pH-Dependence of Spectral Sensitization at Semiconductor Electrodes

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For an interpretation of the pH-dependence of the sensitized photocurrent at semiconductor electrodes, measurements have been carried out on n-type TiO_2 and CdS single crystal electrodes. As sensitizing dyes, rhodamine B and 3,3′-diethylthiacarbocyanine iodide which remain stable in a sufficiently wide pH range were used. It has been found that the logarithm of the sensitized photocurrent at TiO_2 electrode depends linearly on the pH of the electrolyte solution, whereas the sensitized photocurrent shows practically no pH-dependence at CdS electrode. These observations have been accounted for on the basis of the different pH-dependence of flatband potentials of these semiconductor electrodes.

Investigations of spectral sensitization by means of electrochemical arrangements have so far been carried out by a number of authors on ZnO,[1–14] TiO_2,[15] CdS,[16,17] GaAs,[4] GaP,[4,18] AgCl,[12,19] AgBr,[12,19] SnO_2,[20] Cu_2O,[12,21] and organic semiconductors[1,22,23] such as perylene, chrysene and anthracene. By addition of a suitable dye to the electrolyte solution and by subsequent illumination of the semiconductor-electrolyte interface with light of the optical absorption band of the dye, an enhancement of the photocurrent (sensitized photocurrent) is observed. For most n-type and p-type semiconductor electrodes, the sensitized photocurrent is produced under anodic and cathodic polarizations, respectively.

The magnitude of the sensitized photocurrent can be influenced by several factors such as light intensity, dye concentration, additives (reducing or oxidizing agents in particular), and the pH value of the electrolyte solution.

As regards the effect of pH on the sensitized photocurrent, three examples have so far been reported uniquely on ZnO electrode. Gerischer *et al.*[1] measured the rose bengale-sensitized photocurrent as a function of the pH of the solution. The sensitized photocurrent exhibited only a slight pH-dependence in the alkaline region and completely disappeared below pH 3.8 (owing presumably to the protonation of the dye). However, their results show a remarkable increase in the sensitized photocurrent as the pH decreases from 5.5 to 4.5.

Hauffe *et al.*[8] measured the fluorescein-sensitized photocurrent with varying pH. The magnitude of the sensitized photocurrent showed a maximum when the solution pH was around 7.0, and decreased both in alkaline and acidic solutions. However, the decrease in the photocurrent in the acidic condition is due to some structural change of the sensitizing dye, as is indicated by a remarkable decrease in the fluorescent intensity when compared with that in neutral and alkaline solutions.

Gerischer and Tributsch,[2] using rhodamine B as a sensitizing dye, found that the logarithm of the sensitized photocurrent increased almost linearly with the pH of the solution as it decreased from 9.0 to 1.5, but they did not give any plausible interpretation.

The examples cited above suggest that in the pH range where the sensitizing dye undergoes no structural change, the sensitized photocurrent increases as the pH of the electrolyte solution decreases.

In order to obtain further information on the pH-dependence of the sensitized photocurrent, we have investigated the pH-dependence of the sensitized photocurrent at two different semiconductor electrodes, using two kinds of sensitizing dyes which remain quite stable in a sufficiently wide pH range.

Experimental

Materials and Measuring Setup. Single crystals of TiO_2 and CdS, supplied from Nakazumi Crystals Co., Ltd. and Teikoku Tsushin Co., Ltd., respectively, were used as the n-type semiconductor electrodes. Both were in the form of platelets with a surface area of 1.0 cm^2 and thickness of 1.0 mm. In the case of TiO_2, the crystal was treated at around 600 °C under high vacuum for three hours, prior to the preparation of the electrode, in order to increase the electrical conductivity. The crystals were then cemented with an epoxy resin so that usually the (001) face and the (0001) face of TiO_2 and CdS, respectively, were in contact with the electrolyte solution. The opposite face was used for a barrier-free electrical contact by means of vacuum evaporated indium. Before measurements, the electrodes were polished with alumina paste. The CdS electrode surface was chemically etched with concentrated HCl for a few seconds.

As the sensitizing dyes, rhodamine B and 3,3′-diethylthiacarbocyanine iodide were used. The electrolyte was 0.2 M Na_2SO_4 aqueous solution, and the pH of the electrolyte solution was varied by adding a small amount of H_2SO_4 or NaOH aqueous solution. All the chemicals used were of reagent grade.

A 500-W xenon lamp was used as the light source. The wavelength of the illuminating light was selected with the use of colored glass filters or a Shimadzu monochromator. Illumination of the electrode-electrolyte interface was carried out either through the electrode attached as the window of the electrochemical cell or through a quartz window and the dye-containing electrolyte solution. The photocurrent was detected by means of a Keithley picoammeter Model 417.

Adsorption Measurements. Since direct measurement of adsorption of dyes with single crystals is difficult, a powdered TiO_2 (Kishida Kagaku Co., Ltd.) was used as an adsorbent. 0.5 g of TiO_2 powder was added to 20 ml of a dye solution of various concentrations containing 0.2 M of Na_2SO_4. The mixture was put into a glass tube assembled on a stirring machine. The TiO_2 powder was kept in contact with the solution for 30 min at 20 °C, and then separated by centrifuging. The absorbance change of the dye solution was determined by means of a Shimadzu spectrophotometer MPS-5000.

Results and Discussion

Since TiO_2 and CdS are n-type semiconductors with relatively large band gaps (3.0 eV and 2.4 eV, respectively), only a small current flows in darkness under anodic polarization, owing to the formation of a depletion layer for the majority carrier at the surface of the electrode. Figure 1 shows typical current-potential curves for the TiO_2 electrode at two different pH values. In the absence of a sensitizing dye and under illumination with light of longer wavelengths than the intrinsic absorption of TiO_2, a small photocurrent is produced, which is almost independent of the pH of the electrolyte solution. By addition of a sensitizing dye, 3,3′-diethylthiacarbocyanine in the present case, a further photocurrent (sensitized photocurrent) was observed, whose spectral dependence is close to that of the optical absorption of the dye adsorbed to TiO_2. The sensitized photocurrent reaches a saturation value under a slight anodic polarization. As can be seen in Fig. 1, with a decrease in pH from 6.15 to 2.2, the saturation value of the sensitized photocurrent shows a remarkable increase by a factor of more than ten.

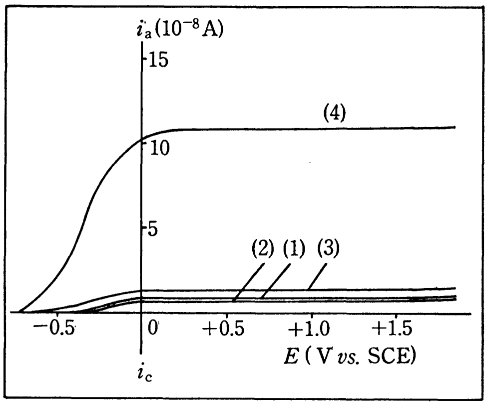

Fig. 1. Current-potential curves for TiO_2 electrode under illumination with $\lambda > 460$ nm.
(1): Blank photocurrent at pH 6.15, (2): same as (1) at pH 2.2, (3): photocurrent by addition of 2×10^{-5} M of 3,3′-diethylthiacarbocyanine at pH 6.15, (4): same as (3) at pH 2.2.

When the sensitized photocurrent is plotted against the dye concentration, in a log-log scale, an almost straight line with a slope of *ca.* 1.0 is obtained in the relatively low concentration region. Figure 2 shows such curves for two different pH values. Decrease in pH enhances the sensitized photocurrent by approximately the same factor, irrespective of the dye concentration.

In the case of the CdS electrode, in contrast to TiO_2 electrode, no pH-dependence of the sensitized photocurrent was observed. Fugure 3 shows the spectra of the rhodamine B-sensitized photocurrent at CdS electrode for four different pH values.

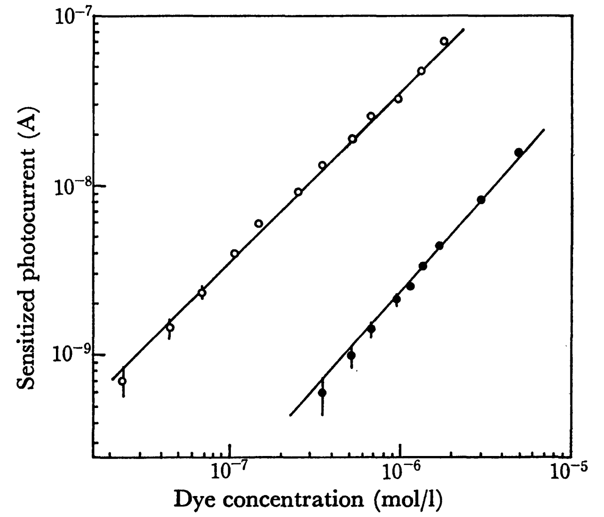

Fig. 2. Dependence of the sensitized photocurrent at TiO_2 electrode upon the concentration of the sentitizing dye (3,3′-diethylthiacarbocyanine iodide) at two different pH values; —○—: pH 2.2, —●—: pH 6.15.

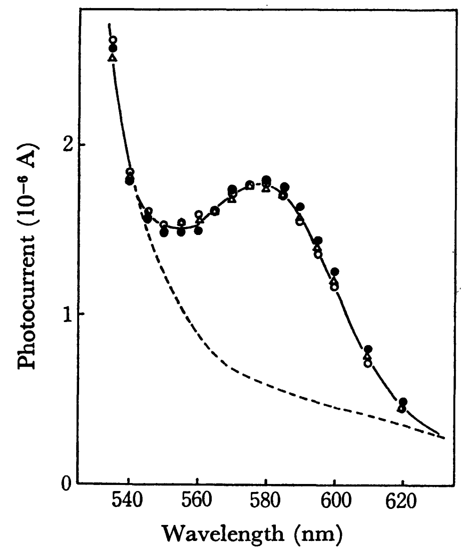

Fig. 3. Spectral dependence of the sensitized photocurrent at CdS electrode with varying pH: ——: pH 5.2, —○—: pH 4.0, —△—: pH 3.0, —●—: pH 2.4, ······: blank photocurrent.

The experimental results of spectral sensitization measurements at TiO_2 and CdS electrodes are summarized in Fig. 4 as a function of pH of the electrolyte solution, together with the data reported by Gerischer and Tributsch[2] on ZnO electrode. In the cases of TiO_2 and ZnO electrodes, the logarithm of the sensitized photocurrent depends almost linearly upon the pH of the solution containing rhodamine B or 3,3′-diethylthiacarbocyanine iodide as a sensitizing dye, while no detectable dependence being observed for the CdS electrode.

As regards the pH-dependence of the sensitized photocurrent at TiO_2 electrode, it is necessary in the first place to check the possible contributions from any

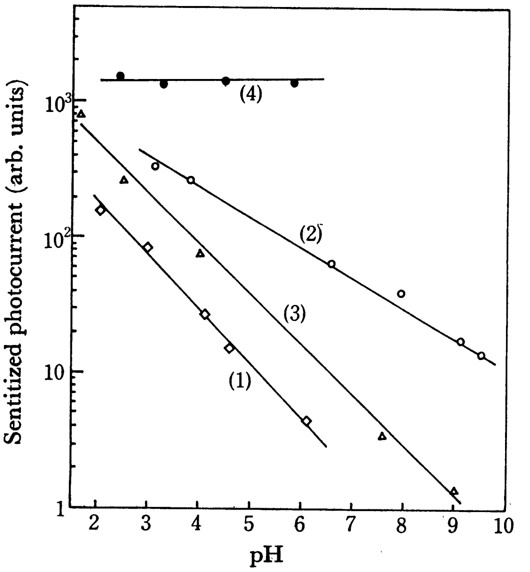

Fig. 4. pH-dependence of the sensitized photocurrents at several semiconductor electrodes;
(1): TiO_2 with 3,3′-diethylthiacarbocyanine, (2) TiO_2 with rhodamine B (3) ZnO with rhodamine B (Gerischer and Tributsch[2]), (4) CdS with rhodamine B.

pH-assisted structural change of the dye molecule and from the pH-dependence of the adsorption characteristics of dyes on TiO_2. The absorption spectra of rhodamine B and 3,3′-diethylthiacarbocyanine iodide were measured in the pH range 2—12, but no detectable change was observed. From this the possibility of the structural change of dye molecules through pH could be ruled out.

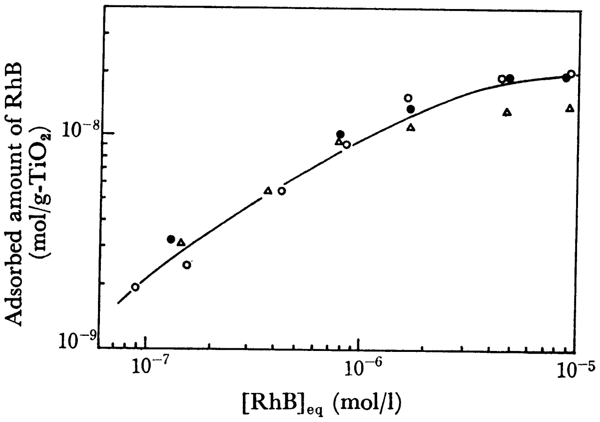

Fig. 5. Adsorption characteristics of rhodamine B on TiO_2 at 20 °C at different pH values; —○—: pH 2.0, —●—: pH 6.15, —△—: pH 10.0.

The adsorption characteristics of the two dyes employed here on TiO_2 have been measured with varying pH of the solution. The results for rhodamine B are shown in Fig. 5. We see that the adsorbability of rhodamine B in the pH range 2—12 falls on the same curve within experimental error. The adsorption of 3,3′-diethylthiacarbocyanine iodide on TiO_2 also is hardly affected by the pH of the solution.

The observations suggest that, in the case of the TiO_2 electrode, a decrease in pH of the electrolyte solution brings about a favorable condition for the occurrence of the spectral sensitization (possibly the electron transfer from the excited dye molecule to the conduction band of the semiconductor).

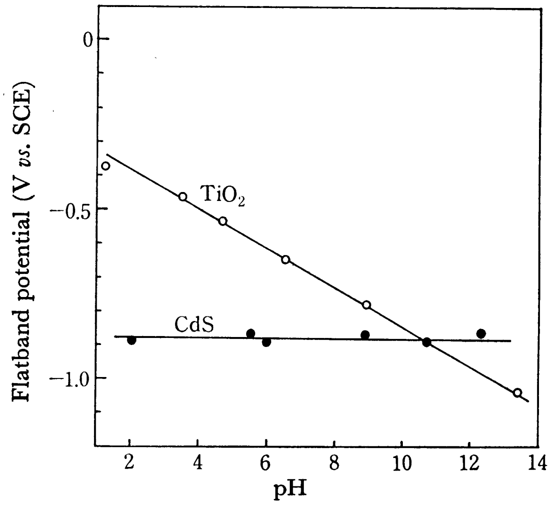

Fig. 6. pH-dependence of flatband potentials of TiO_2 and CdS single crystal electrodes.

In this connection we notice a quite good correlation between the results shown in Fig. 4 and the pH-dependence of the flatband potentials of TiO_2 and CdS electrodes (Fig. 6).[24] The pH-dependence of the flatband potential of the TiO_2 electrode could be elucidated by assuming a dissociation equilibrium[25] at the electrode surface facing the electrolyte solution, such as

$$\text{Ti-O}^{2-} + \text{H}^+ \rightleftarrows \text{Ti-OH}^- \qquad (1)$$

where Ti-O^{2-} denotes a lattice element of the TiO_2 surface, H^+ a proton in the bulk of the electrolyte solution, and Ti-OH^- the lattice element protonized. A thermodynamic consideration on the dissociation equilibrium (1) leads to the following formula:

$$\mu^\circ_{\text{Ti-O}^{2-}} + RT\ln a_{\text{Ti-O}^{2-}} - 2F\Phi_e + \mu^\circ_{\text{H}^+} + RT\ln a_{\text{H}^+} + F\Phi_s = \mu^\circ_{\text{Ti-OH}^-} + RT\ln a_{\text{Ti-OH}^-} - F\Phi_e \qquad (2)$$

where Φ_e and Φ_s are the potentials of the electrode surface and of the bulk of the solution, respectively. Other symbols have their usual meanings. It follows that the potential difference $\Delta\Phi$ $(=\Phi_e-\Phi_s)$ at the phase boundary TiO_2—electrolyte is expressed as

$$\Delta\Phi = \text{const.} + \frac{RT}{F}\ln\frac{a_{\text{Ti-O}^{2-}}}{a_{\text{Ti-OH}^-}} - \frac{2.3RT}{F}\text{pH} \qquad (3)$$

Provided that the second term in Eq. (3) is not significantly affected by the pH change of the electrolyte solution, the electrode potential of TiO_2 shifts by *ca.* 60 mV (at room temperature) per unit decrease in the pH value. This is shown in Fig. 6.

In the ordinary polarization of a semiconductor electrode through the external circuit, most part of the applied voltage operates within the space charge region inside the semiconductor, and the potential difference across the electrical double layer (in the solution-side of the interface) can hardly be changed, owing to much lower carrier concentration in the electrode than in the bulk of the electrolyte solution. Therefore, the rate of the electron transfer from the excited dye to the semiconductor (sensitized photocurrent) exhibits no detectable dependence on the anodic polarization (practically up to 10 V or more *vs.* S.C.E.) as shown in Fig. 1. The effect of polarization appears only under cathodic polarization where an accumulation layer, which obstructs the electron transfer towards the electrode, is formed at the surface of the semiconductor electrode.

Since the potential difference $\Delta\Phi$ due to pH change of the electrolyte solution is brought about at the electrode surface-electrolyte interface, as is ordinarily the case for the polarization of metal electrodes, the rate of the electron transfer from the excited dye to a semiconductor is expected to depend on the pH of the solution. Postulating an ordinary rate equation for the anodic process and tentatively assuming the one-electron transfer, the anodic sensitized photocurrent i_s can be expressed as

$$i_s \propto \exp\left(\frac{\alpha F}{RT}\eta\right) \tag{4}$$

where α is the transfer coefficient and η the overpotential. In view of the above discussion, the latter can be written as

$$\eta = \text{const.}' + \Delta\Phi \tag{5}$$

Combining Eqs. (3)—(5), one obtains the following formula for the sensitized photocurrent:

$$\log i_s = \text{const.}'' - \alpha\text{pH} \tag{6}$$

This equation seems to hold for the pH-dependence of the sensitized photocurrent at TiO_2 and ZnO electrodes shown in Fig. 4. The value of α falls within 0.26—0.40.

A similar treatment has been reported by Vetter and Gorn[26] concerning the corrosion process taking place at the iron oxide-electrolyte interface. They demonstrated a pH-dependence of the corrosion current, which they accounted for by assuming the potential variation caused by the dissolution equilibrium of oxygen ions at the phase boundary.

In contrast to the sensitized photocurrent, the rate-determining step for the blank photocurrent under long wavelength illumination would be the transport of positively-charged species such as ionized donors from interior to the surface of the electrode, since the latter current originates from light absorption inside the semiconductor. This assumption can be verified by the fact that the magnitude of the blank photocurrent shows practically no pH-dependence (Fig. 1) and that it increases gradually with the increase in the anodic polarization.

The fact that no pH-dependence of the sensitized photocurrent was observed at the CdS electrode would be ascribed to the pH-independence of the potential difference within the double layer, as is indicated by the pH-independence of the flatband potential (Fig. 6). This suggests that no dissociation equilibrium, similar to Eq. (1), could be established at the surface of the CdS electrode.

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