May, 1984] © 1984 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 57, 1179—1183 (1984) 1179

Photoelectrochemical Oxidation of Alcohols on Polycrystalline Zinc Oxide

Ju-seong Lee,[†] Tamihiko Kato,[††] Akira Fujishima,* and Kenichi Honda
Department of Synthetic Chemistry, Faculty of Engineering, The University of Tokyo, Bunkyo-ku, Tokyo 113

(Received August 29, 1983)

The current doubling behavior of alcohols was studied on an n-type ZnO polycrystalline electrode. The increase in photocurrent due to alcohols on the ZnO depended on pH of the solution. The photocurrent was almost doubled in alkaline solution. It was found that the ZnO photoanode dissolved in the neutral aqueous solution but the dissolution reaction of ZnO was completely suppressed in alkaline solution at a sufficiently large pH. From the experimental results obtained by the rotating ring disk electrode and gas chromatographic and mass spectrometric analyses, a mechanism of the current-doubling reaction is proposed.

Most recent investigations of semiconductor electrodes have been concerned with the utilization of solar energy in which water is photoelectrolyzed to hydrogen and oxygen.1–8)

Some studies of the electrochemical behavior of organic substances at semiconductor electrodes have been reported.9–13) For example, Morrison *et al.*14,15) reported a "current doubling effect" due to the anodic behavior of aqueous formate ion or alcohols at an illuminated zinc oxide single crystal semiconductor electrode. To account for the mechanism of current doubling they suggested that holes formed by photoirradiation of an n-type semiconductor react with the current doubling agent R to give $R^{\dot{+}}$, which then donates an electron to the conduction band and becomes R^{2+}. However, the photodissolution reaction of zinc oxide was not mentioned.

Subsequently, similar effects were reported on other semiconductor electrodes. Gerischer *et al.*16,17) found current doubling behavior on a cadmium sulfide single crystal electrode when alcohols or aldehydes were added to the electrolyte. Tamura *et al.*18) observed that the photooxidation current for a titanium dioxide single crystal electrode was increased by the addition of alcohols in acidic aqueous solution.

Our earlier studies19–22) with the zinc oxide electrode in neutral aqueous solution showed that as the photocurrent was increasd, oxygen evolution could not be observed but zinc ions were detected in the electrolyte solution after the photoelectrolysis. The amount of zinc ions dissolved was almost equivalent to the charge of holes that flowed to the zinc oxide surface. These facts indicated that the current doubling effect may not always follow Morrison's mechanism.

In this paper, we re-examine the mechanism of current doubling by using a polycrystalline zinc oxide electrode and alcohols as the current doubling agent in solutions of various pH. Experimental measurements were made by rotating ring-disk electrode (RRDE) and gas chromatographic and mass spectrometric analyses of reaction products produced from a photoelectrolysis.

Experimental

Polycrystalline n-type zinc oxide pellets were made by pressing ZnO powder of reagent grade with a pressure of 0.5 t/cm^2 and then heating the pellets for 3 h at 1300 °C in air.21) Two kinds of semiconductor electrodes were made; one was of the conventional type and another was for a ring-disk electrode system. The pellet for photoelectrochemical measurements and macrophotoelectrolysis was 17 mm-diameter and about 2 mm-thick. The pellet for a smaller size cell, which was used for mass spectrometric analysis was 8 mm-diameter and about 2 mm-thick. After an ohmic contact was made with an In–Ga alloy, a lead wire was connected with silver paste, and then all surfaces except one side were covered with an epoxy resin.

The pellet for the ring-disk electrode was assembled with a 6 mm-diameter zinc oxide disk and an amalgamated gold ring 7 mm in inner diameter and 9 mm in outer diameter. The ring-disk electrode is schematically shown in Fig. 1 (a). The experimental setup of the RRDE followed previous paper.23)

The faces of both zinc oxide electrodes, which were exposed to the electrolyte solution, were polished with alumina powder, etched in 1 : 1 HCl–water mixed solution for 10 s, and then washed with distilled water.

A macroelectrolysis cell consisted of two compartments separated by a cation exchange membrane (Asahi Garasu, Selemion CMV). The volumes of anolyte and catholyte chambers were 100 and 80 ml, respectively. As shown in Fig. 1 (b), the cell was equipped with the polycrystalline n-type zinc

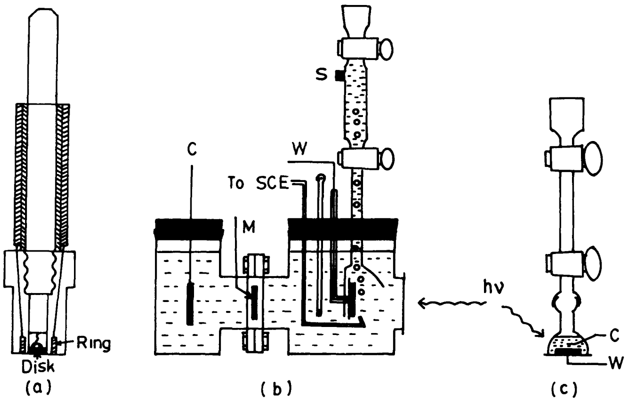

Fig. 1. Schematic diagrams of ring-disk electrode and photoelectrolysis cells.
(a) Ring-disk electrode, (b) macrophotoelectrolysis cell, (c) microphotoelectrolysis cell.
W: Working electrode, C: counter electrode, M: ion exchange membrane, S: rubber stopper.

[†] Department of Industrial Chemistry, College of Engineering, Hanyang University, Seoul 133, Korea.

[††] Department of Industrial Chemistry, Nagoya Institute of Technology, Gokiso, Showa-ku, Nagoya 466.

oxide working electrode, a platinum wire counter electrode, and a saturated calomel electrode (SCE) as a reference electrode. A smaller size cell, which was used for mass spectrometric analysis, was equipped with two electrodes, such as ZnO photoanode and Pt cathode, and the volume of electrolyte was 1 ml, as shown in Fig. 1 (c).

The light source was a 500 W high pressure mercury arc lamp (Ushio Denki) and the wavelength of the illuminating light was fixed at 360±30 nm by means of a glass filter (Toshiba Kasei, UV-D2). Current-potential behavior of the zinc oxide electrode was measured with a potentiostat/galvanostat system (Hokuto Denko), with a saturated calomel electrode as a reference and platinum as a counter electrode. All chemicals were of reagent grade. The oxygen and organic compounds produced were analyzed by means of gas chromatography (Hitachi Model 163) and mass spectrometry (Ulvac YTP-150). In the case of the gas chromatographic analysis, all liquid compounds except formaldehyde were analyzed by using polyethylene glycol 2000, polyethylene glycol 20 M and Chromosorb 101 (FID, temp 120 °C), and formaldehyde was chromatographed with Porapax N (TCD, temp 100 °C). The electrolyte solutions after electrolysis were injected into the gas chromatograph. Oxygen evolved was analyzed with Molecular Sieve SA on 60/80 mesh. The carrier gas was helium at a flow of 40 ml/min. The zinc ions in the electrolyte solutions were analyzed spectrophotometrically by using Zincon reagent in a pH 9.0 buffer solution. Before all experiments, the solutions were purged with nitrogen gas for more than 30 min.

Results

Typical current-potential curves for the electrolyte solution at pH 6 and 13 are shown in Fig. 2. In the dark, no anodic current was observed in both the presence or the absence of a current doubling agent, such as methyl alcohol. In the solution at pH 6, the anodic photocurrent appeared at −0.45 V *vs.* SCE, and then reached saturation under anodic polarization. With the addition of methyl alcohol to the solution, the saturated photoanodic current was increased by a factor of only 1.1. On the other hand, in the solution at pH 13, the onset potential of the anodic photocurrent was more negative by 0.4 V than the potential in the neutral solution. By addition of methyl alcohol to the alkaline solution, the photocurrent was almost doubled.

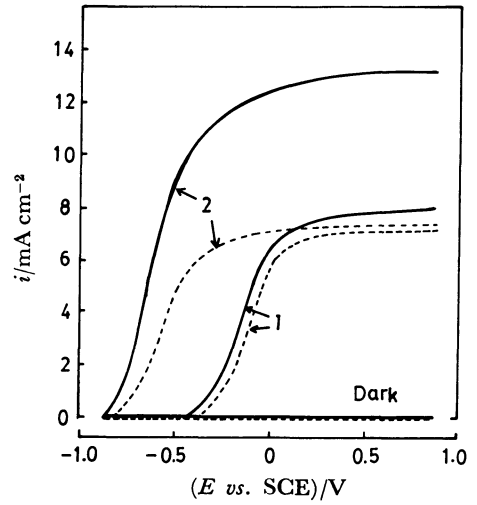

Fig. 2. Current-potential curves for polycrystalline n-type ZnO under illumination (λ=360+30 nm).
1: 0.2 M Na_2SO_4(pH 6), 2: 0.2 M Na_2SO_4+0.1 M NaOH (pH 13).
Dotted lines: $[CH_3OH]=0$; solid lines: $[CH_3OH]=$ 0.5 M

The pH dependences of the photocurrent ratio (i/i_0) of ZnO for various alcohols added to solution are shown in Fig. 3, where i and i_0 are the photocurrent in the presence and in the absence of a current doubling agent, respectively. The ratio i/i_0 increased for the solution containing a primary or secondary alcohol above pH 10, whereas the increase was not observed for a tertiary alcohol solution. Thus it was found that the increase in the photocurrent of ZnO for given alcohol depended very much on the pH of the solution, an effect which is important for the discussion of the reaction mech-

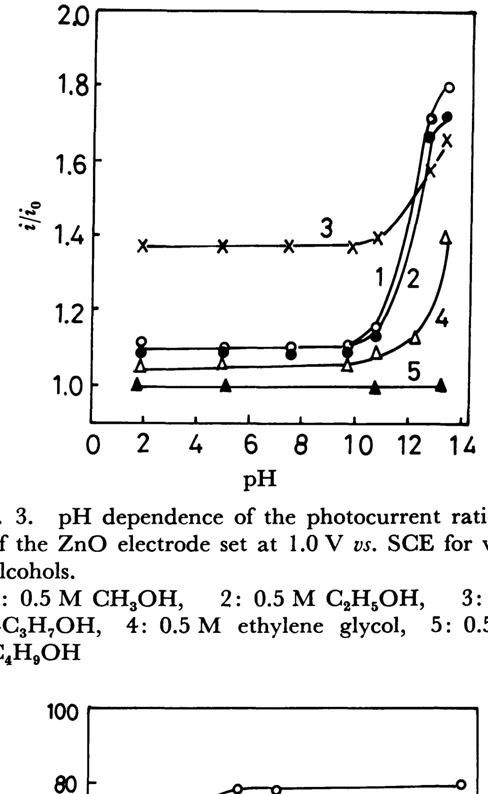

Fig. 3. pH dependence of the photocurrent ratio (i/i_0) of the ZnO electrode set at 1.0 V *vs.* SCE for various alcohols.
1: 0.5 M CH_3OH, 2: 0.5 M C_2H_5OH, 3: 0.5 M *i*-C_3H_7OH, 4: 0.5 M ethylene glycol, 5: 0.5 M *t*-C_4H_9OH

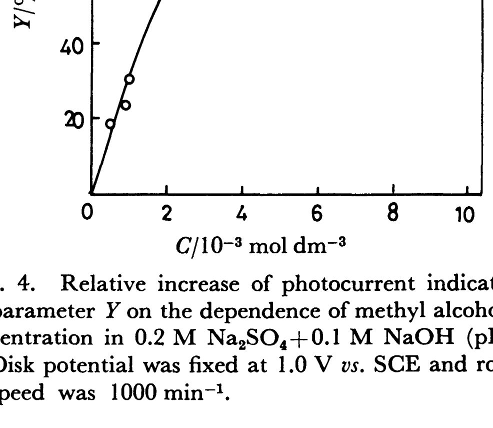

Fig. 4. Relative increase of photocurrent indicated by parameter Y on the dependence of methyl alcohol concentration in 0.2 M Na_2SO_4+0.1 M NaOH (pH 13). Disk potential was fixed at 1.0 V *vs.* SCE and rotating speed was 1000 min^{-1}.

anism. In addition to the pH effect, the α hydrogen of alcohols may be involved with the current doubling photoelectrochemical oxidation reaction.

To obtain more information on the current doubling behavior, the rotating disk electrode method was employed. For convenience, the effects of methyl alcohol concentration was evaluated by the parameter $Y=100(i-i_0)/i_0$ which references the increase in current to the photocurrent in an alkaline electrolyte. The dependence of the value of Y on the concentration of methyl alcohol in a solution containing 0.2 M Na_2SO_4+0.1 M NaOH (pH 13) (1 M=1 mol dm^{-3}) is shown in Fig. 4. The maximum Y value of 80% was obtained for CH_3OH at concentrations $\geq 4\times10^{-3}$ M. In case of methyl alcohol, the RRDE technique was applied to determine which reaction occurred on the ZnO photoanode in neutral and alkaline solutions. The current-potential curves at the disk and the ring electrode in solutions containing 0.2 M Na_2SO_4 are shown for pH 6 and 13 in Figs. 5 and 6, respectively. As shown in Fig. 5, for dark conditions at pH 6, the disk current was negligibly small at the fixed potential of +1.0 V *vs.* SCE, and at the ring electrode hydrogen evolution occurred at potentials more cathodic than −1.5 V *vs.* SCE. Under illumination in the absence of methyl alcohol, an anodic photocurrent flowed at the zinc oxide electrode. At the same time, a reduction current appeared at the ring electrode in the potential ranges more cathodic than −0.2 and −1.0 V, which corresponds to the reduction of oxygen and zinc ion, respectively. By addition of methyl alcohol to the solution, the magnitude of the disk photocurrent increased almost 1.1 or 1.2 times, but the ring current due to the reduction of zinc ion showed little change and the ring current for oxygen reduction disappeared from the current-potential curves.

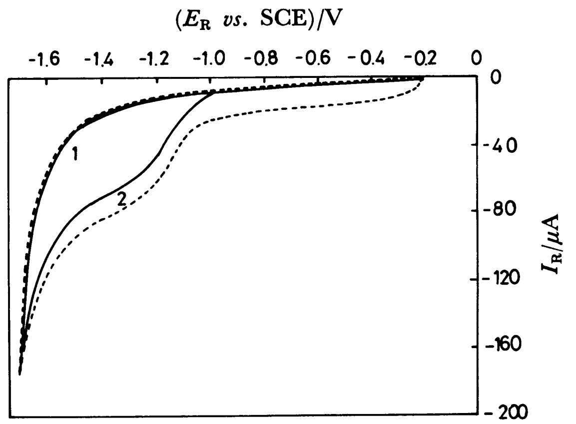

Fig. 5. Dependences of Au(Hg) ring current on the ring potential in a solution of 0.2 M Na_2SO_4(pH 6).
1: I_0: 0 μA (in dark), 2: I_0: dotted line 142 μA, solid line 182 μA (under illumination).
Dotted line is for $[CH_3OH]=0$ and solid line for $[CH_3OH]=5\times10^{-3}$ M.
The disk ZnO potential was fixed at 1.0 V *vs.* SCE. Rotating speed and scan rate were 1000 min^{-1} and 30 sV^{-1}, respectively.

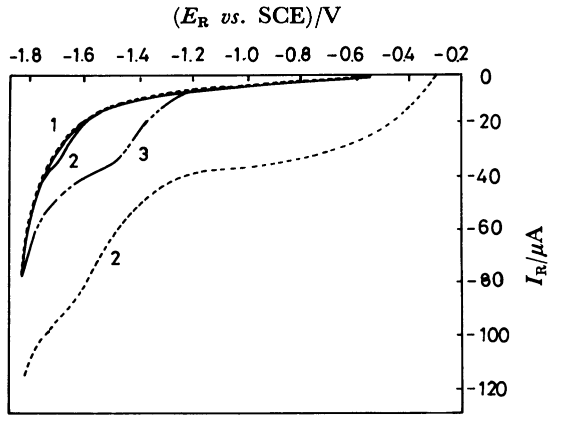

Fig. 6. Dependences of Au(Hg) ring current on the ring potential in a solution of 0.2 M Na_2SO_4+0.1 M NaOH(pH 13).
1: I_0: 0 μA (in dark), 2: I_0: dotted line 290 μA, solid line 540 μA (under illumination), 3: $[Zn^{2+}]=5\times10^{-5}$ M was added in dark.
Other conditions are the same as in Fig. 5.

However, in the alkaline solution (pH 13) the behaviors of the ring and the disk currents were different from those in the neutral solution. As shown in Fig. 6, under illumination on the disk electrode of the ZnO in the absence of methyl alcohol, the ring reduction current due to oxygen appeared from −0.3 V *vs.* SCE but that due to the zinc ion was not observed. The dotted curve 2 of the ring current in Fig. 6 almost coincides with the reduction of oxygen at the dropping mercury electrode reported by Kolthoff.[24] Therefore, the first cathodic wave corresponds to the reduction of dissolved oxygen to hydrogen peroxide and the second wave to the reduction of peroxide to hydroxide ion.

By addition of methyl alcohol to the solution of pH 13, the disk photocurrent increased nearly two times that of the initial photocurrent. At the same time, the reduction current which corresponds to the reduction of oxygen disappeared in the potential range between −0.3 and −1.6 V, but a new wave appeared at a potential of about −1.6 V *vs.* SCE. This new wave might correspond to a reduction current due to formaldehyde formed by photoelectrolysis of methyl alcohol. If dissolution of ZnO photoelectrode occurred in alkaline solution as well as in the neutral solution, the reduction wave of Zn^{2+} should have been observed in Fig. 6. Upon addition of zinc ion to the solution of pH 13, the ring current corresponding to the reduction of Zn^{2+} appeared at a potential of −1.25 V (curve 3 in Fig. 6).

From the experimental results shown in Figs. 5 and 6, it is concluded that the n-type ZnO photoanode dissolved in the neutral aqueous solution but not in the alkaline aqueous solution around pH 13, with or without a current doubling reagent.

In addition to the experimental results of the RRDE measuremnt, the weight changes of the ZnO anode before and after macroelectrolysis under illumination were measured. The weight loss in neutral solution was quantitatively proportional to the quantity of electricity flowed, but a weight change of ZnO could not detect in the alkaline solution at pH 13. Consequently, the ZnO photoanode does not dissolve in adequately alkaline solution during macrophotoelectrolysis, a result which confirms the RRDE measurements.

The data in Table 1 show the results obtained by

TABLE 1. PHOTOELECTROCHEMICAL REACTION OF POLYCRYSTALLINE *n*-TYPE ZnO ELECTRODE IN ALCOHOLIC SOLUTION

Electrolyte	Av. photocurrent density/mA cm^{-2}	Quantity of electricity / C	Current efficiency/% Zn^{2+}	O_2	Org. compd
Without alcohol					
1	6.8	50	98.2	95.5	—
2	7.0	50	0	100.2	—
With 0.5 M MeOH					Formaldehyde
1	7.8	100	99.3	0	18.5
2	13.5	100	0	0	75.0
With 0.5 M EtOH					Acetaldehyde
1	8.2	100	97.9	0	93.8
2	11.8	100	0	0	95.3
With 0.5 M *i*-PrOH					Acetone
1	11.2	100	98.8	0	81.1
2	12.5	100	0	0	90.7

Electrolyte: 1; 0.2 M Na_2SO_4 (pH 6), 2; 0.2 M Na_2SO_4+0.1 M NaOH (pH 13). Illumination wavelength; 360± 30 nm.

macrophotoelecrolysis. In neutral solution in the absence of alcohol, the current efficiencies of evolved oxygen and dissolved Zn^{2+} ion are almost 100%, respectively. On the other hand, in the alkaline solution in the absence of alcohol, the current efficiency for dissolved Zn^{2+} was zero but that of evolved oxygen was maintained at 100%. By addition of alcohols (0.5 M) to the neutral or alkaline solution, oxygen evolution was not observed. In these cases, aldehyde or ketone which corresponds to the oxidation product of a primary or secondary alcohol was observed. During photoelectrolysis the pH of the anolyte decreased gradually in the alkaline alcoholic solution but in the case of the neutral solution the pH of the anolyte was almost constant.

Photoelectrolysis resulted in formation of a small amount of formaldehyde compared with the amount of acetaldehyde or acetone produced. To examine this phenomena, the gas evolved from the electrolyte solution was analyzed by mass spectrometry after the continuous photoelectrolysis to one half the theoretical charge (quantity of electricity) in the alkaline 0.1 M CH_3OH solution (pH 13) using the small size cell. The mass spectrum showed strong signals of H_2 (*m/z* 2), unreacted methyl alcohol (*m/z* 31, 32), formaldehyde (*m/z* 18, 29, 30), CO_2 (*m/z* 44), and a very weak signal of formic acid (*m/z* 46).[25] Hydrogen probably was evolved from the Pt cathode during the electrolysis. The CO_2 is the oxidation product of methyl alcohol on ZnO where part of the formaldehyde produced is oxidized to CO_2.

Discussion

In general, when an oxide or hydrous oxide is immersed in an aqueous solution, protons and hydroxide ions become adsorbed.[26] The pH-dependence of the adsorption on the surface of the ZnO electrode could be explained by assuming reactions (1) and (2) at the electrode surface facing the electrolyte solution, that is, hydroxide ions are adsorbed on Lewis acid sites in alkaline solution and protons are adsorbed on Lewis base sites in weak acid or neutral solution.

$$ZnO + OH^- \longrightarrow ZnO\text{-}OH^- \text{ (in alkaline solution)}, \quad (1)$$

$$ZnO + H^+ \longrightarrow ZnO\text{-}H^+ \text{ (in weak acid or neutral solution)}. \quad (2)$$

The photo-produced holes coming to the ZnO surface may interact with, and oxidize, these adsorbed hydroxide ions or surfaces adsorbed protons. For example, hydroxyl radicals could be produced by reactions (3) and (4)

$$ZnO\text{-}OH^- + h^+ \longrightarrow ZnO + \cdot OH, \quad (3)$$

$$ZnO\text{-}H^+ + h^+ \longrightarrow Zn^{2+} + \cdot OH. \quad (4)$$

Thus the corrosion of the ZnO can occur readily in the neutral solution and be suppressed in alkaline solution. Then, the $\cdot CH_2OH$ radical formed by the reaction between the $\cdot OH$ radical and the α hydrogen of alcohol as in reaction (5) can result in donation of an electron to the conduction band of ZnO, as in reaction (6),

$$\cdot OH + CH_3OH \longrightarrow \cdot CH_2OH + H_2O, \quad (5)$$

$$\cdot CH_2OH + OH^- \longrightarrow HCHO + H_2O + e^-. \quad (6)$$

The net reaction occurring in alkaline solution is obtained by combining reactions (1), (3), (5), and (6)

$$CH_3OH + 2OH^- + h^+ \longrightarrow HCHO + 2H_2O + e^-. \quad (7)$$

The net reaction in weak acid or neutral solution is obtained by combining reactions (2), (4), (5), and (6).

$$ZnO + CH_3OH + h^+ \longrightarrow Zn^{2+} + HCHO + H_2O + e^- \quad (8)$$

Yamase *et al.*,[27] using an esr spin trapping method, detected simultaneously $\cdot OH$ and $\cdot CH_2OH$ radicals as intermediate of the photocatalytic reaction in an aqueous methyl alcohol solution containing polytungstate ion. Thus, reaction (5) is substantiated by their results.

The pH of the alkaline methyl alcohol solution after photoelectrolysis decreased in proportion to the quantity of electricity, but the pH of the neutral solution was much the same as that of the initial solution.

Hence, the observation of current increase (*e.g.* current doubling) makes it clear that hydroxide ion is involved in the reaction mechanism, as in Eq. (6). It is apparent that the current increasing reaction easily takes place in the alkaline solution for which $[OH^-] \geq 10^{-4}$M. In the case of the neutral solution, the small current increasing can be accounted for by the low concentration of hydroxide ions.

As a result of mass spectrometric and chemical analysis, considerable amount of carbon dioxide is detected after photoelectrolysis. This result supported the fact that formaldehyde is produced by oxidation of methyl alcohol on a ZnO photoanode and that the formaldehyde which is produced seems to be oxidized further up to carbon dioxide.

It is also concluded that the n-type ZnO photoanode dissolved in the neutral aqueous solution but not in the alkaline aqueous solution around pH 13, with or without a current doubling reagent.

References

1) A. Fujishima and K. Honda, *Nature*, **238**, 37 (1972).
2) H. Gerischer, *J. Electroanal. Chem.*, **58**, 263 (1975).
3) A. J. Nozik, *Ann. Rev. Phys. Chem.*, **29**, 189 (1978).
4) M. Tomkiewicz and H. Fay, *Appl. Phys.*, **18**, 1 (1979).
5) M. S. Wrighton, *Acc. Chem. Res.*, **12**, 303 (1979).
6) F. F. Fan, B. L. Wheeler, A. J. Bard, and R. N. Noufi, *J. Electrochem. Soc.*, **128**, 2042 (1981).
7) R. A. Simon, A. J. Ricco, and M. S. Wrighton, *J. Am. Chem, Soc.*, **104**, 2031 (1982).
8) D. G. Canfield and S. R. Morrison, *Appl. Surface Sci.*, **10**, 493 (1982).
9) T. Freund and W. P. Gomes, *Cat. Rev.*, **3**, 1 (1969).
10) S. N. Frank and A. J. Bard, *J. Am. Chem. Soc.*, **99**, 4667 (1977).
11) K. Nakatani and H. Tsubomura, *Bull. Chem. Soc. Jpn.*, **50**, 783 (1977).
12) B. Kraeutler and A. J. Bard, *J. Am. Chem. Soc.*, **99**, 7729 (1977).
13) J. Ludvik, J. Klima, J. Volke, A. Kurfurst, and J. Kuthan, *J. Electroanal. Chem.*, **138**, 131 (1982).
14) S. R. Morrison and T. Freund, *J. Chem. phys.*, **47**, 1543 (1967); *Electrochim. Acta,* **13** 1344 (1968).
15) W. P. Gomes, T. Freund, and S. R. Morrison, *J. Electrochem. Soc.*, **115**, 818 (1968); *Surface Sci.* **13**, 201 (1968).
16) H. Gerischer and H. Rösler, *Chemie-Ing.-Tech.*, **42**, 176 (1970).
17) K. Micka and H. Gerischer, *J. Electroanal. Chem.*, **38**, 397 (1972).
18) M. Miyake, H. Yoneyama, and H. Tamura, *Chem. Lett.*, **1976** 635; *Denki Kagaku,* **45**, 411 (1977).
19) A.Fujishima, Ph. D Thesis, The University of Tokyo (1971).
20) A. Fujishima and K. Honda, *Denki Kagaku,* **40**, 33 (1972).
21) A. Fujishima, T. Kato, E. Maekawa, and K. Honda, *Bull. Chem. Soc. Jpn.*, **54**, 1671 (1981).
22) Y. Maeda, A. Fujishima, and K. Honda, *J. Electrochem. Soc.*, **128**, 1731 (1981).
23) T. Inoue, T. Watanabe, A. Fujishima, K. Honda, and K. Kohayakawa, *J. Electrochem. Soc.*, **124**, 719 (1977).
24) I. M. Kolthoff and C. S. Miller, *J. Am. Chem. Soc.*, **83**, 1013 (1941).
25) J. G. Grasselli, Edited, "Atlas of Spectral Data and Physical Constants for Organic Compounds," CRC Press, Ohio (1973).
26) S. R. Morrison, "Electrochemistry at Semiconductor and Oxidized Metal Electrodes," Plenum Press, N. Y. (1980).
27) T. Yamase and N. Takabayashi, Symposium on Catalytic Chemistry to be concerned in Solar Energy Conversion, Abstract p. 46, held on June 3, 1983 at Institute of Physical and Chemical Research, Saitama, Japan.