Photoelectrochemical Behavior of n-Type TiO2 and Other Semiconductor Electrodes in Acetonitrile Solutions Containing Various Aromatic Amines

Kenji NAKATANI and Hiroshi TSUBOMURA

Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560

(Received November 18, 1976)

The electrode behavior of n-type TiO_2 in acetonitrile solutions containing one of a variety of aromatic amines under illumination has been investigated. The onset potential of the anodic photocurrent leading to the oxidation of the amines changed from the most negative -0.51 V *vs.* SCE for *N*,*N*,*N'*,*N'*-tetramethyl-*p*-phenylenediamine to the least negative -0.27 V for aniline. These values parallel the change of the flat band potential by the amine and become more negative as the ionization potential of the amine decreases. The influence of the amine on the flat band potentials of ZnO, CdS, and GaP was also studied and found to be much less than in the case of TiO_2. From these results, the reason for the change of the flat band potential in the case of TiO_2 is attributed to a specific charge transfer interaction between the semiconductor and the amine.

The electro-photochemical behavior of semiconductor electrodes in aqueous solutions has been extensively studied for various semiconductors such as GaP,[2] ZnO,[3,4] CdS,[5,6] TiO_2,[7-9] and others.[13] The photocurrents observed for the n-type semiconductors such as GaP, ZnO and CdS under illumination are attributed to the anodic dissolution of the electrodes. Honda and Fujishima found that the n-type TiO_2 electrode is electrochemically stable and the electrode reaction under illumination is the decomposition of water.[7,8] A similar photoeffect may also play a role in organic electrosynthesis using sunlight as an energy source. However, very few studies have been made on the electrode behavior of semiconductors in non-aqueous solutions,[14] although it seems important for the elucidation of semiconductor properties as well as for use in organic synthesis.

We have now carried out studies in this relatively unexplored area and, in this paper, report the results on the n-type TiO_2 electrodes under illumination in acetonitrile solutions.

Experimental

Single crystals of TiO_2 in the form of a wafer with optically flat (001) surfaces were obtained from Nakazumi Crystals Corp. The electrodes were constructed in a way similar to those used in our previous work.[9] Figure 1 shows the experimental setup. High purity nitrogen gas was bubbled through the solution in order to remove oxygen. A saturated calomel electrode (SCE) was used as the reference electrode. Acetonitrile was purified according to the literature.[10] In order to prevent contamination by water, the SCE was placed in a vessel connected with a tube to the electrochemical cell. Both the vessel and the tube were filled with the same solution as that in the cell. Lithium perchlorate, dried at 180 °C for 6 h *in vacuo*, was used as a supporting electrolyte at the concentration of 0.1 M (mol dm^{-3}). Aromatic amines were purified from reagent grade materials by recrystallization or sublimation *in vacuo*. A 250 W super high pressure mercury lamp was used as the light source. The light was passed through a Toshiba UV-35 filter. A Hokutodenko HA 101 potentiostat and a Shimadzu VM 101 voltammeter were used for measurements of the voltage and current of the photo-cells. Differential capacitance measurements were made by use of a Yokogawa Hewlet-Packard 4265B Universal Bridge.

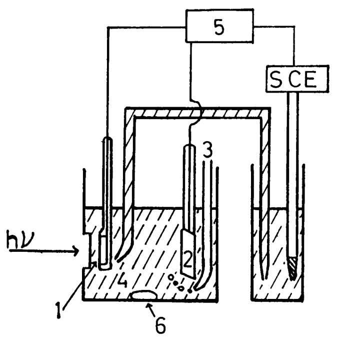


Fig. 1. Schematic diagram of the electrochemical cell. 1: TiO_2 electrode, 2: Pt electrode, 3: N_2 gas inlet, 4: CH_3CN solution containing 0.1 M $LiClO_4$, 5: potentiostat, 6: magnetic stirrer.

Results

Figure 2 shows typical current-voltage curves. In the dark, no anodic current was observed. From curves 1 and 2, we can see that the photocurrent for the acetonitrile solution shows no change in the onset potential, but an increase in the saturation current by addition of 0.8 M water. This result shows that the anodic photocurrent observed in the range 0 to +1 V, in the

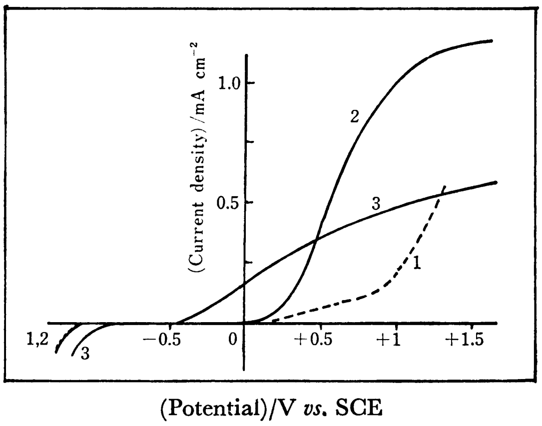


Fig. 2. Photocurrent density-potential curves for the TiO_2 electrode in acetonitrile solutions (0.1 M $LiClO_4$). 1: CH_3CN solution, 2: CH_3CN solution containing 0.8 M H_2O, 3: CH_3CN solution containing 10^{-3} M *p*-PD.

absence of amine, is not due to the oxidation of the solvent but to the decomposition of water dissolved in a trace amount. On the other hand, the anodic photocurrent of the solution containing 10^{-3} M *p*-phenylenediamine (*p*-PD) appeared at around −0.4 V, showing that the onset potential of the photocurrent shifted to the cathodic side by *ca.* 0.4 V by the addition of the amine. The onset potentials of the photocurrents for the other amines, *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD), *N,N*-dimethyl-*p*-phenylenediamine (DMPD), *N,N*-dimethylaniline (DMA), *p*-toluidine (PTD) and aniline (AN), differed from each other as shown in Fig. 3.

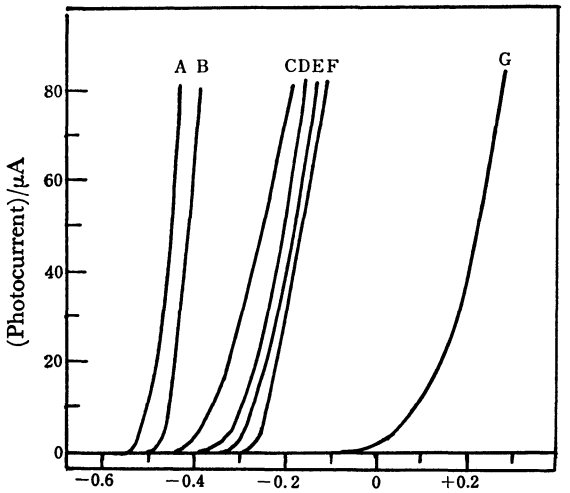


Fig. 3. Photocurrent-potential curves for the TiO_2 electrode in acetonitrile solutions containing 10^{-3} M amines.
A: TMPD, B: DMPD, C: *p*-PD, D: DMA, E: *p*-TD, F: AN, G: 0.8 M H_2O.

Although the onset potential is usually regarded to be approximatly equal to the flat-band potential (V_{fb}), more exact information about V_{fb} can be obtained from the differential capacitance measurements. A plot of $1/C^2$ against the electrode potential, V, according to the Schottky-Mott equation[1]

$$1/C^2 = (2/\varepsilon\varepsilon_0 eN_D)(V - V_{fb} - kT/e) \quad (1)$$

gives the flat band potential and the donor density (N_D), where C represents the space charge capacitance, e the electronic charge, ε the dielectric constant of the TiO_2, and ε_0 the permittivity of vacuum. Some typical results of the measurements are shown in Fig. 4. The donor concentration determined from these plots by assuming ε for TiO_2 to be 120[12] is about 8×10^{18} cm^{-3}. Though the V_{fb} for the TiO_2 in acetonitrile obtained from the Schottky-Mott plot varied with specimen between −0.64 V and −1.1 V (the value most frequently obtained being *ca.* −1.0 V), a constant shift of V_{fb} to the cathodic direction was obtained by adding an amine into the solution as shown by ΔV_{fb} in Table 1. An almost constant value was obtained for the V_{fb} for the aqueous solution of 0.1 M $LiClO_4$ to be −0.80 V. The onset potentials of the photocurrents, V_0, given in Table 1 are more positive than the V_{fb} in each of the

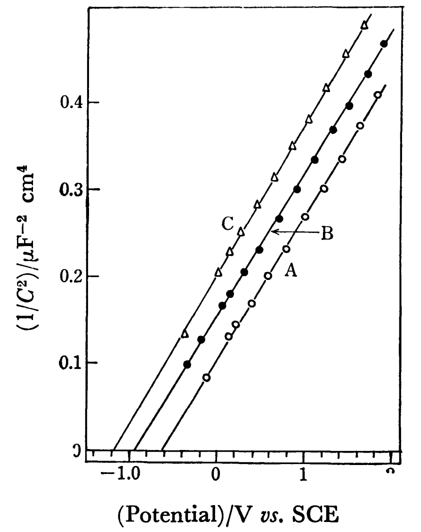


Fig. 4. Schottky-Mott plots of the capacitance *vs.* electrode potential for the TiO_2 in acetonitrile solutions.
A: 0.1 M CH_3CN solution of $LiClO_4$, B: CH_3CN solution containing 2×10^{-3} M DMA, C: CH_3CN solution containing 2×10^{-3} M TMPD.

TABLE 1. ONSET POTENTIALS OF THE PHOTOCURRENT OF THE TiO_2 ELECTRODE FOR VARIOUS ACETONITRILE SOLUTIONS CONTAINING 10^{-3} M AMINES AND THE RELATED QUANTITIES

	E_0[a] (V *vs.* SCE)	I_p^v(eV)[b]	V_0[c] (V *vs.* SCE)	ΔV_{fb}(V)[h]
N,N,N′,N′-Tetramethyl-*p*-phenylenediamine		6.75[d]	−0.51	−0.50
N,N-Dimethyl-*p*-phenylenediamine		6.97[d]	−0.46	−0.44
p-Phenylenediamine	0.20	7.4[e]	−0.41	−0.40
N,N-Dimethylaniline		7.51[f]	−0.33	−0.30
p-Toluidine	0.73	7.78[f]	−0.30	−0.24
Aniline	0.87	8.04[f]	−0.25	−0.20
Water		12.61[g]	−0.05	

a) Oxidation potential of amine on Pt in CH_3CN solution. K. Sakaki, A. Kitani, and M. Tsuboi, *Nippon Kagaku Kaishi*, **1973**, 2269. b) Vertical ionization potential in gas phase. c) Onset potential of the photocurrent in acetonitrile solution. d) Y. Nakato, M. Ozaki, and H. Tsubomura, *Chem. Phys. Lett.*, **9**, 615 (1971). e) T. Tani, *Denki Kagaku*, **41**, 683 (1973). f) A. D. Baker, D. P. May, and B. W. Turner, *J. Chem. Soc., B*, **1968**, 22. g) W. C. Price, *J. Chem. Phys.*, **4**, 147, 539 (1936). h) Shift of V_{fb} caused by addition of amine.

Table 2. Flat band potentials of TiO_2, ZnO, CdS, and GaP in acetonitrile solutions (V *vs.* SCE)

	TiO_2	ZnO	CdS	GaP
in CH_3CN	−1.05	−0.20	−0.80	−1.24
p-PD(2×10^{-3} M/l)	−1.45	−0.25	−0.84	−1.54

corresponding solutions. However, the onset potentials for various amines parallel the corresponding ΔV_{fb} values. This change in V_{fb} by the addition of the amine does not occur in water but only in the acetonitrile solutions. The sequence of the V_{fb}'s for various amines did not change even when the supporting electrolyte concentration was increased from 0.1 to 0.4 M or the donor concentration of the TiO_2 was altered. Table 2 gives the V_{fb} values for other semiconductors, CdS, GaP, and ZnO in acetonitrile solutions with and without 2×10^{-3} M *p*-PD.

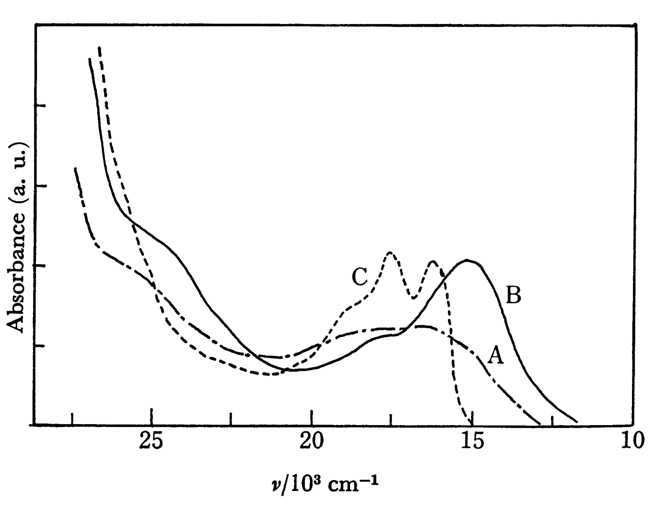
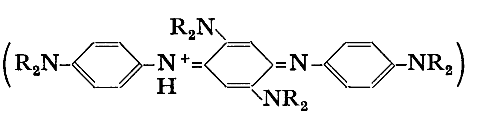


Fig. 5. The absorption spectra of acetonitrile solutions of 0.1 M $LiClO_4$ and 10^{-3} M amine after photo-anodic reactions A: *p*-PD, B: DMPD, C: TMPD.

The absorption spectra of the acetonitrile solutions were measured after letting the anodic photocurrent flow in the cell in order to identify the reaction products formed from the amines (Fig. 5). The spectra for the case of *p*-PD and DMPD resemble those of the Bandrowski's bases



formed by the oxidation of the respective amine.[16] As it has been established that these Bandrowski's bases are formed by the reactions between the radical cations *p*-PD^{+} or $TMPD^{+}$ and the neutral amines, the detection of the Bandrowski's bases shows that the primary products of the photo-anodic reactions at the electrodes are the cation radicals of the amines. The absorption spectrum, in the case of TMPD, resembles that of $TMPD^{+}$.[17] On the other hand, for aniline and dimethylaniline, the solutions remained colorless, a black solid substance being formed on the Pt surface, presumably the condensation reaction products formed from oxidized amines.

Discussion

On excitation of the TiO_2 electrode at the wavelength corresponding to the band gap (3.0 eV),[7] electrons are promoted from the valence band to the conduction band and driven inward by the electric field existing in the space charge layer, while the holes created in the valence band move onto the surface and presumably oxidize the molecules having oxidation potentials lower than the higher limit of the valence band (E_v) at the surface. The ionization potentials in acetonitrile, I_p(sol), of the amines used in this experiment are calculated to be 5.8 eV for TMPD and 6.3 eV for AN by the use of Born's equation,

$$I_p(\mathrm{sol}) = I_p(\mathrm{g}) - (e^2/2r)(1-1/n^2)$$

where I_p(g) represents the gas phase ionization potential of the amine, r the radius of the amine molecule, and n the refractive index of acetonitrile.[20]

The lower limit of the conduction band of TiO_2 (E_c) is calculated to be 3.7 eV by use of the flat band potential −1.0 V (*vs.* SCE) and the absolute energy level of SCE, *ca.* 4.7 eV.[21] Then, the higher limit of the valence band of the TiO_2 (E_v) is obtained to be *ca.* 6.7 eV using the band gap energy 3.0 eV of TiO_2.[7] Therefore, it is reasonable to assume that the amines are oxidized by the photoexcited TiO_2 electrode. The oxidation of the amine was experimentally verified from the absorption spectra of the solutions after illumination at the closed circuit condition, which showed the spectra of the oxidation products.

As described earlier, the onset potentials of the photocurrents and the flat band potentials are changed by adding amines to the solution. The magnitudes of the changes of these two types of potentials are parallel to each other and both become more negative, as the ionization potential of the amine is lowered. The flat band potential, V_{fb}, of the TiO_2 electrode has been reported to shift to the more negative direction with increasing pH of the electrolyte solution.[11] This shift of V_{fb} is explained by taking account of the increase of the negative charge at the surface of the TiO_2, which is produced by the following proton dissociation equilibrium.

$$-\overset{|}{\underset{|}{\mathrm{Ti}}}\mathrm{OH} \rightleftarrows -\overset{|}{\underset{|}{\mathrm{Ti}}}\mathrm{O}^- + \mathrm{H}^+$$

It was also reported that the V_{fb}'s of ZnO[15] and GaP[19] have the similar pH dependence as that of the TiO_2, while CdS does not.[11]

It might be concluded therefore that the shift of V_{fb} of TiO_2 is caused by the enhanced proton dissociation by the amine. In order to verify this, we studied the V_{fb} of TiO_2 by changing the concentration of *p*-toluidine, whose basicity is relatively weak, from 10^{-6} to 5×10^{-2} M in the acetonitrile solution. The V_{fb} changed from −0.64 to −0.9 V as the amine concentration increased from 10^{-6} to 10^{-5} M and then remained almost constant up to the amine concentration of 5×10^{-2} M. This result shows that if the proton dissociation were to occur by the addition of the amine, it comes to equilibrium at a very small concentration of amine. Therefore, it is clear that the difference of the ΔV_{fb} given in Table 1, which are for solutions containing 2×10^{-3} M amine, is not explained by the proton dissociation equilibrium.

As shown in Table 2, the change of V_{fb} for TiO_2 by the addition of *p*-PD is indeed large. But the change for GaP is much less and there is hardly any change for ZnO and for CdS. These results for GaP and especially for ZnO show also that the change in V_{fb} for these semiconductors cannot be explained by the proton dissociation equilibrium.

It seems, therefore, that there is a specific interaction, which affects the V_{fb}, between the semiconductor and the amine on the interface. One possibility is a charge transfer interaction. If one assumes that the TiO_2 electrode has unoccupied intrinsic surface states, the charge transfer interaction (S⋯D) between the amine (D) and the surface state (S) might bring about a surface dipole on the semiconductor, and cause a potential drop at the interface. Consequently, the V_{fb} of the TiO_2 electrode will shift towards the negative direction. The degree of the shift at a given concentration of amine depends on the degree of charge transfer between the amine and the surface state. The stronger the charge transfer force is, the greater is the negative shift of V_{fb}. The degree of charge transfer, X, is expressed approximately as $\sqrt{X}=\beta/(I_p-W_s)$,[18] where $-W_s$ is the energy of the surface state, I_p the ionization potential of the amine, and β the interaction energy between the ground state (S⋯D) and the ionized state ($S^-\cdots D^+$). It can then be expected that the change of the onset potential for the anodic photocurrent and that of V_{fb} will be proportional to $\sqrt{X}$. As shown in Fig. 6, straight lines are obtained for the plots of V_0 and ΔV_{fb} *vs.* $\sqrt{X}$ by assuming W_s to be 5.3 eV, which seems to be of a fairly reasonable magnitude (Fig. 6). These results seem to support our present interpretation by use of the specific charge transfer interaction of the surface state with the amine.

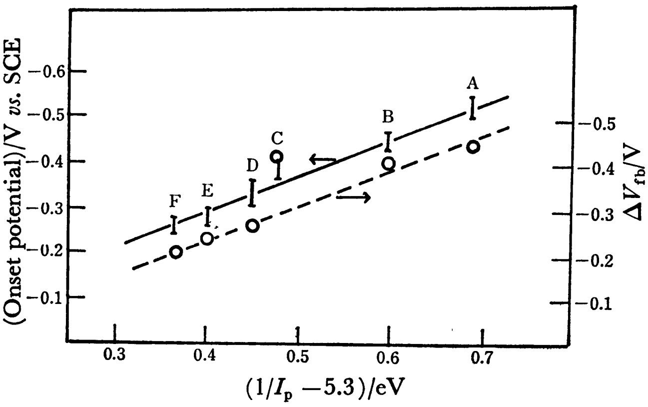


Fig. 6. Dependence of the onset potential of the photocurrent and that of V_{fb} on the ionization potential of amines.

A: TMPD, B: DMPD, C: *p*-PD, D: DMA, E: *p*-TD, F: AN.

As stated in the Results, the V_{fb} of the TiO_2 electrode in aqueous solution does not change by addition of the amine. This is explained by taking account of the hydrogen bonding of water, or protonation, with amine, which decreases or prevents the charge transfer interaction of the amine with TiO_2.

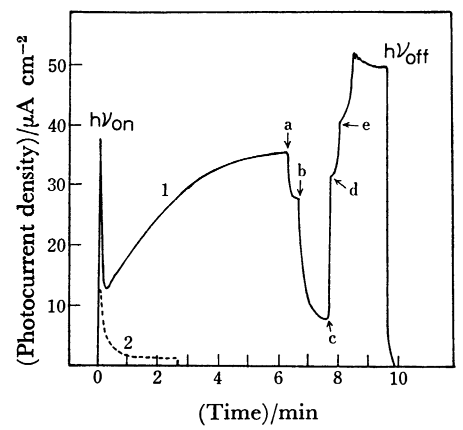


Fig. 7. Change of the photocurrent density of acetonitrile solution containing TMPD with time.

1: 0.1 M CH_3CN solution of $LiClO_4$, 2: the same solution containing 10^{-3} M TMPD.

a: Stirring stopped, b: N_2 gas bubbling stopped, c: N_2 gas started, d: stirring started, e: strong N_2 gas bubbling.

Performance of the Photoelectric Cell. The performance of the system <TiO_2|CH_3CN– amine| Pt> as a photocell has been examined with TMPD used as the amine. The photocurrent for 10^{-3} M acetonitrile solution of TMPD changes with time as shown in Fig. 7. It shows a spike just after illumination, which might be attributable to the charging on the surface of the Pt electrode because there is initially no cathode active species in the solution. With continued illumination, the generation of $TMPD^{\dagger}$ is observed by the development of blue color in the solution, and the photocurrent increases gradually until saturation. When the nitrogen gas bubbling was stopped, the photocurrent decreased immediately, reappearing on stirring. These results suggest that the photocurrent depends on the diffusion rate of the charge carrier, the amine cation, in the solution. The photocurrent for the acetonitrile solution containing 5×10^{-4} M TMPD became constant after 6 min, began to decrease gradually after 20 min, and became one half

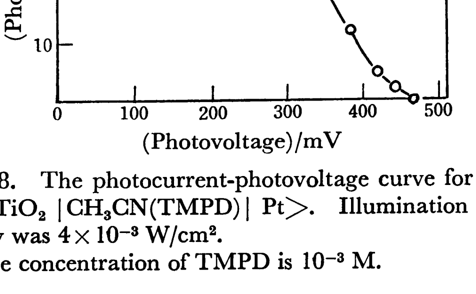


Fig. 8. The photocurrent-photovoltage curve for a cell <TiO_2 |CH_3CN(TMPD) | Pt>. Illumination intensity was 4×10^{-3} W/cm².

The concentration of TMPD is 10^{-3} M.

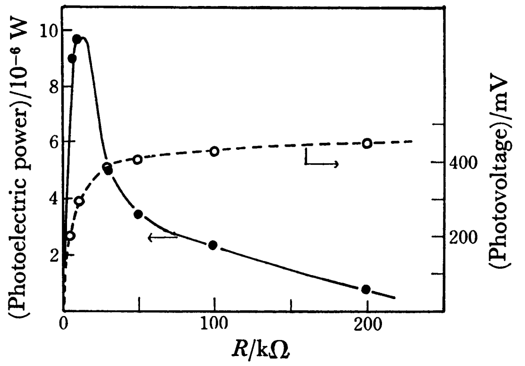


Fig. 9. The photoelectric power and photovoltages *vs.* outer resistance for same cell at the same working conditions as that of Fig. 8.

after about 3 h. This decrease of the photocurrent was proportional to the decrease of the absorbance of TMPD†. These results indicate that TMPD† undergoes further reaction to form an electrochemically inactive colorless product.

Figure 8 shows a photocurrent-photovoltage curve obtained by illuminating the TiO_2 electrode in the cell $<TiO_2|CH_3CN\text{-}TMPD|Pt>$ with the electrodes connected by a variable resistance (R). Figure 9 shows the corresponding relation between photogenerated power output ($i \times V$) and the resistance, R. The maximum power was obtained to be 9.6×10^{-6} W/cm^2 at $R = 10$ kΩ. The power efficiency with respect to the light intensity (4×10^{-3} W/cm^2) was 2.4×10^{-3}.

It was found that the CdS electrode which has a smaller band gap (2.4 eV) than TiO_2 can also be used in a similar photocell. In this case, the oxidation reaction of TMPD occured in competition with the dissolution reaction of the CdS electrode.

The present work partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education (No. 911504).

References

1) H. Gerischer, "Advances in Electrochemistry and Electrochemical Engineering," Vol. 1, ed by P. Delahay and C. Tobias, Interscience, New York (1961).
2) R. Memming and G. Schwandt, *Electrochim. Acta*, **13**, 1299 (1968).
3) F. Lohmann, *Ber. Bunsenges. Phys. Chem.*, **70**, 87 (1966).
4) H. Gerischer, *J. Electrochem. Soc.*, **113**, 1174 (1966).
5) D. M. Kolb and H. Gerischer, *Electrochim. Acta*, **18**, 987 (1973).
6) R. Williams, *J. Chem. Phys.*, **32**, 1505 (1960).
7) A. Fujishima, K. Honda, and C. Kikuchi, *Nippon Kagaku Zasshi*, **72**, 108 (1969).
8) A. Fujishima and K. Honda, *Nature*, **238**, 37 (1972).
9) T. Ohnishi, Y. Nakato, and H. Tsubomura, *Ber. Bunsenges. Phys. Chem.*, **79**, 523 (1975).
10) C. K. Mann, "Electroanalytical Chemistry," Vol. 3, ed by A. J. Bard, Marcel Dekker (1969).
11) T. Watanabe, A. Fujishima and K. Honda, *Chem. Lett.*, **1974**, 897.
12) F. Mollers, H. J. Tolle, and R. Memming, *J. Electrochem. Soc.*, **121**, 1160 (1974).
13) H. Gerischer, *Ber. Bunsenges. Phys. Chem.*, **69**, 578 (1965).
14) S. N. Frank and A. J. Bard, *J. Am. Chem. Soc.*, **97**, 7427 (1975).
15) F. Lohmann, *Ber. Bunsenges. Phys. Chem.*, **70**, 428 (1966).
16) Private communication from T. Sakata, Institute for Molecular Science.
17) Y. Nakato, N. Yamamoto, and H. Tsubomura, *Bull. Chem. Soc. Jpn.*, **40**, 2480 (1967).
18) R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952).
19) R. Memming, *J. Electrochem. Soc.*, **116**, 785 (1969).
20) Y. Nakato, T. Chiyoda, and H. Tsubomura, *Bull. Chem. Soc. Jpn.*, **47**, 3001 (1974).
21) F. Lohmann, *Z. Naturforsch.*, **229**, 843 (1967).