Photocurrents in the ZnO and TiO_2 Photoelectrochemical Cells Sensitized by Xanthene Dyes and Tetraphenylporphines. Effect of Substitution on the Electron Injection Processes

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The photocurrents in zinc oxide and titanium dioxide electrodes sensitized by anionic xanthene dyes (Eosine Y, Phloxine B, Erythrosine, and Rose Bengal) and metal tetraphenylporphines were studied in aqueous solutions. The quantum efficiencies of the photocurrents sensitized by anionic xanthene dyes were unaffected by substitution of the dye with various halogen atoms, while those sensitized by the tetraphenylporphines were affected by changing the central metal. It is concluded from these results that the electron injection from the excited xanthene dyes to the semiconductor electrodes is a process so rapid ($\ll$0.1 ns) that no internal quenching processes can compete with it, while that from the tetraphynelporphines is relatively slow competing with the internal deactivation processes. It is also concluded that the electron back transfer from the semiconductor conduction band to the oxdized dye decreases the sensitization efficiency.

Many studies have been made on the dye-sensitized photocurrents in the semiconductor electrodes for the semiconductor/solution[1-13] and the semiconductor/gas[14,15] interfaces. The sensitization technique is important for efficient electrochemical solar cells, because most of small band-gap semiconductors are unstable in aqueous solutions. We have reported on a series of work on the dye-sensitization effect of n-type semiconductor electrodes in solution.[4-13] It is now clear that the dye-sensitized photocurrents are produced by the electron transfer from the excited dye directly adsorbed on the electrode surface to the conduction band of the semiconductor,[7] followed by electron supply from donor-type species in the aqueous phase.[11] We found that the highest photocurrent quantum efficiency was obtained by using Rose Bengal[6] or similar xanthene dyes.[10] The reason for this was attributed to a strong bonding between the metal atoms in the semiconductor and the oxygen atoms in the dye which made both the adsorption and the electron transfer rate high.[9] We also found that the photocurrent was proportional to the amount of adsorbed dyes, dependent on the pH and dissolved salts in the solution.[12] It was found that the dye sensitization effect became highly efficient when porous sinter electrodes were used. Aluminium doped sinter gave the best results.[12,13]

Little is known, however as to the nature of the excited states of the dye from which electrons are injected. In this paper, we report the effect of substitution of the sensitizing dyes on the photocurrent, from which an important aspect of the nature of transient dye states can be elucidated.

Experimental

The titanium dioxide (TiO_2) single crystals used as electrodes were obtained from Nakazumi Crystal Co., Ltd. and were heated at 650 °C under high vacuum for 1 h, to make them semiconducting. The zinc oxide (ZnO) electrodes used were obtained by sintering compressed ZnO powder (Kanto Chemical Co., Ltd.) at 1300 °C for 1 h. The properties of the ZnO sinter were described in a previous paper.[13] The xanthene dyes were of reagent grade and purified by passing through an alumina column. The tetraphenylporphines were prepared from pyrrole and benzaldehyde, and purified as described previously.[16]

The photocurrents were measured in aqueous solutions of 0.2 M (1 M=1 mol dm^{-3}) potassium nitrate under potentiostatic conditions with a saturated calomel electrode (SCE) as a reference electrode and a platinum plate as a counter electrode. For the illumination, a 500 W xenone lamp (Ushio Electric, Inc.) and a grating monochromator (Japan Jarrell-Ash Co.) were used. The intensity of the monochromatic light incident on the electrode was measured with a bismuth-silver thermopile (The Eppley Lab., Inc.). The photocurrent sensitized by the xanthene dyes was studied using aqueous solutions of the dyes and the electrolyte. The photocurrent sensitized by the tetraphenylporphines was studied either by spraying toluene solutions of the porphines or by the vacuum evaporation method.

The fluorescence was measured with an Aminco-Bowman spectrofluorimeter.

Results and Discussion

The Sensitization by Xanthene Dyes. The result of the dye-sensitized photocurrents for ZnO electrodes immersed in aqueous solutions of anionic xanthene dyes (1.2×10^{-5} M) are given in Table 1, which were measured at the electrode potential of 0.3 V (*vs.* SCE) and at the wavelengths where the highest sensitized photocurrents were obtained. The amounts of the adsorbed dyes on the ZnO electrodes, Γ, in the dye solutions used for the photocurrent measurements were also shown in Table 1.

The quantum efficiency of the sensitized photocurrent, η, (number of flowing electrons over number of absorbed photons) can be calculated from i_{dye}, Γ, and the number of incident photons obtained from the intensity measurement of incident light. The η values thus obtained for the four dyes were found to agree with each other to within the experimental error, although the life times of the excited singlet states of the dyes in aqueous solutions reported by Robinson[17] differ greatly from each other as shown in Table 1.

As mentioned before, the dye-sensitized photocurrent is caused by the electron injection from the ex-

Table 1. Sensitized photocurrent density (i_{dye}) and its quantum efficiency (η), for the ZnO sinter electrodes at 0.3 V (*vs.* SCE) sensitized by anionic xanthene dyes. Adsorptivity (Γ) and the lifetime of excited singlet state (τ) are also given

	$i_{dye}/\mu A\ cm^{-2}$	$\eta/\%$	Γ[a)]	τ/ns[b)]
Eosine Y	0.7	28±5	0.011	1.425
Phloxine B	0.8	25±5	0.014	—
Erythrosine	1.2	26±5	0.021	0.115
Rose Bengal	1.4	28±5	0.022	0.095

a) The Γ here is actually the absorbance of the dye adsorbed on ZnO at the wavelength of its absorption peak, which is proportional to the amount of the adsorbed dye.[12] b) Ref. 17.

cited dye adsorbed on the electrode into the conduction band as shown in Fig. 1. Then, the question arises whether the electron injection occurs from the singlet or the triplet state of the dye. It was reported, and we have partly reconfirmed, that hydroquinone, *p*-benzoquinone, oxygen, and hexacyanoferrate(II) quench the triplet states of the xanthene dyes.[18,19] In spite of this, we have found that the efficiencies of the photocurrents sensitized by these dyes are hardly affected by the presence of these triplet quenchers. Spitler *et al.*[20] reported that the quantum efficiency of the photocurrent was decreased by the addition of hexacyanoferrate(II) in solution. However, we actually concluded that the efficiency was hardly affected by hexacyanoferrate(II), from the precise measurements of the photocurrent and the amounts of dye adsorbed on the electrode. These results suggest that the electron injection occurs from the excited singlet state. This is also supported by our finding that the fluorescence of the dyes is almost completely quenched when they are adsorbed on ZnO. These facts and the agreement of the η values between the dyes shown in Table 1, have led us to conclude that the electron injection from the excited dyes occurs very quickly, *i.e.*, in a time much shorter than the life time of the dyes in their excited singlet states ($\ll$0.1 ns), and hence the quantum efficiency of electron injection from the excited dye is most probably nearly 100%.

The reason why the current quantum efficiencies, η, are much less than 100% in spite of the above mentioned result can be explained by assuming the existence of an electron back transfer process from the conduction band to the solution (Process 2 in Fig. 1). One of the evidences to support this idea is the observation by Pettinger *et al.*[21] of a transient counter current in a dye sensitized ZnO electrode. The η value may, therefore, be given as the ratio of the number of the electrons drifting inward (Process 1 in Fig. 1) to the total number of injected electrons.

In a previous paper, we reported that smaller sensitized photocurrents, *i.e.* η values, were obtained if the surface of the electrode was ground with abrasive on a glass plate.[13] This can be attributed either to the generation of surface states or to the reduction of the migration speed of the electrons toward the

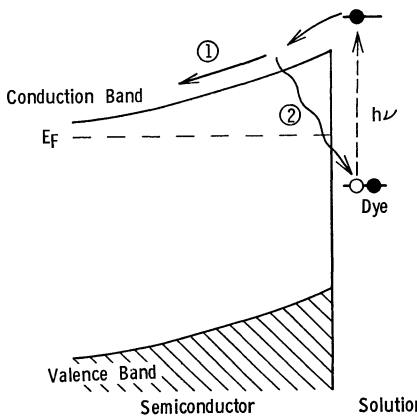

Fig. 1. The energy diagram of a semiconductor surface explaining the mechanism of the dye-sensitization at an n-type semiconductor.

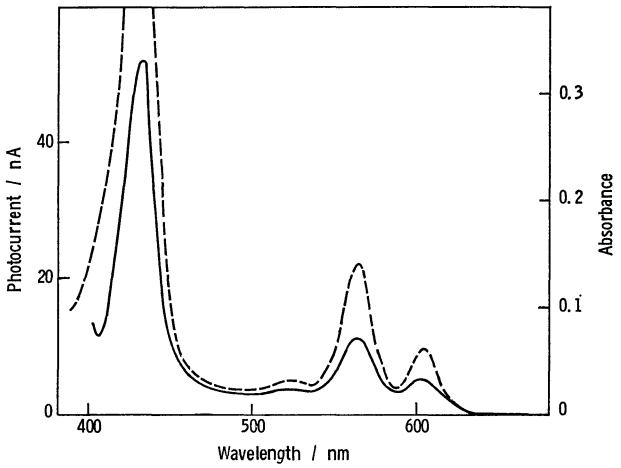

Fig. 2. The action spectrum of the photocurrent at the ZnO electrode sensitized by Mg-TPP (——), and the absorption spectrum of the 5.9×10^{-6} M Mg-TPP in toluene (----).

bulk of electrode. The η values given in Table 1 are those obtained after etching the electrodes. No higher η values was obtained either by further etching or by applying higher anodic potential.

The η values for the sensitized photocurrent in the TiO_2 electrodes were *ca.* 1/15 those for ZnO electrodes. In this case, the fluorescence of the adsorbed dye was also quenched drastically. These results indicate that though the electron injection occurs efficiently in the case of TiO_2, similar to the case of ZnO, the migration of the injected electrons into the bulk of TiO_2(Process 1) is less efficient than the migration into the bulk of ZnO.

The Sensitization by Tetraphenylporphines. The ZnO electrodes coated with metal-free and metal tetraphenylporphines (TPP) showed sensitized photocurrents in the visible region, the action spectra of which agreed well with the absorption spectra of the porphines. An example is shown in Fig. 2 for the case of Mg-TPP. When the amount of the porphines on the electrodes was less than a monolayer coverage, a sensitized anodic photocurrent was observed. Its dependence on the potential, the effect of reducing

Table 2. Quantum efficiencies of the sensitized photocurrent at ZnO electrode (η), effective oxydation potentials of the exited singlet state (U^*_{ox}), and fluorescence intensities in toluene solution, for tetraphenylporphines (M-TPP)

M	η/%	(U^*_{ox} *vs.* SCE)/V	Fluorescence[a)]
Mg	2.3±0.5	−1.32	S
Cd	1.4±0.3	−1.21	W
Zn	1.4±0.3	−1.17	M
Pb	0.8±0.2	−1.01	none
Cu	0.5±0.2	−1.01	none
H_2	0.5±0.2	−0.74	S
Ni	<0.1	−1.02	none

a) S; Strong, M; medium, W; weak.

agents on it *etc.*, were essentially identical to those previously reported for the semiconductor/dye solution systems. On the other hand, when the coverage was *ca.* 20 monolayers, a sensitized cathodic photocurrent appeared at potentials near the flat band potential of the ZnO electrode. This cathodic photocurrent probably arises from the electrical property of the p-type semiconductors of the porphine films.[22,23] In this work, we concentrated our efforts for the case of the coverage less than a monolayer, so are all results described in this paper.

The quantum efficiencies, η, of the photocurrents sensitized by porphines for the above mentioned case are shown in Table 2, decreasing in the order, Mg> Cd≃Zn>Pb>Cu≃H_2>Ni-TPP. Similar to the case of xanthene dyes, the electron of the dye is thought to be injected from the excited singlet state of the porphines, since tetracene, peryrene, and oxygen, which are known to quench the triplet state of porphines,[24,25] did not affect the photocurrent. The effective oxidation potential of the excited dyes, U^*_{ox}, can be written as

$$U^*_{ox} = U_{ox} - (\Delta E - \lambda)/e,$$

where U_{ox} is the oxidation potential in the ground state, ΔE the energy defference between the excited and the ground states, λ the reorganization energy, and e the elementary charge. The U^*_{ox} values for the porphines are shown in Table 2, which are obtained from the oxidation potentials measured in acetonitrile by Stanienda and Bieble,[26] ΔE taken from the absorption edge, and λ tentatively taken to be 0.1 eV. It can be seen from Table 2 that, as a general trend, η becomes the higher, the more negative the U^*_{ox} is. The energy level of the conduction band edge of ZnO at the surface, E^s_c, is estimated to be *ca.* −0.5 V (*vs.* SCE) at pH 6, from the flat band potential measured by us and by assuming that the energy difference between the Fermi level and the conduction band edge is 0.1 eV. The E^s_c value is more positive than all the U^*_{ox} values. The above result that η values depend on the U^*_{ox} values of the porphines shows that a considerably high energy barrier exists for the electron injection from the excited porphines. It is also expected that the η value must depend on the life times of the excited states of the

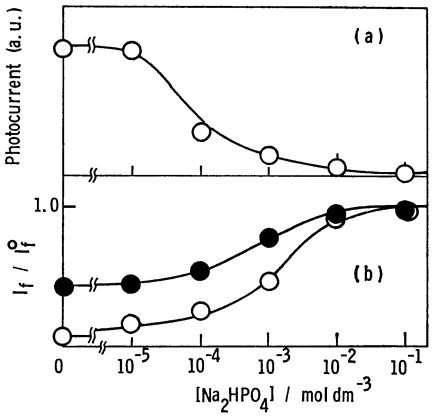

Fig. 3. The effect of the treatment of the ZnO electrode with aqueous solutions of Na_2HPO_4 on the photocurrent sensitized by Mg-TPP (a), and the fluorescence intensities, I_f, of Mg-TPP (○) and H_2-TPP (●) adsorbed on ZnO (b). The ordinate of Fig. 3b indicates the normalized I_f by the values observed at 0.1 M Na_2HPO_4, I_f°.

porphines, because the electron injection is a process competing with the deactivation of the excited states. Therefore, the anomaly in the relation between η and U^*_{ox} of H_2-TPP and Ni-TPP (see Table 2) can be explained as follows. Since H_2-TPP in toluene shows strong fluorescence, while Pb-, Cu-, and Ni-TPP are non-fluorescent, fast radiationless deactivation processes must be present in the metal substituted TPP's. Therefore, the electron injection for H_2-TPP will be more efficient as a sensitizer than Ni-TPP and nearly equal to those of Cu-, and Pb-TPP in spite of the disadvantage of the former in the energetical relation.

Some of the porphines, *e.g.*, H_2-, Mg-, and Zn-TPP, adsorbed on ZnO show fluorescence caused by photoexcitation, while the fluorescence of the xanthene dyes is almost completely quenched. This suggests that the electron injection is less efficient and competing with the fluorescing process in the former case as seen from the η values for tetraphenylporphines, which are lower than those of xanthene dyes (Tables 1 and 2). Such a difference probably arises from the negative U^*_{ox} values of the xanthene dyes, *ca.* 0.2 to 0.8 V more negative than those of porphines, or from the stronger bond formation between the adsorbed xanthene dyes and the zinc atoms in ZnO[9], which should be relevant to the probability of electron injection processes in these cases.

The competing relation mentioned above for the case of the porphines becomes clear by inspection of the results shown in Fig. 3. The sensitized photocurrent became smaller when a ZnO electrode was used which had been immersed in aqueous solutions of disodium hydrogenphosphate (Na_2HPO_4) for a while, dried, and then coated by spraying a Mg-TPP solution (Fig. 3a). The similar effect of disodium hydrogenphosphate was observed for the case of H_2-TPP. On the other hand, the fluorescence of the porphines adsorbed on ZnO was increased by the same treatment of the electrode (Fig. 3b). These results can be understood by assuming that the hy-

drogenphosphate ion adsorbed on ZnO inhibits the electron injection by acting as a spacer between the porphines and ZnO. This assumption is supported by the fact that the adsorption of the xanthene dyes on ZnO from aqueous solutions is inhibited by the presence of a small amount of the hydrogenphosphate ion (*ca.* 10^{-2} M) in the solution. That the effect was smaller in the case of H_2-TPP than for Mg-TPP (see Fig. 3b) is probably due to the difference in the quantum efficiency of the electron injection. Since the quantum efficiency of the photocurrent for H_2-TPP is low even in the absence of the spacer, the fluorescence of H_2-TPP is less affected by the electrode treatment.

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