that the recombination between electrons and holes photogenerated in the particles can be controlled using suitable capping agents and consequently, the quantum efficiency of photocatalytic reactions can be improved.

Therefore, we consider it is important to examine primary photochemical events, especially, trapping and decay processes of electrons and holes photogenerated, of the surface-

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modified semiconductor particles from the standpoint to design effective photocatalyst by use of capping agents. From such standpoint, we have so far prepared acetonitrile-soluble CdS nanoparticles with the surface modified by some thiols and investigated their primary photochemical events by the measurements of their time-resolved transient absorption with nano- and subpicosecond spectroscopy as a beginning [26–28].

As a part of them, in the present study, the behavior of photogenerated electrons and holes was investigated from kinetic analysis of the transient absorption spectra for thioglycerol-capped cadmium sulfide (TG-CdS; it is known as the surface-modified semiconductor particles with a clear exciton absorption maximum and a relatively narrower size distribution [19]) in water, water + acetonitrile, and DMF to elucidate dynamics of electrons and holes photoproduced on the surface-modified semiconductor Q-particles. In particular, detailed discussion for the behavior of trapped and hydrated electrons was done. So far, several studies on photoproduction of trapped holes and electrons and/or hydrated electrons have been reported in non-capped CdS colloidal solutions by analysis of their transient absorption [29–36]. However, there are a few reports [34] which dealt with the dynamics of electrons and holes together in analysis of the transient absorption. Especially, it seems that there is no report which took both trapped and hydrated electrons into consideration for aqueous CdS colloidal solutions.

2. Experimental section

2.1. Preparation of TG-CdS particles and their colloidal solutions

TG-CdS particles used were synthesized from cadmium acetate, thiourea as sulfide source, and thioglycerol as a capping agent according to a literature [19] as reported in our previous study [28]. The colloidal solutions of TG-CdS particles were prepared by dispersing a necessary amount of the synthesized particles into each solvent using a sonicator. The concentration of TG-CdS in the solutions was calculated on the basis of the Cd content of the particles which was determined by EDTA titration [28].

Absorption spectra of TG-CdS colloidal solutions showed the same spectral shape and onset wavelength in all water, water + acetonitrile (4 : 1), and DMF solvents. CdS core size of the particles estimated from the relationship [37] between sizes of CdS particles and the longer wavelength edge of their absorption spectra is about 25 Å.

2.2. Measurements of the transient absorption

The measurements of the time-resolved transient absorption spectra were carried out with our subpicoseond laser flash photolysis system [27]. The light source of the system is a fundamental output (792 nm, ~1 mJ/pulse, ca. 250 fs FWHM (full width at half maximum), 10 Hz) from a Ti:sapphire regenerative amplifier system (TR 70, Continuum) with a Q-switched Nd:YAG laser (Surelite, 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. The pump pulse was a 396 nm pulse generated by frequency doubling of the fundamental output from the regenerative amplifier using a BBO crystal and the probe was a white light continuum generated by focusing the residual of the fundamental output into a 10 mm quartz cell containing water. The wavelength region of the probe pulse used was from 430 nm to 730 nm. The pump pulse was adjusted to 150 μJ/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. 2.0 mm in a spot size at the position of the sample cell.

The transient absorption spectra were acquired as follows. At each delay time, 10 shots of signals were accumulated and the calculation of ΔA (A, absorbance) was carried out using them while changing the delay time from short to long. By repeating similar acquisition and calculation, five 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 cross-correlation of a pump pulse and a probe pulse was taken by detecting sum frequency generated by a BBO crystal at sample cell position. The determination of the temporal dispersion (chirp) with wavelength of the probe pulse was carried out by utilizing the rise time for the transient absorption of perylene in acetone at each wavelength. For all the transient absorption spectra at early time stage within 10 ps 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 was performed for the spectra.

In the measurements, the concentration of TG-CdS colloidal solutions were adjusted as their absorbance at 396 nm (pumping wavelength) becomes 0.6 with a 2 mm-cell in all solvents. All the TG-CdS colloidal solutions were circulated between a non-fluorescent sample flow cell (2 mm in pass length) and a sample reservoir by a roller pump (FURUE SCIENCE, PR-NE3) during the measurements to avoid the damage from the pump pulse. The removal of dissolved oxygen from the colloidal solutions was not made since the effects of deoxygenation on the shape and intensity of the transient absorption spectra for the sample solutions were not observed in preliminary experiments. And further, there were no changes on the ordinary absorption spectra of the sample solutions after being used in pump-probe experiments.

Other details for the measurements of the transient absorption and data processing are described elsewhere [27].

3. Results and discussion

3.1. *Time-resolved transient absorption spectra of TG-CdS particles in various solvents*

3.1.1. *Shape and intensity of the transient absorption spectra*

Subpicosecond time-resolved transient absorption spectra of TG-CdS particles in water are shown in Fig. 1. In the entire, visible wavelength region except the wavelength shorter than ca. 530 nm, where there is the influence of stimulated Raman emission of water, the transient absorption grows considerably within duration of a pump laser pulse and shows a very broad spectrum in which its absorption peak is not clear. Subsequently, at the time (1.6 ps), when ΔA attains maximum, the spectrum changes to a broad one with absorption maximum around 700 nm and its intensity is predominant in the longer wavelength region than in the shorter one. Then, although the transient absorption decreases with the elapse of time, about 50% of its maximum ΔA remains in the entire wavelength region even at 1 ns after laser excitation and the spectral shape is also maintained.

The absorption maximum wavelength and the behavior for growth and decay of the transient absorption of TG-CdS particles in water + acetonitrile (4 : 1) mixed solvent are similar to those in water (Fig. 2). However, the maximum transient absorption decreases to about 70% of that in water and also decreases to about 25% of the former in the entire wavelength region at 1 ns after laser excitation.

The spectral shape and intensity of the transient absorption of TG-CdS in DMF, measured immediately after laser excitation, are almost similar to those in water + acetonitrile mixed solvent except the absorption in the wavelength region shorter than ca. 520 nm which is presumably attributable to DMF itself (Fig. 3). However, its decay dynamics is different from that in water + acetonitrile mixed solvent, namely, the transient absorption almost disappears in whole wavelength region at 1 ns after laser excitation.

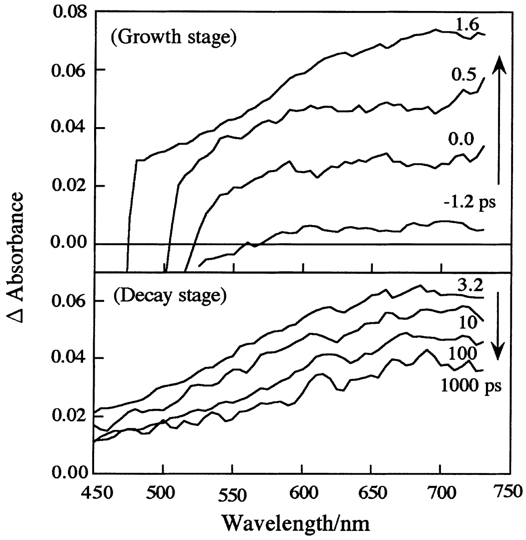

Fig. 1. The time-resolved transient absorption spectra of TG-CdS particles in water at various delay times. The spectra are corrected for temporal dispersion (chirp) of a probe pulse.

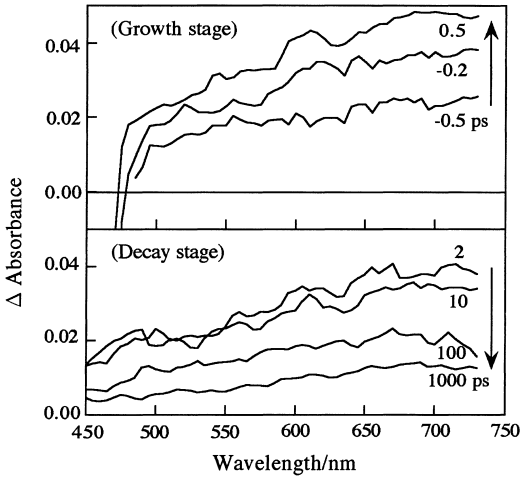

Fig. 2. The time-resolved transient absorption spectra of TG-CdS particles in water + acetonitrile (4 : 1) mixed solvent at various delay times. The spectra are corrected for chirp of a probe pulse. The experimental conditions are the same as those of Fig. 1.

It is known that the transient absorption spectra concerning the electrons and holes produced by photoexcitation of usual non-capped CdS particles appears in the visible wavelength region. Haase et al. [32], observed that the transient absorption attributed to trapped holes appears in the visible wavelength region by photoexcitation of aqueous CdS colloidal solutions and its absorption peak is around 500 nm and 450 nm for CdS particles with diameter of 3–5 nm and 1.5–2.0 nm, respectively. Namely, the absorption peak shifts to shorter wavelength region with decreasing particle size. Further, Kamat et al. [34] attributed the broad transient absorption with absorption maximum around 480 nm which

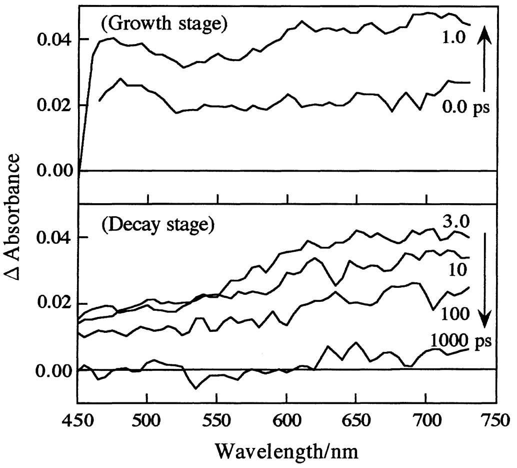

Fig. 3. The time-resolved transient absorption spectra of TG-CdS particles in DMF at various delay times. The spectra are corrected for chirp of a probe pulse. The experimental conditions are the same as those of Fig. 1.

spread over ca. 400–600 nm to trapped holes in the picosecond laser flash photolysis of CdS particles in acetonitrile. From analogy with these reports, it seems that the absorption due to trapped holes has an absorption maximum around 500 nm and is a broad one spreading until ca. 700 nm in the case of TG-CdS particles with particle size of 25 Å in the present study. In the nanosecond laser flash photolysis of TG-CdS particles in water reported previously [28], similar transient absorption with absorption maximum around 500 nm was observed at 500 ns and later after laser excitation by which time the absorption due to hydrated electrons produced from photoproduced electrons is supposed to disappear.

On the other hand, it is known that the transient absorption concerning electrons produced by photoexcitation of CdS particles also appears around 700 nm in longer wavelength region. In the measurements of the transient absorption spectra of CdS particles in water containing sodium hexametaphosphate (HMP) as a stabilizer for colloids [32,35,36], it is confirmed that hydrated electrons are produced by electron ejection from CdS particles. The production of hydrated electrons was also indicated in the nanosecond laser flash photolysis of TG-CdS in water [28]. Furthermore, Skinner et al. [29] and Zhang et al. [30] investigated the behavior of photogenerated electrons in CdS particles by monitoring the transient absorption in the wavelength longer than 600 nm. From analogy with these reports, it is considered that the transient absorption due to photogenerated electrons (hydrated electrons and trapped electrons) on TG-CdS particles is also a broad one which has an absorption maximum around 700 nm and spreads over the whole visible region. Therefore, it seems that the transient absorption spectra of TG-CdS particles in each solvent, which spread over whole visible region, are superposition of very broad transient absorptions due to trapped holes which has an absorption maximum around 500 nm and hydrated electrons and/or trapped electrons which have an absorption peak around 700 nm.

Therefore, as described above, it can be understood that the reason why the transient absorption of TG-CdS particles in water + acetonitrile mixed solvent is weaker than that in water is that the production of hydrated electrons decreases in the mixed solvent than in water. It is reported that the ability of acetonitrile for solvation of electrons is lower than that of water and further the absorption due to dimer anions of acetonitrile produced by the capture of an electron is very weak compared to that due to hydrated electrons in visible region [29,38].

3.1.2. The production rate of trapped holes, trapped electrons, and hydrated electrons

Fig. 4 shows the plots of the time profile of the transient absorption of TG-CdS in water until several picoseconds after laser excitation at several wavelengths. There is a tendency that the growth of the absorption becomes slower at shorter wavelength at which there is the influence from the stimulated Raman emission of water, but at the wavelength region longer than ca. 500 nm, the absorption grows fully within ca. 1 ps. Similar growth of the transient absorption of TG-CdS particles was observed in both water + acetonitrile and DMF solvents. Taking it into account that the instrument response was not considered in the growth process of the transient absorption and the pulse width of the pump pulse was estimated from the cross-correlation using BBO crystal to be <0.8 ps, it seems that the growth time of the transient absorption, ca. 1 ps, is governed by the instrument response time in addition to the pulse width. Therefore, it is considered that the transient absorption attributable to trapped holes, trapped electrons, and hydrated electrons grows in whole visible region within 1 ps at the latest. As 90 ± 20 fs [29] and <100 fs [30] are reported as the trapping time for the photogenerated electrons in CdS particles in which the instrument response and the pump pulse width were taken into account, our result is not essentially a conflict with them. On the other hand, it seems that there are no reports in which the trapping time for holes photogenerated in CdS particles is estimated directly, though Kamat et al. [34] have reported that the trapping of the photogenerated holes in CdS particles is completed within the pulse duration (18 ps) of the laser used.

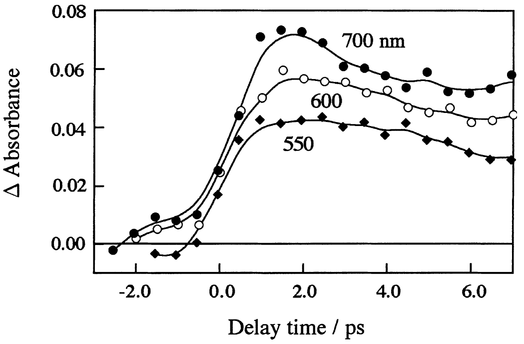

Fig. 4. The time profiles of transient absorption spectra of TG-CdS particles in water up to several picoseconds at various wavelengths.

3.2. Time profiles for the decay parts of the transient absorption of TG-CdS in various solvents

In order to discuss the recombination processes of photogenerated electrons and holes in TG-CdS particles, the time profiles for the decay parts of the transient absorption were investigated at several wavelengths in various solvents. Fig. 5 shows the time profiles (up to 100 ps) of the transient absorption of TG-CdS in water at 550 nm and 700 nm. The curves shown by solid lines in the figure are the best curves fitted with the sum of two exponentials and a base line [30]. At 100 ps, about 60% and 70% of the transient absorption exist at 550 and 700 nm, respectively. Further, although it is not shown in the figure, about 50% of the transient absorption at both wavelengths survives even at 5 ns. Furthermore, the transient absorption with spectral shape and absorption maximum (around 700 nm) similar to those at 5 ns in the

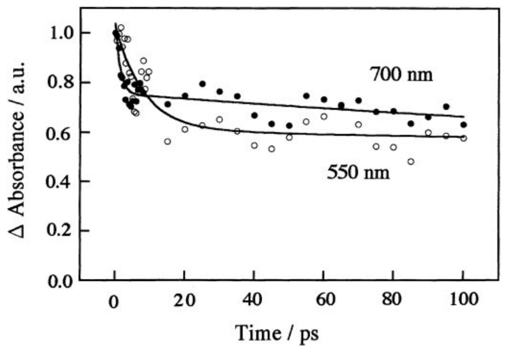

Fig. 5. The curve fitting for the decay parts of transient absorption spectra of TG-CdS particles in water up to 100 ps at 550 and 700 nm. The solid lines in the figure are the best curves fitted with sum of two exponentials and one constant. ΔA is normalized to its maximum and the time when it attained maximum is adopted as time zero at each wavelength.

present subpicosecond study of TG-CdS particles in water had been observed in their previous nanosecond laser flash photolysis [28]. From these results, the decay process for the transient absorption of TG-CdS in water can be classified roughly into three parts; namely, (1) the fast process with the lifetime of few picoseconds, (2) the process which decays with a time constant of several tens to several hundred picoseconds, and (3) the process which decays hardly up to several nanosecond time domain.

From the curve fitting for the decay part up to 100 ps shown in the figure, 0.12 ps^{-1} ($\tau_1 = 8.1$ ps) and 0.74 ps^{-1} ($\tau_1 = 1.4$ ps) were estimated as the first order rate constant k_1 for the fast decay process (first decay process) at 550 and 700 nm, respectively. The value of the rate constant k_1 at 700 nm is almost consistent with those for thiophenolate-capped CdS (PhS-CdS) and mercaptobenzoxazole-capped CdS (MBO-CdS) particles in acetonitrile reported previously [27]. The rate constant k_1 for the fast decay part of TG-CdS in water, estimated by the curve fitting, is smaller at shorter wavelength than at longer one, as well as that of PhS-CdS in acetonitrile. The main reason may result from the fact that the transient absorption at shorter wavelength region is more influenced by stimulated Raman emission of water than that at longer one. Therefore, it is considered that the decay of the transient absorption at any wavelength is essentially due to the recombination of trapped electrons and holes. This fast recombination process is explicable if plural electron–hole pairs (exciton) are produced in a particle with radius smaller than Bohr radius of the exciton in bulk CdS crystal. Namely, it is considered that if plural excitons exist in a particle, these excitons are influenced by their mutual electric fields and consequently, the recombination of trapped electron and hole becomes faster than that in the case where an exciton exists independently in a particle. As described later, it seems that the fast recombination of trapped electron and hole due to the interaction among plural excitons occurs in the present study because four photons are absorbed by one TG-CdS particle and further ca. 25 Å of CdS core diameter of TG-CdS particles is smaller than 29 Å of Bohr radius [39] for the exciton in bulk CdS crystal. Zhang et al. [30] and Ernstring et al. [40] reported that the fast decay component with the lifetime within few picoseconds (0.8–2.0 ps) in the electron–hole recombination process in semiconductor particles appears clearly with increasing the laser intensity for excitation. Zhang et al. called it the nongeminate recombination process and Ernsting et al. interpreted that it was due to the increase of concentration of trapped charge carrier and the decrease of tunnel distance for their recombination.

On the other hand, the values in the wide range of 30–300 ps were obtained as a time constant of a first-order rate for the decay part in the time range of 20–100 ps (second decay process) from the curve fitting at various wavelengths in Fig. 5 (Although the periodical fluctuation of ca. 30 ps appears in the figure, it is an inadvertent phenomenon and not a meaningful one because it is presumably attributable to the intensity fluctuation of a pump pulse in pump-probe experiments.). In a few studies of the electron–hole recombination process in semiconductor particles, the decay process with the time constant of several tens of picoseconds have been observed in the transient absorption due to photogenerated electrons. For example, 50 ps for CdS [30], 30 ps for $Zn_{0.95}Cd_{0.05}S$ [40], and 50 and 100 ps for two glasses with doped CdS_xSe_{1-x}($x \sim 0.9$) [41] have been reported so far as the time constant for the decay process. It seems that the matter which participates in such a recombination process are the trapped electrons and holes with various stabilities and lifetimes due to their different trapping states. From the measurements of the emission lifetime for CdS particles, Chestnoy et al. [42] related the stability of trapping states to the depth of the traps, namely, the emission with a longer lifetime to deep traps and that with a shorter one to shallow ones. Therefore, as the trapped electrons and holes exist in the traps with various depths in semiconductor particles, distribution of their recombination rates becomes very wide. Taking such considerations into account, it is deduced that the decay process with the time constant of several tens to a few hundred picoseconds in the case of TG-CdS particles in water is the sum of the recombination of individual electrons and holes trapped in various trapping states which have different recombination rates.

The third process that decays hardly up to a few nanoseconds may be related to hydrated electrons which exist in the vicinity of the particles. Haase et al. [32] showed that the hydrated electrons produced by ejection of electrons from CdS particles react again with CdS particles in water and their lifetime was estimated to be about 20 µs at the concentration different from that in the present study. Therefore, it is considered that the component of the transient absorption which does not decay even at a few nanoseconds, observed for TG-CdS particles in water in the present study, is mainly attributable to the hydrated electron produced by electron emission from the particles and its lifetime is extended due to low probability for the recombination with trapped holes. On the contrary, the presence of such a long-lived component in the transient absorption indicates the production of hydrated electrons.

The time profiles and the curve fittings for the decay part (up to 100 ps) of the transient absorption of TG-CdS in both water + acetonitrile and DMF solvents are also shown together with those in water in Fig. 6. In the curve fitting, the best fitting was obtained with two exponentials for that in DMF solvent though it was obtained with the sum of two exponentials and a base line for the transient absorption in water + acetonitrile mixed solvent as well as that in water, at both 550 and 700 nm. Although, the figure shows considerable scatter, there are the trends that the fraction of the fast decay component in whole transient absorption in both water + acetonitrile and DMF solvents is larger than that in water. Especially, in the case of DMF solvent, the transient absorption disappears almost perfectly at 1 ns though it is not shown in the figure, namely, the curve fitting for the decay part is possible with only two exponentials as described above. As will be discussed in detail later, the difference in the decay process between solvents containing water and DMF, namely, whether a long-lived decay component (lifetime > 1 ns) is contained or not, is explainable by the fact that the hydrated electrons are not produced in DMF even if electrons were emitted from TG-CdS particles to solvent by the laser excitation. Therefore, only the electrons and holes trapped at the surface of the particles are observed in the transient absorption of TG-CdS particles in DMF and consequently, the decay process of the transient absorption consists of the fast decay due to interaction among plural electron–hole pairs and the decay with the time constant of several tens of picoseconds due to the recombination of trapped electrons and holes in various trapping states. Furthermore, the fraction of the fast decay component in whole transient absorption is larger in DMF than in water and water + acetonitrile as described above. It seems that such an increase in the fraction of the fast decay component suggests that electron ejection from TG-CdS particles to solvent does not occur in DMF.

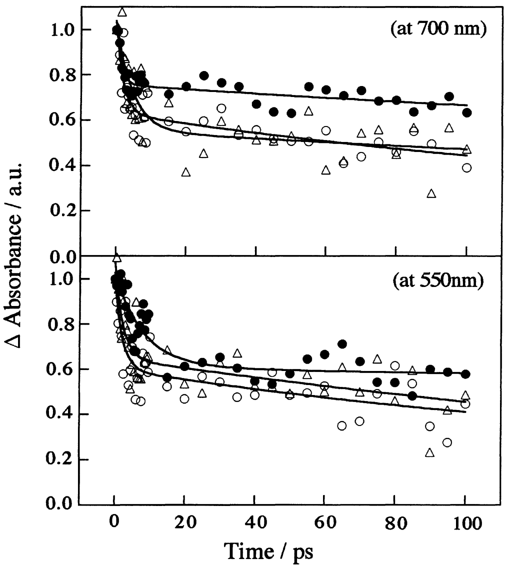

Fig. 6. The curve fitting for the decay parts of transient absorption spectra of TG-CdS particles in various solvents up to 100 ps at 550 and 700 nm. The solid lines in the figure are the best curves fitted with sum of two exponentials and one constant in water (●) and in water + acetonitrile mixed solvent (○), and with sum of two exponentials in DMF (△). ΔA is normalized to its maximum and the time when it attained to the maximum is adopted as time zero at each wavelength.

3.3. The shape of the transient absorption of TG-CdS and production of the hydrated electron in various solvents

As seen from the growth stage of the transient absorption of TG-CdS particles in water in Fig. 1, the absorption around 700 nm increased considerably compared to that in shorter wavelength region when the transient absorption grew sufficiently. And further, the transient absorption at the wavelength longer than 700 nm was enhanced on the way of the growing process, though such a phenomenon was not observed in both water + acetonitrile (Fig. 2) and DMF solvents (Fig. 3). As described above, the transient absorption of TG-CdS particles in water, observed at 500 to 730 nm, consists of the absorptions due to trapped electrons and holes and hydrated electrons.

According to the mechanism for the production of hydrated electrons by multiphoton ionization of neat water reported by Shi et al. [43], photoemitted electrons first change to wet electrons (lowest excited state of hydrated electrons, lifetime: 540 fs) with the absorption maximum at 850 nm and then transfer to the hydrated electrons with the absorption maximum at 720 nm via their relaxation process. Therefore, it seems that the production of the hydrated electron with absorption maximum around 720 nm by laser excitation of TG-CdS particles in water becomes somewhat slower than those of trapped electrons and holes. Consequently, the time dependency of the spectral shape at growth stage in Fig. 1 is explicable provided that the peak of the absorption due to the electrons ejected to solvent shifts from 850 to 720 nm in the production process of hydrated electrons.

According to Kaschke et al. [35], for the production of the hydrated electron by electron ejection from CdS particles in water, the emitted electron should necessarily have the energy larger than −2.9 V versus NHE. In the present study, in which a 395 nm laser pulse was used as a pump pulse, two-photon participation is also necessary to produce hydrated electrons from CdS particles. For TiO_2 particles colloidal solutions, Colombo Jr. et al. [44] proposed the similar process concerning two photons via Auger transition for the production of hydrated electrons. However, for such a two-photon process to occur, it is necessary to absorb another photon or to produce another electron hole pair in an identical particle during the lifetime of the electron hole pair produced by the absorption of one photon. In the present study, from the calculation using 396 nm, 150 μJ/pulse, 2.0 mm, 0.6, 2.4 mM, 25 Å, and 4.82×10^6 g/m^3 as the excitation wavelength, the pulse energy for excitation, beam diameter of the pump pulse at the cross point with a probe pulse in the sample cell, absorption of TG-CdS colloidal solutions (with a 2 mm cell), cadmium concentration in TG-CdS particles, the diameter of the CdS core part of TG-CdS particles, and density of CdS particles, respectively, it follows that about four photons are absorbed per TG-CdS particle within duration (several hundreds of femtoseconds) of the pump pulse. From this result, as described above, there is the possibility that the hydrated electrons are produced by electron ejection from TG-CdS particles via the process such as Auger-like process in which two photons participate [35,43]. Consequently, it is considered that the broad transient absorption having the absorption maximum around 720 nm and spreading over whole visible wavelength region, attributed to hydrated electrons, was contained in the spectra for the subpicosecond time-resolved transient absorption of TG-CdS particles in water in the present study as well as the case of their nanosecond laser flash photolysis reported previously [28].

In addition, it was confirmed that 150 μJ/pulse of excitation energy used in the present study can produce the transient absorption due to hydrated electrons from neat water without TG-CdS particles by multiphoton process which amounts to 25% of that produced from an aqueous colloidal solution containing TG-CdS particles. However, in the case of aqueous TG-CdS colloidal solutions with $A = 0.6$ at 396 nm used in the present study, contribution of laser pulse for production of hydrated electrons from solvent water itself is 25% of total laser pulse because 75% of the pump pulse is absorbed by the particles in the solutions. And further, if the production of the hydrated electron from solvent water itself occurs by the absorption of two photons, the intensity of the transient absorption due to hydrated electrons produced from solvent water itself may become 6% (0.25×0.25) of that for the neat water without the particles. Therefore, it corresponds to 1.5% (6×0.25) of the total transient absorption for aqueous TG-CdS colloidal solutions and the influence of hydrated electrons produced by biphoton absorption of solvent water itself may be negligible in the present study.

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