© 1982 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 55, 2010—2014 (1982) [Vol. 55, No. 7

Photoreduction of Silver Ion in a Titanium Dioxide Suspension

Hiroshi HADA,* Yoshiro YONEZAWA, and Masahiko SAIKAWA
Department of Industrial Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606

(Received September 19, 1981)

Quantum yields ranging from 0.084 to 0.191 were obtained for the reduction of Ag^+ by irradiation of light at 365 nm on a TiO_2 surface in aqueous solutions containing 1×10^{-4} to 1×10^{-2} mol dm^{-3} $AgClO_4$. Some features of the reduction were preliminarily examined with the aid of an electrochemical measurement of TiO_2 sinter. It is proposed that some conduction-band electrons, produced in the TiO_2 by irradiation, transfer to Ag^+ adsorbed on the TiO_2 surface and that positive holes react with water molecules. The photoreduction of Ag^+ is optically sensitized by addition of Uranine. The apparent quantum yield (the number of reacted ions/the number of photons incident to the suspension) of the dye-sensitized photoreduction of Ag^+ is 0.01.

Photodeposition of metals at semiconductor surface is interesting in that it is related to many applications including the solar energy conversion: the solid-state photogalvanic cell capable of storing light energy in the form of deposited metal and supplying electrical energy from it;[1)] semiconductor photocatalysis and anticorrosion of semiconductors;[2—6)] non-silver halide imaging materials of interesting use.[7,8)] However, only a few reports have dealt with the mechanism of the photodeposition.[9)] This may be first because even deposition of colloidal metal by either photolysis or radiolysis of aqueous solution of metal ions is rather a complex reaction as revealed by several investigators,[10,11)] and second because deposited metal may considerably change semiconductor surface in its physical and chemical properties. For these reasons, investigations on photodeposition of metals are limited to SnO_2–, ZnO–, and TiO_2–Ag^+ systems,[9,12,13)] TiO_2–Pd^{2+} system,[14)] TiO_2–Pd^{2+} and –$PtCl_6^{2-}$ systems,[15)] TiO_2– and WO_3–Cu^{2+} systems,[16)] and TiO_2–$PtCl_6^{2-}$, –$PdCl_4^{2-}$, –Ag^+, and –Cu^{2+} systems.[17)] As to dye-sensitized reduction of metal ions, only a few reports have been published which treat TiO_2–Ag^+–triphenylmethane dye[9)] and ZnO–Ag^+–xanthene dye systems,[13)] apart from a qualitative study for photographic application.[18)]

We have been interested in photochemical reactions of the ZnO–Ag^+ system and carried out photochemical and electrochemical studies on photoreduction of Ag^+ both in ZnO suspension and at ZnO sinter surface.[13)] We have found that the net photochemical reaction induced by irradiation of UV-light obeys the local-cell mechanism. In photochemical reactions at TiO_2 surface, positive holes produced by optical excitation of TiO_2 will not induce dissolution of the semiconductor itself, in contrast to the ZnO system, which suggests some different situation involved in this case. We thus investigated photoreduction of Ag^+ in a TiO_2 aqueous suspension by using 365 nm light, which is within the fundamental absorption band of TiO_2, and examined optical sensitization of this reaction by Uranine. Also, we carried out preliminary measurements of electrochemical properties of the TiO_2–aqueous solution interface. We have thus clarified several characteristics of the photoreduction of Ag^+ at TiO_2 surface.

Experimental

The experimental set-up and procedure were almost the same as those previously reported for the ZnO–Ag^+ aqueous suspension.[13)] The TiO_2 used was a highly purified powder offered from Teikoku Kakou Co., Okayama. This material had a surface area of 7.3 m^2/g-TiO_2, an average particle size of 0.5 μm, and low-level impurities of Nb, Al, and P (below 0.01%). In an 50 ml aqueous solution containing 1×10^{-4} to 1×10^{-2} M[†] $AgClO_4$ and 0.5 M KNO_3 was suspended 0.5 g TiO_2 powder. For the study of dye-sensitized reduction, Uranine was added to the aqueous suspension. Before the reaction, dissolved oxygen was purged by introduction of high-purity nitrogen gas.

The same combination of the light source, monochrometer, and glass filter as in our previous work[13)] was used to select either the 365 nm light (designated TiO_2-light) or 500 nm light (dye-light). The half-band width of the monochromator was about 20 nm. Irradiation was commenced after the adsorption equilibrium of Ag^+ at the TiO_2 surface had been established. After irradiation, the amount of photoreduced silver was determined by atomic absorption spectrometry with a Jarrel-Ash AA-780 spectrophotometer. The number of incident photons was 1.10×10^{15} cm^{-2} s^{-1} for TiO_2-light and 2.00×10^{15} cm^{-2} s^{-1} for dye-light.[19)] The transmittance and reflectance for suspensions were measured with Shimadzu spectrophotometers, MPS-5000 and QV-50 equipped with an integrating sphere, respectively. The quantum yield of photoreduction of Ag^+ for the unsensitized system and the apparent quantum yield for the dye-sensitized system were evaluated by use of the equation:

$$\Phi_{Ag} = \frac{1}{Q}\frac{d[Ag]}{dt}, \qquad (1)$$

where Φ_{Ag} is the quantum yield for the unsensitized system or the apparent quantum yield for the dye-sensitized system, d[Ag]/dt is the initial rate of formation of the reduced silver (atoms s^{-1}), and Q is either the number of the photons absorbed by the suspension (unsensitized system) or of those incident to the suspension (sensitized system) (photons s^{-1}). The amount of Ag^+ adsorbed at adsorption equilibrium was determined after TiO_2 powder had been immersed in a solution of 1×10^{-4} to 1×10^{-2} M $AgClO_4$ plus 0.5 M KNO_3 for 3 h under constant stirring.

Electrochemical measurements on a TiO_2 sinter electrode were carried out in the conventional manner.[20,21)] A pellet from TiO_2 powder was placed on a disk 12 mm in diameter and 0.5 mm thick and then sintered at 1300 °C for 2 h in air. After cooling to room temperature, the pellet was reduced at 600 °C in a hydrogen atmosphere for 2 h. Indium was evaporated onto one face of the sinter to provide an ohmic contact, and a copper wire was soldered on it. Then, all surfaces, except the other face of the sinter to be exposed to the electrolyte solution (*ca.* 0.64 cm^2), were cov-

---

[†] 1 M=1 mol dm^{-3}.

ered with epoxy resin. The electrode prepared in this manner was dipped into aq HNO_3 for 30 s and washed in water before use. The construction of the electrochemical cell and electrochemical measurements were carried out by employing the same procedures previously described.[13] The number of incident photons on the electrode (TiO_2-light) was $9.00\times10^{14}\ cm^{-2}\ s^{-1}$. The electrolyte solutions were composed of 0.5 M KNO_3 or a mixed solution of 0.5 M KNO_3 and 1×10^{-5} to 1×10^{-3} M $AgClO_4$. High purity nitrogen gas was bubbled through the solution in order to remove oxygen before the measurement.

Results

Photoreduction in the Unsensitized System. The dependence of the amount of reduced silver on the irradiation time of TiO_2-light for the TiO_2–Ag^+ aqueous suspension is given in Fig. 1. The reduced silver resulting from thermal reduction in the dark was about 0.15 μmol irrespective of either irradiation time or $AgClO_4$ concentration. This value was previously subtracted before constructing this figure. Quantum yields of the photoreduction of Ag^+ are 0.191 ± 0.014 ($AgClO_4$; 1×10^{-2} M), 0.159 ± 0.005 (2×10^{-3} M), 0.090 ± 0.003 (1×10^{-3} M), 0.090 ± 0.003 (5×10^{-4} M), and 0.084 ± 0.0 (1×10^{-4} M). The pH of the suspension was about 4.5. The quantum yields obtained here are in the same magnitude as those reported for TiO_2 thin film–Ag^+ system.[9] However, the dependence of Φ_{Ag} on the initial Ag^+ concentration, C_{Ag^+}, significantly deviates from the Stern-Volmer relation proposed by Fleischauer *et al.* (Fig. 2).

The adsorption of Ag^+ on the TiO_2 surface was measured at 20 °C, the adsorption isotherm being given in Fig. 3. The equilibrium concentration of Ag^+ in the aqueous phase, $C^{eq}_{Ag^+}$, and the equilibrium amount of Ag^+ adsorbed on the surface of 1.0 g TiO_2, N_{Ag^+}, satisfy Freundlich's adsorption formula at $AgClO_4$ concentrations less than 5×10^{-3} M:

$$N_{Ag^+} = A(C^{eq}_{Ag^+})^{1/n}, \tag{2a}$$

$$\log N_{Ag^+} = \log A + \frac{1}{n}\log C^{eq}_{Ag^+}, \tag{2b}$$

where A and n are constants. The adsorption index $1/n$ is 0.78. However, at higher concentrations, N_{Ag^+} began to increase more steeply than expected from Eq. 2. Substitution of N_{Ag^+} for C_{Ag^+} in Fig. 2 could scarcely improve the linear relation of Stern-Volmer plot (Fig. 2).

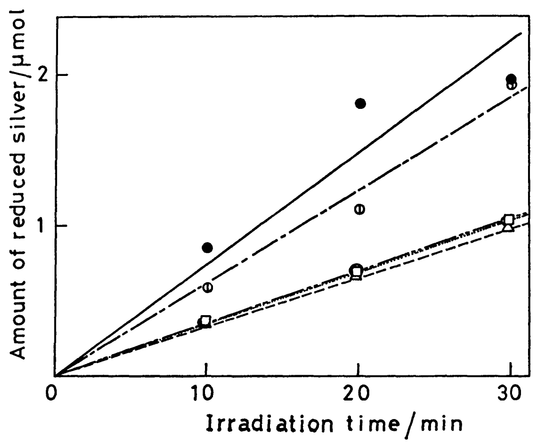

Fig. 1. Growth of the amount of reduced silver in TiO_2 suspension containing $AgClO_4$ and 0.5 M KNO_3 with irradiation time.
●: $[AgClO_4]=1\times10^{-2}$ M, ◐: 2×10^{-3} M, ○: 1×10^{-3} M, □: 5×10^{-4} M, and △: 1×10^{-4} M.

We tried to clarify the behavior of positive holes through detection of increase in the dissolved oxygen in the aqueous phase during the photoreaction. A 200 ml aqueous suspension composed of 2.0 g of TiO_2, 0.5 M KNO_3, and 1×10^{-3} M $AgClO_4$ was prepared.

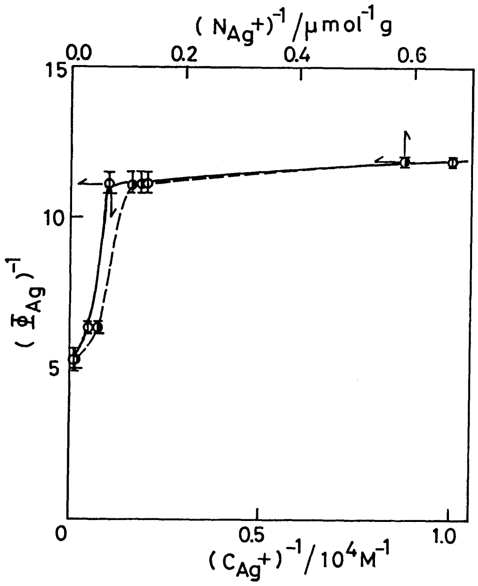

Fig. 2. Stern-Volmer plots for the reduction of Ag^+ on TiO_2.
◐: Reciprocal plot between the quantum yield Φ_{Ag} and C_{Ag^+}, ◑: reciprocal plot between Φ_{Ag} and N_{Ag^+}. C_{Ag^+} and N_{Ag^+} denote the initial concentration of $AgClO_4$ and the amount of adsorbed Ag^+ on TiO_2 surface.

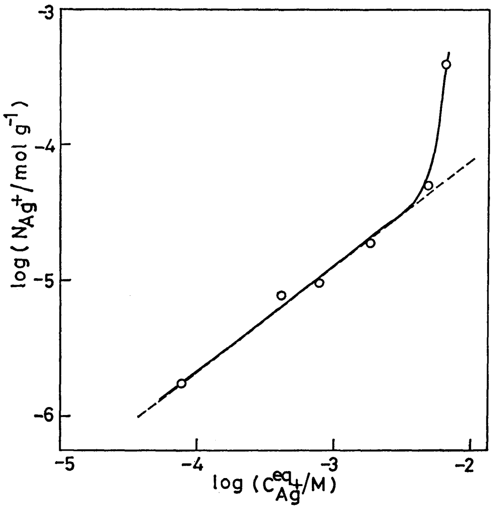

Fig. 3. Freundlich type plot for Ag^+ adsorption on TiO_2 surface.
N_{Ag^+} and $C^{eq}_{Ag^+}$ denote the amount of adsorbed Ag^+ on TiO_2 surface and the concentration of Ag^+ in aqueous phase.

After bubbling nitrogen, the suspension was irradiated by 365 nm light from a 500 W high-pressure mercury lamp (Ushio Denki Type USH-500D), and the increase in dissolved oxygen was recorded on an oxygen meter (Nisshin Rika Model OX-36). After 30 min irradiation, the increase of dissolved oxygen and the amount of reduced silver were registered as 8.2 μmol and 39.6 μmol, respectively. The observed O_2/Ag ratio is close to the theoretical value of 1/4. With suspensions containing no $AgClO_4$, on the contrary, dissolved oxygen after irradiation was at somewhat a lower level than that before irradiation. These facts lead to a conclusion that the positive hole produced by TiO_2-light can react with water and generate oxygen in the presence of Ag^+.[22-24]

Photoreduction in the Dye-sensitized System. The dependence of the amount of photoreduced silver on the irradiation time is given in Fig. 4. The concentrations of $AgClO_4$ and Uranine were 1×10^{-4} and 1×10^{-5} M, respectively. The apparent quantum yield of the photoreduction of Ag^+ is 0.01. The optical absorption spectrum of Uranine solution and the diffuse reflection spectrum of TiO_2 suspension were recorded on an MPS-5000 spectrophotometer (Fig. 5). The dependence of apparent quantum yield on the wavelength of incident light (photochemical action spectrum) was determined from the amount of photoreduced silver after 2 h irradiation. It has a maximum at *ca.* 500 nm (Fig. 5).

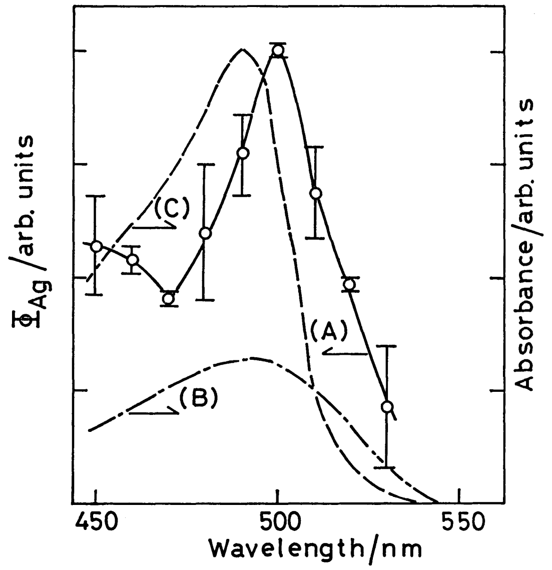

Fig. 5. Photochemical action spectrum for sensitized reduction of Ag^+ on TiO_2 (A) and absorption spectra of Uranine adsorbed on TiO_2 (B) and in aqueous solution (C).
Bulk solution contains 1×10^{-4} M $AgClO_4$, 1×10^{-5} M Uranine and 0.5 M KNO_3.

Discussion

Reaction Scheme for the Unsensitized System. In our previous paper,[13] we examined, with a help of electrochemical study, a simple reaction scheme proposed by Fleischauer *et al.*[9] and concluded that the scheme is capable of interpreting the general feature of Ag^+ reduction at ZnO surface. Such a simple scheme, as it is, is not applicable to the present TiO_2–Ag^+ system, as seen from the significant departure from linear plot shown in Fig. 2. Nevertheless, aside from the detailed mechanism, it is natural to assume, as the above scheme does, that the photoreduction at semiconductor surface will proceed under the local-cell condition, *i.e.*, that the rate of net cathodic reaction is equal to that of net anodic reaction in the photostationary state.

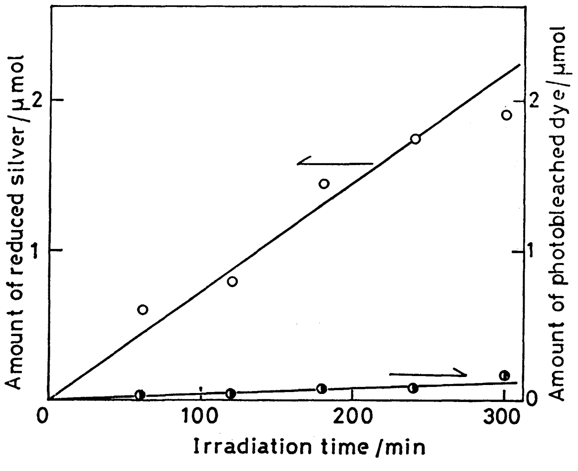

Fig. 4. Growth of the amount of reduced silver in TiO_2 suspension containing $AgClO_4$, KNO_3, and Uranine with irradiation of 500 nm light (O——O). Growth of the amount of photobleached dye is also given (◑——◑).

To examine this assumption, we carried out the present photoelectrochemical study on the TiO_2 sinter electrode. Figure 6 shows polarization curves of the TiO_2 electrode in 0.5 M KNO_3 solutions with and without 5×10^{-4} M $AgClO_4$. The curves indicate both the current measured in the dark and the partial anodic photocurrent as obtained by subtracting the current measured in the dark from the current measured under irradiation. The irradiation did not affect the cathodic current in our study, contrary to the finding of Sprünken *et al.*[25] Therefore, the partial anodic photocurrent indicates the real anodic element of the current under irradiation. From these curves, we have obtained both the zero-current-potential, E_{zcp}, at which the total current under irradiation is zero, and the cathodic current at this potential, i_{dzcp}. If all the cathodic current contributes to the reduction of Ag^+, we can estimate the rate of photoreduction of Ag^+ on this electrode from the value of this current. Indeed, the rate evaluated in this manner at 1×10^{-3} M $AgClO_4$ is in accord with the value obtained by the chemical-analysis method for the same electrode system, within the limit of experimental error. Therefore, almost all the cathodic current at the zero-current-potential can be said to contribute to the silver reduction.

Now, let us assume that the results on the TiO_2 suspension can be analyzed through electrochemical study of the TiO_2 sinter. On the local-cell model for the photoreduction at TiO_2 surface, the electrode

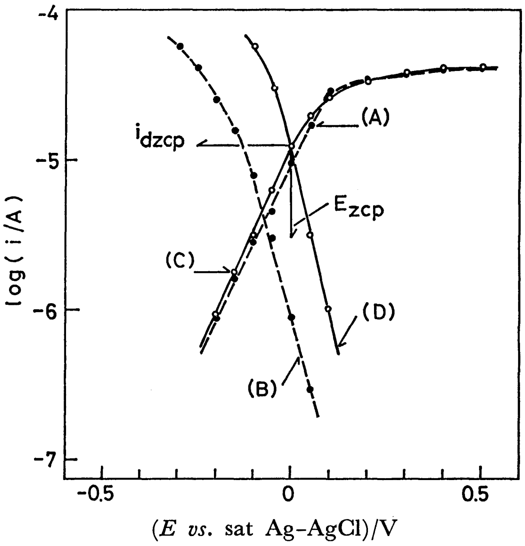

Fig. 6. Polarization curves of TiO_2 electrode in 0.5 M KNO_3 solution with and without 5×10^{-4} M $AgClO_4$.
(A) ●— —●: Partial anodic photocurrent without $AgClO_4$, (B) ●— —●: dark cathodic current without $AgClO_4$, (C) ○——○: partial anodic photocurrent with $AgClO_4$, (D) ○——○: dark cathodic current with $AgClO_4$. E_{zcp} and i_{dzcp} denote the zero-current-potential and the corresponding cathodic current in solution with $AgClO_4$.

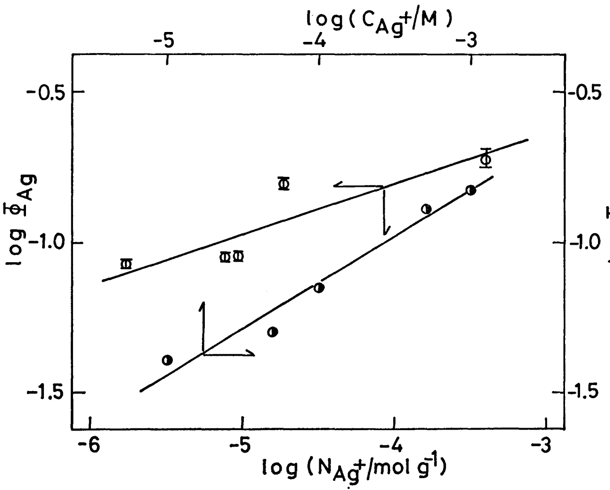

Fig. 7. Relation between the quantum yield and the concentration of $AgClO_4$.
⦶——⦶: Logarithmic plot between the quantum yield Φ_{Ag} and N_{Ag^+}, ◑——◑: logarithmic plot between the quantum efficiency of the photocurrent $\Phi_{h\nu}$ and C_{Ag^+}.

potential (Fermi level) of the TiO_2 immersed in a solution under irradiation is equal to the E_{zcp}. According to Fig. 6, the upward band bending still exists in the space-charge layer of TiO_2, because the onset potential of the partial anodic photocurrent of the TiO_2 electrode is more negative than E_{zcp}. Furthermore, the photopotential measurement on this electrode showed that the electrode potential shifts to a more positive value when the TiO_2-light is cutoff. From these facts, the surface barrier of the TiO_2 in the $AgClO_4$ solution seems to be much smaller under irradiation of TiO_2-light. The photoelectrons in the conduction band can react with the adsorbed Ag^+ over the surface barrier, which is considerably smaller than that in the dark.

We have determined the quantum efficiency of the photocurrent at $E=E_{zcp}$, $\Phi_{h\nu}$, as

$$\Phi_{h\nu}=\frac{1}{eI}i_{dzcp}, \tag{3}$$

which corresponds to the quantum yield of the photoreduction of Ag^+ at the TiO_2 sinter surface. Here, I denotes the number of photons incident to the electrode surface and e the elementary electric charge. A linear relation is observed between the logarithms of $\Phi_{h\nu}$ and C_{Ag^+} (Fig. 7). We have next examined a similar relation between Φ_{Ag} and N_{Ag^+} for the TiO_2 suspension. The linearity shown in Fig. 7 seems to be better than that in Fig. 2. If we note a small amount of the Ag^+ adsorbed on the TiO_2 sinter surface, we may state that log (Φ_{Ag^+}) for both the TiO_2 suspension and sinter systems depends linearly on log (N_{Ag^+}). Such a relation seems to be characteristic of the TiO_2–Ag^+ reaction systems studied here. It contrasts markedly with a Stern-Volmer relation previously reported for ZnO– and TiO_2–Ag^+ systems.[9,13] We have further found that E_{zcp} depends linearly on log(C_{Ag^+}) and that i_{dzcp} is proportional to $I^{0.64}$ irrespective of the Ag^+ concentration. These findings will offer a clue to the mechanism of photoreduction at the TiO_2–Ag^+ system. However, the details of actually operative reaction mechanisms will considerably change depending on physicochemical properties of semiconductor surfaces. It is, therefore, desirable to employ the same semiconductor sample for both photochemical and electrochemical studies; a research along this line is now in progress.

The Mechanism of Dye Sensitization. Though there have been many studies on the dye-sensitization of TiO_2 electrode,[26–29] little is known about the sensitized photoreaction at TiO_2 surface. We have shown in Fig. 4 that silver reduction proceeds by dye-light in the presence of both TiO_2 and Uranine. However, the amount of photoreduced silver after 4 h irradiation of dye-light was only 0.1 μmol in the absence of Uranine and it was still as small as about 0.15 μmol even when Uranine–$AgClO_4$ aqueous solution was irradiated by dye-light for 2 h. Such findings further support the role of both TiO_2 and Uranine in this reaction. The photochemical action spectrum in Fig. 5 may suffer the influence of the filter effect due to the optical absorption of dye molecules in the solution bulk. However, apart from the somewhat longer wavelength maximum in the photochemical action spectrum, the general features of these three spectra may be considered not to be so different from one another, if we note the relatively large half-width of the monochromator employed. The sensitized reaction at TiO_2 surface will be initiated by either electron transfer (the electron transfer mechanism) or energy transfer (the energy transfer mechanism) from excited dye molecules to TiO_2, which results in increase in the concentration of conduction-band electrons. Then, conduction-band electrons are transferred to the Ag^+ adsorbed on the surface. In this way, TiO_2 serves to accept electrons and send them to Ag^+ in such a manner that the reverse electron transfer is prevented from proceeding.

It was observed that a photobleach of dye occurs in the course of silver reduction. The amount of photobleached dye in the suspension was determined by employing the same procedures previously described[13] and is given in Fig. 4. Apparent quantum yield of the photobleach is only 0.0005. However, a similar reaction proceeds to some extent even in the absence of Ag^+, because the photobleached dye in the TiO_2–Uranine system amounted to 0.12 μmol after 5 h irradiation of dye-light. It is remarkable that the amount of photoreduced silver after more than 2 h irradiation is larger than the amount of Uranine initially added to the suspension. To interpret the discrepancy between them, we may as well take into consideration complicated reactions of dye molecule following its sensitizing action, including its regeneration, at least in the case of the electron transfer mechanism for spectral sensitization. Similar phenomena have been reported for the ZnO–Ag^+–Uranine system by us.[13] The mechanism of the sensitized reduction of Ag^+ seems to be much more complicated than that of the unsensitized one and must be far beyond the simple local-cell consideration.

The authors wish to thank Teikoku Kakou Co., for kindly providing us with the TiO_2 powder. This work was carried out with a financial support from the Ministry of Education, Science and Culture of Japan (Grant-in-Aid No. 311607).

References

1) H. Hada and Y. Yonezawa, *Denki Kagaku,* **49**, 60 (1981); H. Hada, K. Takaoka, M. Saikawa, and Y. Yonezawa, *Bull. Chem. Soc. Jpn.*, **54**, 1640 (1981).

2) Y. Nakato, K. Abe, and H. Tsubomura, *Ber. Bunsenges. Phys. Chem.*, **80**, 1002 (1976); Y. Nakato, S. Tonomura, and H. Tsubomura, *ibid.*, **80**, 1289 (1976).

3) B. Kraeutler and A. J. Bard, *J. Am. Chem. Soc.*, **100**, 5985 (1978); H. Reiche and A. J. Bard, *ibid.*, **101**, 3127 (1979).

4) K. Kogo, H. Yoneyama, and H. Tamura, *J. Phys. Chem.*, **84**, 1705 (1980).

5) T. Kawai and T. Sakata, *J. Chem. Soc., Chem. Commun.*, **1980**, 694; *Nature*, **286**, 474 (1980); *Chem. Phys. Lett.*, **72**, 87 (1980).

6) M. Grätzel, *Ber. Bunsenges. Phys. Chem.*, **84**, 981 (1980); E. Borgarello, J. Kiwi, E. Pelizzetti, M. Visca, and M. Grätzel, *Nature*, **289**, 158 (1981).

7) H. Jonker, C. J. Dippel, H. J. Houtman, C. J. G. F. Janssen, and L. K. H. van Beek, *Photogr. Sci. Eng.*, **13**, 1 (1969); H. Jonker, L. K. H. van Beek, C. J. Dippel, C. J. G. F. Janssen, A. Molenaar, and E. J. Spiertz, *J. Photogr. Sci.*, **19**, 96 (1971).

8) G. L. McLeod, *Photogr. Sci. Eng.*, **13**, 93 (1969).

9) P. D. Fleischauer, H. K. Alan Kan, and J. R. Shepherd, *J. Am. Chem. Soc.*, **94**, 283 (1972); A. W. Adamson and P. D. Fleischauer, "Concepts of Inorganic Photochemistry," John Wiley & Sons, New York (1975), p. 400.

10) J. Pukies, W. Roebke, and A. Henglein, *Ber. Bunsenges. Phys. Chem.*, **72**, 842 (1968); M. Kelm, J. Lilie, A. Henglein, and E. Janata, *J. Phys. Chem.*, **78**, 882 (1974); M. Kelm, J. Lilie, and A. Henglein, *J. Chem. Soc., Faraday Trans. 1*, **71**, 1132 (1975); M. Breitenkamp, A. Henglein, and J. Lilie, *Ber. Bunsenges. Phys. Chem.*, **80**, 973 (1976); A. Henglein, *ibid.*, **81**, 556 (1977); R. Tausch-Treml, A. Henglein, and J. Lilie, *ibid.*, **82**, 1335 (1978); A. Henglein, *J. Phys. Chem.*, **83**, 2209 (1979).

11) H. Hada, Y. Yonezawa, A. Yoshida, and A. Kurakake, *J. Phys. Chem.*, **80**, 2728 (1976).

12) H. Lerner, *Photogr. Sci. Eng.*, **13**, 103 (1969).

13) H. Hada, H. Tanemura, and Y. Yonezawa, *Bull. Chem. Soc. Jpn.*, **51**, 3154 (1978).

14) F. Möllers, H. J. Tolle, and R. Memming, *J. Electrochem. Soc.*, **121**, 1160 (1974).

15) H. Yoneyama, N. Nishimura, and H. Tamura, *J. Phys. Chem.*, **85**, 268 (1981).

16) M. S. Wrighton, P. T. Wolczanski, and A. B. Ellis, *J. Solid State Chem.*, **22**, 17 (1977).

17) B. Kraeutler and A. J. Bard, *J. Am. Chem. Soc.*, **100**, 4317 (1978); H. Reiche, W. W. Bunn, and A. J. Bard, *J. Phys. Chem.*, **83**, 2248 (1979).

18) R. H. Sprague and J. H. Keller, *Photogr. Sci. Eng.*, **14**, 401 (1970).

19) C. A. Parker, *Proc. R. Soc. London, Ser. A*, **220**, 104 (1953).

20) D. M. Shub, A. A. Remnev, and V. I. Veselovskii, *Elektrokhimiya*, **9**, 676, 680, 1043 (1973).

21) M. Shiozawa, K. Narita, Y. Fujita, S. Kurita, and H. Yanagida, *Yogyo Kyokai Shi*, **83**, 471 (1975).

22) A. Fujishima and K. Honda, *Nature*, **238**, 37 (1972).

23) T. Ohnishi, Y. Nakato, and H. Tsubomura, *Ber. Bunsenges. Phys. Chem.*, **79**, 523 (1975).

24) P. Clechet, C. Martelet, J. R. Martin, and R. Olier, *Electrochim. Acta.*, **24**, 457 (1979).

25) H. R. Sprünken, R. Schumacher, and R. N. Schindler, *Ber. Bunsenges. Phys. Chem.*, **84**, 1040 (1980).

26) A. Fujishima, E. Hayashitani, and K. Honda, *Seisan Kenkyu*, **23**, 363 (1971); T. Watanabe, A. Fujishima, O. Tatsuoki, and K. Honda, *Bull. Chem. Soc. Jpn.*, **49**, 8 (1976).

27) M. T. Spitler and M. Calvin, *J. Chem. Phys.*, **66**, 4294 (1977).

28) A. Hamnett, M. P. Dare-Edwards, R. D. Wright, K. R. Seddon, and J. B. Goodenough, *J. Phys. Chem.*, **83**, 3280 (1979).

29) W. D. K. Clark and N. Sutin, *J. Am. Chem. Soc.*, **99**, 4676 (1977).