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Mechanism of Photocatalytic Decomposition of Water into H_2 and O_2 over NiO–$SrTiO_3$

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The mechanism of the photocatalytic decomposition of H_2O into H_2 and O_2 over NiO–$SrTiO_3$ powder was studied on the basis of the structure of the catalyst. It was elucidated that H_2 evolution occurs over NiO while O_2 evolution takes place over $SrTiO_3$. The importance of the existence of Ni metal between the interface of NiO and $SrTiO_3$ suggested the transfer of an electron between both materials. Two possible mechanisms, a one-photon process and a two-photon process, were discussed.

INTRODUCTION

Photoelectrochemical decomposition of water has been achieved using some semiconductors as photoelectrodes (*1–5*). Especially, Wrighton *et al.* (*3*) reported that photoelectrolysis of water into H_2 and O_2 proceeds over a reduced $SrTiO_3$ electrode with a platinum counterelectrode without an external bias in an electrochemical cell.

On the other hand, some attempts for catalytic decomposition of water have been done over those semiconductor powders (*5–16*). We found that NiO–$SrTiO_3$ powder with proper pretreatment can steadily decompose water photocatalytically (*6–8*). Lehn *et al.* also showed the activity of photodecomposition of water over $SrTiO_3$ powders modified by rhodium oxide (*10*).

Although the principle of photoelectrolysis of water in a photoelectrochemical cell has been established, that of the photocatalytic decomposition of water over a powder system is not definitely understood.

In our previous paper (*17*) the structures of NiO–$SrTiO_3$ catalysts after various pretreatments were investigated by means of several spectroscopic methods. In this paper, the activities of those NiO–$SrTiO_3$ catalysts for the photocatalytic decomposition of water, as well as for H_2 evolution from aqueous CH_3OH solution and O_2 evolution from aqueous $AgNO_3$ solution, were studied. Comparing those results with the corresponding structures of the catalysts, the mechanism of the photocatalytic reactions over NiO–$SrTiO_3$ powder was discussed.

EXPERIMENTAL

$SrTiO_3$ powder (average particle size 2×10^{-6} m, surface area 3.9 m^2/g) was purchased from Alfa-Ventron. $Ni(NO_3)_2 \cdot 6H_2O$, CH_3OH (Wako Pure Chemical), and $AgNO_3$ (Kanto Chemical Co.) were used without further purification.

NiO–$SrTiO_3$ powder was impregnated with aqueous $Ni(NO_3)_2$ solution as described in the previous papers (*7, 17*). NiO–$SrTiO_3$ powder after the calcination in air is hereafter noted as "nontreated" catalyst. The pretreatments of the catalysts and reactions were carried out in a closed gas circulation reaction system (300 ml) connected with a vacuum line as shown in Fig. 1. At first, NiO–$SrTiO_3$ powder was reduced by H_2 at 500°C for 2 h (hereafter, R500 catalyst), and then was reoxidized at 200°C (R500-O200 catalyst) or at 500°C

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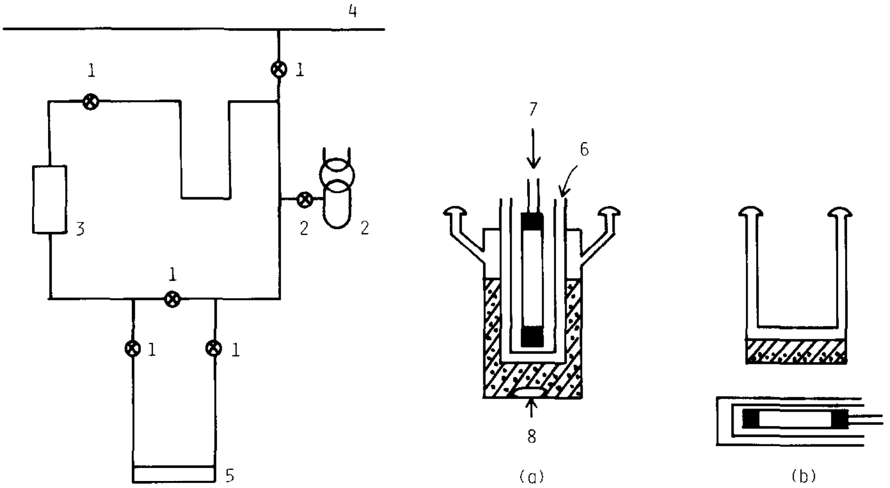

FIG. 1. The apparatus for the photocatalytic reaction. (1) Stopcocks, (2) sampling cell, (3) circulation pump, (4) vacuum line, (5) reaction cell. (a) Inner irradiation reaction cell: (6) cooling water, (7) high pressure mercury lamp, (8) magnetic stirrer. (b) Flat-bottom reaction cell.

(R500-O500 catalyst) for 1 h. Two kinds of reaction cells were used as shown in Figs. 1a and b. For the photocatalytic decomposition of water, an inner irradiation reaction cell made of Pyrex was used. The solution (300 ml) suspended with catalysts (0.5 g) was stirred magnetically. For the H_2 evolution from aqueous CH_3OH solution (50 vol%) and the O_2 evolution from aqueous $AgNO_3$ solution (0.1 *N*), the reaction cell with a flat bottom (ca. 30 cm^2) made of quartz was used. The catalyst (2.0 g) was dispersed on the bottom and dipped in the solution of 10 ml. The vessel was irradiated through the bottom.

The light sources used were high pressure mercury lamps (Ushio UM452, 450 W) in both cases. In the closed circulation system, the solution was degassed completely before the reaction until residual O_2 and N_2 could not be detected by a gas chromatograph. The evolved gases, H_2 and O_2, were analyzed quantitatively by a gas chromatograph (TCD, Ar carrier) with a molecular sieve 5A column. The sampling cell for a gas chromatograph was attached directly to the gas circulation system as shown in Fig. 1.

RESULTS AND DISCUSSION

(*1*) *Photocatalytic Decomposition of Water over NiO–SrTiO₃*

The evolution of H_2 and O_2 from distilled water over NiO(1.5 wt%)–$SrTiO_3$ photocatalysts with various pretreatments took

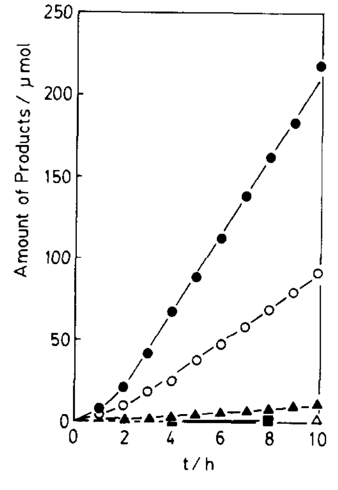

FIG. 2. Time courses of H_2 and O_2 evolution from distilled water over NiO(1.5 wt%)–$SrTiO_3$ catalysts after various pretreatments under irradiation. (■) H_2, nontreated catalyst; (●) H_2, (○) O_2, R500-O200; (▲) H_2, (△) O_2, R500-O500. Inner irradiation reaction cell, catalyst = 0.5 g, high pressure mercury lamp (450 W).

place as shown in Fig. 2. The nontreated catalyst showed very low activity for H_2 evolution (0.1 μmol/h) and no O_2 was detected during the reaction. On the other hand, the R500-O200 catalyst evolved H_2 and O_2 steadily after an induction period for 2–3 h. The ratio of the rate of H_2 evolution (24 μmol/h) to that of O_2 (11 μmol/h) was almost 2 : 1. When the catalyst was reoxidized at higher temperature, the R500-O500 catalyst, the rate of H_2 evolution decreased markedly (1.2 μmol/h) and that of O_2 (0.05 μmol/h) was not stoichiometric. These results showed clearly the effect of the pretreatment of catalysts for photodecomposition of water.

In Fig. 3, the evolution of H_2 and O_2 from aqueous NaOH solution (5 *N*) as well as from distilled water over the R500-O200 catalyst are shown. The activity in aqueous NaOH solution was higher than that in distilled water as previously reported. (*8*).

The quantum yield at 365 nm was measured using a monochrometer (H.20, ISA JOBIN YVON Instrument) and a thermopile (The Eppley Laboratory Inc.). Although the activity changed by the factor of 2 to 3 due to the small difference of pretreatment conditions or to the difference of the origin of $SrTiO_3$ powder, the value attained for R500-O200 catalyst in aqueous NaOH solution (5 *N*) was ca. 1%.

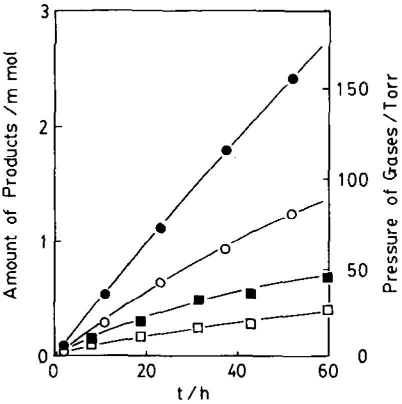

FIG. 3. Time courses of H_2 and O_2 evolution from aqueous NaOH (5 *N*) solution and distilled water over NiO(1.7 wt%)–$SrTiO_3$, R500-O200 catalyst. (●) H_2, (○) O_2, in aqueous NaOH solution; (■) H_2, (□) O_2, in distilled water. Inner irradiation reaction cell, catalyst = 0.5 g, high pressure mercury lamp (450 W).

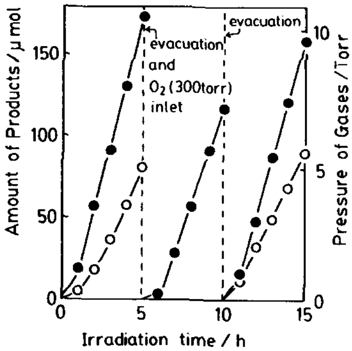

FIG. 4. The effect of O_2 on the activity of photodecomposition of water over NiO(1.7 wt%)–$SrTiO_3$, R500-O200 catalyst, in aqueous NaOH solution (5 *N*). At 5 h, the gas phase was evacuated and O_2 (300 Torr) was introduced and saturated for 1 h in the dark. After 10 h, the gas phase was evacuated again. (●) Evolved H_2, (○) evolved O_2. Inner irradiation reaction cell, catalyst = 0.5 g, high pressure mercury lamp (450 W).

As shown in Fig. 3, the rates of H_2 and O_2 evolution decreased gradually both in aqueous NaOH solution and in distilled water with the irradiation time. To study the effect of the evolved O_2 during the reaction over R500-O200 catalyst in aqueous NaOH solution (5 *N*), O_2 (300 Torr, 1 Torr = 133.3 N m^{-2}) was intentionally introduced in the gas phase after the reaction had proceeded for 5 h as shown in Fig. 4. In the presence of O_2 of 300 Torr the rate of H_2 evolution was suppressed by about 25%. When the gas phase was evacuated after a 10-h reaction, the activity of the H_2 evolution was almost recovered. As mentioned previously (*6*) the reverse reaction, $2H_2 + O_2 \rightarrow 2H_2O$, is very slow in the dark over NiO–$SrTiO_3$ catalyst and therefore the effect should be due to the photoreaction of O_2 over the catalyst, i.e., $O_2 + e^- \rightarrow O_2^-$ etc.

The evolution of H_2 and O_2 in water over the R500 catalyst which contained Ni metal on the surface of $SrTiO_3$ were also studied as shown in Fig. 5. The rate of H_2 evolution was lower than that over the R500-O200 catalyst, and O_2 did not evolve at all. The activity of the H_2 evolution decreased rapidly

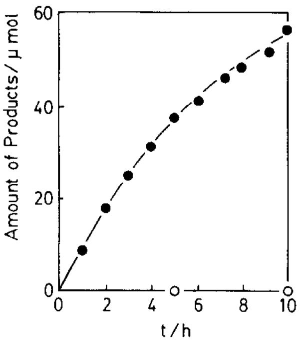

FIG. 5. Time courses of H_2 and O_2 evolution from distilled water over R500 catalyst under irradiation. (●) H_2, (○) O_2. Catalyst = 0.5 g, inner irradiation reaction cell, high pressure mercury lamp (450 W).

with the irradiation time. In this case the surface of Ni metal was oxidized instead of OH^- and/or H_2O. $Ni(OH)_2$ formation over the catalyst during the reaction was observed by XPS (*17*).

The ratio of the amounts of produced H_2 and O_2 gases should be 2 : 1 when the photodecomposition of water proceeds catalytically. However, in the present experiments, the amount of O_2 produced was sometimes smaller than that expected. When the catalyst was reduced by H_2 at lower temperature such as 200°C and then reoxidized at 200°C, it was found that O_2 did not evolve in stoichiometric amount, as shown in Fig. 6. Even after long time irradiation, the ratio of evolved H_2 and O_2 was not 2 : 1. Further, the activity is lower than that of R500-O200 catalyst. Although the reason is not clear, the oxidation of water into O_2 seems not to proceed catalytically over these catalysts.

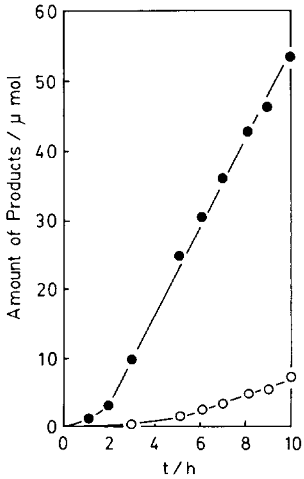

FIG. 6. Time courses of H_2 and O_2 evolution from aqueous NaOH solution (5 *N*) over R500-O200 catalyst. (●) H_2, (○) O_2. Catalyst = 0.5 g, inner irradiation reaction cell, high pressure mercury lamp (450 W).

(2) *Activities of H_2 Evolution from Aqueous CH_3OH Solution (1 : 1 in volume) and O_2 Evolution from Aqueous $AgNO_3$ Solution (0.1 N)*

The rate of H_2 evolution from aqueous CH_3OH solution and the initial rates of O_2 evolution from aqueous $AgNO_3$ solution are summarized in Table 1, along the rates of H_2 and O_2 evolution from distilled water. Evolution of O_2 from aqueous $AgNO_3$ solution over the R500-O500 catalyst is shown in Fig. 7. The rate of O_2 evolution decreased with time due to the deposition of silver metal on the catalyst surface. To compare the activities, the amount of evolved O_2 for the first hour was regarded as those activities.

The activities for H_2 evolution from aqueous CH_3OH solution over various pretreated catalysts changed markedly, similarly to that of the activity for H_2O decomposition. On the other hand, the activities

TABLE 1

Activities of some Photocatalytic Reactions over NiO(1.5 wt%)–$SrTiO_3$ after Various Pretreatments

Catalyst	Rate of gas evolution (μmol/h)			
	H_2O^a		$CH_3OH_{aq}{}^b$	$AgNO_{3\,aq}{}^c$
	H_2	O_2	H_2	O_2
Nontreated	0.1	0	0.2	76
	0^d	0^d	0.2^d	99^d
R500	8.5	0	9.8	47
R500-O200	24.4	10.6	16.8	124
R500-O500	1.2	0.05	1.8	66

[a] Catalyst; 0.5 g, inner irradiation reaction cell, H_2O; 300 ml.

[b] Catalyst; 2 g, flat-bottom reaction cell, $CH_3OH + H_2O$ (1 : 1 in vol); 10 ml.

[c] Catalyst; 2 g, flat-bottom reaction cell, $AgNO_{3\,aq}$ (0.1 *M*); 10 ml.

[d] Only $SrTiO_3$.

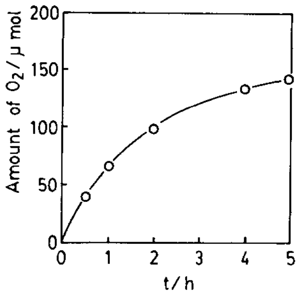

FIG. 7. Time course of O_2 evolution from aqueous $AgNO_3$ solution (0.1 *N*) over R500-O500 catalyst. Flat-bottom reaction cell, high pressure mercury lamp (450 W), solution = 10 ml, catalyst = 2g.

of O_2 evolution were not much different among those catalysts treated under various conditions, although the R500-O200 catalyst showed the highest activity. This difference is probably caused by the difference of the reduction site for H^+ and Ag^+. The reduction of H^+ ion proceeds only over the NiO surface, on the other hand, the reduction of Ag^+ ion occurs both over the NiO and $SrTiO_3$ surfaces.

(3) *The Nature of the Interface of Ni Metal and SrTiO₃*

Recently, Bard *et al.* have conducted studies on the interface between Pt metal and TiO_2 (rutile) (*19*). They found that the electrical properties of the contacts were strongly altered by thermal treatment of the sample, where extended annealing produced a low-resistance ohmic junction and not a Schottky type junction. In the present case, a similar ohmic junction seems to be formed at the interface between Ni metal and $SrTiO_3$, since NiO–$SrTiO_3$ catalyst was activated by the reduction at 500°C. In the previous paper (*8*), we found that the lower the reduction temperature below 500°C, the lower the photocatalytic activity of NiO–$SrTiO_3$. After the reoxidation at 200°C, Ni metal still remained at the interface between $SrTiO_3$ and NiO. When the reduced catalyst was reoxidized at higher temperature above 500°C, Ni metal disappeared completely (*17*), and the activity of the catalyst was very low, as mentioned above. In this case, the ohmic interface between NiO and $SrTiO_3$ would be destroyed. These results seem to suggest that the electron in the conduction band, excited by the photon, flows into Ni metal through the ohmic junction, at the interface.

(4) *Roles of SrTiO₃ and Nickel Oxide*

According to the electrochemical model, the surface of *n*-type semiconductor, $SrTiO_3$, is suitable for the oxidation of H_2O or OH^- by the hole in the valence band, while that seems not to be suitable for evolution of H_2 because of the large excess potential. When $SrTiO_3$ powder, without NiO, was illuminated in aqueous $AgNO_3$ solution, O_2 evolved efficiently as shown in Table 1. On the other hand, when $SrTiO_3$ powder alone was illuminated in aqueous CH_3OH solution, very low activity of the H_2 evolution was found, while evolution of H_2 over NiO–$SrTiO_3$ steadily takes place under the same condition. These experimental facts indicate that the hole at the surface of $SrTiO_3$ can oxidize OH^- and/or methanol, and the electron at the surface can reduce Ag^+, but cannot reduce H^+ to H_2. Taking these results into consideration, it can be concluded that evolution of H_2 occurs on the surface of NiO.

Lehn *et al.* (*10*) have reported the system of $SrTiO_3$ powder modified by Rh deposition, which could also decompose water into H_2 and O_2 photocatalytically. They found that $SrTiO_3$ loaded with Rh(III) species is active, whereas that with reduced Rh showed no catalytic activity. Their catalytic system is similar to the one discussed here. In our case, without reoxidation of the reduced catalyst (R500 catalyst) at proper temperature (200°C) the evolution of H_2 and O_2 does not take place, although H_2 is evolved slowly. The important role of NiO must be to prevent the reverse reaction, i.e., $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$, over the catalyst surface. Further NiO is stable during the reaction, although the surface seems to be hydrated in part (*17*).

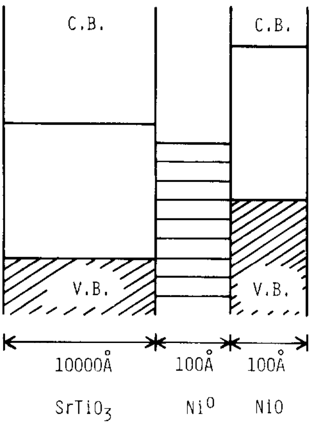

FIG. 8. Energy diagram of NiO–$SrTiO_3$ system.

On the other hand, NiO is well known as a *p*-type semiconductor containing excess oxygen. Goodenough *et al.* (*20*) studied the photoelectrochemical properties and proposed the band structure of NiO. They also proposed the mechanism of H_2 evolution over NiO. Koffyberg and Benko (*21*) studied the band structure of NiO by the electrochemical method. By referring to these studies it is possible to describe an energy level diagram of the NiO–$SrTiO_3$ system as shown in Fig. 8. An ohmic contact at the interface between Ni metal and NiO is expected although the structure is not clear. The electron donation to H^+ over the Sr TiO_3 surface should be considered. In that case, NiO would act only as the catalyst for the recombination of H atoms to form H_2. Such a mechanism, however, does not appear probable in this case, because Ni metal must be present at the interface between NiO and $SrTiO_3$ for an efficient photoreaction. We propose the model in which the electron donation to H^+ occurs on the NiO surface. The thickness of NiO on $SrTiO_3$ powder was estimated to be in order of 100 Å according to the results of SEM and TEM (*17*). Therefore, two possible ways for the electron transfer can be taken into consideration. These two models are illustrated schematically in Fig. 9. One is a direct electron transfer from Ni metal to H^+ which is adsorbed on the NiO surface, and another is an electron transfer from the conduction band of NiO. In the latter case, both NiO and $SrTiO_3$ have to be excited by photons. Actually NiO as well as $SrTiO_3$ are irradiated in the working state. This model would be regarded as an example of a particulate system of a *p–n* type photochemical diode which was proposed by Nozik (*22*). Goodenough *et al.* (*20*) concluded that the low efficiency of photoresponse of NiO single crystal is due to the small diffusion length of electrons. In the present case, the thickness of NiO may be comparable to the diffusion length (≈100 Å) of NiO.

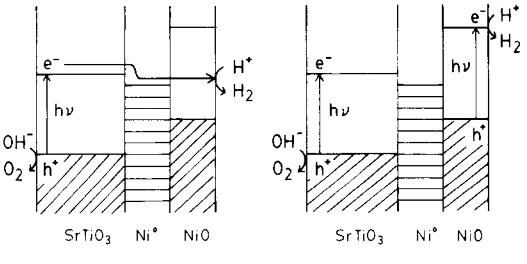

FIG. 9. The possible mechanisms of H_2O decomposition over NiO–$SrTiO_3$ powder system under irradiation. (a) One-photon scheme: photon is absorbed in $SrTiO_3$. (b) Two-photon scheme: photons are absorbed both in $SrTiO_3$ and in NiO.

So far, we have discussed the mechanism of the reaction on the basis of an electrochemical model of a semiconductor electrode. However, there may be critical differences between the particulate system at the submicrometer level and the electrode system, and some of those have already been pointed out (*23*). Based on these points of view, further studies are now proceeding in our laboratory.

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REFERENCES

1. Fujishima, A., and Honda, K., *Bull. Chem. Soc. Jpn.* **44,** 1148 (1971).

2. Fujishima, A., and Honda, K., *Nature* (*London*) **238,** 37 (1972).
3. Wrighton, M. S., Ellis, A. B., Wolczanski, P. T., Morse, D. L., Abrahamson, H. B., and Ginley, D. S., *J. Amer. Chem. Soc.* **98,** 2774 (1976).
4. Ellis, A. B., Kaiser, S. W., and Wrighton, M. S., *J. Phys. Chem.* **80,** 1325 (1976).
5. Leygraf, C., Hendewerk, M., and Somorjai, G. A., *Proc. Natl. Acad. Sci. USA* **79,** 5739 (1982).
6. Domen, K., Naito, S., Soma, M., Onishi, T., and Tamaru, K., *J. Chem. Soc., Chem. Commun.* **543** (1980).
7. Domen, K., Naito, S., Soma, M., Onishi, T., and Tamaru, K., *J. Phys. Chem.* **86,** 3657 (1982).
8. Domen, K., Naito, S., Onishi, T., and Tamaru, K., *Chem. Phys. Lett.* **92,** 433 (1982).
9. Lehn, J. M., Sauvage, J. P., and Ziessel, R., *Nouv. J. Chim* **4,** 623 (1980).
10. Lehn, J. M., Sauvage, J. P. Ziessel, R., and Hilaire, L., *Israel J. Chem.* **22,** 168 (1982).
11. Sato, S., and White, J. M. *Chem. Phys. Lett.* **72,** 83 (1980).
12. Sato, S., and White, J. M., *J. Catal.* **69,** 128 (1981).
13. Kawai, T., and Sakata, T., *Chem. Phys. Lett.* **72,** 87 (1980).
14. Grätzel, M., *Ber. Bunsenges. Phys. Chem.* **84,** 981 (1980).
15. Borgarello, E., Kiwi, J., Pelizzetti, E., Visca, M., and Grätzel, M., *Nature* **289,** 158 (1981).
16. Borgarello, E., Kiwi, J., Pelizzetti, E., Visca, M., and Grätzel, M., *J. Amer. Chem. Soc.* **103,** 6324 (1981).
17. Domen, K., Kudo, A., Onishi, T., Kosugi, N., and Kuroda, H., *J. Phys. Chem.* **90,** 292 (1986).
18. Wagner, F. T., and Somorjai, G. A., *J. Amer. Chem. Soc.* **102,** 5494 (1980).
19. Hope, G. A., and Bard, A. J., *J. Phys. Chem.* **87,** 1979 (1983).
20. Dare-Edwards, M. P., Goodenough, J. B., Hamnett, A., and Nicholson, N. D., *J. Chem. Soc., Faraday Trans. 2* **77,** 643 (1981).
21. Koffyberg, F. P., and Benko, F. A., *J. Electrochem. Soc.* **128,** 2476 (1981).
22. Nozik, A. J., *Appl. Phys. Lett.* **30,** 567 (1977).
23. Fujii, M., Kawai, T., and Kawai, S., *Chem. Phys. Lett.* **106,** 517 (1984).