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Photoreduction of silver ions in a colloidal titanium dioxide suspension

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Abstract

The photoreduction of Ag^+ ions at the surface of colloidal TiO_2 nanoparticles has been investigated. Irradiation of an aqueous solution containing TiO_2 and Ag^+ ions with near-UV light brings about the growth of a sharp absorption band of colloidal silver in absorption spectrum. The photoreduction of Ag^+ ions by TiO_2 is optically sensitized by a simple cyanine dye, 3,3′-disulfopropyl-5,5′-dichloro-thiacyanine sodium salt (TC). TC molecules are adsorbed at the surface of TiO_2 nanoparticles in the form of the J-aggregate (JA). Visible-light irradiation of the solution containing TiO_2, Ag^+ ions, and TC causes the growth of a broad absorption band of the colloidal silver and the decrease of whole absorption bands of TC. Experimental results have been interpreted in terms of electronic energy levels of the colloidal silver and the TC aggregate, as well as energy bands of TiO_2. In the sensitized photoreduction, TiO_2 could play the role of a medium to facilitate efficient electron transfer from the excited TC aggregate to Ag^+ ions adsorbed at the surface.

Keywords: Titanium dioxide; Nanoparticle; Photocatalysis; J-aggregate; Colloidal silver

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1. Introduction

The discovery that O_2 is produced when a titanium dioxide (TiO_2) single crystal electrode is illuminated with near-UV light by Fujishima and Honda in 1972 triggered a lot of activities to find photoelectrochemical systems capable of splitting water into H_2 and O_2 [1]. An important aspect of the TiO_2 electrode superior to other semiconductor electrodes is its tolerance to corrosion under irradiation of light. In 1991, O'Regan and Grätzel proposed a low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO_2 films [2]. This cell consisted of a 10 μm thick, optically transparent film of TiO_2 nanoparticles coated with sensitizing dye layers. Since then, dye sensitization of TiO_2 particulate electrodes has attracted much attention. Another important application of TiO_2 to environmental cleaning technology [3]; purification of air and water deodorizing, treatment of waste fluids, relies on generation of oxidizing species such as positive holes, OH radicals, O_2 by light. Photocatalytic actions of TiO_2 have been extensively studied [4]. An exploration of novel imaging materials [5], recovery of precious metals, as well as removal of harmful metals from waste water [6,7] are based on reduction of metal ions by photoelectrons at the TiO_2 surface.

In 1980s, one of the authors studied the photoreduction of Ag^+ ions in the TiO_2 suspension whose particle size was about 0.5 μm [8]. With the help of a comparative photoelectrochemical study on the TiO_2 single crystal electrode [9], we proposed a reaction scheme that some conduction-band electrons in the TiO_2 produced by near-UV light transfer to Ag^+ ions, while positive holes in the valence band react with water molecules. Moser and Grätzel [10] and Henglein [11]

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group reported early experimental works with colloidal solutions of TiO_2 nanoparticles in 1980s. A great advantage of using colloidal TiO_2 nanoparticles in place of the TiO_2 powder would lie in the possibility of a number of spectroscopic measurements for the study of interfacial reactions. Recently, aiming at the exploration of nanometer-sized optics and optoelectronics devices, metal and semiconductor nanoparticles have been extensively studied [12–14]. On the other hand, the investigations of composite nanoparticles which are formed by coating the surface of metal or semiconductor nanoparticles with e.g., organic dye layers, have not advanced so much. We have attempted to fabricate dye-coated Ag and Au nanoparticles by adsorbing dye molecules from an aqueous solution [15]. When anionic dye, 3,3′-disulfopropyl-5,5′-dichloro-thiacyanine sodium salt (TC), is used, Ag and Au nanoparticles covered with the J-aggregate (JA) of TC; Ag/TC, Au/TC, are formed [16]. It appeared that absorption spectrum of the composite nanoparticle, Au/TC, is not a simple sum of the colloidal absorption band of Au nanoparticles and the J-band of the TC aggregate. The absorption spectrum is characterized by a spectral dip at the wavelength near the J-band. These spectroscopic properties have been interpreted in the context of electromagnetic coupling of the surface plasmon band of metal nanoparticles and the exciton band of the J-aggregate (JA).

Synthesis, excitation dynamics, photochemistry and photoelectrochemistry of semiconductor/dye composite nanoparticles have been studied by a number of groups [17]. However, there have been a few reports on the TiO_2/JA composite nanoparticles. Arakawa and coworkers have examined photoelectrochemical properties of the JA of a series of benzothiazole merocyanine dyes on a nanoporous TiO_2 electrode [18]. It has been reported that the J-aggregation could improve the performance of solar cells having a TiO_2 photoelectrode due to densely packed dye molecules: extension of the sensitivity towards the longer wavelength, broadening of the absorption band. Xiang et al. reported photoinduced electron transfer from the excited JA of 3,3′-disulfopropyl-4,5,4′,5′-dibenzo-9-phenyl-thiacarbocyanine triethylammonium salt (NC) to colloidal TiO_2 nanoparticles [19]. We have observed that TC molecules are adsorbed as the JA at the TiO_2 surface. In this article, we have examined photocatalytic actions of TiO_2/TC nanoparticles under irradiation with near-UV light absorbed by TiO_2 and also with visible light absorbed by the TC aggregate. The photoreduction of Ag^+ ions at the TiO_2 surface has been taken up as a typical photocatalytic reaction.

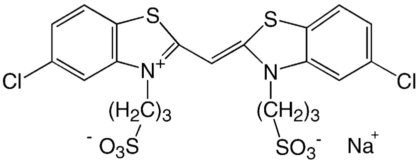
2. Experimental

2.1. Colloidal synthesis and characterization

Colloidal TiO_2 was synthesized by hydrolysis of Ti(IV) tetraisopropoxide ($Ti(OCH(CH_3)_2)_4$, Ti(*i*-OPr)$_4$) according to Grätzel and coworkers [20] and Hoffmann and coworkers [21]. Ti(*i*-OPr)$_4$, 2-propanol and HNO_3 were purchased from Kishida Chemicals Co. Singly distilled water was used for preparation of aqueous solutions. 0.5 g of Ti(*i*-OPr)$_4$ was dissolved with 10 ml of 2-propanol. The solution was dropped under vigorous stirring at room temperature onto 100 ml of an aqueous HNO_3 solution whose pH was adjusted to 1.5. After completion of the addition of the Ti(*i*-OPr)$_4$ solution, the reaction vessel was closed and the reaction mixture was continuously stirred several days for aging at room temperature until the solution became almost transparent. According to transmission electron microscopy (TEM) observations using a Hitachi H-7000 electron microscope, the particle size of colloidal TiO_2 nanoparticles was 5–30 nm. X-ray diffraction analysis by means of RINT-2100 (Rigaku Denki Co.) showed that the TiO_2 particles are of anatase-type. Absorption spectra of the TiO_2 colloidal solution were recorded on a UV–vis spectrophotometer, V-560 (Nihon Bunko Co.).

2.2. Photochemical reactions

TC was obtained from Hayashibara Biochemical Laboratories Inc. The structure of TC is illustrated in Scheme 1. $AgNO_3$ and $AgClO_4$ were purchased from Wako Chemicals Co. Singly distilled water was used for preparation of all aqueous solutions. The reaction cell was a rectangular quartz vessel of 10 mm × 10 mm × 40 mm in size which was also used for spectroscopic measurements (lightpath-length 10 mm). A 3.0 ml aqueous solution was usually composed of a colloidal TiO_2 solution and $AgNO_3$ or $AgClO_4$, together with or without TC. A 500 W high-pressure mercury lamp, Type USH-500D, with a Type HB-501A power supply (Ushio Denki Co.), was used as the light source. Near-UV light ($\lambda = 300$–400 nm, TiO_2-light) was selected by the combination of a glass filter, UV-D35 (Toshiba Co.), and a $CuSO_4$ solution filter. Visible light ($\lambda = 460$ nm, dye-light) was selected with a glass filter, KL-46 (Toshiba Co.), and a water filter. The incident intensities of TiO_2-light and dye-light on the reaction vessel were monitored with the aid of a photometer, Type IL-600 (International Light Co.). In this work, the ratio of the photon numbers of TiO_2-light to dye-light was about 1.5. Irradiation of the solution was carried out at room temperature in air. The progress of photochemical reactions was monitored intermittently by recording the absorption spectra of the reaction mixture with a V-560 spectrophotometer.



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Scheme 1. Schematic structure of TC.

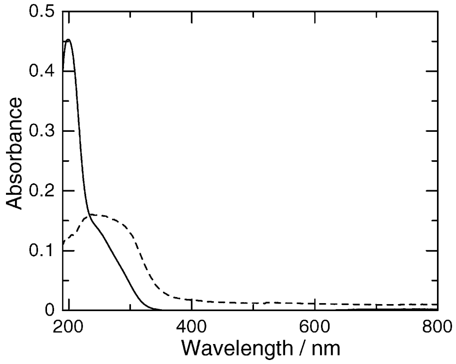

Fig. 1. Absorption spectra of the solution of colloidal TiO_2 nanoparticles obtained by hydrolysis of Ti(*i*-OPr)$_4$. Lightpath-length; 10 mm. (—) before dialysis, $[TiO_2] = 1.6 \times 10^{-5}$ M; (- - -) after dialysis, $[TiO_2] = 1.6 \times 10^{-4}$ M; $[TiO_2] = 1$ M corresponds to 80 g TiO_2/l.

3. Results

3.1. Photochemical reactions with TiO_2-light

Absorption spectrum of a colloidal TiO_2 solution is shown in Fig. 1. The absorption rose rapidly at the wavelength λ shorter than about 350 nm, which corresponds to the band gap energy of TiO_2. After purification of TiO_2 particles by dialysis with deionized water, the band edge of TiO_2 became more evident (Fig. 1). However, because colloidal TiO_2 nanoparticles tend to coagulate themselves after dialysis, we have employed for the study of photocatalytic reactions a colloidal TiO_2 solution without dialysis. The photoreduction of Ag^+ ions at the TiO_2 surface under irradiation with TiO_2-light has been examined. The change in the absorption spectra of a solution containing TiO_2 and $AgNO_3$ upon irradiation is shown in Fig. 2. A characteristic absorption band around λ = 400 nm, which is assigned to surface plasmon resonance of colloidal silver, developed with irradiation. Almost the same results were obtained when $AgClO_4$ was used in place of $AgNO_3$. However, irradiation of an aqueous $AgNO_3$ or $AgClO_4$ solution without TiO_2 had practically no effect. It is evident that Ag^+ ions are reduced by conduction-band electrons of TiO_2, giving rise to colloidal silver. The general tendency was the same when TiO_2 concentrations were varied for $[TiO_2] = 1.6 \times 10^{-5}$ to 1.6×10^{-4} M.

We have next examined the adsorption of TC molecules at the TiO_2 surface. Aqueous solutions of TC were prepared whose concentration $[TC] = 10^{-6}$ to 10^{-4} M was low enough to avoid J-aggregation in the bulk solution. The dye solution was mixed with the colloidal TiO_2 solution (8×10^{-5} M) at room temperature. Absorption spectra of dye solutions with and without TiO_2 are shown in Fig. 3. In the absence of TiO_2, a 10^{-6} M TC solution had a monomer absorption band (M-band) at λ = 428 nm and a shoulder of the dimer absorption band (D-band) around λ = 408 nm. An addition of TiO_2 nanoparticles brought about J-aggregation of TC as evidenced by the development of intense J-band at λ = 462 nm. A peak around λ = 428 nm is a remainder M-band. Peak positions of these bands are practically the same as those reported by our group [16,22]. Similar results were obtained in the 10^{-5} M TC solution. On the other hand, TiO_2 addition did not cause a serious spectral change in the 10^{-4} M TC solution because of high dye concentrations. We have found that the TiO_2/JA composite nanoparticles are easily formed by adsorbing TC molecules at the TiO_2 surface from the

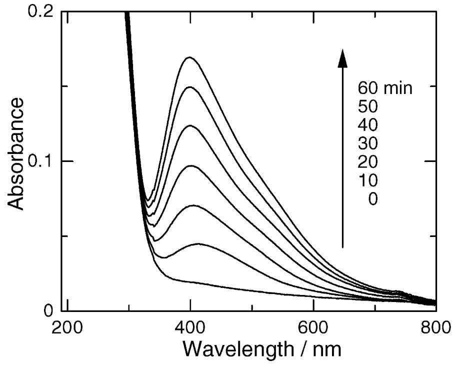

Fig. 2. Variation of absorption spectra of the solution containing TiO_2 and $AgNO_3$ with irradiation of TiO_2-light. $[TiO_2] = 8 \times 10^{-5}$ M, $[AgNO_3] = 10^{-3}$ M.

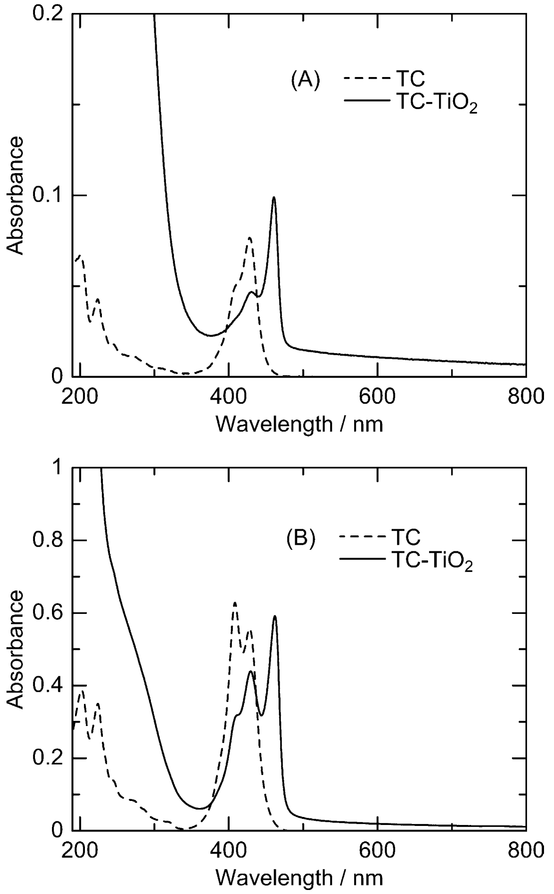

Fig. 3. Absorption spectra of the solution containing TiO_2 and TC. (A) $[TiO_2] = 8 \times 10^{-5}$ M, $[TC] = 10^{-6}$ M; (B) $[TiO_2] = 8 \times 10^{-5}$ M, $[TC] = 10^{-5}$ M.

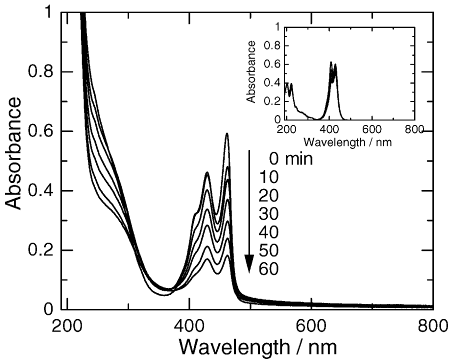

Fig. 4. Variation of absorption spectra of the solution containing TiO_2 and TC with irradiation of TiO_2-light. $[TiO_2] = 8 \times 10^{-5}$ M, $[TC] = 10^{-5}$ M. Insert: $[TC] = 10^{-5}$ M only; irradiation time: 0–60 min.

solution. The TC monomer and dimer are likely to exist in the bulk solution. About five-fold increase of the absorbance at the J-band on increasing TC concentrations from 10^{-6} to 10^{-5} M would imply multilayer adsorption of the TC aggregate. When TiO_2/TC composite nanoparticles are irradiated with TiO_2-light, photoholes could oxidize dye molecules at the TiO_2 surface. The change in the absorption spectrum of the solution containing TiO_2 and TC with irradiation is shown in Fig. 4. The progress of the photobleach of TC is demonstrated by the decrease of the absorption in the whole wavelength range. Irradiation of the TC solution without TiO_2 caused a certain decrease in the M- and D-bands; 1 h irradiation of the 10^{-5} M TC solution resulted in about 10% decrease of the absorbance at the M-band (insert of Fig. 4). On the other hand, the photobleach is more evident in the presence of TiO_2; 1 h irradiation brought about ca. 70% decrease of the absorbance at the J-band.

3.2. Photochemical reactions with dye-light

Photocatalytic reactions induced by visible light have attracted attention in relation to dye-sensitized solar cells. We have examined the photoreduction of Ag^+ ions in the presence of both TC and TiO_2. The change in the absorption spectrum of the solution containing TiO_2, $AgClO_4$ and TC upon irradiation with dye-light is shown in Fig. 5. The absorption of TC (J-band, M-band) was decreased with the irradiation time and almost disappeared after 1 h. At the same time, a broad absorption in the region λ = 350–650 nm with a maximum around 460 nm, which is assigned to colloidal silver, became evident. The shape of the colloidal absorption is different from the sharp absorption band in Fig. 2. We have tested the photobleach of TC by dye-light in the presence of TiO_2 nanoparticles. The change in the absorption spectrum of the solution containing TiO_2 and TC upon irradiation is given in Fig. 6. The insert shows the spectral change in the absence of TiO_2. After 1 h irradiation, J-band and M-band of TC almost disappeared in the presence of TiO_2. On the other hand, the absorbance change at the M-band was only about 20% in the absence of TiO_2. Although irradiation of the solution containing $AgClO_4$ and TC caused the photobleach of TC, the decrease of the M-band remained about 20% after 2 h irradiation. These observations clearly indicate catalytic actions of TiO_2 nanoparticles for the photobleach of TC. Spectral change did not occur when the solution containing 8×10^{-5} M TiO_2 and 10^{-3} M $AgClO_4$ was irradiated with dye-light for 1 h. It is obvious that the sensitized photoreduction of Ag^+ ions by TC aggregate proceeds via TiO_2 surface. The reduction of the concentration of TiO_2 or $AgClO_4$ by 1/10 did not affect the results.

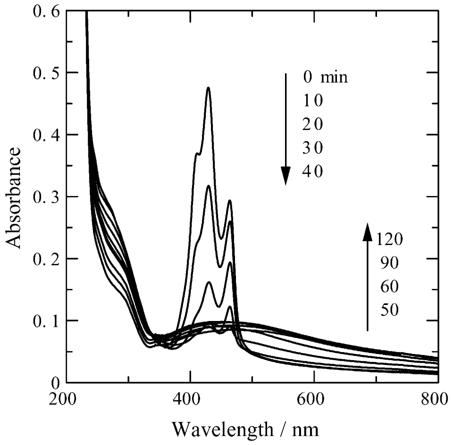

Fig. 5. Variation of absorption spectra of the solution containing TiO_2, $AgClO_4$ and TC with irradiation of dye-light. $[TiO_2] = 8 \times 10^{-5}$ M, $[AgClO_4] = 10^{-3}$ M, $[TC] = 10^{-5}$ M. Note that the intensity of incident dye-light is about 60% of that in Fig. 6.

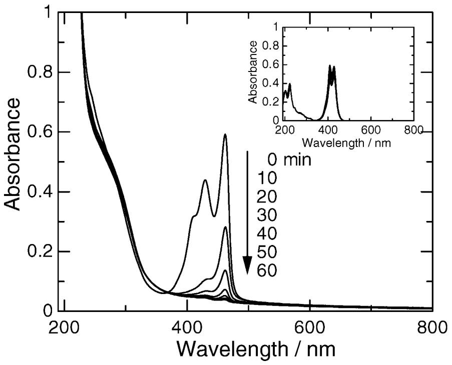

Fig. 6. Variation of absorption spectra of the solution containing TiO_2 and TC with irradiation of dye-light. $[TiO_2] = 8 \times 10^{-5}$ M, $[TC] = 10^{-5}$ M. Insert: $[TC] = 10^{-5}$ M only; irradiation time: 0–60 min.

4. Discussion

One of the authors has studied the photoreduction of Ag^+ ions in ZnO and TiO_2 suspensions [8,23]. The sensitized photoreduction of Ag^+ ions was explored by using xanthene dyes such as uranine and rhodamine B as the spectral sensitizer [24]. Irradiation of near-UV light (λ = 365 nm), which belongs to the fundamental absorption band of ZnO, on the aqueous solution containing ZnO powder and $AgClO_4$ produced deposited silver with a quantum yield of about 10^{-1}.

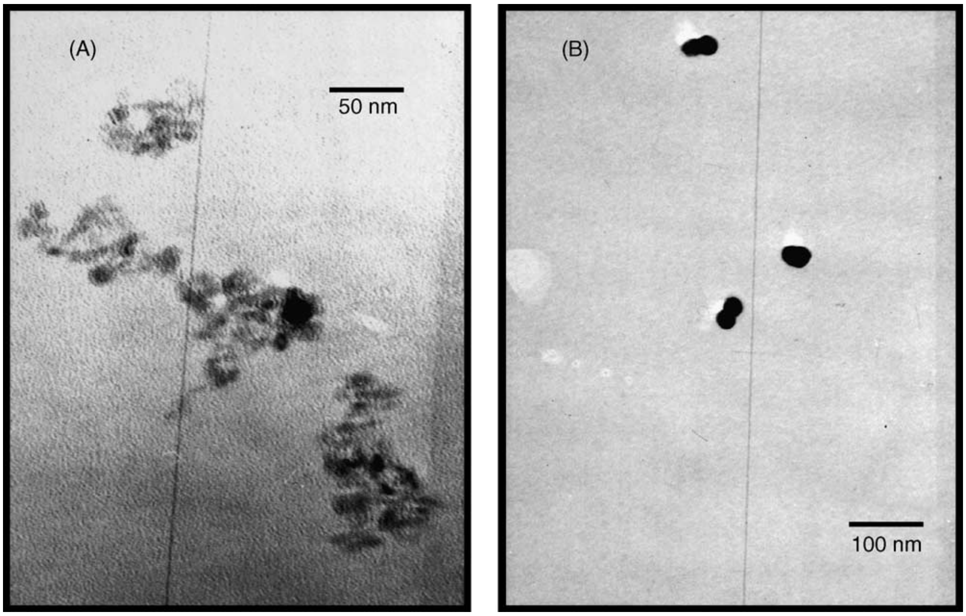

Fig. 7. Transmission electron micrographs of Ag particles formed by photoreduction. (A) Irradiation of the solution containing $[TiO_2] = 8 \times 10^{-5}$ M and $[AgClO_4] = 10^{-3}$ M with TiO_2-light for 1 h. (B) Irradiation of the solution containing $[TiO_2] = 8 \times 10^{-5}$ M, $[AgClO_4] = 10^{-3}$ M and $[TC] = 3 \times 10^{-5}$ M with dye-light for 4 h.

At the same time, positive holes generated in ZnO brought about the dissolution of ZnO into Zn^{2+} and O_2. In the case of the TiO_2 suspension containing $AgClO_4$, the photoreduction of Ag^+ ions (quantum yield 10^{-1}) was accompanied with the generation of O_2. In the present study, colloidal TiO_2 nanoparticles have been used in place of the TiO_2 powder. The molar ratio of Ag^+ ions to TiO_2, $[Ag^+]/[TiO_2] = 6$–60, is considerably larger than $[Ag^+]/[TiO_2] = 10^{-3}$ to 10^{-1} in the previous study [8]. We have assumed that almost the same reaction scheme is available to account for the photochemical reactions induced by TiO_2-light (photon energy $h\nu_{TiO_2}$).

$$\begin{aligned} TiO_2 &\rightarrow e^-(CB) + p^+(VB)(h\nu TiO_2), \\ Ag^+ + e^-(CB) &\rightarrow Ag^0, \\ 2H_2O + 4p^+(VB) &\rightarrow 4H^+ + O_2, \\ Ag^0 &\rightarrow Ag^C \end{aligned} \tag{1}$$

Conduction-band electrons generated in the TiO_2 ($e^-(CB)$) reduce adsorbed Ag^+ ions, giving rise to Ag atoms (Ag^0), which are finally changed into colloidal silver (Ag^C). In case of the colloidal TiO_2 nanoparticles, it has been proposed that positive holes not only oxidize water (reaction scheme) but also corrode TiO_2 itself [25]. To obtain the supporting evidence of the reaction scheme (1), a TEM characterization of the Ag particles was carried out by using a Hitachi H-7000 electron microscope operating at 100 kV. Samples for TEM observation were prepared by placing a small drop of the reaction mixture on a carbon-coated grid. The individual sample was then allowed to dry before it was placed in the specimen holder. A TEM image of Ag particles formed after 1 h irradiation of the solution containing TiO_2 and $AgClO_4$ with TiO_2-light is shown in Fig. 7(A). Ag particles are about 10 nm in size. As the particle size of TiO_2 nanoparticles does not change so much before and after photochemical reactions, the corrosion of TiO_2 nanoparticles is negligible in our study.

Irradiation of the aqueous suspensions containing ZnO, $AgClO_4$ and xanthene dyes with visible light promotes the photoreduction of Ag^+ ions, which is accompanied with the photobleach of dyes. We have examined the mechanism of the sensitized photoreduction in terms of electronic energy levels of ZnO, Ag^+/Ag and dye^+/dye^*. Here dye^+ and dye^* denote the oxidized form and the excited state of dyes, respectively. In the present study, the molar ratio $[dye]/[TiO_2]$ amounts to 10^{-2} to 1, which is much larger than $[dye]/[ZnO] = 10^{-4}$ in the previous work [24]. We have assumed that the same energetic considerations are applicable for the present colloidal TiO_2–Ag^+–TC aggregate system as well. The electronic

Table 1
Electronic energy levels for TiO_2, Ag^+ and TC

	E/V vs. NHE
TiO_2[a]	E_{CB}: −0.20 E_{VB}: +3.0
Ag^+[b]	$E(Ag^+/Ag^0)$: −1.8 $E(Ag^+/Ag^M)$: +0.799
TC[c]	$E(TC^+/TC)$: +1.64 $E(TC^+/TC^*)$: −1.06

[a] Bandgap energy of TiO_2; 3.2 eV [9,19,26].
[b] Sublimation energy of Ag; 2.6 eV [28].
[c] Transition energy of TC aggregate; 2.7 eV [27].

energy levels of TiO_2, Ag^+/Ag and TC^+/TC^* are summarized in Table 1. The conduction-band edge, E_{CB}, and the valence-band edge, E_{VB}, were estimated from the data of the TiO_2 single crystal electrode and the colloidal TiO_2 [9,19,26]. The electronic redox levels, $E(TC^+/TC)$, $E(TC^+/TC^*)$, of the TC aggregate were taken from Hranisavljevic et al. [27]. The electronic redox level $E(Ag^+/Ag^0)$ was taken from our former paper [28]. Relative positions of electronic energy levels in Table 1 are illustrated in Fig. 8. While E_{CB} of TiO_2 is more negative than the standard electrode potential of silver, $E(Ag^+/Ag^M)$, it is more positive than $E(TC^+/TC^*)$. Therefore, the sensitized photoreduction at the TiO_2 surface by dye-light (photon energy $h\nu_{dye}$) is initiated by electron transfer from the excited TC aggregate to TiO_2, which results in increase in the conduction-band electrons. Then, some of the conduction-band electrons transfer to the Ag^+ ions adsorbed on the surface. TiO_2 thus serves to accept electrons and share them to Ag^+ ions in such a manner that reverse electron transfer is prevented:

$$\mathrm{TC} \rightarrow \mathrm{TC}^*(h\nu_{\mathrm{dye}}),$$

$$\mathrm{TC}^* + \mathrm{TiO_2} \rightarrow \mathrm{TC}^+ + \mathrm{e}^-(\mathrm{CB}),$$

$$\mathrm{Ag}^+ + \mathrm{e}^-(\mathrm{CB}) \rightarrow \mathrm{Ag}^0, \qquad \mathrm{TC}^+ \rightarrow \text{decomposition} \qquad (2)$$

A TEM observation of the Ag particles formed by the sensitized photoreduction was carried out. A TEM image of Ag particles formed after 4 h irradiation of the solution containing TiO_2, $AgClO_4$ and TC with dye-light is shown in Fig. 7(B). The particle size is 20–30 nm. In this solution, considerable part of photolytic silver precipitated as a gray deposit. The existence of the gray precipitate and the broad colloidal absorption band (Fig. 5) would suggest a broad particle-size distribution of photolytic silver.

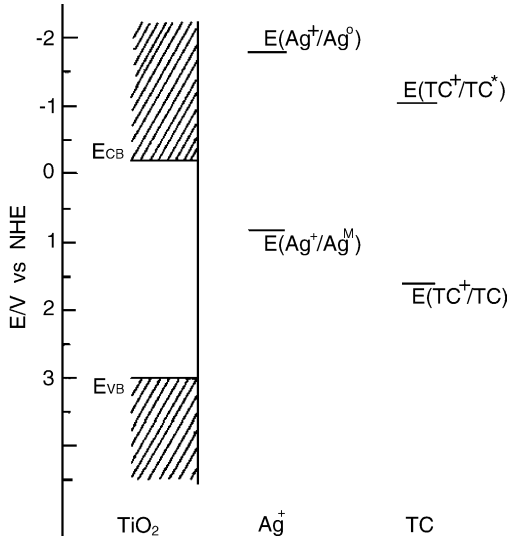

Fig. 8. Schematic energy-level diagram for TiO_2, Ag^+ and TC aggregate. E_{CB}, E_{VB}: conduction band and valence band of TiO_2, $E(Ag^+/Ag^0)$, $E(Ag^+/Ag^M)$; electronic redox levels of Ag atom and Ag metal, $E(TC^+/TC)$, $E(TC^+/TC^*)$; electronic redox levels of TC aggregate in the ground state and excited state, respectively. Electronic energy levels are given as volt vs. NHE.

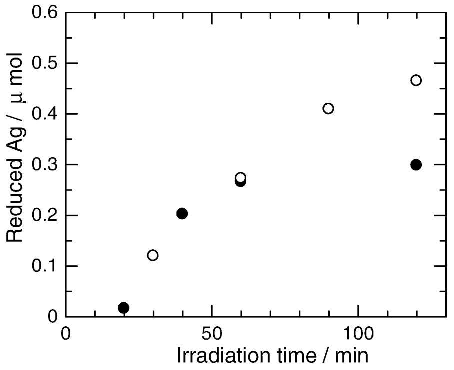

Fig. 9. Growth of the amount of reduced silver with irradiation time. (●) Irradiation of the solution containing $[TiO_2] = 8 \times 10^{-5}$ M and $[AgClO_4] = 10^{-3}$ M with TiO_2-light; (○) irradiation of the solution containing $[TiO_2] = 8 \times 10^{-5}$ M, $[AgClO_4] = 10^{-3}$ M and $[TC] = 2 \times 10^{-5}$ M with dye-light.

We have attempted to evaluate the amount of reduced silver by atomic absorption spectrometry. After irradiation of aqueous solutions containing TiO_2, $AgClO_4$, with or without TC, the reaction mixture was collected and transferred into a dialysis tubing (VISKASE Co.). After dialysis with deionized water for 24 h, the sample in the tubing was transferred to the vessel and deposited silver was dissolved in concentration HNO_3. The solution was then submitted to silver analysis by means of atomic absorption spectrometry with a HITACHI Z-6100 spectrophotometer. The dependence of the amount of reduced silver (ΔN_{Ag}) on the irradiation time is given in Fig. 9. ΔN_{Ag} of the solution containing TiO_2 and $AgClO_4$ amounted to about 0.3 μmol after 1 h irradiation of TiO_2-light and then attained to a saturation value. The conversion of Ag^+ ions, which existed at the beginning, was about 10%. On the other hand, ΔN_{Ag} of the solution containing TiO_2, $AgClO_4$ and TC continued increasing with irradiation of dye-light. After 2 h irradiation, the conversion of Ag^+ ions was ca. 15%. A slowdown of the growth of ΔN_{Ag} with the irradiation time of TiO_2-light would be caused by the electron–hole recombination, as well as a “filter effect” due to photolytic silver at the TiO_2 surface.

Irradiation of the solution containing TiO_2 and TC with either TiO_2-light or dye-light brought about the photobleach of TC molecules (Figs. 4 and 6). The progress of the photobleach is explained in the framework of Fig. 8. It has been known that conduction-band electrons are transferred to dissolved oxygen in solutions [29]. Photochemical reactions induced by TiO_2-light are summarized as

$$\mathrm{TiO_2} \rightarrow \mathrm{e}^-(\mathrm{CB}) + \mathrm{p}^+(\mathrm{VB})(h\nu_{\mathrm{TiO_2}}),$$

$$\mathrm{p}^+(\mathrm{VB}) + \mathrm{TC} \rightarrow \mathrm{TC}^+,$$

$$\mathrm{e}^-(\mathrm{CB}) + \mathrm{O_2} \rightarrow \mathrm{O_2}^-,$$

$$\mathrm{TC}^+ \rightarrow \text{decomposition} \qquad (3)$$

In the same manner, photochemical reactions caused by dye-light are described as

$$\mathrm{TC} \rightarrow \mathrm{TC}^*(h\nu_{\mathrm{dye}}),$$
$$\mathrm{TC}^* + \mathrm{TiO_2} \rightarrow \mathrm{TC}^+ + \mathrm{e}^-(\mathrm{CB}),$$
$$\mathrm{e}^-(\mathrm{CB}) + \mathrm{O_2} \rightarrow \mathrm{O_2}^-, \qquad \mathrm{TC}^+ \rightarrow \text{decomposition} \qquad (4)$$

It is remarkable that the progress of the photobleach by dye-light is more pronounced than by TiO_2-light. Actually, the absorption bands of TC almost disappeared after 1 h irradiation with dye-light (Fig. 6). However, they were still detectable after 1 h irradiation with TiO_2-light (Fig. 4). Considering the weaker incident intensity of dye-light than TiO_2-light, we infer that the higher absorption coefficient of the TC aggregate is responsible to the enhanced photobleach reaction. Such a property can also contribute to the prevalent photobleach in Fig. 5 than in Fig. 4. A similar consideration may be partly related with an observation in Fig. 9 that ΔN_{Ag} formed by dye-light is always equal to or larger than that by TiO_2-light.

It has often been stated that adsorbed Ag^+ ions at the TiO_2 surface can promote the photobleach of dyes due to the capture of conduction-band electrons, preventing back electron transfer to dye$^+$ [26]. However, comparing the results of Fig. 5 with Fig. 6, the photobleach is somewhat suppressed in the presence of Ag^+ ions. In this study, aside from the reduced light intensity by about 60% (Fig. 5), the suppression of the J-aggregation by adsorbed Ag^+ ions seems to be a reason for a little bit inferior reactivity in Fig. 5. It is noticed in Fig. 9 that ΔN_{Ag} after prolonged irradiation with dye-light is considerably larger than the amount of TC, which existed at the beginning. Similar observations have been reported for the ZnO–Ag^+–uranine system by us [24]. The detailed reactions of TC molecules following the sensitizing action seem to be rather complicated, indicating the necessity of further experimental studies for the full understanding of the reaction mechanism.

In recent years, electron injection and recombination dynamics of sensitizing dyes adsorbed at the surface of TiO_2 nanoparticles and thin films have been intensively studied in relation with novel dye-sensitized solar cells [30–33]. TiO_2/JA composite nanoparticles are interesting because most of dye molecules are organized into the J-aggregate. The hole delocalization in the JA may result in the slow charge recombination rate. High-yield of a long-lived charge separation state due to such slow charge recombination would be of relevance for the enhanced performance of dye-sensitized solar cells [34,35].

5. Conclusions

The photoreduction of Ag^+ ions in aqueous solutions containing TiO_2 and Ag^+ ions, together with sensitizing dye TC or not has been studied. Colloidal TiO_2 nanoparticles synthesized by hydrolysis of Ti(IV) tetraisopropoxide were of anatase-type with average diameter 5–30 nm. Irradiation of the solution containing TiO_2 and Ag^+ ions with TiO_2-light brought about the growth of a sharp colloidal absorption band of silver particles, which is formed by the photoreduction of Ag^+ ions at the surface of TiO_2 nanoparticles. It has been found that TC molecules are adsorbed at the TiO_2 surface in the form of the JA. Irradiation of the solution containing TiO_2 and TC with TiO_2-light caused the photobleach of TC. The photoreduction of Ag^+ ions is optically sensitized by the TC aggregate. Irradiation of the solution containing TiO_2, Ag^+ ions and TC with dye-light induced the growth of a broad colloidal absorption band of silver particles and the photobleach of TC. The photoreduction of Ag^+ ions at the TiO_2 surface has been interpreted in terms of electronic energy levels of TiO_2, Ag^+/Ag and TC^+/TC^*. TiO_2/JA composite nanoparticles have relevance to the development of dye-sensitized solar cells, artificial photosynthesis systems as well as novel imaging materials.

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