

# Subpicosecond time-resolved photoluminescence of thioglycerol-capped CdS nanoparticles in water

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## Abstract

Subpicosecond time-resolved photoluminescence (STRPL) of aqueous colloidal solutions of thioglycerol-capped CdS nanoparticles (TG-CdS) was successfully measured by fluorescence up-conversion techniques. In their STRPL obtained within the time range of 30 ps after the excitation, the intensity of photoluminescence (PL) around 500 nm at which their static PL is not noticeable is considerably outstanding compared with that at a longer wavelength region at which PL is attributed to deep trap sites in CdS nanoparticles. From the analysis of the PL decay profile at the wavelength region of 490–550 nm at which PL is mainly attributed to near band edge emission, we observed two fast PL decay components of ca. 1 ps and ca. 10 ps, similar to those already reported for the band edge emission of CdS nanoparticles in a glass matrix. In the present study, former decay component was related to trapping rate of photogenerated holes, following the case already reported for CdS nanoparticles embedded in a glass matrix. However, the origin of the latter PL decay component is not clear at present. It is necessary to study in further detail to elucidate it. © 2005 Elsevier B.V. All rights reserved.

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## 1. Introduction

Many studies have been so far carried out on the primary behavior of electrons and holes photogenerated in semiconductor nanoparticles by ultrafast spectroscopy such as a pump and probe transient absorption measurement because such studies are very important for designing effective photocatalysts [1–16]. We have also studied the primary photochemical events, especially the behavior of the photogenerated charge carriers immediately after the photoexcitation, of thiol-capped CdS nanoparticles, which are convenient for spectroscopic measurements by their subpicosecond time-resolved transient absorption measurements (the pump and probe technique) [17–21].

Photoluminescence (PL) of CdS nanoparticles, which is a radiative recombination process between photogenerated electrons and holes directly reflects the behavior of photogenerated charge carriers. Therefore, their PL measurements are another useful means to understand their photochemical events. Their

time-resolved PL measurements were also carried out by using a streak camera or by the time-correlation single photon counting method in order to investigate dynamic behavior of charge carriers [11,14,22–31]. However, most of the studies are focused on the analysis of PL decay components, which found in the time region more than nanoseconds. It seems that there is no report on the time-resolved PL for the colloidal solutions of CdS nanoparticles measured in time region of a subpicosecond to several tens of picoseconds, which correspond to the subpicosecond time-resolved transient absorption because probably of their low quantum yield. As far as we investigated, there are only a few reports on the up-conversion measurement for PL of CdS nanoparticles in a glass matrix [8,32,33].

In the present study, the subpicosecond time-resolved PL (STRPL) for CdS nanoparticle colloidal solutions, which has not been reported so far, as far as we know, was measured by fluorescence up-conversion techniques using aqueous colloidal solutions of thioglycerol-capped CdS nanoparticles (TG-CdS). TG-CdS nanoparticles were used previously for the subpicosecond time-resolved transient absorption measurements. From their PL decay dynamics obtained, their primary photochemical events were discussed. It was necessary to carry out repetitional

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measurements of 15–20 times and their averaging to obtain analyzable PL decay profiles because of extremely low quantum yield for PL of TG-CdS colloidal solutions. Use of colloidal solutions of CdS nanoparticles seems to facilitate the preparation of semiconductor nanoparticles with various surface conditions, compared to those in a glass matrix. Therefore, we initiated a detailed study of the behavior of charge carriers immediately after photoexcitation, using aqueous colloidal solutions of CdS nanoparticles.

## 2. Experimental section

### 2.1. Preparation of TG-CdS colloidal solutions

TG-CdS colloidal solutions were prepared by redispersing TG-CdS in water. TG-CdS was synthesized from cadmium acetate, thiourea, and 1-thioglycerol [34,35]. The CdS core size of TG-CdS synthesized was estimated to be ca. 2.5 nm from the correlation between the onset wavelength of its absorption spectrum and the particle size of CdS nanoparticles [36,37].

### 2.2. Subpicosecond time-resolved PL measurements

The subpicosecond time-resolved PL (STRPL) measurements for the TG-CdS colloidal solutions were carried out by using the home-made fluorescence up-conversion optics as shown in Fig. 1. The pump pulse (excitation pulse) was a 396 nm pulse generated by frequency doubling of the fundamental output ( $\lambda_{\max} = 792$  nm) from a femtosecond mode-locked Ti:Sapphire laser (76 MHz, FWHM = ca. 170 fs, MIRA 900 Basic, Coherent) using a BBO crystal. The gate pulse (mixing pulse) was the residual of the fundamental output. The PL generated by photoexcitation of samples was collected by an objective lens just behind a sample cell and focused usually after passed through a cut filter (L-42, HOYA) in a BBO crystal together with the gate pulse, which passed through the optical delay stage to generate their sum frequency signal. In order to cover the wide wavelength region, two kinds of BBO crystals with a different phase matching angle were used. The generated sum frequency signal was introduced into a monochromator and then detected by using a photomultiplier tube (R585, Hamamatsu) and a gated photon counter (SR400, Stanford Research Systems Inc.). Applied voltage for the photomultiplier tube was  $-1200$  V. The signals from the photomultiplier tube were amplified to

five-fold by a fast pre-amplifier before they were introduced into the gated photon counter. The sum frequency signals were measured as a function of the delay time between the pump pulse and the gate pulse by operating the optical delay stage. Acquisition and accumulation of the data and operating of the delay stage were carried out using a personal computer equipped with an operation software. Because the sum frequency signals were usually very weak, the measurements at identical wavelength were repeated 15–20 times and their average was used for data analysis. All measurements were carried out with ca. 15 mW for the pump pulse and ca. 190 mW for the gate pulse. The optimization of the optics for the up-conversion measurements (especially, optimization of the angle of incidence of the pulses into a BBO crystal for sum frequency generation at each observing wavelength) was done by utilizing the fluorescence of coumarin 151 in ethanol/water.

In the measurements, the concentration of all colloidal solutions was adjusted as their absorbance at 396 nm (pumping wavelength) to be 0.015 Abs. with a 1 mm cell to avoid the damage from the pump pulse, and then the solutions were circulated between the sample cell and a sample reservoir by a roller pump during the measurements. A non-fluorescent quartz flow cell with 1 mm in path length was used for all measurements. The removal of dissolved oxygen in the colloidal solutions was not done. To remove the influences of a Raman scattering light from water solvent and a stray light due to the excitation pulse, the sum frequency signal of pure water obtained under the identical experimental conditions were subtracted from the up-conversion signals for the samples.

In the measurement of ordinary (non-time-resolved) PL spectra carried out to obtain the fundamental PL properties of the colloidal solutions, the 396 nm subpicosecond pulse described above and a monochromatic light from a 100 W Xe lamp were used as the excitation light source. The PL of the samples was collected with an objective lens placed at a right angle with the excitation light and then led into a monochromator. A cut filter (L-42, HOYA) was usually put just in front of the monochromator to remove a stray light from the excitation light. PL passed through the monochromator was detected with a CCD detector (DV420-OE, Andor tech.). Acquisition and accumulation of the data were carried out using the personal computer equipped with an operation software attached to the CCD detector. Non-fluorescent quartz cells with 10 mm in path length were used as a sample cell. The concentration of the samples and the pump pulse intensity (in the case of laser pulse excitation) were identical with those for the up-conversion measurements described above. The correction of the PL spectra was not done.

## 3. Results and discussion

### 3.1. Analysis for the decay part of STRPL for TG-CdS in water

Before the measurement of STRPL for aqueous colloidal solutions of TG-CdS, its ordinary (non-time-resolved) PL spectrum was measured by the subpicosecond laser pulse excitation (Fig. 2). A broad PL band with the maximum near 600 nm

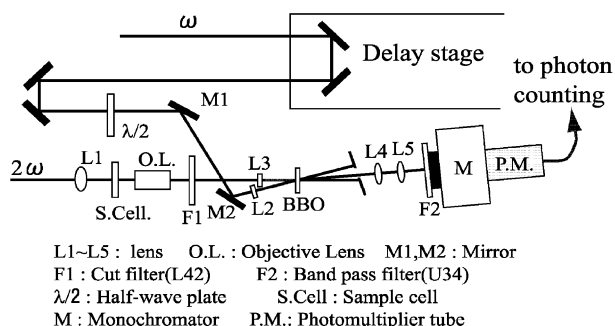


Fig. 1. Schematic representation of fluorescence up-conversion optics.

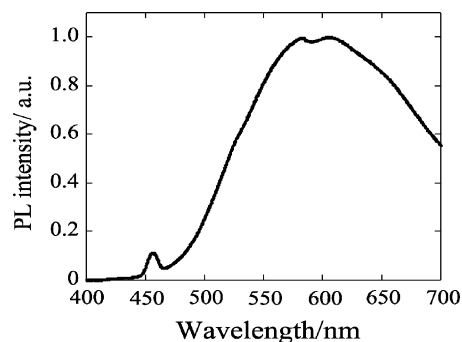


Fig. 2. Ordinary PL spectrum of TG-CdS in water. The subpicosecond laser pulse was used for the 396 nm-excitation. The correction of the spectrum was not done.

was observed in the wavelength region of 450–700 nm. On the analogy of the reports for ordinary colloidal solutions of CdS nanoparticles [22,38], it is considered that the PL band is attributed to deep trap sites due to the sulfur vacancy. However, the band edge emission, which is expected to appear around 430 nm when estimated from their absorption band edge was not observed in the spectrum in Fig. 2. The band edge emission was not observed even under the conditions that the L-42 cut filter was removed and the excitation wavelength was moved at shorter wavelength using a monochromatic light from the 100 W Xe lamp. Therefore, it is considered that the reason why the band edge emission was not observed for TG-CdS in water was not because of the cut filter placed just in front of the monochromator but because of the nanoparticles with a large surface area per volume [27,39]. It is well known that the surface of the nanoparticles has many trap sites in their colloidal solutions. Furthermore, a very broad band suggests that the surface trap sites with various energy states exist near the surface of the nanoparticles together with the existence of their size dispersion. The PL spectrum of TG-CdS colloidal solution was observed at the longer wavelength region compared to that of CdS nanoparticles in glass matrix [32] despite that the size of TG-CdS nanoparticles is smaller than that of CdS nanoparticles in glass matrix. One plausible explanation is due to the temperature at which the solution was prepared. The colloidal solutions of TG-CdS were prepared at room temperature and therefore the surface of TG-CdS nanoparticles has many surface states and consequently their PL spectrum was governed by PL originated from the surface states. On the other hand, CdS nanoparticles in a glass matrix were prepared at high temperature. A small and narrow PL peak observed around 450 nm in Fig. 2 is due to a Raman scattering light from water used as the solvent. The details of ordinary PL of TG-CdS will be reported elsewhere together with that of other thiol-capped CdS nanoparticles.

In order to investigate the rise and decay dynamics for PL of TG-CdS in water, the up-conversion measurements for the PL at several wavelengths in the wavelength region of 430–750 nm were carried out within 30 ps after the laser excitation. The measurement was done at 430 nm at which its ordinary PL was not clear, though the measurements was not done at the wavelength range of 440–480 nm at which the influence of a Raman scattering light was extremely large. The time profiles of PL of

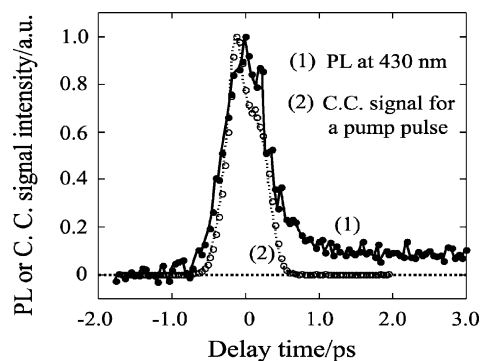


Fig. 3. Time profiles of the up-conversion signals of PL at 430 nm for TG-CdS in water and cross correlation signals of a pump pulse within few ps after the excitation.

TG-CdS in water obtained as up-conversion signals are shown in Figs. 3 and 4. In principle, since the time profile of the PL up-conversion signal is identical with that of the corresponding PL, all time profiles will be handled as those for PL from now on. Furthermore, the wavelengths shown in all figures are for PL. For time profiles at 430 and 490 nm at which the influence of a stray light of excitation pulse and a Raman scattering light of water can not be disregarded, the correction of the influence was carried out by subtracting the up-conversion signal of pure water which was measured under the same experimental conditions, as shown in Fig. 5.

Fig. 3 shows the time profile of the up-conversion signal of PL at 430 nm at which it is possible to observe the band edge emission of TG-CdS, together with that of the pump pulse (the excitation pulse). The time profile of PL of TG-CdS was very similar to that of the pump pulse except for existence of the decay component which remains somewhat at the time longer than 2 ps after the excitation, while most of the PL decays within the duration time (few hundreds of femtoseconds) of the pump pulse. It suggests that the direct recombination of the photo-generated charge carriers and their relaxation (hoping) to lower energy levels occur virtually within the duration time of the pump pulse. However, the data at 430 nm was hereafter excluded

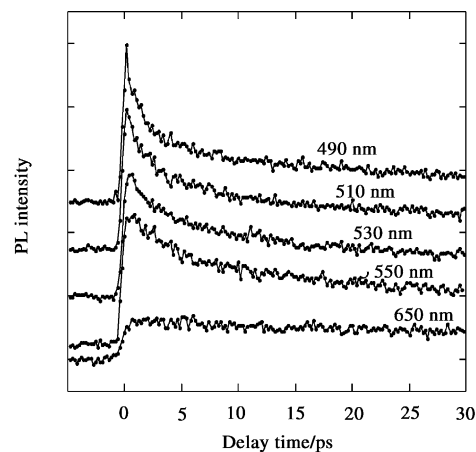


Fig. 4. Time profiles of the up-conversion signals of PL at various wavelengths for TG-CdS in water within 30 ps after the excitation.

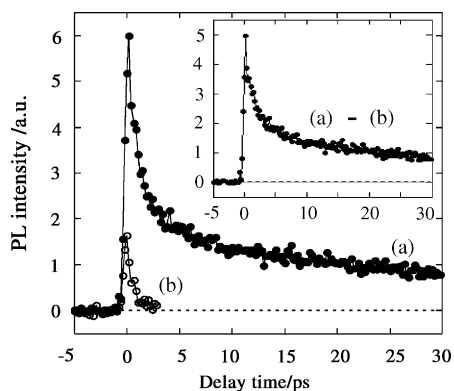


Fig. 5. An example (at 490 nm) for the correction of the influence of Raman scattering light from water solvent on the PL decay time profile for the TG-CdS colloidal solution. The correction was carried out by subtracting the time profile for neat water (b) from that for the TG-CdS colloidal solution (a). The corrected time profile is shown as an inset in the figure.

from the discussion because it was doubtful whether the primitive correction method described above was appropriate for the correction of a relatively intense stray light and consequently whether the corrected PL time profile is reliable. Therefore, the time profiles at wavelengths longer than 490 nm in Fig. 4 will be used for the following discussions.

Although it is difficult to compare exactly the PL intensity at the various wavelengths due to the wavelength dependence of the sum frequency conversion efficiency and the complicated adjustment of phase matching angle of BBO crystal in the up-conversion optics, broadly speaking, as seen from Fig. 4, the intensity of STRPL for TG-CdS in water measured immediately after the pulse excitation increases with decreasing the observing wavelength. This observation is different from the case of its ordinary PL spectrum in Fig. 2. Namely, the PL immediately after the excitation decreased with increasing the observing wavelength and became extremely small at the wavelength longer than 650 nm. It is considered that the wavelength dependence of the conversion efficiencies of the BBO crystals is not so large in the wavelength region used for this study. This result suggests that the origin of STRPL observed within several ps after the excitation is different from that of its ordinary PL spectrum though both measurements were carried out at the same wavelength. Thus, it follows that PL of TG-CdS in water observed by subpicosecond up-conversion measurements reflects mainly the electron–hole recombination at the states concerning with fast decay processes, which differs from its ordinary PL. Probably, that is why its PL up-conversion signals were observed at the wavelengths shorter than 500 nm at which its ordinary PL is extremely weak.

The decay of the PL as a whole was slower at longer wavelengths and was hardly observed up to 30 ps at 650 nm. Furthermore the rise of the PL at 650 nm was several hundreds of fs slower than that at 490 nm as shown in Fig. 6. However, the rising time of the PL at 650 nm, where it is related to relatively deep trap sites was much shorter than the time (20–30 ps) estimated from PL decay dynamics at shorter wavelength region, which is the time required for the trapping of photogenerated electrons into deep trap sites for CdS nanoparticles in a glass

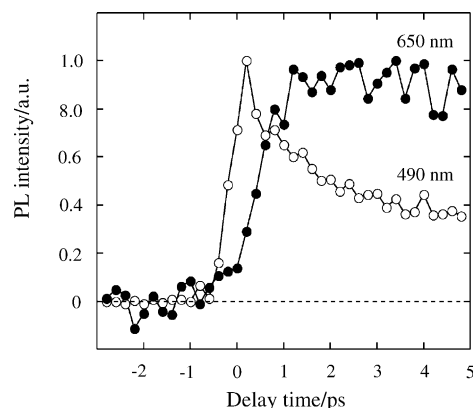


Fig. 6. Comparison of PL time profiles between 490 and 650 nm for TG-CdS in water. The PL intensities were normalized to their maxima at each wavelength.

matrix [32]. Therefore, it seems that the observed rising time of the PL at 650 nm probably does not reflect the overall trapping time of photogenerated electrons into the deep trap sites. Namely, it means that some photogenerated carriers (electrons, holes, or both) arrived to their trap sites and then the recombination of electron–hole occurred within 1 ps even at 650 nm which does not contain short-lived components because the rising of the PL at 650 nm was observed within 1 ps after the laser pulse excitation. On the other hand, the rising time of PL at shorter wavelength region (ca. 500–540 nm) for CdS nanoparticles in a glass matrix was related to carrier intraband relaxation [32]. As far as we investigated, there is no report on STRPL measurements for colloidal solutions of CdS nanoparticles measured within the time range of several tens of ps after the pulse excitation, probably due to their extremely weak PL intensity, though the measurements for CdS nanoparticles in a glass matrix are already reported [32,33,40].

In order to analyse the PL time profiles in Fig. 4, they were normalized for the maximum value at each wavelength (Fig. 7). It was also found from the normalized time profiles that overall decay of the PL becomes slower with increasing the observing wavelength. Decay parts of all time profiles, except for that at

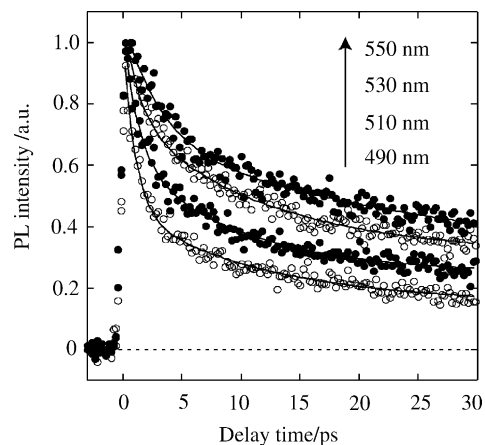


Fig. 7. Curve fitting of the decay part of the PL for TG-CdS in water in Fig. 4. The PL intensities were normalized to their maxima at each wavelength. The solid lines in the figure are the best fitted curves by using Eq. (1) in the text.

Table 1  
Decay lifetimes and pre-exponential factors for PL of TG-CdS in water at various wavelengths

Wavelength (nm)	$\tau_1$ (ps)	$\tau_2$ (ps)	$A_1$	$A_2$	Constant
490	1.0	12	0.55	0.30	0.15
510	1.3	9.5	0.37	0.38	0.25
530	1.4	12	0.25	0.44	0.31
550	3.2	32	0.33	0.43	0.24

650 nm in which PL does not virtually decay, can be fitted using the following Eq. (1) [22]:

$$S(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + \text{Constant} \quad (1)$$

where  $S(t)$  is the PL intensity (the up-conversion signal intensity) at  $t$  ps (delay time) after the pump pulse excitation, and  $\tau_i$  and  $A_i$  are the lifetime of the PL decay component  $i$  and its ratio to whole components at the time zero, respectively. The Constant denotes the PL component, which hardly changes within the time range of several tens of ps. For nanosecond decay dynamics for PL (due to deep trap sites) of ordinary CdS nanoparticles, O'Neil et al. [25] have reported that its PL decay profile could not be fitted by sum of simple exponentials such as Eq. (1) described above. In the present study, however, Eq. (1) was used for the curve fitting to carry out the basic analysis for the PL decay dynamics. The solid lines in the figure are the best fit for the curve fitting by Eq. (1). The values of  $\tau_i$  and  $A_i$  obtained at various wavelengths are summarized in Table 1. As can be seen from the table, the predominant PL components in the time range within several ps after the excitation are two fast decay components with the lifetime of ca. 1 ps and ca. 10 ps, respectively, until 550 nm, which is a relatively long wavelength. The origin for these decay components will be discussed hereinafter.

### 3.2. The origin of the PL decay component (1 ps-component) with the lifetime of ca. 1 ps

A fast PL decay component similar to the 1 ps-component for PL of the aqueous colloidal solution of TG-CdS observed in the wavelength region of 490–550 nm in the present study is already reported for the band edge emission of CdS nanoparticles in a glass matrix [32,33,40]. In the reports, Klimov et al. [32,40] proposed that the lifetime of the fast PL decay component reflects the trapping rate of the photogenerated holes. At the same time, they also proposed that the trap sites for the photogenerated holes are intrinsic states of the particle and/or the surface states which was not modified by various surface-controlling, but not the localized surface defects such as vacancies because decay dynamics for holes is uniformly fast under the any surface conditions, in contrast to that for electrons controlled by modification of the nanoparticle surface [15,40]. We concluded that, similar to the case of the band edge emission of CdS nanoparticles in a glass matrix, the 1 ps-component observed for PL of the aqueous colloidal solution of TG-CdS in the present study also reflects rather the trapping rate of the photogenerated holes than that of the photogenerated electrons because it was hardly influenced

by exchanging solvents from water to DMF (effect of solvent on the PL decay dynamics will be reported in detail elsewhere later).

However, the 1 ps-component obtained for the PL of TG-CdS in the present study appeared until around 550 nm which is considerably longer than the wavelength at which the band edge emission of CdS nanoparticles may appear. It is difficult to consider that the band edge emission appears until around 550 nm, from the distribution of particle size expected for TG-CdS, even if the coupling of the band edge state with vibronic states and the dispersion of particle size are considered as well as the analysis of the decay component with the lifetime of several hundreds of ps in the picosecond time-resolved PL measurements for CdS nanoparticles by O'Neil et al. [25]. Therefore, we concluded so for the present even though there are some questions whether or not the discussion on the band edge emission of CdS nanoparticles in a glass matrix is applicable to the near band edge PL of TG-CdS in the present study.

As described above, in the present study, as the 1 ps-decay component of the PL of TG-CdS was related to trapping rate of holes to relative deep trap states, it is considered that the holes relating to the PL necessarily populate in the valence band or in the relative shallow trap states formed near the valence band. This explanation is consistent with the reports by Klimov et al. [32] and Logunov et al. [41] in which a few ps decay component is observed in the band edge emission and a few ps component exists in the subpicosecond transient photobleaching dynamics of the lowest exciton transition for CdS nanoparticles, respectively. From the above-mentioned discussion on the trapping sites for holes, it is considered that the electrons concerning with the PL around 500 nm which was observed within 30 ps after the excitation are trapped into relatively deep intra-gap states (they are shallow traps) near the bottom of the conduction band. In the present study, it is difficult to obtain a more detailed knowledge of the trap sites of the electrons. However, it may be natural to assume such states as the trap states for the electrons, because in addition to the wide size distribution, it is predicted that many surface states with various energy levels are formed on the surface of TG-CdS particles whose surface-to-volume ratio is much larger than that for ordinary CdS particles.

On the other hand, on the time-resolved transient absorption measurements under the low intensity excitation, the fast decay component with the lifetime less than a few ps was not observed for CdS nanoparticles. However, the absorption decay component due to photogenerated holes with the lifetime (< few ps), virtually similar to that for PL decay component observed for TG-CdS in the present study, was observed for CdS nanoparticles [40].

### 3.3. The origin of the PL decay component (10 ps-component) with the lifetime of ca. 10 ps

As can be seen from Table 1, PL of TG-CdS observed at various wavelengths within 30 ps after the excitation contains the 10 ps-decay component as one of the main components together with the 1 ps-decay component. When the curve fitting was carried out for the time profiles measured up to 100 ps

for comparison, the lifetime of the 10 ps-component became somewhat longer than 10 ps. This suggests that the lifetime of the 10 ps-component obtained by the curve fitting for the narrow time range of 30 ps was estimated shorter than its actual lifetime. However, the most of the PL up-conversion measurements were carried out within 30 ps after the pulse excitation because the main purpose of the present study was to observe the fast PL decay components for TG-CdS colloidal solutions.

Taking into account the above discussion, it is considered that the lifetime of the 10 ps-decay component obtained for TG-CdS in the present study is roughly similar to the lifetime ( $\tau_2 = 20\text{--}30\text{ ps}$ ) of second PL decay component obtained for STRPL measurements of CdS nanoparticles in a glass matrix by Klimov et al. [32]. They have described that the second PL decay component was related to the trapping rate of electrons into the trap sites (sulfur vacancies), which are origin of deep trap emission. Furthermore, to observe the electron trapping process into the deep trap sites in the CdS nanoparticles, O'Neil et al. [24] and Logunov et al. [41] observed the rising time for their PL time profiles at longer wavelength and obtained ca. 30 ps as its time constant. O'Neil et al. [24] pointed out that the time constant of 30 ps is extremely slower than the expected diffusion time (<1 ps) of electrons in nanoparticles and proposed the following model for its explanation. Namely, the model is that the charge carriers photogenerated in CdS nanoparticles are rapidly trapped into the states near their band edge and subsequently are kept diffusing until they encounter with the deep trap sites.

On the other hand, Roberti et al. reported that in the transient absorption measurements of CdS nanoparticles using a 790 nm laser pulse as a probe pulse, the decay time constant of ca. 50 ps for their transient absorption was related to the trapping rate of the photogenerated charge carriers [11]. It was also reported that the transient absorption at 790 nm is attributable to the trapped charge carriers and then the contribution of the free electrons in the conduction band and excitons to the absorption may be little. These views will give the important guideline for the assignment of the states, which relate to the 10 ps-decay component obtained for STRPL of TG-CdS in the present study. It is also reported that there is the component with the time constant of ca. 30 ps relating to the trapping rate of photogenerated electrons in the recovery dynamics obtained on the transient bleaching measurements of the exciton transition for CdS nanoparticles [41].

As described above, it has been reported by many researchers from various spectroscopic measurements that the time constant of several tens of ps appears in the charge carrier dynamics of CdS nanoparticles and it can be related to the trapping rate of the charge carriers. Taking into account these results, it seems to be natural to relate the 10 ps PL decay component obtained in the present study to the trapping rate of electrons. However, it is still a question to some degree whether the 10 ps decay component obtained for TG-CdS colloidal solutions in the present study is related to the trapping rate of electrons to deep trap states as well as the second decay component (lifetime of 20–30 ps) of CdS nanoparticles in a glass matrix because of the following reasons: (1) the PL observed is not band edge emission, (2) the lifetime obtained is somewhat shorter than the value reported for CdS nanoparticles in a glass matrix, and (3) rising of the PL at a longer

wavelength range (at 650 nm) which is related to deep traps is also a fast process which occurs within ca. 1 ps. Therefore, to elucidate the origin of the 10 ps-component, it is necessary to study in detail the PL decay dynamics for the colloidal solutions of TG-CdS under various conditions.

#### 3.4. The origin of the offset component which is contained in the decay process near 500 nm and the PL decay components at 650 nm

In addition to both the 1 ps- and the 10 ps-components, the PL decay process observed near 500 nm for TG-CdS in water also contains the offset component, which hardly decays within the observed time range (30 ps) (Fig. 7 and Table 1). On the other hand, at the decay process at 650 nm, both the fast decay components were not clearly observed, though the offset component was observed (Fig. 4). Although the analysis for the decay lifetimes of the offset component at all wavelengths containing 650 nm were not carried out, it is supposed that their lifetimes are in the time range of several hundreds of ps because they still remain considerably or hardly decayed at 100 ps after the excitation. The values of several hundreds of ps to several ns were reported so far by many researchers as the lifetime of the fast PL decay component for aqueous colloidal solutions of CdS nanoparticles by the ps or ns time-resolved PL measurements and decay component was related to the recombination of electrons and holes. Therefore, it is considered that the offset component observed in the present study which hardly decays within 30 ps after the excitation and presumably has the lifetime of several hundreds of ps corresponds to the PL observed so far in the ps- and ns time-resolved PL measurements for CdS nanoparticle colloidal solutions.

Since neither the 1 ps-component nor the 10 ps one is contained practically in the PL decay profile at 650 nm in Fig. 4, it is suggested that the holes related to the PL at 650 nm exist at the state different from those related to the PL around 500 nm. We consider that the sites where the holes related to the 650 nm-PL exist is the trap site for the holes related to the PL around 500 nm (Fig. 8). As shown in Fig. 6, the rising time of the PL at 650 nm is somewhat slower (several hundreds of fs) than that at 490 nm.

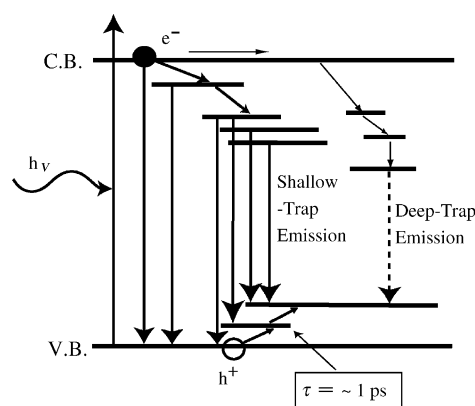


Fig. 8. Schematic representation of the states (energy levels) related to the 1 ps-decay component.

It seems that this result supports the above discussion on the trap sites of holes related to the PL observed in the present study.

### 3.5. Wavelength dependence of the PL decay dynamics

As can be seen from Table 1, there are two characteristic wavelength dependences in the PL decay dynamics for aqueous colloidal solutions of TG-CdS. One is the ratio of the 1 ps-decay component to all decay components decreases with increasing the observing wavelength (from  $A_1 = 0.55$  at 490 nm to  $A_1 = 0.25$  at 530 nm) and the other is the lifetime of the 1 ps-decay component becomes slightly longer with increasing the observing wavelength (from  $\tau_1 = 1.0$  ps at 490 nm to  $\tau_1 = 1.4$  ps at 530 nm).

The wavelength dependence of the PL decay dynamics has been so far reported on  $\mu$ s to ps time-resolved PL measurements for aqueous colloidal solutions of CdS nanoparticles [22,23,25–28,30]. It was generally observed that the lifetime becomes longer with increasing the observing wavelength. And, it follows that these results generally result in the red-shift of the maximum wavelength of the time-resolved PL spectra with time. The PL intensity within several ps after the excitation for TG-CdS in water was the strongest around 500 nm and could not be observed at the wavelength more than 700 nm in the wavelength range (490–750 nm) observed in the present study. This observation suggests that the PL of TG-CdS was governed by the shorter wavelength components rather than the longer ones within few tens of ps after the excitation. In connection with that the time-resolved PL spectra shift to the longer wavelength range with time, Chestnoy et al. [22] have reported that the states concerning with the PL disperse in the band gap and the decay of the PL concerning with them is rapid as their energy is higher and that this observation is explicable by the donor–acceptor pair recombination model applied to bulk semiconductors. It seems that the wavelength dependence observed for the PL of TG-CdS in the present study is also explicable in a similar manner as above.

## 4. Conclusion

The subpicosecond time-resolved PL (STRPL) for aqueous colloidal solutions of TG-CdS was successfully measured by the fluorescence up-conversion technique. It seems that such STRPL measurements for CdS nanoparticle colloidal solutions were not carried out until now, as far as we know, though the measurements were already carried out for CdS nanoparticles in a glass matrix. The PL intensity for TG-CdS within several ps after the excitation was pronounced around 500 nm, at which its ordinary PL is considerably weak, compared with that in the wavelength than 600 nm at which PL observed is attributed to the deep trap states. The two fast PL decay components with the lifetimes of ca. 1 ps and ca. 10 ps, respectively, were obtained by analysis of the PL decay profile around 500 nm. The former component may be related to the trapping rate of holes, following the case already reported for CdS nanoparticles in a glass matrix. However, it is necessary to study in detail in order to elucidate the origin of the latter one.

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