Effect of Etching on Intrinsic and Dye-sensitized Photocurrents in Zinc Oxide Electrodes

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The photoelectrochemical behavior of sintered zinc oxide electrodes was studied. The intrinsic photocurrent, generated by ultraviolet illumination of the zinc oxide electrode, significantly diminished by grinding the electrode surface with an abrasive, and was restored by etching in 2 M(M= mol dm^{-3})HCl for *ca.* 120 s. The dye-sensitized photocurrent caused by rose bengal was also lowered by grinding, but the effect was not as large as in the case of the intrinsic photocurrent, and the photocurrent was restored in a much shorter time of etching. The dye-sensitized photocurrent for an insufficiently etched electrode was enhanced by addition of a reducing agent, *e.g.*, hydroquinone or allylthiourea. However, no enhancement was observed for a well etched electrode. The results, together with the luminescence and reflection spectra of zinc oxide, were discussed by means of models for the semiconductor electronic bands.

Many studies have been carried out on electrochemical solar cells each comprising a semiconductor electrode such as ZnO, TiO_2, or CdS, an electrolyte solution, and a metal counter electrode.[1-6] In these cells, the photocurrent generally arises by the band gap excitation of the semiconductor. The photocurrent is referred to as intrinsic photocurrent, i_{int}, of the semiconductor electrode.

The dye-sensitized photocurrents in the semiconductor electrodes, i_{dye}, have also been studied.[7-11] The dye-sensitized photocurrents are caused by the dye adsorbed on the electrode, but not by those dissolved in the solution.[11-13] Stationary photocurrents can be obtained only when reducing agents are added to the solution.[12,14] Relatively high photocurrents have been obtained by use of rose bengal as a sensitizer and a porous zinc oxide electrode.[15,16] In this paper, further results on some fundamental aspects of the dye-sensitization effects are reported.

Experimental

Zinc oxide sintered disks were prepared by heating compressed zinc oxide powder at 1300 °C in the air for 1 h. The dye adsorptivity on the disk varies a great deal with the source of zinc oxide powder. This seems to be due to impurities such as $ZnCO_3$ present in a small amount. In the present experiment, the powder (Kanto Chemical Co.) was used without further purification. The sinter made from this material has low adsorptivity, giving a reproducible photocurrent. The density of the sinter is almost equal to that of a single crystal. The scanning electron micrograph shows a very compact array of crystalline grains and no visible pore (Fig. 1). The sinter has low electric resistivity $\approx 10\ \Omega$ cm. The shape of the electrode is the same as that described previously.[15] All the other chemicals were of reagent grade and used without further purification.

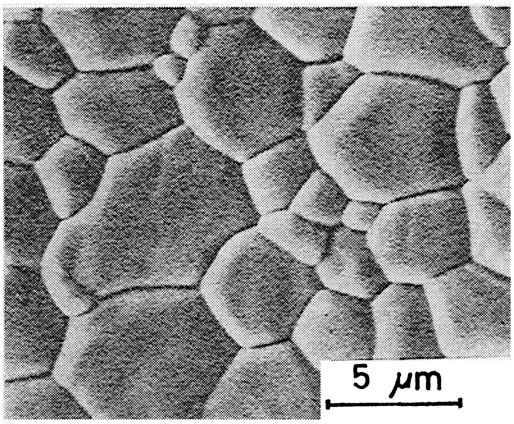

Fig. 1. The scanning electron micrograph of the zinc oxide sinter.

The photocurrents were measured under potentiostatic conditions with a Hokutodenko HA-101 potentiostat and a saturated calomel electrode (SCE). A 500 W xenon lamp (Ushio Electric, Inc.) was used as the light source. The light was monochromatized by use of a Japan-Jarrell Ash 0.25 m Ebert type monochromator. The light intensity was measured with an Eppley bismuth-silver thermopile. The dye-sensitized photocurrents were studied in aqueous solutions of rose bengal and 0.2 M (mol dm^{-3}) potassium nitrate, the pH of the solution being 6.1. For the measurements of intrinsic photocurrents, the pH of the solution was adjusted to 7.8 with a borate buffer. Dissolved oxygen was removed by bubbling the solution with high purity nitrogen. In many cases, the zinc oxide sinter was ground with a silicon carbide abrasive (No. 2000), etched in 2 M hydrochloric acid, washed with water and dried.

The luminescence intensity of zinc oxide sinter excited by the same light source as above was measured by use of an RCA 1P28 photomultiplier equipped with Toshiba B46 and 052 glass filters. The luminescence spectra were measured with an Aminco-Bowman spectrofluorimeter. The absorption spectra and the diffuse reflectance spectra were measured with a Shimadzu MPS-50L spectrophotometer. The ZnO sinter was colored slightly after dipping in the dye solution. The amount of the dye adsorbed on the electrode was estimated from the diffuse reflectance spectra of the ZnO sinter taken out of the dye solution, the residual solution on the sinter being soaked with a filter paper.

The differential capacitance at the semiconductor-electrolyte interface was measured with a Yokogawa Hewlett-Packard 4265B universal bridge at a frequency of 1 kHz.

Results

The dye-sensitized photocurrent under steady illumination decayed exponentially during the first several seconds (curve 1, Fig. 2). The initial value of the dye-sensitized photocurrent, i°_{dye}, was determined by extrapolating the curve to zero time of the illumination. When the dye solution contained a reducing agent such

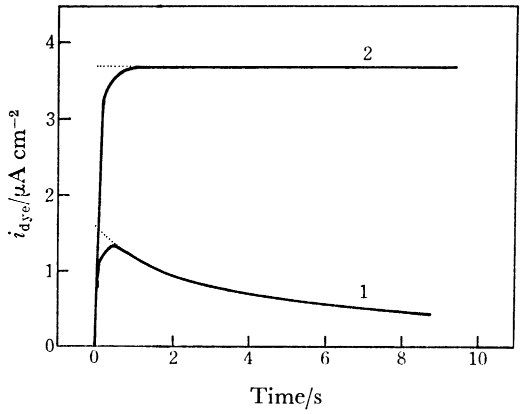

Fig. 2. Change of photocurrent *vs.* time for un-etched electrodes in a solution of 2×10^{-5} M Rose Bengal at potential of 0.4 V (*vs.* SCE). Curve 1, without hydroquinone. Curve 2, with 1.6×10^{-3} M hydroquinone.

as hydroquinone, allylthiourea, or potassium iodide, the decay was suppressed. In some cases the initial value of the photocurrent was enhanced as shown by curve 2 for the case of hydroquinone as a reducing agent. The decay of i_{dye} was suppressed by addition of hydroquinone or allylthiourea at a concentration as low as 5×10^{-5} M, while the increase of i°_{dye} was small at such a low concentration and reached saturation at *ca.* 1×10^{-3} M. In the case of iodide ion, the decay of i_{dye} was not prevented at concentrations below 5×10^{-2} M, and the increase of i°_{dye} could not be observed even at 1.0 M. The difference seems to arise from the weaker electron donor strength of the iodide ion than hydroquinone or allylthiourea. On the other hand, the intrinsic photocurrent did not decay even when the electrolyte solution contained no reducing agent, nor was it affected by the reducing agent.

The photocurrent-potential curves of both i_{int} and i°_{dye} for electrodes etched for various periods of time are shown in Fig. 3. The photocurrents are proportional to the illumination intensity, the shapes of the photocurrent-potential curves not being changed by decrease in the illumination intensity to 1/7. The apparent quantum efficiency of i_{int}, defined as the number of electrons flowing per the number of incident photons on the electrode, is *ca.* 80% for the electrode etched for more than 120 s and polarized at a higher electrode potential than 0.3 V (*vs.* SCE). The onset potentials of the photocurrents did not change with etching. The flat band potentials of ZnO electrodes in the solutions used for the measurements of i_{int} and i_{dye} as determined by the Mott-Schottky plots of the differential capacitance are *ca.* −0.48 and −0.32 V (*vs.* SCE), respectively, agreeing nearly with the onset potentials of photocurrents. The donor densities were determined to be in the range 4.9×10^{22}—7.1×10^{22} m^{-3} by assuming the roughness factor of 2 for the electrode surface.

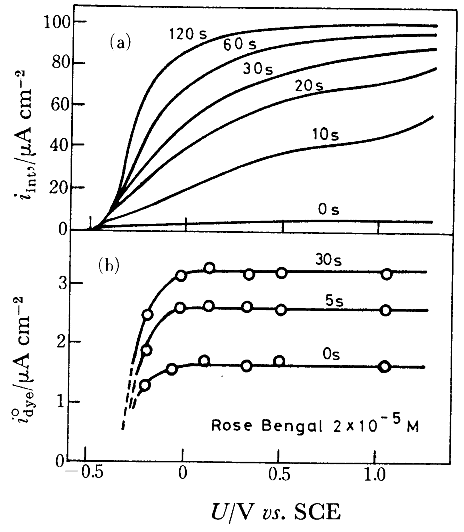

Fig. 3. Current-potential curves of (a) intrinsic photocurrents (excited at λ 360 nm) and (b) the initial values of dye-sensitized photocurrents (λ 562 nm) of ZnO electrode etched for various periods of time.

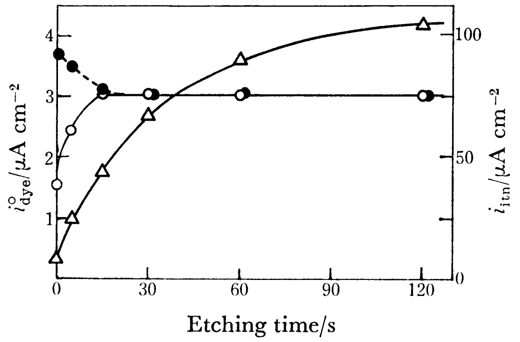

Fig. 4. The photocurrent (at 0.4 V *vs.* SCE) *vs.* etching time in the electrode ground with an abrasive.
○: Initial values of dye-sensitized photocurrent (λ 562 nm) in the presence of 2×10^{-5} M Rose Bengal, ●: the dye-sensitized photocurrent obtained by addition of 1.6×10^{-3} M hydroquinone into the solution; △: the intrinsic photocurrent (λ 360 nm).

The photocurrents observed at the electrode potential of 0.4 V (*vs.* SCE) are plotted against the etching time in Fig. 4. The i°_{dye} value becomes constant at an etching time much shorter than that for the i_{int}. The enhancement of i°_{dye} by hydroquinone occurs only at an etching times less than 15 s. The addition of hydroquinone up to the concentration of 10^{-2} M did not affect the adsorptivity of dye. The amount of the dye adsorbed on the electrode changed slightly by etching, being approximately proportional to the i_{dye} observed in the presence of hydroquinone. This might be due to the change of the surface area caused by etching.

The ZnO sinter emits luminescence when exposed to ultraviolet light. The emission band lies in the range 400—750 nm with a maximum near 530 nm (Fig. 5). The luminescence intensity was quenched drastically by grinding the sinter, but was gradually restored with etching. By etching for 150 s, the luminescence intensity returned to the value before grinding. Figure 6 shows the luminescence intensity at various electrode potentials. The luminescence intensity falls near the onset potential of the photocurrents, decreasing nearly to zero at potentials where the i_{int} value is saturated.

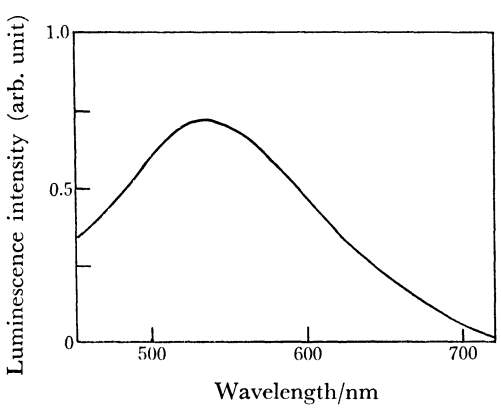

Fig. 5. The luminescence spectrum of ZnO sinter excited at 360 nm.

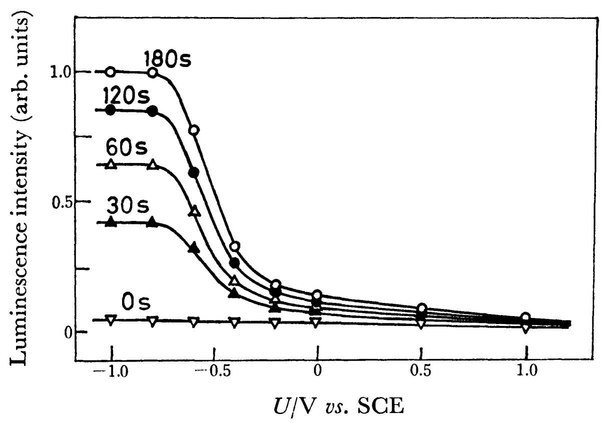

Fig. 6. The luminescence intensity of zinc oxide electrode etched for various periods of time *vs.* electrode potential. The luminescence was excited at 360 nm.

By measuring the weight loss of the ZnO sinter etched in 2 M HCl, the average thickness of the ZnO sinter dissolved by the solution was determined to be 4.3 μm min^{-1}.

Discussion

Our results have revealed that there are fundamental differences between the behavior of the intrinsic photocurrent ($i_{\rm int}$) and that of the dye-sensitized photocurrent ($i_{\rm dye}$):

1. The $i_{\rm int}$ is weakened to a greater extent than $i_{\rm dye}$ by grinding the electrode.
2. The increase in $i_{\rm dye}$ with etching reaches saturation when etching time is *ca.* 15 s. The $i_{\rm int}$ value increaes much more slowly by etching, reaching saturation at *ca.* 120 s.
3. The $i_{\rm int}$ value for an insufficiently etched electrode rises gradually as the electrode becomes anodically polarized up to quite high voltages, whereas $i_{\rm dye}$ rises sharply and is saturated at 0.0 V (Fig. 3).
4. By addition of reducing agents to the solution, the decay of $i_{\rm dye}$ is suppressed. Sometimes $i^{\circ}_{\rm dye}$ increases, whereas $i_{\rm int}$ is hardly affected.

Based on these results, we shall discuss the mechanism of these photocurrents.

Intrinsic Photocurrent. The mechanism of the generation of $i_{\rm int}$ is shown in Fig. 7a. When an n-type semiconductor immersed in an electrolyte is polarized anodically, a potential gradient develops in the space charge layer. By the band gap excitation, the electrons in the valence band are excited to the conduction band. The electron-hole pairs thus generated in the space charge layer are separated efficiently by the electric field.

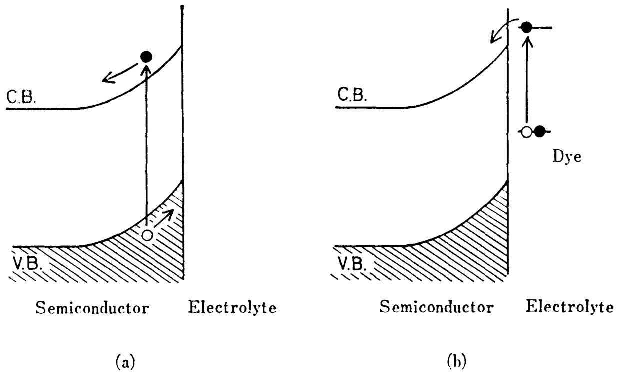

Fig. 7. The energy level diagrams of the semiconductor illustrating the mechanisms of the intrinsic photocurrent (a) and dye-sensitized photocurrent (b).

The $i_{\rm int}$ value of a well etched electrode reaches saturation at the electrode potential of *ca.* 0.3 V (Fig. 3). The quantum efficiency of the saturated $i_{\rm int}$ is regarded to be almost 100% if the reflection of the incident light at the surface is taken into account.

The depth of the space charge layer, L, is approximately given by[17)]

$$L = \sqrt{2(U-U_{\rm fb})\varepsilon\varepsilon_0/N_{\rm d}e} \qquad (1)$$

where U is the electrode potential in the bulk, $U_{\rm fb}$ the flat band potential, ε the dielectric constant, ε_0 the permittivity of vacuum, and e the elementary electric charge. The value of L is calculated to be 110 nm at the electrode potential of 0.3 V, at which $i_{\rm int}$ of a well-etched electrode reaches saturation, by substituting $U_{\rm fb}=-0.48$ V, $\varepsilon=8.5$, $N_{\rm d}=6\times10^{22}$ m^{-3} (the mean value of the observed donor density) into Eq. 1. On the other hand, the penetration depth of the incident light (λ 360 nm) in ZnO, l, defined as the distance at which the light intensity becomes 5%, is calculated to be *ca.* 100 nm from the absorption constant of *ca.* 3×10^{7} m^{-1},[18)] in good agreement with the above derived L value. The result suggests that the recombination is negligible in the space charge layer of a well-etched electrode.

On the other hand, the $i_{\rm int}$ value for an insufficiently etched electrode did not reach saturation even when the electrode potential was raised to 5 V (*vs.* SCE). This cannot be explained by the relation between the penetration depth of the light and the depth of the space charge layer, but by taking into account the recombination center of electron-hole pair in the space charge layer generated by the grinding. At a higher anodic polarization, the electric field strength near the surface of the electrode increases and the electrons and holes are separated more rapidly, leading to a higher photocurrent.

This mechanism is supported by the measurements of luminescence from ZnO. The luminescence drops sharply at around −0.5 V (*vs*. SCE) to the more positive region where i_{int} begins to rise (Figs. 3 and 6). This is reasonable since the luminescence is caused by a recombination of the electron-hole pairs. The figures also indicate that non-radiative recombination centers are generated by grinding the electrode, since both the luminescence and i_{int} are weak when the etching time is short, increasing in a similar way with longer etching.

Dye-sensitized Photocurrent. It is generally admitted that the dye sensitized photocurrent (i_{dye}) is caused by an electron injection from the excited dye into the conduction band, the electrons being driven inward by the electric field in the space charge layer (Fig. 7b). In the case of i_{dye}, free holes do not exist in the valence band, and, therefore, the recombination process does not take place even though defects are present in the space charge layer. This can explain i_{dye} being less affected than i_{int} by grinding of the electrode.

The effect of grinding on i°_{dye} can be explained by assuming the formation of electron traps near the surface which capture electrons injected from the dye and send them back to the dye. The fact that the photocurrent at sufficiently high anodic polarization became constant by etching for 15 s indicates that the density of the traps is high in the region very close to the surface (Fig. 4).

Sintered ZnO, normally slight yellow, turns deep yellow on grinding. The increase in absorbance of the sinter from 380 to 650 nm thus produced can be measured by diffuse reflectance spectroscopy. This can be removed by etching for *ca*. 15 s, which is comparable to that necessary to make i°_{dye} reach saturation. The increased absorbance seems to be due to the surface defects, which trap the injected electrons.

The Effect of Reducing Agents on i_{dye}. There are two features of the effect of reducing agents on i_{dye},[12] the increase of i°_{dye} and the prevention of decay of i_{dye}.

Hydroquinone increases i°_{dye} for an electrode etched for less than 15 s, but not for a sufficiently etched electrode (Fig. 4). This can be explained by assuming the presence of surface traps (Fig. 8). Without a reducing agent, a part of the injected electrons are capturated by the surface traps, returning to the dyes which have injected these electrons. Such a backward movement of electrons is prevented by a rapid electron supply from the reducing agent, increasing i°_{dye}.

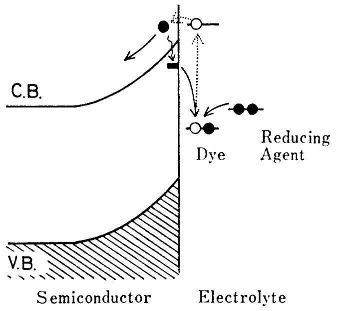

Fig. 8. The energy level diagrams explaining the influence of the surface defect and the reducing agent on the dye-sensitized photocurrent.

Some authors pointed out that the effect of reducing agents on i_{dye} is attributable to either an electron transfer from the reducing agent to the dye in excited state or an exciplex formation between the dye and the reducing agent. In the present case, however, the results are explained in terms of the electron transfer from the reducing agents to the photo-oxidized dye. There seems to be no general "super sensitization" effect of the reducing agents.

From the present study, the dye-sensitized photocurrent has been proved to be less sensitive to the defects in the electrode than the intrinsic photocurrent, especially when the solution contains reducing agents. This is one of the advantages of the dye-sensitized photocurrent as regards utilization of imperfect solid specimens for electrochemical photocells.

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References

1) A. B. Ellis, S. W. Kaiser, and M. S. Wrighton, *J. Am. Chem. Soc.*, **98**, 6855 (1977).

2) B. Miller and A. Heller, *Nature*, **262**, 680 (1976).

3) A. Fujishima, K. Kohayakawa, and K. Honda, *Bull. Chem. Soc. Jpn.*, **48**, 1041 (1975).

4) H. Minoura, M. Tsuiki, and T. Oki, *Ber. Bunsenges. Phys. Chem.*, **81**, 588 (1977).

5) H. Yoneyama, H. Sakamoto, and H. Tamura, *Electrochim, Acta*, **20**, 341 (1975).

6) Y. Nakato, K. Abe, and H. Tsubomura, *Ber. Bunsenges. Phys. Chem.*, **80**, 1002 (1976).

7) H. Gerischer and F. Willig, "Topics in Current Chemistry," Springer, New York (1976), Vol. 61, p. 31.

8) T. Watanabe, A. Fujishima, and K. Honda, *Ber. Bunsenges. Phys. Chem.*, **79**, 1213 (1975).

9) H. Tributsch and H. Gerischer, *Ber. Bunsenges. Phys. Chem.*, **73**, 251 (1969).

10) U. Bode, K. Hauffe, Y. Ishikawa, and H. Pusch, *Z, Phys. Chem. N. F.*, **85**, 144 (1973).

11) R. Memming, *Photochem. Photobiol.*, **16**, 325 (1972).

12) M. Matsumura, Y. Nomura, and H. Tsubomura, *Bull. Chem. Soc. Jpn.*, **50**, 2533 (1977).

13) M. Matsumura, Y. Nomura, and H. Tsubomura, *Bull. Chem. Soc. Jpn.*, **49**, 1409 (1976).

14) M. Matsumura, K. Yamamoto, and H. Tsubomura, *Nippon Kagaku Kaishi*, **1976**, 399.

15) H. Tsubomura, M. Matsumura, Y. Nomura, and T. Amamiya, *Nature*, **261**, 402 (1976).

16) H. Tsubomura, M. Matsumura, K. Nakatani, K. Yamamoto, and K. Maeda, *Solar Energy*, **21**, 93 (1978).

17) H. Gerischer, *J. Electroanal. Chem. Interfac. Electrochem.*, **58**, 236 (1975).

18) G. Heiland, E. Mollwo, and F. Stöckmann, "Solid State Physics," Academic Press, New York (1959), Vol. 8, p. 191.