Unique Effects of Iron(III) Ions on Photocatalytic and Photoelectrochemical Properties of Titanium Dioxide

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Photocatalytic oxidation of water on TiO_2 (rutile) powder proceeded with a fairly high efficiency (about 9%) when iron(III) ions were used as the electron acceptor. The reaction continued until all iron(III) ions added to the solution were reduced into iron(II) ions. This behavior was in marked contrast to other reversible photocatalytic reactions, whose reaction rates decelerate as the result of the back reactions of the products on the photocatalysts. The efficient oxidation of water in the presence of iron(III) ions was attributed to preferential adsorption of iron(III) ions on TiO_2 over iron(II) ions, which enabled efficient oxidation of water, although this reaction was thermodynamically less favorable than oxidation of iron(II) ions. Furthermore, from the measurements of photocurrents at crystalline TiO_2 electrodes, iron(III) ions were concluded to have a catalytic function for the oxidation of water on photoirradiated TiO_2.

Introduction

Photocatalytic reactions on semiconductor powders[1−9] have attracted much attention because of structural simplicity of the reaction systems and their applicability to the treatments of a variety of pollutants and wastes. Another possibility of utilization of semiconductor photocatalysts is the conversion of light energy into chemical energy.[10,11] The reactions for the treatments of wastes and pollutants are usually exothermic and irreversible. Contrarily, the reactions of the latter category should be endothermic and reversible. The difference characterizes the properties of the two classes of reactions and the optimal conditions for the preparation of photocatalysts for these reactions.

Among the chemical reactions suitable for energy conversion is the decomposition of water, because the change of Gibbs energy is largely positive and the needed reactant is solely water. Hence, great efforts have been expended to achieve the photodecomposition of water using semiconductors electrodes such as TiO_2[12] and $SrTiO_3$.[13] Semiconductor particles such as TiO_2,[14] $SrTiO_3$,[15] and $K_4Nb_6O_{17}$[16] have also been studied for this purpose.

The aim of our study is to decompose water by combining two photocatalytic reactions, i.e., oxidation of water and reduction of water.[17] Combination of two photosystems is the strategy of green plants for the utilization of solar energy and is considered to be the practical method for achieving largely endothermic reactions in artificial systems.[18] If both of the oxygen evolving and hydrogen evolving systems are established, they can in principle be linked via a redox couple dissolved in an oil phase.[19] So far, we have demonstrated that water is reduced into hydrogen by a reversible and endothermic reaction using iodide ions as the electron donor.[17] Thus, our next target is the realization of oxidation of water. There have been reports on the oxidation of water on photoirradiated TiO_2 using some kinds of electron acceptors, such as silver(I)[20,21] and iron(III) ions.[22,23] In this paper, we report that iron(III) ions have unique effects on photoirradiated TiO_2, which enable efficient oxidation of water into molecular oxygen.

Experimental Section

Materials. Titanium dioxide powder (JRC-TIO-5) obtained from Catalysis Society of Japan was used as the photocatalyst. The powder had a rutile crystalline form and a surface area of 2.6 to 2.7 m^2/g. Iron(III) compounds were obtained from Wako Pure Chemical as guaranteed reagents. For colorimetry of iron-(II) ions, 2,4,6-tris(2-pyridyl)-*s*-triazine (TPTZ) obtained from Dojindo Laboratories was used as the complexing reagent. All other chemicals used in the experiments were purchased from commercial sources as guaranteed reagents and used without further purification.

Photocatalytic Study. In the experiments of photocatalytic reactions, the TiO_2 powder (100 mg) was added to aqueous solutions containing iron(III) chloride or other electron acceptors. The pH of the solutions was adjusted at 2.4 by adding aqueous solution of sulfuric acid, if necessary. Photocatalytic reactions were carried out in a closed flask under reduced pressure after the air dissolved in the solution was removed by repeating freeze−pump−thaw cycles. A 500 W high-pressure mercury lamp (Wacom, BMO-500DY) was used as the light source. The light beam was passed through a Pyrex glass filter to cut off deep UV radiation. During the photoirradiation, the TiO_2 powder was suspended in the solutions with a magnetic stirrer. Evolution of oxygen was determined using a quadruple gas analyzer (Anelva, AGA-100) and the amounts of evolved oxygen were measured with an oil manometer. Concentrations of iron(II) ions and iron(III) ions in solution were determined from UV-vis absorption spectra, which were measured with a Shimadzu UV-2500PC spectrophotometer. Before the spectroscopic measurements, iron(II) ions were colored by complexing with TPTZ in solutions at pH 4.6 and iron(III) ions by complexing with chloride ions in solutions of 6 mol dm^{-3} hydrochloric acid.

For determining the quantum efficiency of the photocatalytic reactions, suspension of TiO_2 was irradiated with a light beam at wavelengths around 365 nm from the high-pressure mercury lamp. Light at the wavelengths was chosen using band pass filters. The light intensity was monitored with a thermopile (Eppley Laboratory).
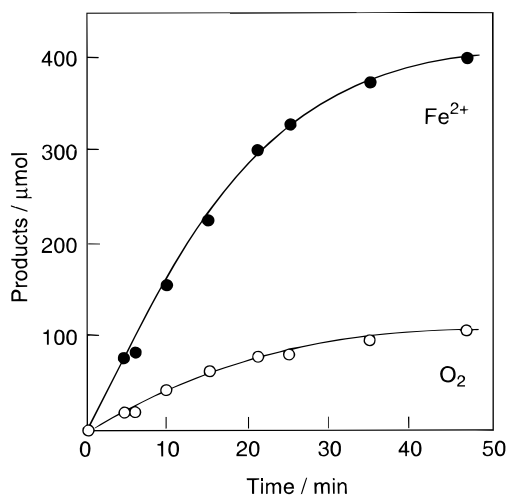
Figure 1. Photocatalytic generation of iron(II) ions and oxygen-using iron(III) chloride as the electron acceptor. The reaction was carried out in an aqueous solution (0.05 dm³) of iron(III) chloride (400 mmol) containing TiO₂ powder (JCR-TIO-5, 100 mg).

Figure 2. Photocatalytic evolution of oxygen using iron(III) chloride as the electron acceptor in the presence of iron(II) ions at different concentrations. The reaction was carried out in aqueous solutions (0.05 dm³) of iron(III) chl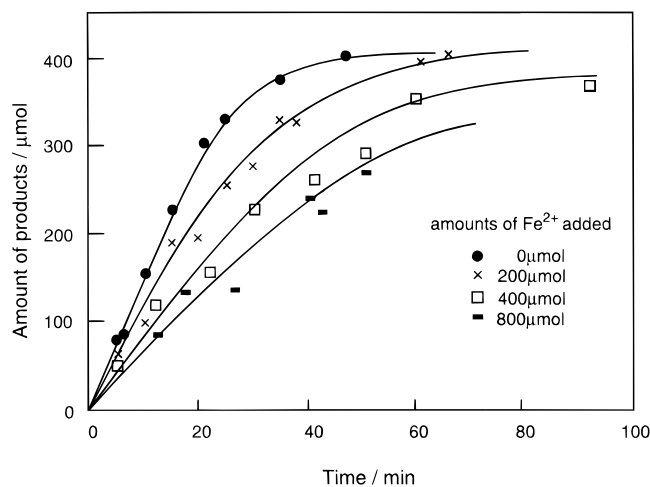oride (400 mmol) containing TiO₂ powder (JCR-TIO-5, 100 mg). Amounts of iron(II) chloride added to the solution are described in the figure.

Photoelectrochemical Study. Single crystals of titanium dioxide (1×1 cm²) were obtained from Earth Chemicals (Kobe, Japan). Some exposed the (110) crystalline face and the others exposed the (100) face. They were all reduced in a hydrogen stream at 650 °C for 1 h to give the electric conductivity. The electrodes for photoelectrochemistry were fabricated by connecting lead wires to the TiO₂ crystals through a Ga−In alloy. A platinum plate and an Ag/AgCl electrode were used as the counter and reference electrodes, respectively. Photoelectrochemical measurements were carried out using a 170 W Xenon lamp (ILC Technology) as the light source. Potential of the TiO₂ electrodes was controlled using a potentiostat (Nikkokeisoku, NPOT-2501).

Results and Discussion

Photocatalytic Oxidation of Water. Photocatalytic reactions on the TiO₂ powder were carried out in flasks containing deaerated aqueous solutions at pH 2.4. In the absence of iron (III) ions or other electron acceptors in the solutions, no oxygen evolved . On the other hand, trace amounts of hydrogen were obtained after prolonged illumination. Evolution of hydrogen under similar conditions has often been reported and attributed to the photocatalytic reactions caused by organic contaminants.[25]

Contrary to the above cases, evolution of oxygen was observed when iron(III) ions were added to the solutions. As oxygen evolves, iron(II) ions were generated in solution. Typical results are shown in Figure 1. Mills and Porter[22] and by Vorgarello et al.[23] have already reported the evolution of oxygen using iron(III) ions as the electron acceptor. Besides the fact that iron(III) ions can be an electron acceptor for oxidation of water on TiO₂, we found that iron(III) ions have very unique effects on TiO₂, which lead to efficient oxygen evolution on TiO₂, as discussed later.

The results shown in Figure 1 were obtained using an aqueous solution of iron(III) chloride (400 mmol) containing TiO₂ powder (100 mg). The amounts of oxygen and iron(II) ions generated by photoirradiation for 47 min are almost 100 and 400 mmol, respectively. They are stoichiometrically in agreement with the amounts expected from the oxidation of water by iron(III) ions. Note that a part of light energy is converted into chemical energy by this reaction because the standard free energy change of oxygen evolution from iron (III) solutions is 108.4 kJ mol⁻¹ at pH 2.4. Note also that the photocatalytic

oxidation of water continues until almost all iron(III) ions in the solution are reduced into iron(II) ions.

In most of the photocatalytic reactions that convert light energy into chemical energy, the reactions practically stop as the concentration of the products in the solutions reaches certain levels because of the back reactions between the products and also as the result of the back reactions of the products on the photocatalysts. The former back process is much prevented if one of the products is gaseous. On the other hand, the latter process is difficult to prevent, unless the products are ingeniously separated from the reactive site of the photocatalyst, on which the back reaction takes place. An example of the prevention of the back reaction on the photocatalyst is the oxidation of water using silver ions as an electron acceptor. In this case, probably because metallic silver is deposited on the reductive site of the photocatalysts, the back reaction (oxidative dissolution of metallic silver) is prevented and the forward reaction proceeds efficiently.[21] Interestingly, in the case of oxidation of water using iron(III) ions as the electron acceptor, the reaction proceeds even when iron(II) ions are present in the solution. Figure 2 shows that the reaction rate is lowered to some extent when the concentration of iron(II) ions is higher than 4 mmol dm⁻³. However, the negative effect by iron(II) ions is much less than that of other electron acceptors added to the solution, such as triiodide ions.[17] This is the most unique property of the reaction system using iron(III) ions as the electron acceptor.

The quantum efficiency of the reaction was measured under irradiation of TiO₂ powder in 8 mmol dm⁻³ iron(III) chloride with light at wavelengths around 365 nm. From the rates of oxygen evolution and iron(II) generation, the quantum efficiency of the reaction was determined to be 9.0%. The initial rate of oxygen evolution on TiO₂ powder under irradiation from a high pressure mercury lamp was about 75 mmol/h and almost independent of the concentration of iron(III) chloride in the range of 4 to 8 mmol dm⁻³, as shown in Figure 3. The rate of oxygen evolution was lowered to some extent by raising the concentrations of iron(III) ions above 12 mmol dm⁻³, probably owing to a filter effect of the solution in high concentration.

Since the above reaction is endothermic, it is expected that we can get the clues to the construction of photochemical energy conversion system by elucidating the unique effects of iron-(III) ions. Hence, we searched for the reasons for the high efficiency of the oxygen evolution. For this purpose we

Effects of Iron(III) Ions on TiO₂

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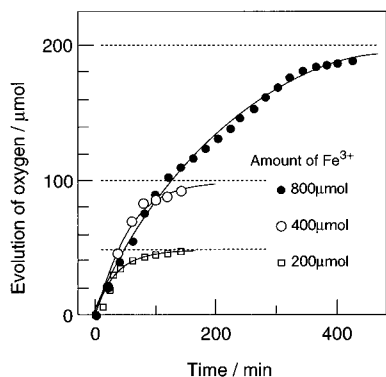
Figure 3. Photocatalytic evolution of oxygen using iron(III) chloride as the electron acceptor at different concentrations. The reaction was carried out in aqueous solutions (0.05 dm^3) of iron(III) chloride (200, 400, and 800 mmol) containing TiO₂ power (JCR-TIO-5, 100 mg). The broken lines show the upper limits of oxygen evolution expected from the amounts of iron(III) chloride added to the solutions.
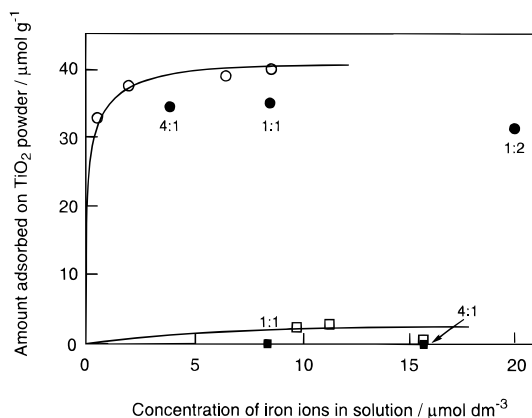

Figure 4. Adsorption isotherms of iron(III) and iron(II) ions on TiO₂ powder at 25 °C: (○) for iron (III) ions and (□) for iron (II) ions. When both iron(II) and iron(III) ions were added to the solution, their adsorptivity was affected each other: (●) for iron (III) ions and (■) for iron(II) ions. The molar ratio of iron(III) ions: iron(II) ions is described in the figure. Measurements were performed using TiO₂ (JCR-TIO-5) powder.

measured the adsorptivity of ion(III) and iron(II) ions on TiO₂, and we studied the photoelectrochemistry of TiO₂ in solutions containing these ions.

The amounts of iron(III) ions adsorbed on TiO₂ were determined by analyzing the concentration of ion(III) ions in solutions before and after addition of certain amounts of TiO₂ powder to the solutions. The results showed that iron(III) ions are easily adsorbed on the surface of TiO₂, as shown in Figure 4. Since 1 g of the TiO₂ powder has the surface area of 2.6–2.7 m^2, the surface of TiO₂ is estimated to be fully covered with iron(III) ions when the concentration of iron(III) ions in solution is above 1×10^{-3} mol dm^{-3}.

Compared to the adsorption of iron(III) ions, iron(II) ions showed much lower adsorptivity. Strikingly, when both iron-(III) and iron(II) ions were added to solution, the amount of iron(II) ions adsorbed on TiO₂ was lowered to be negligibly small, as shown in Figure 4. These results suggest that iron-(II) ions, which are generated on TiO₂ by photocatalytic reduction of iron(III) ions, are promptly replaced by iron(III) ions in solution and the iron(II) ions are removed from the TiO₂ surface. The exchange of the adsorbed ions on TiO₂ leads to a very slow rate for oxidation of iron(II) ions and preferential oxidation of water despite the fact that this reaction is thermodynamically less favorable.

The reaction rates were found to be affected by the counter ions of iron(III) ions in solution. For example, the rates of

(b)
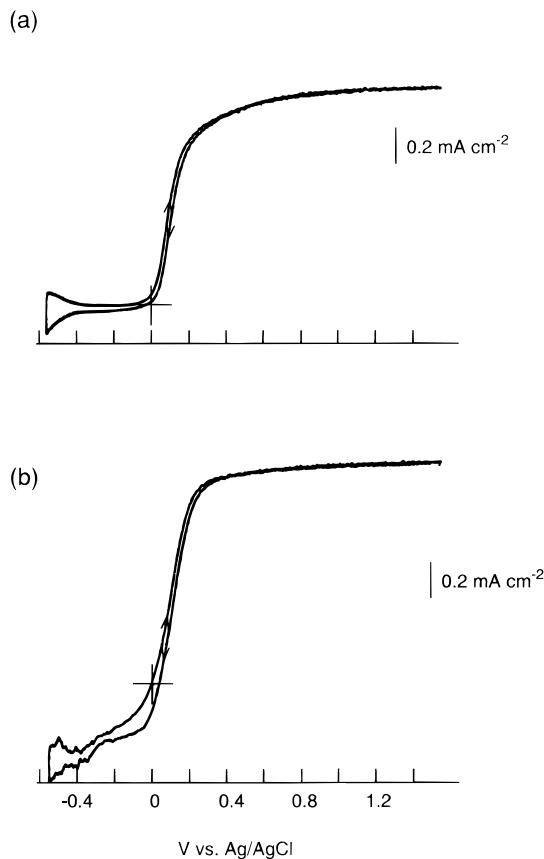
Figure 5. I−V characteristics of a TiO₂ (110) electrode (a) in an aqueous solution containing 0.01 mol dm^{-3} sulfuric acid and 0.5 mol dm^{-3} potassium nitrate and (b) those obtained after addition of iron-(III) nitrate (2.0 mmol dm^{-3}) to the solution. The potential was swept at a rate of 20 mV s^{-1}.

oxygen evolution were lowered to be about 17% of that obtained using iron(III) chloride when iron(III) sulfate were added to the solution in place of iron(III) chloride. This result suggests that adsorptivity of iron(III) and iron(II) ions on TiO₂ is affected by the anionic species in solution.

Effect of Iron(III) ions on the Photoelectrochemical Properties of TiO₂ Electrodes. The photoelectrochemical properties of TiO₂ electrodes exposing either a (110) face or a (100) face were studied after the activation treatment in an aqueous solution of 0.5 mol dm^{-3} sulfuric acid.[25] The I−V characteristics of the electrodes after the activation treatment were measured in the solution containing 0.01 mol dm^{-3} sulfuric acid and 0.5 mol dm^{-3} potassium nitrate; the pH of the solution was 1.9. When small amounts of iron(III) ions were added to the solution, the photocurrent rose more steeply and leveled off at lower potentials than the photocurrents observed in the absence of iron(III) ions, as shown in Figure 5. In other words, the properties of the TiO₂ electrode were improved by the addition of iron(III) ions. As the photocurrent flowed continuous evolution of fine bubbles, probably oxygen gas, was observed at the surface of the electrodes under irradiation at a high light intensity, where the current density was about 1 mA cm^{-2}. Close observation of the I−V characteristics of Figure 5 shows that, when iron(III) ions are present in the solution, the onset potential of the photocurrent is a little more anodic than the potential observed without iron(III) ions. The anodic shift of the photocurrent onset in the presence of iron(III) ions is due to the dark cathodic current caused by the reduction of iron(III) ions on the electrode. In these all properties, no difference was observed between the electrodes exposing a (110) face and those exposing a (100) face.
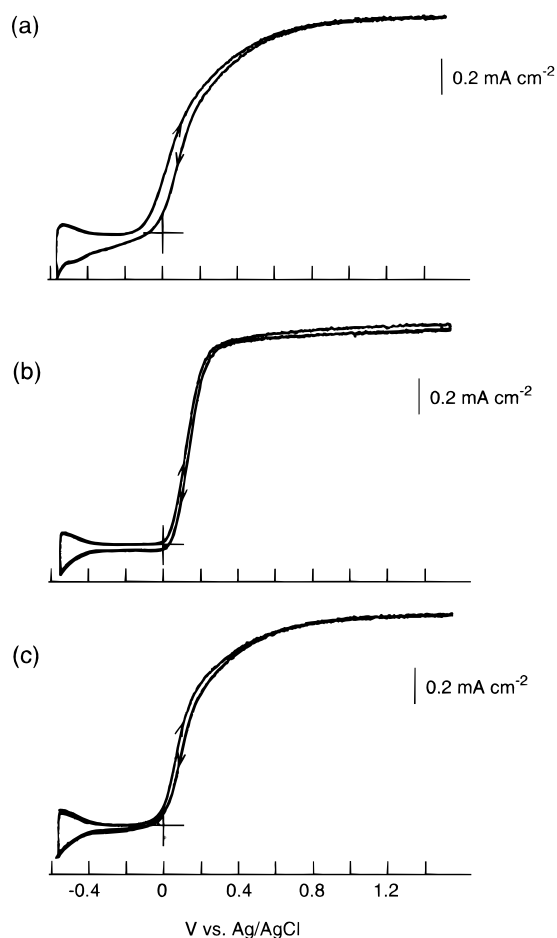
Figure 6. I−V characteristics for a TiO$_2$ (110) electrode measured successively in an aqueous solution containing 0.01 mol dm^{-3} sulfuric acid and 0.5 mol dm^{-3} potassium nitrate: (a) an initial state, (b) after soaking the electrode in a solution containing iron(III) nitrate (10 mmol dm^{-3}) for 15 min, and (c) after application of a cathodic potential (-1.0 V vs. Ag/AgCl) to the solution for 30 min. The potential was swept at a rate of 20 mV s^{-1}.

Even without iron(III) ions in solution, the I−V characteristics of TiO$_2$ electrodes were almost the same as those obtained in the iron(III) containing solution if iron(III) ions were adsorbed on the TiO$_2$ electrodes by soaking them in the solutions containing iron(III) ions, as shown in Figure 6b. The improved I−V characteristics by the adsorption of iron(III) ions was reserved if the electrode was immersed in water for 48 h, the period during which the electrode was disconnected from the circuit. However, by applying cathodic potentials to these electrodes, the I−V characteristics deteriorated and approached those of the electrodes without the adsorbed iron(III) ions, as shown in Figure 6c. Upon application of the cathodic potential to these electrodes, transient cathodic currents flowed, suggesting that iron(III) ions on the electrodes were reduced into iron(II) ions. Besides the experiments of the adsorption of iron(II and III) ions, the above results also indicate that iron(III) ions have strong adsorptivity on TiO$_2$, while iron(II) ions have weak adsorptivity.

The effect of metal ions on the photocurrent of TiO$_2$ electrodes has been surveyed using other metal ions, such as Ga(III), Cr(III), V(III), Ca(II), and Ni(II). Among them, only V(III) ions gave some improvement in the rise of the photocurrent, although the effect was smaller than that of iron(III) ions.

The I−V curves measured in the presence of iron(III) ions (Figures 5 and 6) indicate that iron(III) ions adsorbed on TiO$_2$

have a catalytic effect on the oxidation of water. A possible explanation for the catalytic effect by iron(III) ions is as follows. Before the evolution of molecular oxygen at the photoirradiated TiO$_2$ electrode, several kinds of intermediates are supposed to be formed on the surface of TiO$_2$. The intermediates can be the surface recombination center for electrons and holes. Especially, the intermediates having positive charges are considered to be efficient electron-hole recombination centers, because the majority carriers in TiO$_2$ are electrons. Therefore, iron(III) ions adsorbed on TiO$_2$ are supposed to catalyze the reaction step which determines the amounts of the intermediates. Enhanced deprotonation of hydroxide-type intermediates by making an iron(III)−O bond may be another possibility for their catalytic activity. If the accumulation of positive charge is prevented by the deprotonation, it works favorably to retard the rate of electron-hole recombination. Such assumed functions of iron(III) ions are largely dependent on the structure and the location of iron(III) ions on the TiO$_2$. In rutile, six oxygen atoms compose octahedral units; every second of them is filled with a titanium ion and the other second is vacant.[26] We tentatively assume that iron(III) ions are included in the vacant units at the surface. The determination of the structure of iron-(III) ions adsorbed on TiO$_2$ is now under investigation.

Conclusion

We have demonstrated that water is photocatalytically oxidized into oxygen with high efficiency on TiO$_2$ particles using iron(III) ions as electron acceptor. The unique properties of this reaction are clarified to be due to preferential adsorption of iron(III) ions on TiO$_2$ over iron (II) ions. The iron(III) ions are also demonstrated to have the catalytic activity for the oxidation of water on TiO$_2$. These results are important for improving the properties of TiO$_2$ photocatalysts for the construction of photochemical energy conversion systems. The effects of iron(III) ions are also useful from the viewpoint of the application of TiO$_2$ to the treatments of pollutants and wastes.

References and Notes

(1) Schwitzgebel, J.; Ekerdt, J. G.; Gerischer, H.; Heller, A. *J. Phys. Chem.* **1995**, *99*, 5633.

(2) Willner, I.; Eichem, Y.; Frank, A. J.; Fox, M. A. *J. Phys. Chem.* **1993**, *97*, 7264.

(3) Ohnishi, H.; Matsumura, M.; Tsubomura, H.; Iwasaki, M. *Ind. Eng. Chem. Res.*, **1989**, *28*, 719.

(4) Matsumura, M.; Furukawa, S.; Saho, Y.; Tsubomura, H. *J. Phys. Chem.* **1985**, *81*, 1327.

(5) Jackson, N. B.; Wang, C. M.; Luo, Z.; Schwitzgebel, J.; Ekerdt, J. G.; Brock, J. R; Heller, A. *J. Electrochem. Soc.* **1991**, *138*, 3660.

(6) Kuwabata, S.; Tsuda, R.; Yoneyama, H. *J. Am. Chem. Soc.* **1994**, *116*, 5437.

(7) Fujishima, A.; Cai, R. X.; Otsuki, J.; Hashimoto, K.; Itoh, K.; Yamashita, T.; Kubota, Y. *Electrochim. Acta* **1993**, *18*, 153.

(8) D'Oliveira, J. C.; Minero, C.; Pelizzetti, E.; Pichat, P. *J. Photochem. Photobiol. A* **1993**, *72*, 261.

(9) Pelizzetti, E.; Minerro, C.; Mauniro, V.; Hidaka, H.; Serpone, N.; Terzian, R. *Ann. Chem.* **1990**, *80*, 81.

(10) Duonghong, D.; Borgarello, E.; Grätzel, M. *J. Am. Chem. Soc.* **1981**, *103*, 4685.

(11) Domen, K.; Kudo, A.; Shinozaki, A.; Tanaka, A.; Maruya, K.; Ohnoshi, T. *J. Chem. Soc., Chem. Commun.* **1986**, 356.

(12) Fujishima, A.; Honda, K. *Nature* **1972**, *238*, 37.

(13) Watanabe, T.; Fujishima, A.; Honda, K. *Bull Chem. Soc. Jpn.* **1976**, *49*, 355.

(14) Yamaguchi, K.; Sato, S. *J. Chem. Soc., Faraday Trans. 1* **1985**, *81*, 1237.

(15) Sayama, K.; Arakawa, H. *J. Chem. Soc., Chem. Commun.* **1992**, 253.

(16) Sayama, K.; Tanaka, A.; Domen, K.; Maruya K.; Onishi, T. *J. Phys. Chem.* **1991**, *95*, 1345.

(17) Ohno, T.; Saito, S.; Fujihara, K., Matsumura, M. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 3059.

(18) Linkous, C. A.; Slatteru, D. K.; Ouellette, A. J. A.; McKaige, G. T. B.; Austin, C. N. *Proceedings of the 11th World Hydrogen Energy Conference* **1996**, *11*, 2545.

(19) Ohno, T.; Fujihara, K.; Saito, S.; Matsumura, M. *Sol. Energy Mater. Sol. Cells*, **1997**, *45*, 423.

(20) Osawa, Y.; Grätzel, M. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 197.

(21) Nishimoto, S.; Ohtani, B.; Kajiwara, H.; Kagiya, T. *J. Chem. Soc., Faraday Trans. 1* **1985**, *81*, 61.

(22) Mills, A.; Porter, G. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 3659.

(23) Vorgarello, E.; Kiwi, J.; Grätzel, M.; Pelizzetti, E.; Visca, M. *J. Am. Chem. Soc.* **1982**, *104*, 2996.

(24) Sato, S. *Kagaku to Kogyo* **1988**, *22*, 206.

(25) Nakato, Y.; Kamura, A.; Shimizu, J.; Magari, Y. *J. Electroanal. Chem.* **1995**, *396*, 35.

(26) (a) Cotton F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; John Wiley and Sons: New York, 1988. (b) Glassford, K. M.; Chelikowsky, J. R. *Phys. Rev. B*, **1992**, *46*, 1284.