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## Nanosecond laser flash photolysis of thioglycerol-capped cadmium sulfide particles

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### Abstract

Nanosecond transient absorption spectra of thioglycerol-capped cadmium sulfide particles (TG-CdS) were measured in various solvents containing dissolved oxygen. The transient absorption spectrum of TG-CdS observed immediately after laser excitation in water is a broad one with absorption maximum near 700 nm and is very different from those of TG-CdS in organic solvents (DMF, DMSO) and that of thiophenolate-capped CdS particles (PhS-CdS) in acetonitrile reported previously. This transient absorption around 700 nm is attributable mainly to hydrated electrons, comparing with that of HMP-CdS (aqueous CdS colloidal solutions containing sodium hexametaphosphate as a stabilizer for the colloids) which is known to produce hydrated electrons by electron ejection from the particles with the interaction of two electron-hole pairs. The effects of electron and hole scavengers, solvent and the laser intensity on the transient absorption spectra also support this conclusion. It seems that the large differences in the decay dynamics and the shape of the transient absorption between TG-CdS in water and PhS-CdS in acetonitrile mainly result from the difference in solvent rather than the difference in the hole trapping ability between thiophenol and thioglycerol. © 1998 Elsevier Science S.A. All rights reserved.

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### 1. Introduction

A large number of studies on semiconductor photocatalytic reaction utilizing the strong redox force of electrons and holes produced by band-gap excitation of semiconductor particles have been carried out because it is attractive from the standpoint of potentiality for energy conversion such as the photo-decomposition of water and novel organic synthetic methods [1–3]. When this photocatalytic reaction is utilized, however, its lower quantum efficiency generally becomes significant disadvantage. It is understood that the low quantum efficiency mainly results from the poor charge separation efficiency due to a very fast recombination of photo-produced electrons and holes in primary photochemical events on the semiconductor particles [1,2]. To suppress the recombination and consequently improve the charge separation efficiency, the surface of semiconductor particles is modified by various metals or metal oxides [1,2].

On the other hand, the semiconductor particles with the surface modified by capping agents, which are recently known as the size-quantized semiconductor particles with a narrow size distribution, are convenient for spectroscopic studies of their photochemical processes because one can prepare the transparent colloidal solutions by using them easily [4–6]. However, it is supposed that their photochemical processes such as electron and hole trapping and decay dynamics of trapped charge carriers are affected by capping agents on their surface. Therefore, the charge separation efficiency of photo-produced electrons and holes on semiconductor photocatalysts and consequently whole efficiency of the photocatalytic reactions may be improved by utilizing such capping agents. As a first stage for finding effective capping agents for such a charge separation, we are interested in the primary photochemical events of CdS particles with the surface modified by capping agents [7,8].

In the present study, the photochemical events of TG-CdS were discussed on the basis of the measurements of their nanosecond time-resolved transient absorption spectra in various solvents. The nanosecond laser flash photolysis of HMP-CdS was also carried out under same experimental conditions for comparison.

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## 2. Experimental

### 2.1. Materials

Cadmium acetate dihydrate (Kanto Chem., reagent grade), thiourea (Kanto Chem., reagent grade), thioglycerol (Wako Chem., reagent grade), and dimethylsulfoxide (DMSO, Nakalai Tesque, reagent grade) employed for the synthesis of TG-CdS particles were used as received. Acetonitrile, dimethylformamide (DMF), and DMSO used as solvents in the measurement of the transient absorption were purchased from Kanto Chem. and were spectro grade. All other chemicals were reagent grade and used without further purification. Triply distilled water was used for the preparation of aqueous TG-CdS and HMP-CdS colloidal solutions.

### 2.2. Preparation of TG-CdS particles and their colloidal solutions

The synthesis of TG-CdS particles was carried out in the following way by pyrolysis of thiourea as sulfide source according to the method reported by Vossmeier et al. [6]. A 200 ml of DMF solution containing cadmium acetate (8.82 mmol), thiourea (12.48 mmol) and 1-thioglycerol (11.53 mmol) was heated at 90°C for 1 h while stirring and bubbling with nitrogen gas. Further, the solution was refluxed at 120°C for 5 h while bubbling with nitrogen gas. After the solution was allowed to stand overnight at room temperature, it was concentrated to ca. 25 ml with a rotary evaporator. After it was cooled to room temperature, 10 ml of acetone was added in order to precipitate TG-CdS particles, and the resultant suspension was stirred for 3 h. The precipitate produced was separated by centrifugation and dried *in vacuo* at room temperature for 12 h.

The colloidal solutions of TG-CdS particles were prepared by dispersing a necessary amount of the particles into each solvent using a sonicator. The concentration of TG-CdS in the solution was calculated on the basis of the Cd content of the particles which was determined by EDTA titration [7,9]. The result of titration showed that the weight percentage of Cd in the TG-CdS particles was 39%.

HMP-CdS colloidal solutions were prepared from cadmium chloride, sodium sulfide, and sodium hexametaphosphate by referring the literature [10].

### 2.3. Measurements of the transient absorption

The experiments of nanosecond time-resolved transient absorption were carried out using a nanosecond laser flash photolysis system (Tokyo Instruments, excitation pulse; Nd : YAG, 355 nm, FWHM = 10 ns, pulse energy = 10 mJ/pulse at the position of a sample cell) whose analyzing light source was modified in our laboratory [11]. The average of 16 signals acquired was used for the calculation of transient absorption ( $\Delta$  Abs.). In the experiments of laser power dependency of the transient absorption, the laser

power was changed by varying the pumping voltage of a Nd : YAG laser.

The concentration of TG-CdS colloidal solutions was 1.0 mM and their absorbance was 1.5 with a 10 mm-cell at 355 nm which is excitation wavelength of the laser flash photolysis. Absorbance of HMP-CdS colloidal solutions was also 1.5 with a 10 mm-cells at 355 nm. All the sample solutions were circulated between a sample flow cell (10 mm in pass length for analyzing light) and a sample reservoir by a peristaltic pump (Iwaki Glass, PST-106) during the measurements to avoid the damage from the excitation laser pulse. The removal of dissolved oxygen from the colloidal solutions was not made except the samples for which effect of oxygen on the transient absorption was examined.

## 3. Results and discussion

### 3.1. The size of TG-CdS particles

The absorption spectrum of TG-CdS particles in water is shown in Fig. 1. As seen from the figure, it can be expected that the size distribution of TG-CdS particles synthesized in the present study is relatively narrow because the absorption peak due to excitonic transition of Q-particles appears clearly at ca. 382 nm [6]. Quite similar absorption spectra were also observed in water/acetonitrile mixed solvent, DMF and DMSO. CdS core size of the particles estimated from the relationship [12] between sizes of CdS particles and the longer wavelength edge of their absorption spectra is about 25 Å. Similarly ca. 35 Å was estimated as the particle size of CdS in a HMP-CdS colloidal solution [8].

### 3.2. Transient absorption spectra of TG-CdS particles

Fig. 2 shows the time-resolved transient absorption spectra of aqueous TG-CdS colloidal solutions at various times after laser excitation, obtained from time profiles of transient absorption measured at each wavelength. The transient absorption spectrum immediately after laser excitation has a very broad and distinct absorption band with absorp-

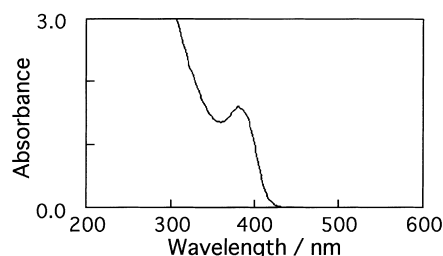


Fig. 1. Absorption spectrum of TG-CdS particles in water. A quartz cell with 10 mm of path length was used in the measurement. [TG-CdS]: 1.0 mM.

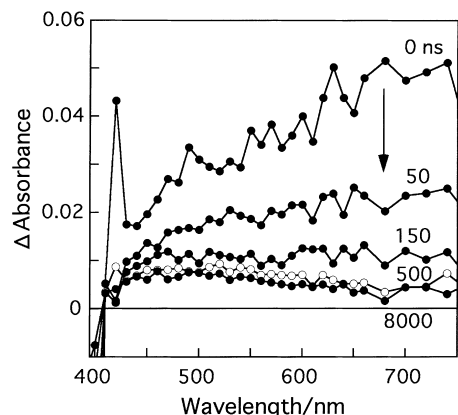


Fig. 2. The time-resolved transient absorption spectra of TG-CdS particles in water. [TG-CdS]: 1.0 mM.

tion maximum near 700 nm besides the negative absorption due to characteristic photo-bleaching [13–15] of semiconductor Q-particles observed below ca. 400 nm. The transient absorption subsequently decays with the elapse of time and its intensity at 700 nm decays to ca. 50% at 50 ns and below 10% at 500 ns though one at 500 nm decays to ca. 60% at 50 ns and ca. 25% at 500 ns. The absorption maximum of this transient absorption at the time of 500 ns shifts to 480 ~ 500 nm which is absorption peak of the trapped holes [7,16–19] and further its shape is very similar to that of transient absorption immediately after laser excitation in the nanosecond laser photolysis of thiophenolate capped CdS (PhS-CdS) particles in acetonitrile [7].

Such distinct transient absorption with absorption maximum around 700 nm observed in water was hardly observed not only in organic solvents such as DMF and DMSO but also in nanosecond laser photolysis of PhS-CdS in acetonitrile reported already [7]. However, it was also observed more clearly in nanosecond laser flash photolysis of HMP-CdS in water, carried out in the present study with the same excitation energy (10 mJ/pulse) as the case of TG-CdS (However, when HMP-CdS prepared from cadmium nitrate was used, the transient absorption with absorption maximum around 700 nm was not observed, presumably because nitrate acts as an electron scavenger [17]). The time profiles of the transient absorption of TG-CdS in various solvents and HMP-CdS in water are shown in Fig. 3. As can be seen from the figure, the distinct transient absorption appears immediately after laser excitation for both TG-CdS and HMP-CdS in water though their decay kinetics (life time for the decay: ca. 100 ~ 150 ns) are considerably faster than that (ca. 10  $\mu$ s) for the deoxygenated-aqueous HMP-CdS colloidal solutions reported [17,18,20].

The time resolved transient absorption spectra of TG-CdS particles were also measured in water containing methylviologen ( $MV^{2+}$ ) or sodium iodide which are known as electron or hole scavengers in order to investigate the behavior of the transient absorption with absorption

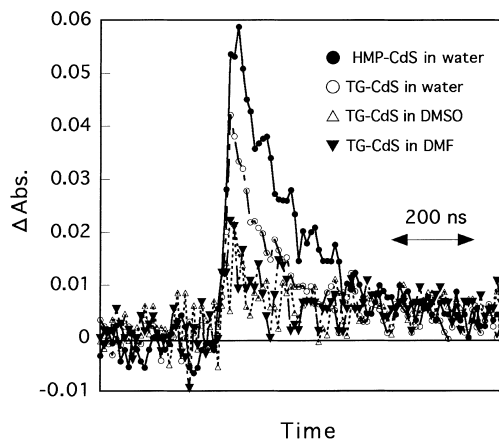


Fig. 3. Time profiles of transient absorption spectra of TG-CdS in various solvents and HMP-CdS in water at 700 nm. The absorbance of all colloidal solutions at 355 nm, which is excitation wavelength for nanosecond laser flash photolysis, was adjusted to 1.5.

maximum around 700 nm observed immediately after laser excitation. Fig. 4 shows the result of addition of  $MV^{2+}$ . As seen from the figure, in the transient absorption of TG-CdS in water containing 1 mM  $MV^{2+}$ , observed immediately after laser excitation, the absorption decreases around 700 nm and consequently absorption around 600 nm predominates relatively compared with that of TG-CdS in water without  $MV^{2+}$ . Further, the shape of the transient absorption at several tens nanoseconds after laser excitation changes markedly, namely, the absorption in the wavelength region longer than 700 nm decreases remarkably and its absorption maximum shifts from near 700 nm to ca. 600 nm, and is very similar to that of methylviologen cation radical ( $MV^{\cdot+}$ ) [21]. Subsequently the changes in the shape and the intensity of the transient absorption are slow up to several hundreds nanoseconds. On the other hand, the addition of 10 mM NaI into the colloidal solution hardly influenced the shape and

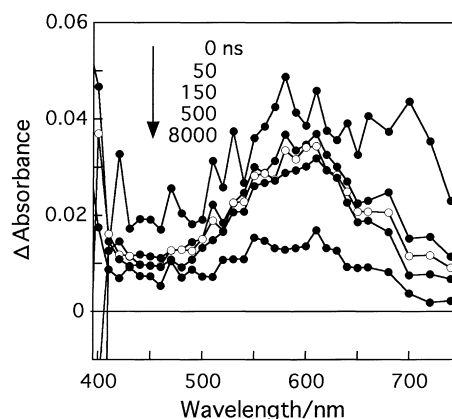


Fig. 4. The time-resolved transient absorption spectra of TG-CdS particles in water in the presence of methylviologen. [TG-CdS]: 1.0 mM. [ $MV^{2+}$ ]: 1.0 mM.

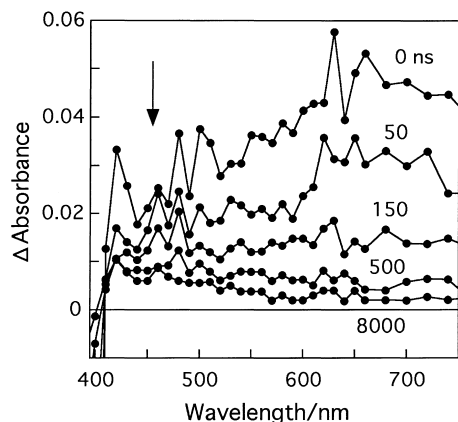


Fig. 5. The time-resolved transient absorption spectra of TG-CdS particles in water in the presence of sodium iodide. [TG-CdS]: 1.0 mM. [NaI]: 10 mM.

the intensity of the transient absorption of TG-CdS in water except that the decay of the transient absorption becomes somewhat slower up to several tens nanoseconds, as shown in Fig. 5.

Furthermore, as can be seen Fig. 6, the intensity of the transient absorption measured immediately after laser excitation in water-acetonitrile (3 : 2) mixed solvent is small wholly and the absorption around 700 nm is not notable compared with that in water. The dependencies of the transient absorption of TG-CdS, observed immediately after laser excitation at 430 and 730 nm, on the content of acetonitrile in the mixed solvents are also shown in Fig. 7. The intensity of the transient absorption at 730 nm decreases clearly with increasing the acetonitrile content though such tendency is not observed at 430 nm.

All of these results strongly suggest that the transient absorption in longer wavelength region, observed at early stage in the nanosecond laser photolysis of TG-CdS in water, is mainly attributable to hydrated electrons as in the case reported for the deoxygenated aqueous HMP-CdS colloidal solutions [17].

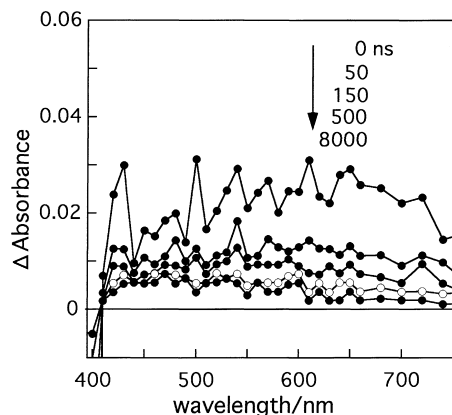


Fig. 6. The time-resolved transient absorption spectra of TG-CdS particles in water-acetonitrile (3 : 2) mixed solvent. [TG-CdS]: 1.0 mM.

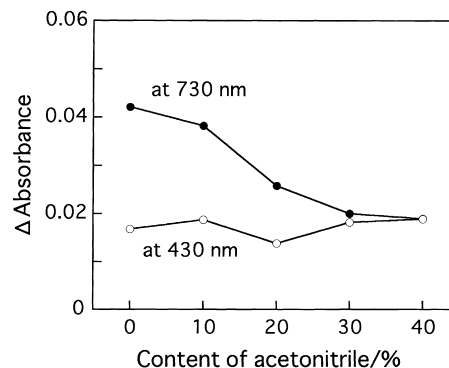


Fig. 7. The dependency of the transient absorption of TG-CdS, measured immediately after laser excitation, on content of acetonitrile in water-acetonitrile mixed solvents. [TG-CdS]: 1.0 mM.

### 3.3. Mechanism for the production of the hydrated electron

The laser power dependency of the transient absorption measured at 700 nm immediately after laser excitation is shown in Fig. 8.  $\Delta$  absorbance at 700 nm due to the production of the hydrated electrons increases almost linearly up to ca. 10 mJ/pulse and subsequently shows a tendency to bend downward slightly with further increase of laser intensities. Almost similar laser intensity dependency of the production of hydrated electrons was reported for the nanosecond and subpicosecond laser flash photolysis of aqueous HMP-CdS colloidal solutions without the dissolved oxygen [17,22].

If the production of the hydrated electron is one photon process, the  $\Delta$  absorbance should be proportional to the square root of the laser intensities [17]. As seen from the figure, the  $\Delta$  absorbance is almost linearly proportional to the laser intensities (Auger-like process in which two photons participate. Details will be described below). Furthermore, it is also reported that the photo-generated electrons in conduction band of CdS particles do not have sufficient energy to produce hydrated electrons via one

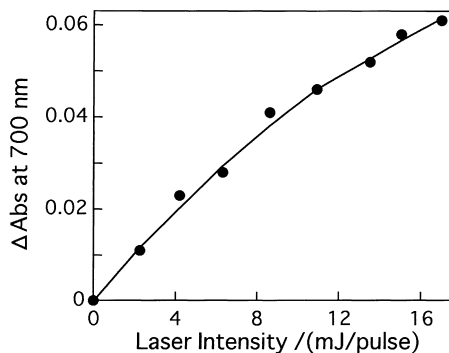


Fig. 8. The laser power dependency of the transient absorption of TG-CdS in water.  $\Delta$  absorbances at 700 nm measured immediately after laser excitation were plotted. Laser powers were measured just behind of the sample cell under condition to remove the cell. [TG-CdS]: 1.0 mM.

photon process [20]. Therefore, one photon process is excluded in the present study for the production of the hydrated electrons.

In the present study, the average photon number absorbed by one TG-CdS particle is ca. 30 and further the mean agglomeration number of TG-CdS particles is about 160. They were estimated from the laser intensity (10 mJ/pulse), the concentration of TG-CdS (1 mM as Cd), their absorbance at excitation wavelength (0.6 at 355 nm with 0.4 cm in path length), the size (25 Å in diameter) and density (4.8 as CdS) of the particles, and the sample volume absorbed photons ( $0.3 \times 0.4 \times 1.0 \text{ cm}^3$ ). The average photon number absorbed by a particle is less than the mean agglomeration number of the particle. Therefore, it seems that there is also no possibility for the production of hydrated electrons by simultaneous or successive absorption of two photons by identical electron under the present experimental conditions.

Haase et al. [17] proposed the mechanism for the production of the hydrated electrons in aqueous HMP-CdS colloidal solutions as follows. Auger-like interaction between two photo-generated electron-hole pairs occurs in identical particle during their life time, consequently an electron is emitted to bulk water, producing a hydrated electron. According to the proposed mechanism, the production rates are proportional to 2nd,  $1 \sim 2$ nd and 1st power of the laser dose at very low, medium and high light intensities, respectively. Furthermore, it is reported that the concentration of hydrated electrons produced shows a tendency to saturate slowly with increasing laser intensities in the region of laser intensities where more than one electron were emitted from CdS particle during a laser pulse because of the increase of the electron-hole recombination rate due to excess holes. Consequently, the light intensity dependency of the yield of the hydrated electron indicates a complex relationship and varies with light intensity.

At 10 mJ/pulse of laser intensity in the present study, the average number of electron emitted from identical TG-CdS particle during a laser pulse is ca. 0.5 which was estimated from  $\Delta$  absorbance (0.045) in Fig. 8 (at 700 nm,  $\epsilon(e_{\text{eq}}^-) = 1.5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  [17]) and the data described above. It seems that the influence of the excess hole on the electron-hole recombination is little, so this electron-hole recombination may be not the reason for the downward bending of the laser intensity dependency curve. Furthermore, one can obtain ca. 0.017 as the quantum yield for the production of the hydrated electron using the average number (ca. 0.5) of electron emitted from TG-CdS particle and the photon number (ca. 30 photon) absorbed by a particle during a laser pulse. This relatively small quantum yield may result from a low probability for Aguer-like interaction between two electron-hole pairs in a particle in the present experimental conditions because only 30 photons are absorbed per particle during a laser pulse (pulse width: ca. 10 ns) and consequently the probability that another electron-hole pair exists in a identical particle during the

life time of one electron-hole pair is considerably low. On the other hand, though the time constant for the trapping process of the photo-produced electrons on the surface of CdS Q-particles is 90 fs [23], it is considered that trapped electrons in CdS Q-particles exist as electron-hole pairs because radius of the Q-particles is smaller than that of exciton in ordinary CdS particles. Therefore, Aguer-like interaction between two (probably trapped) electron-hole pairs in a particle may occur to some extent even by the nanosecond laser excitation.

In the case of TG-CdS particles, furthermore, it is considered that the life time of the photo-generated electrons trapped is relatively long on the TG-CdS particles because thioglycerol binds covalently with CdS core through its sulfur atom [6] traps photo-generated holes, reducing the electron-hole recombination. Therefore, the possibility that the electron is ejected to bulk water by Aguer-like process (two photons participation) are enhanced and the absorption due to hydrated electrons can be observed in water as well as the case of HMP-CdS.

#### 3.4. Effects of capping agents and dissolved oxygen on the transient absorption

From the results and the discussion described so far, it is supposed that the large differences in the decay dynamics and the shape of the transient absorption between TG-CdS in water and PhS-CdS in acetonitrile mainly results from the difference in solvent rather than the difference in the hole trapping ability between thiophenol and thioglycerol.

Furthermore, it seems that there is no large difference between the hole trapping abilities of thioglycerol (non-charged) which binds covalently with CdS of TG-CdS particles and hexametaphosphate (negatively charged) which is adsorbed loosely to the surface of CdS particles because there is no large difference in the intensity of the transient absorption due to hydrated electrons observed immediately after laser excitation of both TG-CdS and HMP-CdS in water. As the main reason why the transient absorption of TG-CdS was not observed in visible region in both DMF and DMSO solvents, it is considered that either stable solvated electrons such as hydrated electrons are not produced or their extinction coefficient is very small in these solvents.

Furthermore, the decay of the transient absorption due to hydrated electrons for the present study of HMP-CdS was considerably faster than the results reported. The reasons are ascribed to the differences in the colloid concentration and further experimental conditions whether oxygen exist or not in the solution. It is known that the decay rate of the hydrated electrons depends on the concentration of CdS particles and further becomes faster in the presence of oxygen [17]. In the present study, actually the decay of the transient absorption spectra of TG-CdS particles in water became somewhat slower by the removal of oxygen from the colloidal solutions

by bubbling nitrogen gas though the shape of the spectra were not influenced.

#### 4. Conclusions

The transient absorption of TG-CdS in water at longer wavelength region, observed immediately after laser excitation, is clearly attributable to hydrated electrons. However, as the photo-generated electrons in conduction band of CdS particles do not have sufficient energy to produce hydrated electrons, they are not produced via one photon process. It is necessary that an Auger-like interaction between two electron-hole pairs in a particle occurs during their life times (namely, two photons participate) for the production of the hydrated electron as already proposed for HMP-CdS by Haase et al. The life times of the photo-generated electron-hole pairs may be somewhat extended on the TG-CdS particles since thioglycerol bound covalently with CdS core traps photo-generated holes. Consequently, the possibilities that electrons are ejected to bulk water via the interaction between two electron-hole pairs by participation of two photons are enhanced and the relative large absorption due to hydrated electrons can be observed as well as the case of HMP-CdS in water. Although there was the possibility that an analogous Auger-like process occurs in TG-CdS particles in organic solvents such as DMF and DMSO, the absorption due to the solvated electron was not observed.

The measurements of time-resolved transient absorption spectra of TG-CdS particles is currently under way using a subpicosecond laser system to obtain more detailed knowledge about their photochemical events.

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