The Photoreduction of the Silver Ion in a Zinc Oxide Suspension

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Quantum yields of from 0.235 to 0.385 have been determined for the reduction of Ag^+ by the irradiation of 365 nm light on a ZnO surface in aqueous solutions containing 5×10^{-5} to 1×10^{-3} M $AgClO_4$. It is proposed that these results can be interpreted by a reaction scheme based on the assumption that some conduction-band electron produced in the ZnO by the irradiation transfers to the Ag^+ adsorbed on the ZnO surface. The surface-energy barrier under the present experimental conditions was discussed with the aid of the electrochemical measurement of the ZnO sinter. The photoreduction of Ag^+ is optically sensitized by the addition of xanthene dyes, such as Uranine and Rhodamine B. In this case, it is observed that the photoreduction of Ag^+ is accompanied by the photolysis of dye molecules. The apparent quantum yields (the number of reacted molecules/the number of photons absorbed in the suspension) of the dye-sensitized photoreduction of Ag^+ and the photolysis of dye molecules are 0.015 and 0.007 for Uranine, and 0.003 and 0.0003 for Rhodamine B, respectively.

The electronic energy transfer in the semiconductor-aqueous solution interface is a fundamental process for semiconductor photochemistry and electrochemistry, and the detailed analysis of this process is closely related to the elucidation of related topics in photobiology, photographic science, and catalysis science, as well as the utilization of solar energy. Many reports[1-6] in which ZnO is used as a working electrode have been published in the fields of semiconductor electrochemistry. They cover the investigations of dye-sensitized photocurrents and the redox reactions as well as the construction of solar cells. In the photochemistry of ZnO powder, Cunningham *et al.*[7-13] have investigated the photoreduction of several molecules and ions on the ZnO–gas and ZnO–solution interfaces, and Dixon *et al.*[14] have reported on the photocatalytic reaction of H_2O on the ZnO–solution interface.

As to the photoreduction of metal ions, Tammann[15] has reported the darkening of an emulsion containing ZnO and Ag^+ under UV-irradiation. Recently, Fleischauer *et al.*[16,17] have investigated the photoreduction of $AgNO_3$ on the surface of ZnO and TiO_2 (rutile) single crystals by means of 365 nm light and obtained quantum yields of from 0.08 to 0.4 for the $AgNO_3$ concentrations of from 0.1 to 1.0 M respectively on the ZnO and also obtained quantum yields of from 0.016 to 0.03 for the $AgNO_3$ concentrations of from 0.001 to 0.01 M respectively on the TiO_2.

We have observed that the irradiation of an aqueous suspension of ZnO containing $AgClO_4$ by means of 365 nm light, which belongs to the fundamental absorption band of ZnO, produces colloidal silver adsorbed on the ZnO surface, and that this reaction can be optically sensitized by the addition of xanthene dyes. This reaction seems to be suitable for the study of the electron-transfer process in the interface because of its rather simple reaction. We have thus investigated the photoreduction of $AgClO_4$ in a ZnO aqueous suspension by means of 365 nm light and the optical sensitization of this reaction by two xanthene dyes, Uranine and Rhodamine B. It has been found that these dye molecules are decomposed in the course of the photoreduction of Ag^+. We also carried out preliminary measurements of the electrochemical properties of the ZnO–aqueous solution interface. Hence, we have obtained several significant conclusions regarding the reaction mechanism of the photoreduction of Ag^+ on the ZnO–aqueous solution interface.

Experimental

The ZnO used in the present study was a highly purified powder sample, labeled SAZEX-4000, which had been obtained by courtesy of the Sakai Kagaku Co., Ltd., Osaka. This material has a surface area of 4.6 m^2/g-ZnO, an average particle size of 0.5 μm, and very low impurities of Pb (0.002%) and Cd (0.0002%). $AgClO_4$, $AgNO_3$, and Uranine are of special grade, purchased from the Nakarai Chemicals Co., Ltd. The perchlorate salt of Rhodamine B was provided by the Nippon Kanko Shikiso Co., Ltd., Okayama. Distilled water was used for the preparation of all the aqueous suspensions of ZnO powder and of all the aqueous solutions employed in the study.

The reaction cell was a cylindrical quartz vessel of 4 cm in diameter and 20 cm in height. It was equipped with a flat window of 1.6 cm in diameter at the bottom for the irradiation of light and with a glass cap with a glass cock to introduce N_2 gas at the top. N_2 replacement was not carried out except when measuring the amount of dissolved oxygen in the suspension. All the parts of the reaction cell except for the flat window were covered with black cloth to avoid the entrance of any stray light. The aqueous suspensions were prepared in the dark. For the study of the dye-sensitized reduction, 0.5 g-ZnO powder was suspended in an 50 ml aqueous solution composed of $AgClO_4$ and xanthene dye. The buffer solution was not added in either case, because this might cause some undesirable reactions. The reaction mixture was rigorously mixed by a magnetic stirrer under a constant velocity throughout the reaction.

A 500 W xenon lamp, Type UXL-500D, with a Type DSB-500SS, power supply (Ushio Denki Co., Ltd.), was used as the light source. The monochromatic light for irradiation was selected by the combination of a monochromator (Shimadzu Seisakusho Co., Ltd.) and an appropriate glass filter (Toshiba Co., Ltd.). For the study of the unsensitized reduction, 365 nm light was used. For the study of the dye-sensitized reductions, 490 nm light was used for Uranine and 560 nm light for Rhodamine B (designated as dye-light). The irradiation was commenced after the adsorption equilibrium had been established. It takes about 30 min for the unsensitized system, and about 180 min for the dye-sensitized system, to attain the adsorption equilibrium. After the irradiation, the reaction mixture in the solid state was collected through a sintered glass filter, washed completely with a large excess of distilled water, dissolved by

HNO_3, and then submitted to the quantitative analysis of the Ag^+. The details of the silver analysis by means of the differential potentiometric titration method were presented in our previous paper.[18] The decomposition products of ZnO and dyes by HNO_3 did not hinder the analysis of the reduced silver.

The incident intensities of 365 nm light on the reaction vessel were measured by the use of the ferrioxalate actinometer, using the quantum yields determined by Parker.[19] Those of dye-light were determined with the aid of a photometer, Type IL-600 (International Light Co., Ltd.). In this work, the numbers of incident photons were 9.10×10^{14} photon/cm^2 s at 365 nm, 2.78×10^{15} photon/cm^2 s at 490 nm, and 1.89×10^{15} photon/cm^2 s at 560 nm. To calculate the number of photons absorbed by suspensions, the transmittance and the reflectance of suspensions were measured by the use of the spectrophotometers, MPS-5000 and QV-50 equipped with an integrating sphere (Shimadzu Seisakusho Co., Ltd.). The quantum yields of the photoreduction of Ag^+ for the unsensitized systems and the apparent quantum yield (the number of reacted molecules/the number of photons absorbed by suspension) for the dye-sensitized system were determined as follows:

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

where Φ is the quantum yield for the unsensitized system or the apparent quantum yield for the dye-sensitized system, $d[Ag]/dt$ the initial rate of the formation of the reduced silver (atom/s), and Q the number of photons absorbed by the suspension (photon/s). It is easy to determine the quantum yield for the unsensitized system by means of Eq. 1, because all the photons absorbed by the suspension at 365 nm are absorbed by ZnO itself. On the contrary, it is difficult to determine the quantum yield for the dye-sensitized system because some of the incident photons absorbed by free dye molecules in the solution, not by the dye adsorbed on ZnO, do not contribute to the photoreduction. Therefore, for the dye-sensitized system we have determined only the apparent quantum yield by means of Eq. 1.

The photobleach reactions of Uranine and Rhodamine B were studied in the suspensions described above. After the irradiation by dye-light, the suspension was filtered out and the optical density of the filtrate at this wavelength was measured. From this, the amount of dyes photobleached during the sensitized photoreduction was determined. The adsorption isotherm of Ag^+ adsorbed in equilibrium was determined after the ZnO powders had been immersed in 5×10^{-5} to 1×10^{-3} M solutions of $AgClO_4$ for 3 h under a constant stirring.

The electrochemical measurements of the ZnO sinter electrode were carried out in a conventional manner.[6,20] ZnO powder SAZEX-4000 was placed, in pellets, on a disk of 10 mm in diameter and 0.5 mm thick, and then sintered at 1000 °C for 2 h in air. After cooling to room temperature, it was activated at 550 °C under 1×10^{-4} mmHg for 3 h. The surface of ZnO electrode was etched by 85% H_3PO_4 and washed with distilled water before use. A platinum plate was used as the counter electrode, and a saturated KCl–Ag/AgCl electrode of the double-junction type was used as the reference electrode. The electrochemical measurements of the cell thus constructed were carried out by means of a potentiostat equipped with an electrometer, Type HA-104 (Hokuto Denko Co., Ltd.). The electrolyte solutions were composed of 0.5 M KNO_3 or of a mixed solution of 0.5 M KNO_3 and 1.0×10^{-4} M $AgClO_4$. Before the measurements, dissolved O_2 was purged by the introduction of high-purity N_2 gas.

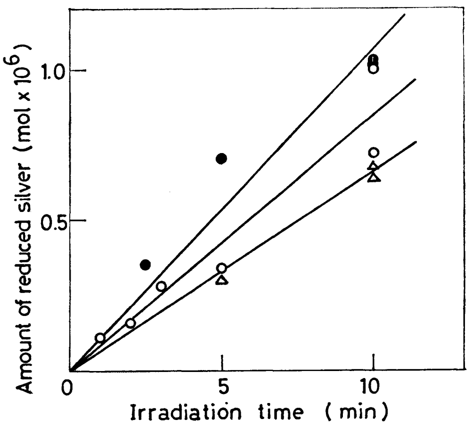

Fig. 1. Growth of the amount of reduced silver in ZnO suspension containing $AgClO_4$ with irradiation time. ●: $[AgClO_4] = 1.0 \times 10^{-3}$ M, ○: 1×10^{-4} M, and △: 5×10^{-5} M.

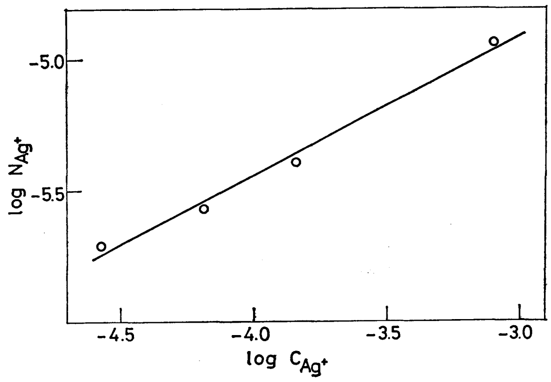

Fig. 2. Plots showing the Freundlich type adsorption for Ag^+ on ZnO surface. Index of adsorption is 0.53. N_{Ag^+}, and C_{Ag^+} denote the amount of adsorbed Ag^+ (mol/g-ZnO) and the concentration of Ag^+ in aqueous phase (mol/l).

Results

Photoreaction in the Unsensitized System. The dependence of the amount of reduced silver on the irradiation time of 365 nm light for the ZnO–$AgClO_4$ aqueous suspension is given in Fig. 1. The thermal reduction in the dark is negligible as compared with the photoreduction. From the rate of Ag^+ reduction obtained by means of the method of least squares in Fig. 1, and the number of photons absorbed at 365 nm in the suspensions, the quantum yield of the photoreduction of Ag^+ was calculated. The values are 0.385±0.016, 0.303±0.021, and 0.235±0.004 for $AgClO_4$ concentrations of 1.0×10^{-3}, 1.0×10^{-4}, and 5.0×10^{-5} M respectively. The pH values of the suspensions are 6.8, 6.6, and 6.5 for $AgClO_4$ concentrations of 1.0×10^{-3}, 1.0×10^{-4}, and 5.0×10^{-5} M respectively. The pH change during the irradiation was not remarkable after 30 min irradiation. The quantum yields obtained here are much larger than those predicted by the extrapolation of the results of Fleischauer *et al.*[16] on the photoreduction of $AgNO_3$ on the ZnO single crystal. Cunningham *et al.*[10] reported that $NaNO_3$ is reduced to $NaNO_2$ by UV-light in the ZnO–aqueous suspension. Therefore, we have carried out the photoreduction of $AgNO_3$ by the same reaction system as $AgClO_4$. The quantum yields for $AgNO_3$ are nearly equal to that for $AgClO_4$. Therefore, these results seem to suggest the differences in the physicochemical properties of the ZnO employed by different investigators.

The adsorption isotherm of Ag^+ on the ZnO surface was measured at 20 °C. It is given in Fig. 2. In the equilibrium state, the concentration of Ag^+ in the aqueous phase, C_{Ag^+}, and the amount of adsorbed Ag^+ on the surface of 1.0 g-ZnO, N_{Ag^+}, satisfy Freundlich's adsorption formula:

$$N_{Ag^+} = \alpha(C_{Ag^+})^{1/n}, \qquad (2a)$$

$$\log N_{Ag^+} = \log \alpha + \frac{1}{n}\log C_{Ag^+}. \qquad (2b)$$

(α, n: constant)

The adsorption index, $1/n=0.53$, is a rather reasonable value.

We tried to clarify the behavior of the positive hole by the detection of the increases in the dissolved O_2 and Zn^{2+} in the aqueous phase during the photoreaction. A 50 ml aqueous suspension of 0.5 g of the ZnO and 1.0×10^{-3} M $AgClO_4$ was prepared. The dissolved O_2 was measured by the use of an oxygen meter, Model DO-2A (Toa Denpa Co., Ltd.). The amount of O_2 dissolved in the suspension is decreased by the introduction of N_2 gas in the dark under constant stirring. Then, the suspension was irradiated with 365 nm light for 40 min, and the increase of the dissolved O_2 was recorded. The observed value of 2.6×10^{-6} mol is nearly equal to the amount of photoreduced silver of 3.9×10^{-6} mol under the same reaction conditions. The increase in Zn^{2+} was examined by colorimetric analysis using Xylenol Orange as an indicator.[21–23] The same suspension described above was also irradiated by 365 nm light for 40 min and then filtered. 0.1% Xylenol Orange and a buffer solution (pH=5.6) were added to the filtrate, and the absorption spectra were recorded. A characteristic peak was observed at 571 nm which was not distinct in the unirradiated case. This surely implies that Zn^{2+} increases after the irradiation. From these results, the positive hole produced by 365 nm light can be thought to react with the chemisorbed oxygen ion or water molecule on the ZnO surface, as well as with the oxygen ion in the ZnO lattice.[14,24,25]

The current-voltage characteristics of the ZnO sinter electrode were also studied. The electrolyte solution was composed of either 0.5 M KNO_3 or a mixture of 0.5 M KNO_3 and 1.0×10^{-4} M $AgClO_4$. The polarization curves obtained are given in Figs. 3 and 4. The solid line and the dashed line indicate the currents measured under the irradiation and in the dark respectively. The dotted line indicates the partial anodic photocurrents.[26–28] This is obtained by the subtraction of the current in the dark from the current measured under the irradiation. Because the irradiation should not affect the cathodic current, the cathodic current measured in the dark is equal to that under the irradiation. Therefore, the partial anodic photocurrent indicates the real anodic element of the current under the irradiation.

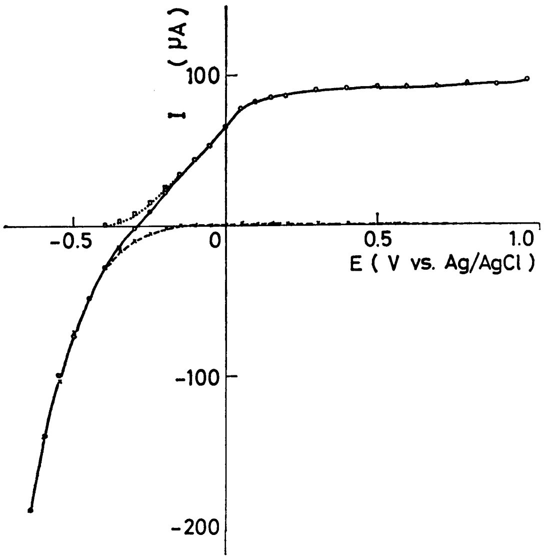

Fig. 3. Polarization curves of ZnO electrode in 0.5 M KNO_3 solution. ○——○: Measured currents under irradiation, ×----×: measured currents in the dark, □······□: the partial anodic photocurrents defined in the text.

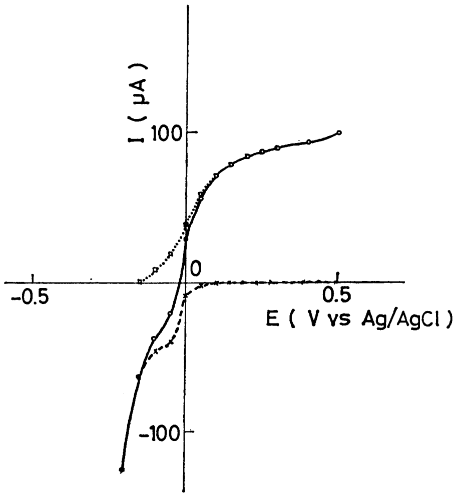

Fig. 4. Polarization curves of ZnO electrode in 0.5 M KNO_3 solution containing 1×10^{-4} M $AgClO_4$. ○——○: Measured currents under irradiation, ×----×: measured currents in the dark, □······□: the partial anodic photocurrents defined in the text.

Under the irradiation at the electrode potential of −0.030 V *vs.* Ag/AgCl in Fig. 4, the cathodic current cancels the anodic current on the ZnO sinter electrode, so the total current is zero (Zero-current-potential). The cathodic current at this potential is 24 μA in Fig. 4, but it is almost zero at this potential in Fig. 3. If all the cathodic current contributes to the reduction

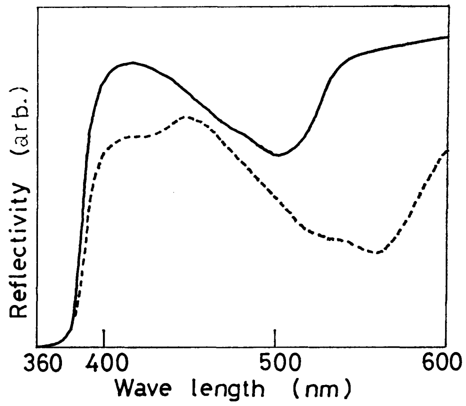

Fig. 5. Reflection spectra of ZnO-$AgClO_4$-Uranine (——) and ZnO-$AgClO_4$-Rhodamine B (----) aqueous suspensions.

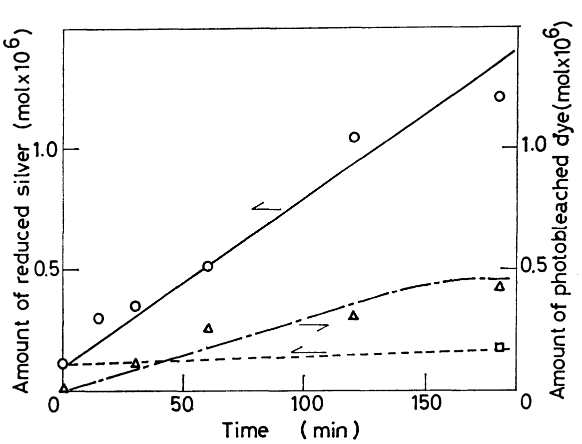

Fig. 6. Growth of the amount of reduced silver in ZnO suspension containing $AgClO_4$ and Uranine with irradiation of 490 nm light (○——○) and in the dark (□----□). Growth of the amount of photobleached dye is also given (△———△).

of Ag^+, we can determine the rate of photoreduction of Ag^+ on this electrode from this value. Indeed, the rate evaluated in this manner is in accord with the value obtained by the chemical-analysis method in the same electrode reaction system, within the limits of experimental error. Therefore, almost all the cathodic current at the zero-current-potential can be said to contribute to the photoreduction of Ag^+.

The onset point of the partial anodic photocurrents corresponds to the flat-band potential. We can see that this potential (−0.40 V *vs.* Ag/AgCl in Fig. 3) is shifted to a more positive value (−0.15 V *vs.* Ag/AgCl in Fig. 4) when $AgClO_4$ is added to the electrolyte solution.

Photoreaction in the Dye-Sensitized Systems. The diffuse reflection spectra of ZnO–$AgClO_4$ aqueous suspensions containing dye were recorded on a MPS-5000 spectrophotometer. The results are given in Fig. 5. The absorption band shorter than 385 nm corresponds to the fundamental absorption of ZnO. The monomer absorption maxima of dyes exist at 490 nm for Uranine and 560 nm for Rhodamine B. No peaks due to the dye aggregation were found.

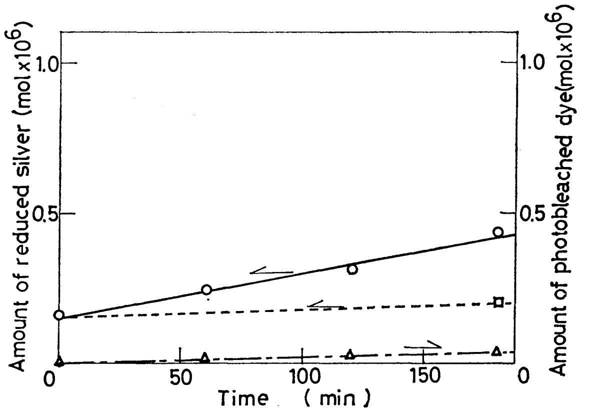

Fig. 7. Growth of the amount of reduced silver in ZnO suspension containing $AgClO_4$ and Rhodamine B with irradiation 560 nm light (○——○) and in the dark (□----□). Growth of the amount of photobleached dye is also given (△———△).

In the case of the Uranine system, the dependence of the amounts of photoreduced silver on the irradiation time is given in Fig. 6. The concentrations of $AgClO_4$ and dye are 1.0×10^{-4} and 1.0×10^{-5} M respectively. From the initial slope of the photoreduction curve and the number of absorbed photons, the apparent quantum yield of the photoreduction of Ag^+ is found to be 0.015. It is observed that a photobleach of the dye proceeds simultaneously with the Ag^+ reduction. The dependence of the amount of photobleached dye on the irradiation time is also shown in Fig. 6. The apparent quantum yield of this reaction is 0.007. We have found that the photoreduction of Ag^+ and the photobleach of the dye cannot occur in the absence of ZnO. Therefore, it is impossible that Ag^+ is directly reduced by the dye molecules without the participation of ZnO. The amount of reduced silver is about twice as large as the amount of Uranine which exists in the suspension at the beginning. This means that at least two Ag^+s are reduced by one Uranine molecule.

As to the Rhodamine B system, the amounts of reduced silver and photobleached dye are given in Fig. 7. The concentrations of $AgClO_4$ and dye are the same as in the Uranine system. The apparent quantum yields of 0.003 and 0.0003 were obtained for the photoreduction of Ag^+ and the photobleach of Rhodamine B respectively. These values are smaller than those in the Uranine system.

Discussion

Reaction Scheme. The amount of adsorbed Ag^+ plays a significant role in the photoreduction. We tried to interpret the dependence of the quantum yields on the $AgClO_4$ concentrations with the help of the simple reaction scheme of Fleischauer *et al*:¹⁶⁾

$$ZnO + h\nu \xrightarrow{\theta} e(s) + p, \tag{3a}$$

$$e(s) + Ag^+(s) \xrightarrow{k_1} Ag(s), \tag{3b}$$

$$e(s) \xrightarrow{k_2} \text{non-reactive state}, \tag{3c}$$

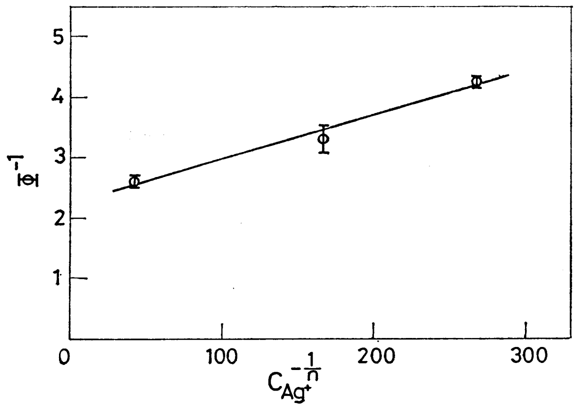

Fig. 8. Reciprocal plots between the quantum yield Φ and $(C_{Ag^+})^{1/n}$.

where e(s) and p denote the surface electron and the free hole produced by the light, and where $Ag^+(s)$ and Ag(s) denote the silver ion and the atom adsorbed on ZnO surface, respectively. In this scheme, the excitation of ZnO produces a surface electron with an efficiency of θ. This electron reacts with the adsorbed silver ion at the solid-liquid interface with the rate constant of k_1. Some part of this electron will be converted to the non-reactive state, with the average rate constant of k_2, by trapping, recombination, or reaction with some impurites on ZnO. Assuming the stationary concentration of e(s), the quantum yield of the Ag formation is expressed as

$$\Phi = \frac{\theta k_1 N_{Ag^+}}{k_2 + k_1 N_{Ag^+}}. \tag{4}$$

From Eqs. 2a and 4, we can obtain

$$\Phi^{-1} = \frac{k_2}{\alpha k_1 \theta}(C_{Ag^+})^{-1/n} + \frac{1}{\theta}. \tag{5}$$

The experimental relation between Φ^{-1} and $(C_{Ag^+})^{-1/n}$ given in Fig. 8. confirms our assumption that the adsorption equilibrium of Ag^+ on the ZnO surface is not perturbed very much in the earlier stage of the photoreaction and that the dependence of the quantum yield on the Ag^+ concentration can be interpreted by means of this scheme.

ZnO–Aqueous Solution Interface. It is well known[12,25,29] that there exists a surface-energy barrier for electrons in the space-charge layer of ZnO left in air due to electron localization on the surface-energy levels of the chemisorbed oxygen. When ZnO is in contact with an aqueous solution, the surface barrier will change with the pH or some other properties of the solution. In the aqueous suspension of ZnO studied here, both Ag^+ and ClO_4^-, as well as H^+, OH^-, and H_2O exist in the solution. Therefore, the surface barrier would be considerably changed from that in air.

Now, let us assume that the results of the ZnO suspension can be analyzed by an electrochemical study of the ZnO sinter. This is supported by the fact that the quantum yield of the photoreduction of Ag^+ on the ZnO sinter is almost the same as that in the ZnO suspension. First, let us consider the surface-energy barrier of the ZnO sinter in view of the results of the electrochemical measurements. In the "local cell model" of the photoreaction on the ZnO sinter, the electrode potential of the ZnO sinter immersed in the solution under the irradiation is equal to the zero-current-potential, noted before. We also found from the photopotential measurement of the ZnO electrode, that the electrode potential is indeed −0.030 V *vs.* Ag/AgCl under the irradiation and that it shifts to a more positive value (0.315 V *vs.* Ag/AgCl was measured), when the 365 nm light is cut off. According to the results of the photocurrent and the photopotential measurements cited above, it may be concluded that the upward band bending still exists in the space-charge layer of ZnO, because the flat-band potential of the ZnO electrode in the presence of Ag^+ is more negative than the electrode potential either in the dark or under the irradiation. It is evident that the bottom of the conduction band at the surface does not change so much as the electrode potential on the irradiation. From these facts, the surface barrier of the ZnO sinter in the $AgClO_4$ solution can surely be said to be much smaller under the irradiation of 365 nm light. This effect may be due to the rapid consumption of the positive hole, and the resultant accumulation of photoelectrons in the conduction band under the influence of the electric field of the space-charge layer. The photoelectrons in the conduction band can react with $Ag^+(s)$ over the surface barrier, which is considerably smaller than that in the dark. The rate of the photoreduction of Ag^+ is equal to the rate of hole consumption in the photostationary state. This corresponds to a "local cell model."[26–28]

In Figs. 3 and 4 the shift of the flat-band potential is observed upon the addition of $AgClO_4$. Lohmann[4] has demonstrated that the flat-band potential of a ZnO electrode is shifted as the pH of the solution is changed. The pH value of the solution containing 0.5 M KNO_3 is 5.1, and that of the solution containing 0.5 M KNO_3 and 1×10^{-4} M $AgClO_4$ is 5.2, so the shift of the flat-band potential observed in our case is much larger than that to be expected from the pH change by the addition of $AgClO_4$. Therefore, we can assume that when $AgClO_4$ is added, the pH change and also the specific adsorption of Ag^+ on the ZnO surface contribute to the shift of the flat-band potential. Ag^+ is specially adsorbed in the Helmholtz layer on the surface of ZnO and causes the changes in the physicochemical properties of the surface. This is not inconsistent with Freundlich's adsorption isotherm of Ag^+ on the surface of ZnO, which can be interpreted in terms of the assumption that the adsorbate can occupy various surface points whose adsorption energies are distributed exponentially. Morrison[3] reported that the flat-band potential of a ZnO electrode does not change when several other metal ions are added to the electrolyte solution. However, we think that Ag^+ may play a specific role, in contrast to the ions reported by him. The exact determination of the flat-band potential of the ZnO electrode by the impedance measurement when Ag^+ is added to the electrolyte solution is in progress. Our results will be published in forthcoming paper.

In the reaction scheme discussed in the previous section, it was assumed that the surface barrier under the irradiation does not change even if the concentrations of Ag^+ in the solution are varied. In fact, the differences between the flat-band potential and the electrode potential under the irradiation in Figs. 3 and 4 are almost the same. This means that, although the flat-band potential of the electrode is changed by the addition of $AgClO_4$, the surface barrier under the irradiation does not change very much by the addition of $AgClO_4$.

Cunningham *et al.*[7,10] have obtained that quantum yields of about 10^{-5} for the photoreduction of N_2O on the surface of ZnO powder and of 10^{-1} to 10^{-3} for the photoreduction of various molecules and ions in a ZnO aqueous suspension. They interpreted the greatly enhanced quantum efficientcies of the photoreaction at ZnO–water interface relative to the ZnO–gas interface, at least in part, by the assumption that there exists a rather downward band bending due to the predominance of H^+ over OH^- on the surface of ZnO at a neutral pH, but such bending would not be reasonable in our case. The much larger quantum yields and the relatively small dark reaction rates obtained by us must be mainly the result of the decrease in the surface barrier for the conduction-band electron, as has been described above.

The Mechanism of Dye Sensitization. There have been many studies of the dye sensitization of ZnO in terms of both photoelectric and electrochemical properties. In these studies, the external electric field was applied to the ZnO material, and the photocurrent caused by the energy transfer or the charge transfer from the dye in contact with them was measured. In our study, the photoelectron is moved by the electric field of the space-charge layer originally present in the ZnO–aqueous solution interface.

Because ZnO plays a decisive role in the dye-sensitized photoreduction of Ag^+, the following reaction mechanism seems probable. In the first step, the energy transfer or the charge transfer from the dye molecules adsorbed to ZnO occurs, and the concentration of the conduction-band electron increases, then the conduction-band electron in ZnO transfers to the Ag^+ adsorbed on the surface through the interface in the same manner as the unsensitized reduction of Ag^+. If we assume that the surface barrier of ZnO in the presence of $AgClO_4$ can hardly be affected by the addition of dyes, the quantum yield of the dye-sensitized photoreduction of Ag^+ would be of the same magnitude as the product of the quantum yields of the photocurrent generation and the unsensitized photoreduction of Ag^+. According to Tsubomura *et al.*,[20] the quantum yield of the photocurrent of a ZnO electrode by Rose Bengal, one of the xanthene dyes, is 0.22. In our study, the quantum yields of 0.23 to 0.50 have been determined for the reduction of Ag^+ by 365 nm light on the ZnO surface. Therefore, the apparent quantum yields of 0.015 and 0.003 obtained by us for the dye-sensitized photoreduction of Ag^+, which correspond to the minimum of the real quantum yields, are rather reasonable.

A large difference was found in quantum yields of the photobleach between the two dyes. The ratios of the apparent quantum yields of the photoreduction of Ag^+ by dyes to those of the photobleach of dyes are 2.2 for Uranine and 10 for Rhodamine B. It seems that these numbers show how many times one dye molecule contributes to the photoreduction of Ag^+. We think that the photobleach and the reproduction of dyes are related to the sensitization mechanism of a semiconductor.

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