

Subpicosecond spectroscopy of thioglycerol-capped CdS colloidal solutions: influences of the solvent composition and the pump pulse intensity

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Abstract

The dependencies of the transient absorption of thioglycerol-capped CdS (TG-CdS) particles on the solvent and the pumping pulse intensity were investigated in water, dimethylformamide (DMF) and their mixtures by excitation with a subpicosecond laser pulse of $\lambda_{\text{max}} = 396 \text{ nm}$ to elucidate the more detailed contribution of hydrated electrons to the transient absorption of the surface modified CdS particles in longer wavelength region. It was observed that the transient absorption of TG-CdS in water–DMF mixed solvents, obtained immediately after the excitation, reflected the difference in the amount of the hydrated electron produced that depending on both the water content of the mixed solvents and the pump pulse intensity. As the relationship between the pump pulse intensity and the intensity (at 0.5 ps after laser excitation) of the transient absorption of TG-CdS at 720 nm which nearly corresponds to the absorption maximum wavelength of the hydrated electron is non-linear, it seems that the absorption of two or more photons per a particle is essential for the production of the hydrated electron. The production of hydrated electron in TG-CdS colloidal solutions seems to occur by electron ejection via an Auger-like process which needs two electron–hole pairs per a particle as in the case of non-capped CdS particles. However, even at the pump pulse energy of 160 μJ per pulse, where TG-CdS particles absorb about four photons per a particle, the production of the hydrated electrons was not observed in the water–DMF solvents with the water content of less than 40%. This result suggests that the mixed solvent containing water of more than about 50% is necessary for the production and stabilization of the hydrated electron following electron ejection from TG-CdS particles in water–DMF mixed solvents. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

In order to understand the behavior of electrons and holes photo-produced on the semiconductor particles immediately after photo-excitation of the particles, the time-resolved transient absorption spectra have been studied for the colloidal solutions of CdS and TiO_2 particles [1–23].

In the case of ordinary (non-capped) CdS particles in organic solvents such as acetonitrile, it is known that the transient absorption maximum of trapped electrons exists in the wavelength region longer than 600 nm [19] and the transient absorption for trapped holes spreads over the wavelength region from about 400 to 640 nm [14]. For the aqueous CdS colloidal solutions, in addition to those, the transient absorption attributed to the hydrated electron has been also confirmed in the longer wavelength region [15].

It is also known that the production of hydrated electron via the direct electron transfer from the conduction band of CdS to bulk water is energetically impossible [2,15]. Instead of such a direct electron transfer, an Auger-like process in which two photons participate was proposed as the mechanism for the production of the hydrated electron by the excitation of the conduction band of CdS particles [15].

In the case of capped CdS particles such as thioglycerol-capped CdS (TG-CdS), the transient absorption attributed to the hydrated electron, which has a relative longer lifetime and may be produced via the two-photons concerning process, was also observed immediately after photo-excitation of the particles in water besides the transient absorption attributed to trapped electrons and holes [22,23].

In the present study, to elucidate in more detail the characteristics of the transient absorption of the hydrated electron photo-produced on the surface-modified CdS particles in water, the dependence of the transient absorption on the solvent composition and the pump pulse intensity

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was investigated using TG-CdS particles which are soluble in both water and DMF. And further the mechanism for the production of the hydrated electron in aqueous TG-CdS colloidal solutions was discussed on the basis of the results.

2. Experimental section

TG-CdS colloidal solutions were prepared by dispersing TG-CdS particles, which were synthesized by pyrolysis of thiourea in the presence of cadmium acetate and thioglycerol, into solvents [22,24]. The ordinary absorption spectra of TG-CdS particles used in the present study were identical in both water and DMF solvents and further coincided with those in both water and DMSO solvents already reported [22,25]. The size of CdS core of TG-CdS particles, estimated from the absorption edges of their spectra by use of the relationship between the particle size and the absorption edge for CdS [26], was ca. 2.5 nm in both water and DMF solvents.

The measurements of time-resolved transient spectra were carried out with the subpicosecond laser flash photolysis system. The system is composed of a cw self mode-locked Ti:sapphire laser pumped by an argon ion laser, a Ti:sapphire regenerative amplifier system and a pump and probe optical system [21,23]. The pump pulse was a 396 nm (λ_{max}) pulse generated by frequency doubling of the fundamental output ($\lambda_{\text{max}} = 792$ nm). The probe pulse was a white light continuum generated by focusing a part of the fundamental output into a 10 mm-quartz cell containing water. The transient absorption spectra at each delay times were calculated from five or ten sets of the data accumulated 10 shots of the signal. All the colloidal solutions were circulated between a non-fluorescent flow cell (2 mm in pass length) and a sample reservoir by a roller pump during the measurements to avoid the damage from the pump pulse. The pump pulse intensity was usually 90 μJ per pulse (ca. 2.2 mJ cm^{-2}). In the experiment for the dependence of pump pulse intensity on the transient absorption, ND filters with various transmittance were used to change the pump pulse intensity. The difference in the arrival time of the pump pulse into a sample cell due to use of ND filters with various thickness was compensated by changing the light-path length of the probe pulse in advance with a delay stage. The pump pulse intensity was measured with a laser power meter (SCINTECH362, BOULDER Co.). Other details for the measurements and data processing are described elsewhere [21,23].

3. Results and discussion

3.1. The transient absorption spectra of TG-CdS in both water and DMF solvents

The transient absorption spectra of TG-CdS in both water and DMF solvents, measured at 0.5 ps after laser excitation, are shown in Fig. 1. In DMF the transient absorption

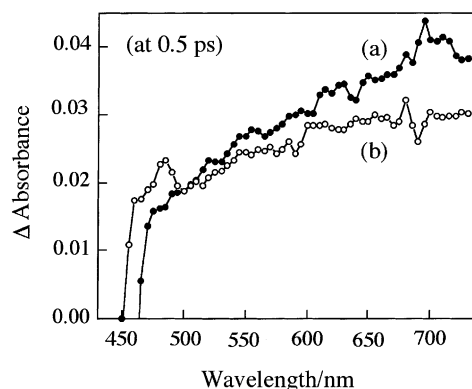


Fig. 1. The transient absorption spectra of TG-CdS in water (a); and DMF (b) at the delay time of 0.5 ps. The spectra were corrected for the chirp of a probe pulse.

spectrum spreads over the whole visible region and its spectral shape is very broad. And further its absorption maximum is not clear though supposed to exist in longer wavelength region. The spectrum seems to consist of the absorption attributed to trapped electrons and holes as in the case of non-capped CdS particles [14,19,23]. On the other hand, the transient absorption spectrum of TG-CdS in water predominates in a longer wavelength region compared with that in DMF because of the production of hydrated electrons as already reported [23]. As can be seen from the figure, in both solvents, an abrupt drop is observed in the transient absorption immediately after laser excitation in shorter wavelength region. The drop is attributed to the serious influence of the stimulated Raman emission of solvents due to the pump pulse and the negative absorption of TG-CdS particles owing to characteristic photo-bleaching of Q-particles [21]. The stimulated Raman emission of water appears up to longer wavelength region compared to that of DMF. This may be the reason why the transient absorption of TG-CdS in water is influenced even in the longer wavelength region compared with that in DMF under the same pump pulse intensity. And further the influence of both the stimulated Raman emission and the photo-bleaching of the particles becomes larger and extends to the longer wavelength region with increasing the pump pulse intensity.

The time profiles (up to several picoseconds) of the transient absorption at 720 nm are shown in Fig. 2. It is known that the absorption maximum of the trapped electron exists around 720 nm as well as that of the hydrated electron [15]. As can be seen from the figure, the rise time of the transient absorption is ca. 1 ps in both solvents. However, it is considered that the transients (trapped electrons in DMF, and trapped and hydrated electrons in water) responsible for absorption at 720 nm have been produced within the time shorter than 1 ps, because the laser pulse width containing the instrumental response time is ca. 0.8 ps in the present study. For ordinary CdS particles with the same size as that of TG-CdS used in the present study, it is reported that the

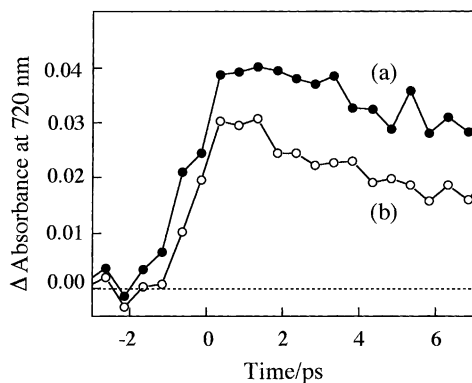


Fig. 2. Time profiles of the transient absorption of TG-CdS in water (a); and DMF (b) at 720 nm.

trapping time for electrons and charge carriers photo-produced are <100 [19] and <250 fs [15], respectively.

As the difference between both spectra in Fig. 1 seems to be due to the production of the hydrated electron in aqueous TG-CdS colloidal solutions, it is considered that the hydrated electron is also produced immediately after laser excitation. The difference spectrum obtained by subtracting the transient absorption spectrum of TG-CdS in DMF from that in water in Fig. 1 is shown in Fig. 3. The shape of the obtained spectrum is similar to that of the hydrated electron reported by Kaschke et al. [15]. The difference spectrum is also almost consistent with that of the hydrated electron produced by the photo-dissociation of an electron from pure water, reported by Shi et al. [27]. They described that the hydrated electron with absorption maximum at 720 nm is produced from the photo-dissociated electron via the electron state (excited state of hydrated electron) called “wet electron” with absorption peak at 850 nm. Taking their discussion into account, it is also analogized for aqueous TG-CdS colloidal solutions that the wet electron is first produced by electron ejection from the conduction band of TG-CdS after laser excitation and subsequently the hydrated electron is produced via the relaxation process. As can be seen from Fig. 2, since

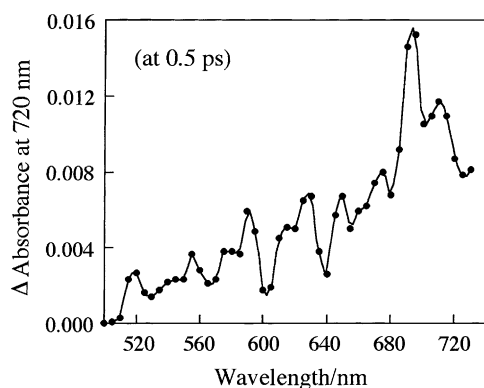


Fig. 3. A difference spectrum obtained by subtracting the spectrum of TG-CdS in DMF from that in water in Fig. 2.

the transient absorption at 720 nm of TG-CdS colloidal solutions has fully grown within ca. 1 ps after incidence of a pump pulse, it is presumed that the relaxation from the wet electron to the hydrated electron occurs at a considerably early stage. Consequently the relaxation process may have not been observed with our subpicosecond pump and probe system with instrumental response of ca. 1 ps.

On the other hand, Kaschke et al. [15] have reported for CdS particles that the two photon-concerning process such as an Auger-like electron ejection process is necessary to produce the hydrated electron, because the energy of the first excited state (conduction band; -1.0 V versus NHE) of CdS is not enough for an electron ejection as the energy level of the hydrated electron is -2.9 V versus NHE. Colomb et al. [18] have also proposed the process via an Auger process for the production of the hydrated electron in aqueous TiO_2 colloidal solutions. Therefore, it is also essential to absorb two or more photons per a particle for the occurrence of such an Auger-like process in TG-CdS particles. Under the ordinary experimental conditions in the present study (the wavelength of the pump pulse, the pump pulse intensity, the diameter of the pump pulse at the cross point with the probe pulse in the sample cell, the absorbance of TG-CdS colloidal solutions at 396 nm with a 2 mm-cell and cadmium concentration in TG-CdS particles are 396 nm, 90 μJ per pulse, ca. 2 mm, 0.6, and 2.4 mM, respectively, calculated using 25 Å and $4.58 \times 10^6 \text{ g m}^{-3}$ as diameter and density of the CdS core part of TG-CdS particles), about 2.4 photons are absorbed per a TG-CdS particle within duration time (several hundreds of femtoseconds) of the pump pulse. Therefore, it may be possible under our experimental conditions to produce the hydrated electron by the electron ejection via an Auger-like process that needs two electron–hole pairs per a particle.

3.2. Influence of solvent composition on the transient absorption of TG-CdS particles

To confirm the contribution of the hydrated electron to the transient absorption of aqueous TG-CdS colloidal solutions, the transient absorption of TG-CdS particles was also measured in water–DMF mixed solvents with various mixing ratios. The absorption intensity (ΔA) at 720 nm, absorption maximum wavelength of hydrated electrons, obtained from the transient absorption spectra of TG-CdS at 0.5 ps after laser excitation are shown as a function of the solvent composition in Fig. 4. As can be seen from the figure, at the low pump pulse intensity (53 μJ per pulse) in which TG-CdS particles absorb one photon per a particle, the dependence of the absorption intensity on the solvent composition was hardly observed in the mixed solvents with any mixing ratios. Therefore, this result seems to suggest that the transient absorption of TG-CdS colloidal solutions observed at the longer wavelength region under such a low pump pulse intensity is mainly attributable to the trapped electrons on the surface of the particles which is independent of solvents. The result suggests that the transient absorption spectrum of

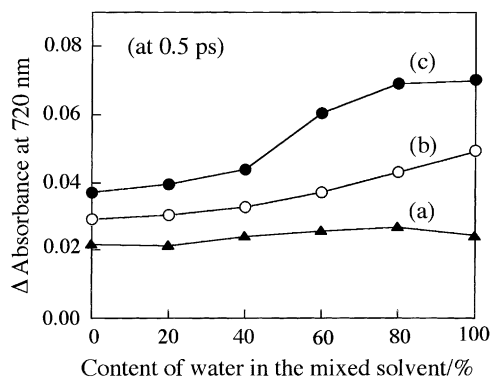


Fig. 4. Relationships between the transient absorption of TG-CdS in water-DMF mixed solvents at 720 nm, measured at various pump pulse intensities, and the content of water in the solvents. Pump pulse intensities used were 53 (a); 108 (b); and 158 μJ per pulse (c); respectively.

TG-CdS hardly contains the absorption due to the hydrated electrons even in water.

On the other hand, under the condition of the high pump pulse intensity (108 and 158 μJ per pulse), where TG-CdS particles absorb more than two photons per a particle, the increase in the absorption intensity with increasing the water content of the mixed solvents was clearly observed different from the results for the low pump pulse intensity when the water content is more than 60%. But the increase was not observed when the water content is less than 40%. Therefore, the increase of the absorption intensity of TG-CdS in the mixed solvents with high water-content may be attributable to the increase in the amount of the hydrated electron produced by multi-photon process as an Auger-like process described in previous section.

These results suggest that the simultaneous production of plural electron-hole pairs in a particle is necessary to produce the hydrated electron by photo-excitation of TG-CdS in the mixed solvents. The results also suggest that the mixed solvents with water content of less than about 50% are inconvenient for the production and/or stabilization of the hydrated electron.

3.3. Influence of pump pulse intensity on the transient absorption of TG-CdS particles

The dependence of the transient absorption of TG-CdS colloidal solutions on pump pulse intensity was also investigated to obtain the information about the production of the hydrated electron by the excitation of TG-CdS in water-DMF mixed solvents. Plots of the transient absorption (ΔA) at 720 nm measured at 0.5 ps after laser excitation against the pump pulse intensity for TG-CdS in water-DMF mixed solvents with various mixing ratios are shown in Fig. 5. The measurements were carried out in the pulse intensity range from 20 to 160 μJ per pulse in which a TG-CdS particle absorbs about 0.5–4 photons by the incidence of a shot of a pump pulse. The plot shows

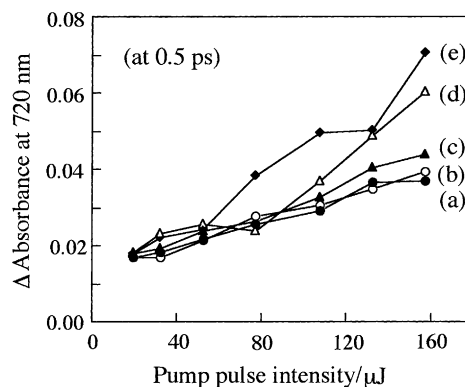


Fig. 5. Relationships between the transient absorption (at 720 nm) of TG-CdS, measured in water-DMF mixed solvents with various mixing ratios, and pump pulse intensities (μJ per pulse). The percentages of water in the mixed solvent were 0 (a); 20 (b); 40 (c); 60 (d); and 100% (e); respectively.

nearly linear in DMF solvent where the hydrated electron is not produced because of the absence of water. In both the mixed solvents with the water content of 20 and 40%, the transient absorption also increases linearly with increasing the pump pulse intensity like that in DMF solvent without water. Therefore, the linear increases observed in the DMF-water mixed solvents with the water content of 0–40% are attributable to the increase in the amount of the trapped electron and not to the hydrated electron.

On the other hand, in pure water and water-DMF mixed solvents with the water content of 60 and 80%, although the transient absorption increases with increasing the pump pulse intensity, the plots display upward curvature, different from that in the mixed solvent with low water content. This curvature results from the fact that the transient absorption attributable to the hydrated electron produced via a multi-photon process such as an Auger-like process appears more clearly with increasing the pump pulse intensity in addition to the increase of the absorption due to the trapped electron.

To clarify the contribution of the hydrated electron to the transient absorption with increasing the pump pulse intensity, the results obtained by subtracting ΔA for TG-CdS in DMF from those in water and water-DMF mixed solvents with various mixing ratios in Fig. 5 are plotted against the pump pulse intensity in Fig. 6. In the mixed solvents with the water content less than 40%, the transient absorption (ΔA at 720 nm) obtained is relatively small at the whole region of the pump pulse intensity, whereas in the mixed solvents with the water content more than 60%, the transient absorption increases clearly with increasing the pump pulse intensity at the pump pulse intensity region of more than 80 μJ per pulse. Namely, the curves have upward curvature and display a non-linear relationship between the intensity of the transient absorption due to the hydrated electron and the pump pulse intensity. In the nanosecond laser photolysis of CdS particles in water, Haase et al. [12] have reported

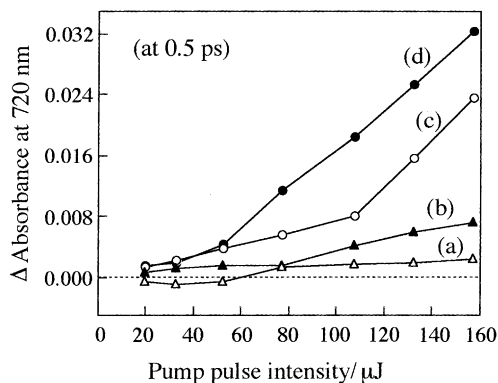


Fig. 6. Relationships between the estimated transient absorption (at 720 nm at the delay time of 0.5 ps), attributable to hydrated electrons, and pump pulse intensities for TG-CdS in the water–DMF mixed solvents with various mixing ratios. Percentages of water in the mixed solvents were 20 (a); 40 (b); 60 (c); and 100% (d); respectively. The transient absorption, attributable to the hydrated electron, was estimated by subtracting the spectrum of TG-CdS in DMF from those in the water–DMF mixed solvents with various mixing ratios.

that the transient absorption attributable to the hydrated electron is proportional to the square of pump pulse intensity. Although the transient absorption attributable to the hydrated electron, estimated at subpicosecond time region as described above in the present study, was not proportional for certain to the square of the pump pulse intensity because of the difficulty in the estimation of the transient absorption attributable to the hydrated electron in the subpicosecond time domain, it is understandable that their relation is at least non-linear. Therefore, it may be also considered that the hydrated electron is produced via a multi-photon process such as an Auger-like process as described above.

3.4. Dependence of the decay kinetics for the transient absorption of TG-CdS on solvent and the pump pulse intensity

The dependence of the decay kinetics for the transient absorption of TG-CdS on solvent and the pump pulse intensity was investigated under some different experimental conditions. The time profiles for the decay part of the transient absorption (at 720 nm) of TG-CdS in water, obtained from its time-resolved transient absorption spectra measured under the two different pump pulse intensities, are shown in Fig. 7. ΔA in the figure is normalized to its maximum and the time when it attained maximum is adopted as time zero. The curves shown by solid lines in the figure are the best curves fitted with the sum of two exponentials and one constant as already reported [23]. From the curve fitting for the decay parts up to 100 ps shown in the figure, 0.16 ($\tau_1 = 6.3$ ps) and 0.50 ps^{-1} ($\tau_1 = 2.0$ ps) were estimated as the first order rate constant k_1 for the fast decay process at 720 nm under the pump pulse intensity of 90 and 150 μJ per pulse, respectively. As shown in the inset of Fig. 7, al-

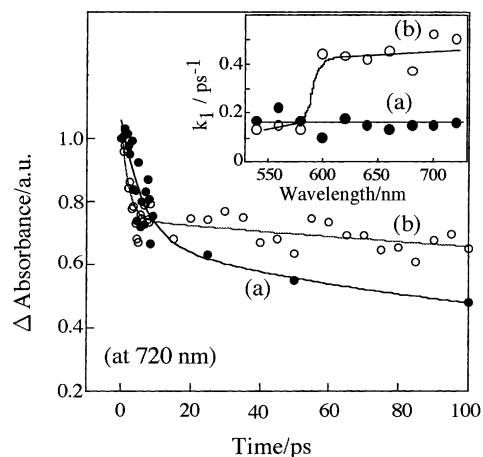


Fig. 7. The curve fitting for the decay parts (up to 100 ps) of the transient absorption spectra (at 720 nm) of TG-CdS in water. Plots (a) and (b) in the figure are the data measured under pump pulse intensities of 90 and 150 μJ per pulse, respectively. The solid lines in the figure are the best curves fitted with sum of two exponentials and one constant. ΔA is normalized to its maximum and the time when it attained to the maximum is adopted as time zero for each decay part. The inset is wavelength dependence of the first-order rate constant (k_1) obtained by the curve fitting at various wavelengths.

most same values are obtained as the rate constant k_1 in whole wavelength region for each pump pulse intensity except shorter wavelength region (<600 nm) for 150 μJ per pulse. The rate constant k_1 for 150 μJ per pulse is apparently larger than that for 90 μJ per pulse in the longer wavelength region. For 150 μJ per pulse, however, k_1 decreases steeply at the shorter wavelength region (<600 nm). It seems that this steep decrease is not meaningful, because it may be attributable to the influence of the stimulated Raman emission and the photo-bleaching, as mentioned above.

On the other hand, the proportion of the long-lived decay component to the whole decay one increases somewhat with increasing the pump pulse intensity. This observation is contrary to the previous report [17] for an aqueous CdS colloidal solution in which Zhang et al. reported that the proportion of the fast decay process with the lifetime of a few picoseconds, due to the non-geminate recombination of electron and hole, to the whole decay process increases with increasing the pump pulse intensity. This discrepancy may be attributable to whether the hydrated electron exists or not. Namely, in the present study, in addition to the transient absorption attributed to the trapped electron, the transient absorption due to the hydrated electron was clearly observed as well as previous report [15] though it was not confirmed in their study. Therefore, it is considered that the dependence of the fast decay process on the pump pulse intensity appeared oppositely in the present study because the increase of the fast decay component was hidden by the production of hydrated electrons. However, it seems that the hydrated electron produced hardly influences the decay kinetics for the fast decay process attributed to fast electron–hole recombination

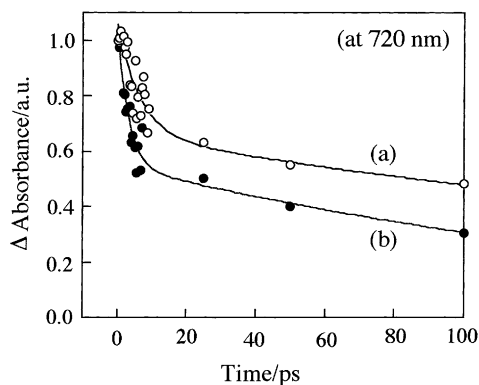


Fig. 8. The curve fitting for the decay parts (up to 100 ps) of transient absorption spectra (at 720 nm) of TG-CdS in water (a); and DMF (b) solvents. The solid lines in the figure are the best curves fitted with sum of two exponentials and one constant (a); and with sum of two exponential (b). ΔA is normalized to its maximum and the time when it attained to the maximum is adopted as time zero at each decay part.

because the lifetime of the hydrated electron is considerably longer compared to that of the fast decay process. This may be the reason why the rate constant for the fast decay process is almost constant in wide wavelength region. Therefore, as the rate constant obtained in the present study becomes larger with the increase in the pump pulse intensity, this fast decay process may be basically a non-geminate recombination process for electrons and holes photo-produced on the particles as proposed by Zhang et al. [17]. Ernsting et al. [28] have explained that this fast decay process becomes faster as the concentration of the trapped charge carrier increases and the tunneling distance of the recombination decreases. In the present study, it seems that the fast recombination process of electron and hole due to the interaction among electron-hole pairs (excitons) was observed for TG-CdS in water, because the particles absorb 2–3 and ca. 4 photons per a particle for 90 and 150 μJ per pulse, respectively, and consequently plural excitons are generated on a particle simultaneously. Therefore, it is considered that the difference in the lifetime for the fast decay process depending on the pump pulse intensity in the present study results from the difference in the number of electron-hole pairs produced simultaneously.

Fig. 8 is the time profiles of the decay part of the transient absorption (at 720 nm) of TG-CdS particles in both water and DMF, which were measured with the pump pulse intensity of 90 μJ per pulse. The curves shown by solid lines in the figure are the best curves fitted with the sum of two exponentials and one constant for TG-CdS in water and with the sum of two exponentials for TG-CdS in DMF, as already reported [23]. From the curve fitting for the decay parts up to 100 ps shown in the figure, 0.15 ($\tau_1 = 6.6$ ps) and 0.32 ps $^{-1}$ ($\tau_1 = 3.0$ ps) were obtained as the first order rate constant k_1 for the fast decay part of the transient absorption of TG-CdS in water and DMF solvents, respectively. Since both TG-CdS colloidal solutions were prepared so that their absorbances at 396 nm, the maximum wavelength of the pump pulse,

become equal each other and further the measurements were carried out under the same pump pulse intensity, the concentration of electron-hole pairs on the particles produced immediately after laser pulse excitation may be identical in both solvents. Therefore, since it is expected that the extent of the interaction among electron-hole pairs on the particles is almost same in both solvents, similar values should be obtained as the rate constant k_1 for the fast decay process in both solvents. However, the rate constant obtained in DMF was larger than that in water. The result may suggest that the production of the hydrated electron, which needs to absorb two or more photons per a particle, occurs in water though similar electron ejection from the particles to solvent does not occur in DMF. From these discussions, it is considered that the difference in the concentration of electron-hole pairs on the particles exists between in both solvents because of the consumption of electron-hole pairs due to the production of hydrated electrons in water solvent. Consequently the rate constant k_1 for the fast decay process in DMF, where the concentration of the electron-hole pairs is higher compared to that in water, becomes larger than that in water. On the other hand, the second decay process in the figure is attributable to the recombination for the geminate electron-hole pairs, as discussed already elsewhere [23]. The lifetime for the decay process obtained in the present study is roughly in the time range of the several tens picoseconds in both solvents though the lifetime depends on the time range of the curve fitting and further its accuracy is not good. Chestnoy et al. [29] have reported that there are the trapped electrons and holes in the trap sites with various depths on the particles and the time constants for their recombination has a wide distribution.

As can be seen from Figs. 7 and 8, significant amounts of the transient at 720 nm survives up to 100 ps for aqueous TG-CdS colloidal solutions though its extent reflects the amount of the hydrated electrons produced and hence depends on the pump pulse intensity. Although it is not shown in the figure, ca. 50% of the transient absorption survives even at 5 ns for the pump pulse intensity of 150 μJ per pulse (in the case of DMF solvent, the transient absorption disappears almost perfectly at 1 ns, as already described [23]). The transient absorption which does not decay up to few hundreds picoseconds is mainly attributable to hydrated electron in the bulk solutions. It is known that the hydrated electron produced by electron ejection from ordinary CdS particle reacts with the original particle (emitted the electron) [12]. It is considered that the analogous recombination also occurs in aqueous TG-CdS colloidal solutions. The production of the hydrated electron has been also confirmed on the nanosecond laser flash photolysis of aqueous TG-CdS colloidal solutions and it took about 500 ns for the disappearance of its transient absorption [22].

In conclusion, it is recognized that the transient absorption of TG-CdS in water-DMF mixed solvents, obtained immediately after subpicosecond laser pulse excitation, reflects the difference in the amount of the hydrated electron produced which depends on both the water content of the

mixed solvents and the pump pulse intensity. Since the relationship of the pump pulse intensity and the intensity (ΔA at 0.5 ps after laser excitation) of the transient absorption of TG-CdS at 720 nm which nearly corresponds to the absorption maximum wavelength of the hydrated electron is non-linear, it is suggested that the absorption of two or more photons per a particle is essential for the production of the hydrated electron. The production of the hydrated electron seems to occur by electron ejection via an Auger-like process, which needs two electron–hole pairs per a particle, in TG-CdS colloidal solutions. However, even at the pump pulse intensity of 160 μJ per pulse, where TG-CdS particles absorb about four photons per a particle, the production of the hydrated electrons was not observed in the water–DMF solvents with the water content of less than 40%. This result also suggests that the mixed solvents are required to have the water content of more than about 50% for the production of the hydrated electron by electron ejection from TG-CdS particles in water–DMF mixed solvents and for its stabilization.

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