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Stability of colloidal solutions containing various surface-modified cadmium sulfide particles under stationary illumination

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Abstract

Stability of the various colloidal solutions containing CdS particles with the surface modified by thiols such as thioglycerol (TG-CdS), mercaptophenyltetrazole (MPT-CdS), mercaptobenzimidazole (MBI-CdS), and mercaptoacetate (MA-CdS) (capped CdS particles) under the stationary illumination was studied by monitoring the changes in the absorption spectra to obtain knowledge about the influence of these capping agents on photocatalytic events such as electron and hole transfer processes at the capped semiconductor particle-solution interface. By the stationary illumination of the capped CdS particles, the photo-aggregation of the particles was observed in water and the photo-dissolution in organic solvents. The observed difference may be ascribed to the oxidative elimination of the capping agents from the CdS particles which occurs assisted by proton dissociation from the agents in water but not in organic solvents with aprotic nature. Addition of iodide which is known as a hole scavenger enhanced the photo-dissolution of both the capped and ordinary non-capped CdS particles, contrary to the expected photo-aggregation. ©2000 Elsevier Science S.A. All rights reserved.

Keywords: Cadmium sulfide; Capped CdS; Nanoparticles; Photo-dissolution; Photo-aggregation

1. Introduction

The semiconductor photocatalytic reaction has attracted considerable attention because of potentialities for the photo-decomposition of water, novel organic synthetic methods, and others [1–4]. The photocatalytic reaction has, however, significant disadvantage, because of its low quantum efficiency. It is expected that the capping agent used to modify the surface of the semiconductor particles influences the photochemical processes such as trapping and recombination of electrons and holes photo-generated on the particles. Therefore, the charge separation efficiency of photo-generated electrons and holes on photocatalysts and consequently whole efficiency of the photocatalytic reactions may be improved by utilizing suitable capping agents. From such a standpoint, we have so far investigated the primary photochemical events of the capped CdS particles by means of nano- and subpicosecond laser flash photolysis techniques [5–8].

In order to complement our previous discussion on the photochemical processes of the capped CdS particles based on the time-resolved transient absorption spectra measured by laser flash photolysis [6–8], the stability of various capped CdS particles under the stationary illumination was investigated in the present study by monitoring the absorption spectra. The influence of capping agents on the photochemical processes such as interfacial electron and hole transfer processes and their mechanism are discussed on the basis of the photo-dissolution mechanism of aqueous colloidal solutions containing ordinary non-capped CdS particles [9,10]. As semiconductor particles with the surface modified by organic molecules which are chemically bonded to the surface of semiconductor particles have relatively narrow size distribution and generally their transparent colloidal solutions can be easily prepared by redispersing them into solvents [11–13], these particles are convenient for spectroscopic studies on the photochemical processes.

For the purpose of comparision, the stability of ordinary non-capped CdS particles stabilized by hexametaphosphate (HMP-CdS) was also investigated under the same illumination conditions. It is known that n-type compound semiconductors such as CdS, CdSe, GaP and GaAs un-

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dergo the photo-dissolution in the ordinary solutions containing electrolytes by light illumination. The mechanism for photo-dissolution of CdS is also established. Furthermore, attempts to suppress the photo-dissolution of CdS have been carried out with a view to use it as an electrode of photoelectrochemical cell [14–20] and preparation of the mono-dispersed CdS Q-particles has been attempted utilizing photo-dissolution of CdS particles [21,22].

2. Experimental section

2.1. Materials

5-Mercapto-1-phenyltetrazole (MPT, Acros Org.), 2-mercaptobenzimmidazole (MBI, Acros Org.), thioglycerol (TG, Wako Chem.), and sodium mercaptoacetate (MA, Tokyo Kasei) employed as the capping agents were reagent grade and used as received. All other chemicals were also reagent grade and used without further purification. Triply distilled water was used for the preparation of aqueous colloidal solutions.

2.2. Apparatus

A cool stirrer (FDC-900, FINE) was used for the temperature control of the solutions in the preparation of CdS colloidal solutions. A 396 nm monochromatic light obtained by passing the light from 500 W xenon lamp (UI-501C, Ushio Denki) through a monochromator (CT-10, Japan Spectro.) was used as a light source for the stationary illumination. Absorption spectra of the colloidal solutions were measured with a spectrophotometer (U-2000, Hitachi).

2.3. Preparation of capped CdS particles and their colloidal solutions

TG-CdS particles were synthesized from cadmium acetate, thiourea, and thioglycerol according to the literatures [7,8,13] and their colloidal solutions were prepared by redispersing them into the solvents by the sonication.

MPT-CdS colloidal solutions were prepared employing the synthetic method [23] used for ordinary CdS colloidal solutions in the following way. 25 ml of 0.02 M cadmium acetate in DMF and 25 ml of 0.02 M MPT in DMF were mixed and stirred for 30 min in a 200-ml Erlenmeyer flask in a cool stirrer maintained at 25°C. While stirring the mixed solution, 25 ml of 0.02 M sodium sulfide in DMF/water (1 : 1) mixed solvent was poured quickly into it with a buret (injection rate: ca. 0.6 ml/s). The yellow-tinged colloidal solution containing MPT-CdS particles was obtained. After continued stirring of the colloidal solution for 1 h, it was allowed to stand in the dark until use. In order to remove insoluble large particles from the solution and make sure that the solution is transparent, it was centrifuged before use.

The preparation of the colloidal solution containing MBI-CdS particles was carried out using a similar method as that for MPT-CdS described above except the order of mixing of reagents. Namely, 0.02 M cadmium acetate in DMF was added into the mixed solution of 0.02 M sodium sulfide in DMF/water (1 : 1) and 0.02 M MBI in DMF. The treatment after that was similar to the case of MPT-CdS.

MA-CdS colloidal solutions were also prepared employing the synthetic method reported by Ramsden et al. [23] as follows. Fifty milliliters of 0.006 M cadmium chloride in water and 50 ml of 0.021 M sodium mercaptoacetate in water were mixed and stirred for 30 min in a 200-ml Erlenmeyer flask in a cool stirrer maintained at 25°C. While stirring the mixed solution, 5 ml of 0.06 M sodium sulfide in water was poured into it with a buret (injection rate: ca. one droplet/s). The yellow-tinged, transparent colloidal solution containing MA-CdS particles was obtained. After continued stirring of the colloidal solution for 1 h, it was allowed to stand in a refrigerator until use. The colloidal solutions were used after returned to room temperature.

CdS colloidal solutions stabilized with HMP (HMP-CdS) were also prepared using the synthetic method reported by Ramsden et al. [23] as follows. Fifty milliliters of 0.01 M sodium sulfide in water and 50 ml of 0.015 M HMP in water were mixed and stirred for 30 min in a 200-ml Erlenmeyer flask in a cool stirrer maintained at 25°C. While stirring the mixed solution, 2 ml of 0.255 M cadmium nitrate in water was injected quickly into it with a syringe. The yellow-tinged, transparent colloidal solution containing MA-CdS particles was obtained. The treatment after that was similar to the case of MPT-CdS.

All colloidal solutions were diluted with each solvent so as their absorbance at 396 nm to become 1.8 with a 10-mm cell before the stationary illumination experiments. For the experiments under deoxygenation, the colloidal solutions in a square quartz cell were deoxygenated by bubbling nitrogen gas through them for 15 min and sealed.

2.4. Stationary illumination experiments

The stationary illumination experiments were usually carried out as follows. 3 ml of the colloidal solution was transferred into a square quartz cell (path length: 10 mm) with glass stopper using a volumetric pipet. The colloidal solutions in the cell were illuminated with 396 nm monochromatic light for 4 h while stirring with magnetic stirrer. During that, the illumination was interrupted and their absorption spectra were measured every 30 min. The change in absorption spectra of the colloidal solutions under the stationary illumination was monitored, and the decrease in absorbance at 396 nm was taken as the measure for photo-dissolution of the CdS particles and the increases at 396 and 600 nm photo-aggregation (The increase in absorbance at 600 nm, where no absorption of CdS particles exists, is attributable to the scattering of the light due to aggregation of the particles).

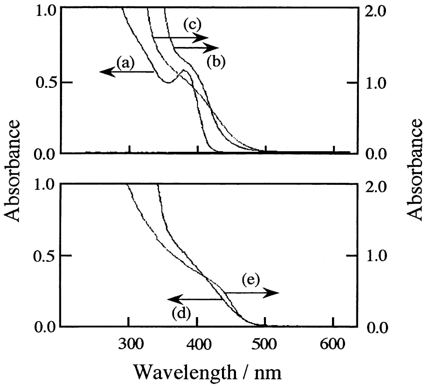

Fig. 1. Absorption spectra of capped and non-capped CdS colloidal solutions. (a) TG-CdS in DMSO; (b) MPT-CdS in DMF; (c) MBI-CdS in DMF; (d) MA-CdS in water, and (e) HMP-CdS in water.

3. Results and discussion

3.1. The sizes of the capped CdS particles

The absorption spectra of capped CdS particles in water and organic solvents used in the present study are shown in Fig. 1. On the basis of the relationship [24] between sizes of CdS particles and the longer wavelength edge of their absorption spectra, CdS core sizes of the capped CdS particles are estimated to be ca. 25, 30, and 35–40 Å for TG-CdS, MPT-CdS, and both MBI-CdS and MA-CdS from the spectra, respectively. The particle size of HMP-CdS is estimated similarly as 35–40 Å.

3.2. Stabilitiy of the capped CdS particles in water under the stationary illumination

First, the stability of HMP-CdS (ordinary non-capped CdS) in water under the stationary illumination was investigated for various conditions to compare with that of capped CdS particles under the same experimental conditions. The results are shown in Fig. 2. In this figure, the absorbances normalized to those measured before illumination at each wavelength are plotted as a function of illumination time for aqueous HMP-CdS colloidal solutions with and without 2 mM methyviorogen (MV^{2+}) together with deoxygenated one without MV^{2+}. One of the monitoring wavelength 396 nm is same as that of illuminating light which enables to monitor the photo-aggregation and the photo-dissolution of the particles because the CdS particles have absorption band in this wavelength region. Another monitoring wavelength 600 nm also enables to monitor photo-aggregation of CdS particles because the influence of light scattering due to aggregation and turbidity of the particles on their normalized absorbances appears sensitively in this wavelength region where transparent colloidal solutions containing small CdS particles have no absorption band.

As seen from the figure, the normalized absorbance at 396 nm for the solution containing dissolved oxygen decreases linearly with increasing illumination time and becomes about 90% of that before illumination at the illumination time of 4 h. On the other hand, the absorbance for the deoxygenated solution does not change even after illumination of 4 h. This observation means that oxygen is essential for photo-dissolution of CdS particles as shown by the following reaction mechanism reported already [9,10].

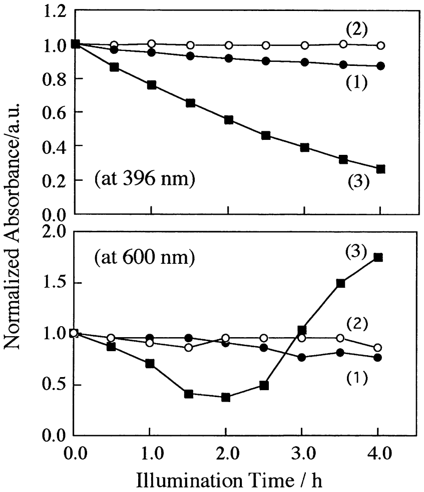

Fig. 2. Relationships between the normalized absorbances and illumination times for HMP-CdS in water under various conditions. (1) non-treated (●); (2) deoxygenated (○), and (3) with 2 mM methylviologen (MV^{2+}) (■). Each absorbance is normalized to that measured before the illumination.

$$CdS + h\nu \rightarrow CdS(e^- + h^+) \tag{1}$$

$$e^- + O_2 \rightarrow O_2^- \tag{2}$$

$$h^+ + CdS \rightarrow Cd^{2+}S^- \tag{3}$$

$$Cd^{2+}S^- + O_2^- + O_2 \rightarrow Cd^{2+} + SO_4^{2-} \tag{4}$$

As a whole,

$$CdS + 2O_2 \rightarrow Cd^{2+} + SO_4^{2-} \tag{5}$$

Therefore, it is considered that in the absence of oxygen, Eq. (2) in the mechanism is inhibited and simultaneously the efficiency of the recombination between photo-generated electrons and holes (Eq. (1)) is enhanced. Consequently the photo-dissolution reaction of CdS particles is inhibited in the deoxygenated solution. On the other hand, in the presence of MV^{2+}, the photo-dissolution of CdS particles was significantly accelerated owing to both the increase of the holes escaped from the recombination with electrons and the mediator action of MV^{2+} for electron transfer to oxygen. It is known that MV^{2+} acts as both electron scavenger and mediator for the electron transfer to oxygen for the photo-generated electrons on the surface of the particles.

The relative absorbance of HMP-CdS containing 2 mM MV^{2+} at 600 nm decreases with increasing illumination time

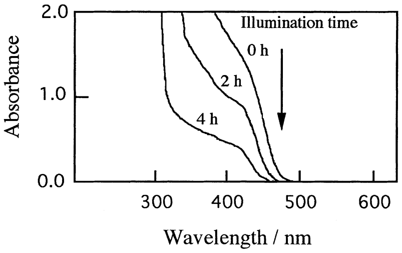

Fig. 3. Absorption spectra of HMP-CdS in water containing 2 mM MV^{2+} at various illumination times.

until 2 h and then increases steeply (notice that the change in the normalized absorbance at 600 nm by illumination is considerably larger than that at 396 nm though the absorbance observed at 600 nm is actually extremely small). The decrease in the absorbance at the early illumination time may be attributable to the dissolution of large-size CdS particles which are slightly contained in an aqueous HMP-CdS colloidal solution. However, it hardly seems that the steep increase at the latter stage of the illumination time results from the light scattering by the aggregation of the particles because the colloidal solution is apparently transparent. This observation may be explicable as follows. At the early illumination time when oxygen exists sufficiently in the colloidal solution, the dissolution of the particles proceeds to some extent because MV^{2+} acts as mediator for the electron transfer to oxygen via its radical (MV^{+}). On the other hand, at the latter stage of the illumination time, the amount of oxygen in the colloidal solution decreases by progress of the dissolution reaction, and the steep increase of relative absorbance is observed because of the accumulation of MV^{+} radical with a relatively large extinction coefficient at the absorption maximum near 600 nm.

For the HMP-CdS colloidal solution containing MV^{2+}, the blue shift of absorption spectra was observed together with the decrease of absorption intensity by the illumination because band gap energy of the particles increase owing to the decrease of the particle sizes. Their absorption spectra at various illumination time are shown in Fig. 3.

Next, the stabilities of capped CdS particles (TG-CdS, MA-CdS) in water under the stationary illumination were investigated as mentioned above. For both TG-CdS and MA-CdS particles in water, the absorbances normalized by the method described above are plotted as a function of illumination time in Fig. 4. The result for HMP-CdS already shown in Fig. 2 is also plotted in the figure for comparison. As can be seen from the figure, the normalized absorbances at both 396 and 600 nm for both TG-CdS and MA-CdS increase almost linearly with increasing illumination time in contrast to the case of HMP-CdS. The result seems that the oxidative elimination of capping agents from the particles takes place by the stationary illumination and consequently the particles aggregate to make the colloidal solutions turbid with increasing illumination time. In addition, yellow precipitate (presumably CdS) is observed at the bottom of the cell beyond 4 h illumination. The photo-aggregation of the capped CdS may be caused by that the capping agents bonded to the surface of the particles are oxidized by the photo-generated holes and detached from CdS core to make particles coagulate or grow the size. Further discussion will be given in the next section together with that for the capped CdS particles in organic solvents.

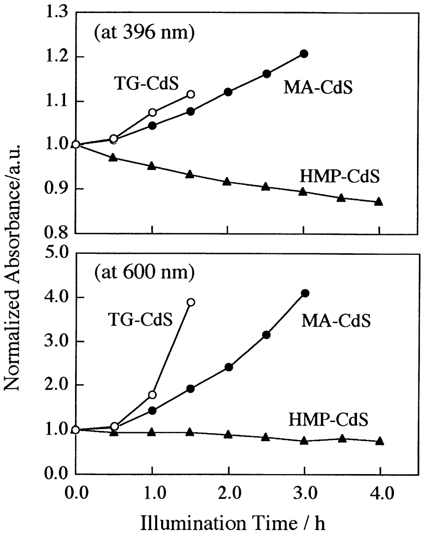

Fig. 4. Relationships between the normalized absorbances and illumination times for capped and non-capped CdS particles in water. Each absorbance is normalized to that measured before the illumination.

3.3. *Stabilitty of the capped CdS particles in organic solvents under the stationary illumination*

The stability of capped CdS particles (TG-CdS, MPT-CdS, MBI-CdS) in organic solvents under the stationary illumination was also investigated under the illumination conditions similar to the case in water. For TG-CdS in DMSO, MPT-CdS in DMF, and MBI-CdS in DMF, the absorbances at 396 and 600 nm, normalized to those measured before illumination at each wavelength, are plotted as a function of illumination time in Fig. 5. In contrast to both TG-CdS and MA-CdS in water for which the photo-aggregation was observed, stationary illumination of TG-CdS and MBI-CdS in organic solvents caused the photo-dissolution. Namely, decrease of absorbance at 396 nm was observed, as the case of HMP-CdS in water. As the capped CdS particles were illuminated in both solvents under the identical illumination conditions, the initial quantities of electrons and holes photo-produced may be same in both solvents. Therefore, if the hole trapping ability of each capping agents does not change from water to organic solvent, the identical phenomenon (either photo-dissolution or photo-aggregation) should be observed in both solvents. However, different phenomena were observed by the stationary illumination of TG-CdS under same conditions.

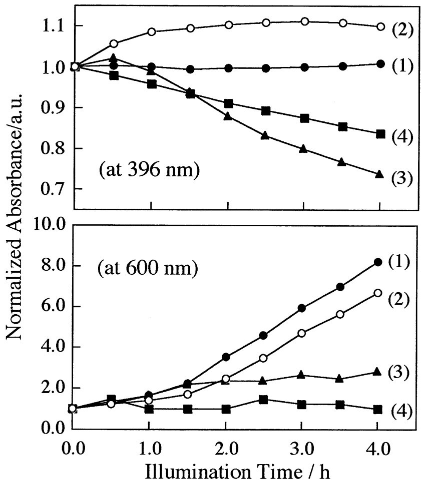

Fig. 5. Relationships between the normalized absorbances and illumination times for capped CdS in organic solvents; (1) MPT-CdS in DMF (●); (2) MPT-CdS in DMF without O_2 (○); (3) MBI-CdS in DMF (▲), and (4) TG-CdS in DMSO (■). Each absorbance is normalized to that measured before the illumination.

If there is the decay process for photo-generated electrons that does not exist in organic solvents but does in water, these results are explicable. In such a case the number of holes which escaped from the recombination with electrons increases in water compared with that in organic solvents. Consequently, the percentage of capping agents which are oxidized by holes on the surface of capped CdS particles increases and then the photo-aggregation is observed in water. In such a decay process for photo-generated electrons, one is apt to consider the direct reduction of water (or proton) by photo-generated electrons since the level of conduction band of CdS is more negative than reduction potential of water (or proton). However, it is known [9] that the electrochemical reduction of dissolved oxygen (Eq. (2)) takes place preferably to reduction of water (or proton), and moreover, reduction of water (or proton) by photo-generated electrons hardly occurs even in the absence of dissolved oxygen because of the fast recombination with holes. Therefore, the reaction with water (or proton) may be ruled out from the decay process of photo-generated electrons which exists only in water. However, we have no alternative idea for the decay process which works only in water . Accordingly, it may be difficult to ascribe the difference in the behavior of TG-CdS particles in both solvents under the illumination to the decay process of photo-generated electrons that does not occur in organic solvents but occurs only in water Eq. (5)

Alternatively, this difference depending on solvent may be attributed to the difference in the oxidative elimination process of capping agents in both solvents as being explained below. When organic compounds were oxidized electrochemically in water, the stepwise oxidation proceeds usually accompanying the stepwise proton elimination as Eq. (6). However, this stepwise oxidation becomes difficult in certain aprotic organic solvents which have weak affinity for proton [25].

$$\mathrm{RH_2} \xrightarrow{-e^-} (\mathrm{RH_2})^+ \rightarrow \mathrm{H^+} + ({}^\bullet\mathrm{RH}) \xrightarrow{-e^-} ({}^\bullet\mathrm{RH})^+ + \mathrm{H^+} \rightarrow 2\mathrm{H^+} + \mathrm{R} \qquad (6)$$

Taking into account the molecular structure of capping agents (TG and MA) used in the present study, it is expected that the stepwise proton elimination from the capping agents oxidized by photo-generated holes occurs in water as Eq. (6). Therefore, the oxidative elimination of capping agents from the surface of the capped CdS particles may be accelerated and consequently photo-aggregation proceeds in water by the stationary illumination. On the other hand, in aprotic organic solvents such as DMSO and DMF, photo-generated holes may be used mainly for dissolution reaction (Eq. (3)) of CdS core rather than for oxidation of capping agents on the surface because such stepwise proton elimination from the oxidized capping agents does not occur. This may be the reason for the fact that photo-dissolution was observed predominantly rather than photo-aggregation by the stationary illumination of TG-CdS in DMSO.

Furthermore, it is known that Cd^{2+} can be stabilized in aprotic organic solvents such as DMSO and DMF. Tsubomura et al. [26] reported that when the photocurrent of a crystalline CdS electrode was measured in various non-aqueous solvents, decomposition of CdS was observed in all solvents together with an anodic current under the sufficiently positive electrode potential and moreover in some solvents such as alcohols, DMF, and DMSO, an anodic current flows at potentials more negative than that in water with higher dielectric constant. They explained these results based on the donicity (donor number, DN) of the solvents proposed by Guttman rather than the dielectric constant of the solvents, that is, the higher donor number (the stronger electron-donating ability) of solvents, the stronger the solvation for ions such as Cd^{2+} becomes. Taking their discussion into account, the reason why the photo-dissolution of CdS core of the capped CdS particles is observed in DMSO (DN = 28 [27]) and DMF (DN = 27 [27]) on contrary to the case in water (DN = 18 [27]) may be ascribed to their higher donor numbers.

On the other hand, if most holes are trapped by capping agents, the photo-dissolution of the particles may be suppressed because Eq. (3) in the reaction mechanism is inhibited. However, the photo-dissolution of the capped CdS particles has been observed in organic solvents as seen from Fig. 5. This suggests that hole trapping by capping agents on the surface of the capped CdS particles is insufficient and holes which participate in the dissolution process of the particles remain to some extent on the surface of the particles in organic solvents. This also implies that the hole trapping ability of the capping agents depends on the solvent as indicated by the fact that proton elimination from the oxidized capping agents occurs in water but not in organic solvents.

In the case of MPT-CdS in DMF under the stationary illumination, although the change of absorbance at 396 nm is not observed, the photo-aggregation seems to occur because the increase in absorbance at 600 nm and turbidity of the solution are recognized. And further the absorbance at 396 nm for the solution without dissolved oxygen increases by the illumination. Therefore, it seems that the photo-aggregation and the photo-dissolution of the particles occur simultaneously by illumination of the solution containing dissolved oxygen. That is the reason why the absorbance change at 396 nm is not observed for MPT-CdS in DMF by the illumination. The difference in the behavior for the illumination between MBT-CdS and both TG-CdS and MBI-CdS may be attributable partly to the fact that the stability of MPT-CdS colloidal solution in the dark is poor compared to other colloidal solutions.

3.4. The influences of dissolved oxygen and electron and hole scavengers on the stability of the capped CdS particles under the stationary illumination

The stability of the capped CdS particles under the stationary illumination was also investigated in the presence of electron and hole scavengers. Iodide and cadmium ions were used as hole and electron scavengers, respectively. Their effects appeared pronouncedly for the stability of both TG-CdS and MBI-CdS in organic solvents though their effects were not clear in water because the photo-aggregation of the capped CdS particles occurred rapidly even in the absence of them. These effects in organic solvents can be interpreted on the basis of the reaction mechanism (Eqs. (1)–(4)) for the photo-dissolution of CdS particles in the presence of dissolved oxygen.

The relationships between absorbances at 396 nm and illumination times for TG-CdS and MBI-CdS in organic solvents are shown together with those for the colloidal solutions without dissolved oxygen in Fig. 6. In the case of the absence of both electron and hole scavengers, although the decrease in the absorbance due to the photo-dissolution was observed for both TG-CdS and MBI-CdS, but not for the deoxygenated solutions as described in the preceding section. This suggests that the dissolved oxygen is necessary for the photo-dissolution of the capped CdS particles despite of kinds of solvents and capping agents used, as can be expected from Eq. (2). Cd^{2+} ion which acts as an electron scavenger suppresses somewhat the photo-dissolution of CdS core of TG-CdS (capped CdS particles) by competing with oxygen for the transfer of photo-generated electrons. However, the extent of the suppression is smaller than that for HMP-CdS (non-capped CdS particles) in Fig. 7, for which access of Cd^{2+} ions seems to be easy because the surface of the particles is covered with HMP having negative charges. On the other hand, addition of iodide ion known as a hole scavenger enhanced the photo-dissolution of the particles as shown in Fig. 6(a) contrary to our expectation that iodide ions react with photo-generated holes and consequently Eq. (3) in the photo-dissolution mechanism is inhibited. And further, its effect becomes larger with increasing the concentration (Fig. 6b). The similar effect of iodide was also observed in an aqueous HMP-CdS colloidal solution (Fig. 7). Furthermore, analogous results were already observed for usual CdS powders and CdS electrodes by Matsumura et al. [28]. As one of the reason why iodide ions enhance the photo-dissolution of the CdS particles, it may be considered that iodide ions stabilize the dissolved cadmium ions by the formation of complex ions (for example, CdI_4^{2-}) though its identification has not been carried out in the present study.

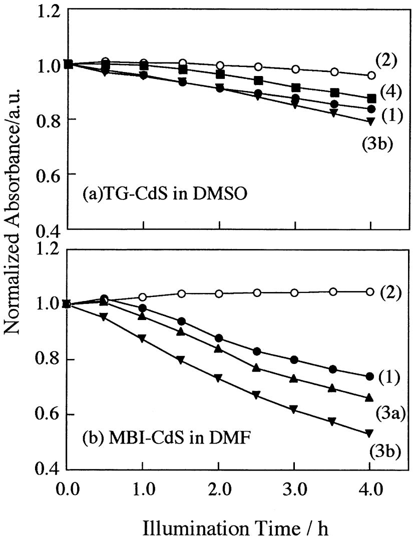

Fig. 6. Relationships between the normalized absorbances at 396 nm and illumination times for TG-CdS in DMSO (a) and MBI-CdS in DMF; (b) under various conditions: (1) non-treated (●); (2) deoxygenated (○); (3a) with 1 mM I^- (▲); (3b) with 10 mM I^- (▼) , and (4) 2.5 mM Cd^{2+} (■). Each absorbance is normalized to that measured before the illumination.

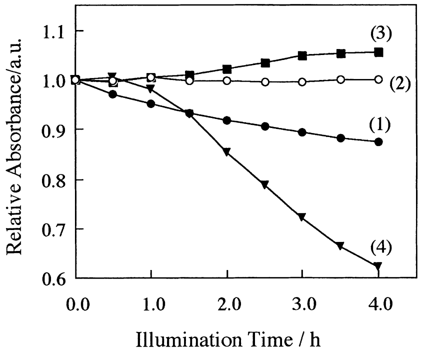

Fig. 7. Relationships between the normalized absorbances at 396 nm and illumination times for HMP-CdS in water under various conditions; (1) non-treated (●); (2) deoxygenated (○); (3) 2.5 mM Cd^{2+} (■), and (4) with 10 mM I^- (▼). Each absorbance is normalized to that measured before the illumination.

4. Conclusion

The capped CdS particles aggregate in water by the stationary illumination, contrary to the non-capped HMP-CdS particles for which the photo-dissolution is observed. The photo-aggregation may be caused by the oxidative elimination of capping agents which are bonded directly to the surface of the particles. The elimination of capping agents is, in turn, supposed to be assisted by the proton elimination from the oxidized capping agents. On the other hand, the capped CdS particles undergo the photo-dissolution in organic solvents such as DMSO and DMF. In these solvents, the photo-dissolution rather takes place by the assistance of strong electron donating ability of the solvents than the photo-aggregation which seems to be difficult to occur because the proton elimination from the oxidized capping agents becomes hard due to aprotic nature of the solvents. The effects of Cd^{2+} ion and deoxygenation of the colloidal solutions on the stability of the capped CdS particles are consistent with the photo-dissolution mechanism already proposed for usual CdS particles. Addition of iodide ion, which is known as a hole scavenger, enhanced the photo-dissolution of the capped and non-capped CdS particles contrary to the expected photo-aggregation.

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