# COMPETITIVE PHOTOSENSITIZED OXIDATION AT TiO_2 PHOTOANODE

Tooru INOUE, Tadashi WATANABE, Akira FUJISHIMA, and Kenichi HONDA

Department of Synthetic Chemistry, Faculty of Engineering,
The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

The rotating ring-disk electrode (RRDE) technique has been applied to the study of photosensitized oxidation of various redox agents in competition with the oxidation of water on a TiO_2 photoanode. The results are discussed referring to the standard redox potentials of the reducing agents.

In a previous paper,[1] we investigated the competitive oxidation between a CdS electrode and several reducing agents by photogenerated holes, by means of the RRDE technique which facilitated a rapid and quantitative determination of the oxidation rates. In the present study similar measurements have been extended to the case of a TiO_2 photoanode. In this case the photosensitized electrolytic oxidation of water proceeds at the electrode surface according to

$$2H_2O + 4h^+ \longrightarrow O_2 + 4H^+ \qquad (1)$$
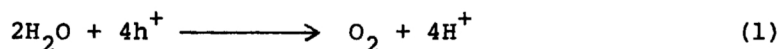
When a reducing agent (Red) is present in the electrolyte solution, it can be oxidized by photoholes(h^+),

$$Red + nh^+ \longrightarrow Ox \qquad (2)$$

in competition with process (1). Although this competitive oxidation at a TiO_2 photoanode has so far been studied by ourselves,[2] Dutoit et al.[3] and Frank and Bard,[4] it was felt that a more systematic investigation was necessary for a better understanding of the mechanism of photoelectrochemical processes. Such an investigation is also expected to provide useful information concerning the selection of electroactive (redox) substances for use in an electrochemical photocell.

An n-type TiO_2 single crystal (Nakazumi Crystal Ltd.) employed in the present study had been reduced under vacuum at 500 $^\circ$C for three hours. The crystal was shaped into a disk 6.0 mm in diameter and 1.0 mm in thickness. The method of ring-disk electrode preparation and of establishment of an ohmic contact has been described elsewhere.[2] The RRDE measurement apparatus was the same as that used in the previous study.[1] The light source was a 500 W high pressure mercury arc lamp and the wavelength range from 300 to 410 nm was used for illumination. All reducing agents, $Fe(CN)_6^{4-}$, hydroquinone (H_2Q), Fe^{2+}, I^-, Br^-, Cl^- and Mn^{2+} were reagent grade. The rotation speed of the RRDE was set at 1000 rpm. The solutions were deaerated with highly purified nitrogen in all experiments.

Figure 1(a) shows the dependences of the disk (I_D) and ring (I_R) currents on the ring potential (E_R), with and without Br^- added in the electrolyte solution. In darkness (curve 1), a negligibly small current is observed at the TiO_2 disk electrode fixed at +1.0 V vs. SCE, while hydrogen evolution (E < -0.3 V) and oxygen evolution (E> +0.9 V) occur at the Pt ring electrode. Illumination of the TiO_2 disk gives rise to an anodic photocurrent (curve 2) and at the same time a reduction current appears at the Pt ring electrode in the potential range more cathodic than +0.1 V vs. SCE. The latter current corresponds to the reduction of oxygen produced by the photosensitized reaction (1). Since the ratio of the limiting reduction current at the Pt ring electrode to the anodic photocurrent at the TiO_2 disk electrode fairly coincides with the theoretical collection efficiency for the ring-disk electrode employed, it is evident that the process (1) is totally responsible for the anodic photocurrent.

By addition of 0.1 M KBr in the electrolyte solution, the magnitude of the disk photocurrent undergoes practically no change, while a new ring current (curve 3) appears at potentials more cathodic than +0.8 V vs. SCE, corresponding to the reduction of Br_2 generated by the process (2). The occurrence of this process can also be verified by the dependence of the disk and ring currents on the disk potential (E_D), with the ring potential fixed at +0.4 V where only Br_2 can be reduced, as shown in Fig. 1(b).

With illuminated TiO_2 disk electrode, the reduction current at potentials more cathodic than +0.1 V vs. SCE remains approximately the same irrespective of the presence or absence of Br^- in the electrolyte solution. If we denote the magnitude of the total ring current (at e.g. -0.2 V) by I_R^o and that due to Br_2 reduction by I_R, the value $100I_R/I_R^o$ can be termed the percentage of the competitive oxidation of Br^- in the course of the photoelectrochemical process at the TiO_2 disk electrode.

Figure 2 shows the percentage (P) of the competitive oxidation of Br^- thus determined as a function of its concentration and the pH value of the electrolyte solution. It is seen that the value of P increases with the increase in
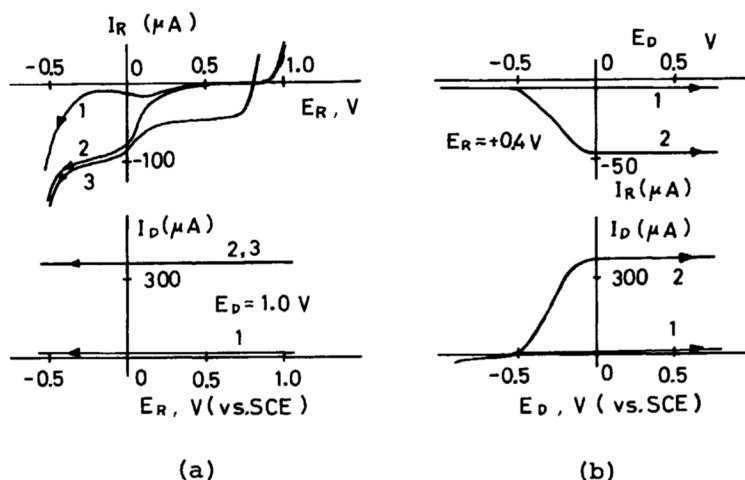

(a)   (b)

Fig. 1. Current-potential curves at the Pt/TiO$_2$ RRDE. rotation: 1000 rpm; electrolyte: 0.2 M Na$_2$SO$_4$, acetate buffer (pH=4.5).
(a) Dependence on the ring potential. E_D=+1.0 V vs. SCE. 1: in darkness, $[Br^-]$=0; 2: illuminated, $[Br^-]$=0; 3: illuminated, $[Br^-]$=0.1 M.
(b) Dependence on the disk potential. E_R=+0.4 V vs. SCE. 1: in darkness, $[Br^-]$=0.1 M; 2: illuminated, $[Br^-]$=0.1 M.

[Br$^-$], as has been described in an earlier report.[2] The decrease in P with the increase in the pH value is explained by invoking the fact that the redox potential for H_2O/O_2 couple is cathodically shifted with increasing pH, whereas that for Br$^-$/Br$_2$ couple is pH-independent (i.e., H_2O is more oxidizable at higher pH). Other halide ions, Cl$^-$ and I$^-$, were also oxidized at the TiO$_2$ photoanode in competition with the oxygen evolution. The values of P for these halide ions also decreased with the increase in pH. When a comparison is made under the same halide ion concentration and the pH of the electrolyte solution, the magnitude of P is in the order I$^-$ >Br$^-$> Cl$^-$. This indicates that a reducing agent with a more cathodic redox potential is more effective in the competitive oxidation (2) at the illuminated TiO$_2$ disk electrode.

When two kinds of reducing agents are added to the electrolyte solution, each reducing agent can be photoelectrochemically oxidized with different efficiency in competition with the oxygen evolution (1). Figure 3 shows the percentage of the competitive oxidation for H_2Q-Cl$^-$ mixed system as a function of H_2Q concentration. Curve 1 corresponds to the case where only H_2Q is present in the electrolyte solution, while curve 2 shows the total effect for the H_2Q-Cl$^-$ mixture with the fixed concentration of 0.01 M Cl$^-$. Curve 3 corresponds to the percentage of the competitive oxidation of Cl$^-$ alone in the mixed system. From the results shown in Fig. 3, one can estimate the effectiveness of photosensitized oxidation of each reducing agent at the TiO$_2$ photoanode under particular conditions. For example, the ratio of the competitive oxidation of H_2O : Cl$^-$: H_2Q, at concentrations of 55M, 10^{-2}M, 10^{-4} M, respectively, is approximately 73 : 15 : 12. Further, the ratio of the oxidizability of Cl$^-$ to that of H_2Q, at a common concentration of 0.01 M for both reducing agents, is nearly 1 : 50.

Figure 4 summarizes the percentages of competitive oxidation for a total of seven reducing agents (each 0.01 M) in 1.0 N
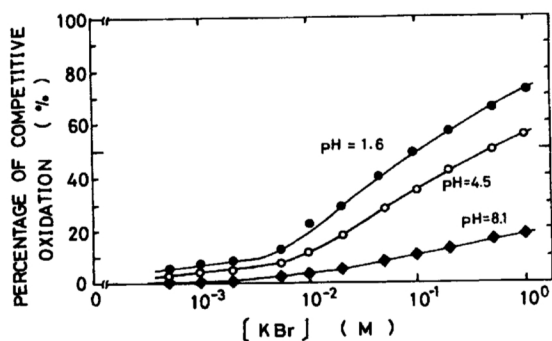

Fig. 2. Percentage of the competitive oxidation of Br$^-$ as a function of its concentration and solution pH.
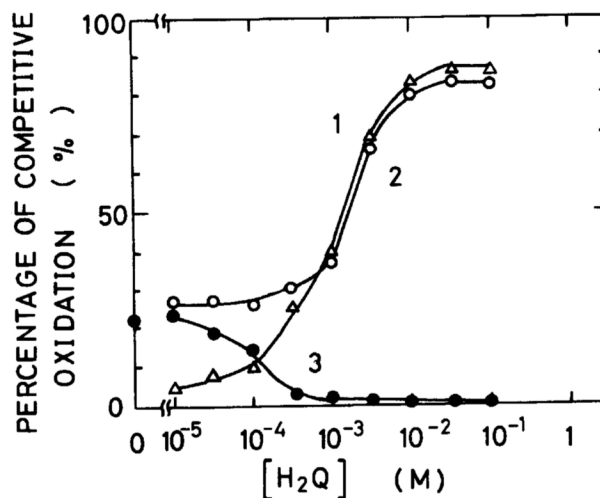

Fig. 3. Dependence of the competitive oxidation of H_2Q, Cl$^-$ and H_2O on [H_2Q]. electrolyte: 0.2 M Na$_2$SO$_4$ + 1.0 N H$_2$SO$_4$ 1: H_2Q alone; total effect of H_2Q and Cl$^-$ in the mixed system ([Cl$^-$]=0.01 M]; 3: effect of Cl$^-$ alone in the mixed system.
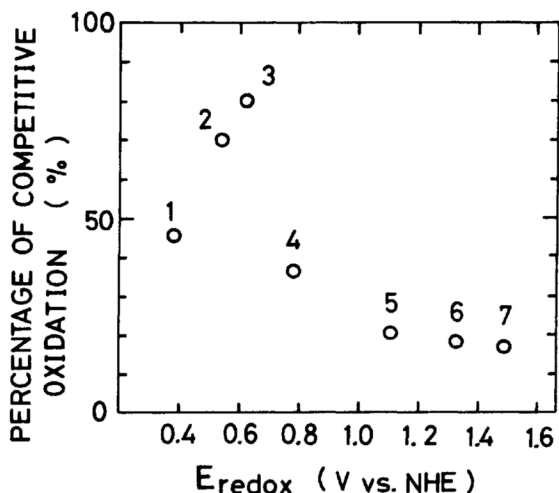
Fig. 4. Percentage of the competitive oxidation of reducing agents (0.01 M) in 1.0 N H_2SO_4 as a function of their standard redox potentials.
1: $Fe(CN)_6^{3-/4-}$, 2: I_2/I^-, 3: Q/H_2Q, 4: $Fe^{3+/2+}$, 5: Br_2/Br^-, 6: Cl_2/Cl^-, 7: $Mn^{3+/2+}$.

H_2SO_4 aqueous solution, as a function of their redox potentials vs. NHE. Frank and Bard,[4] who studied the competitive oxidation of H_2Q, I^-, Br^-, Cl^- and Ce^{3+} on a TiO_2 photoanode by means of chemical analysis, obtained the result similar to that in Fig. 4. According to Gerischer,[5] an efficient charge transfer at a semiconductor/electrolyte interface can take place only when the distribution function of the electronically occupied state in one phase overlaps well with that of unoccupied state in another. The conduction and the valence band of the TiO_2 electrode is situated at ca. 0.0 V and 3.0 V vs. NHE, respectively, for the pH value used in the present measurement. Even when one postulates a reorganization energy as high as 1.5 eV for the redox couple Q/H_2Q, a satisfactory overlap between the occupied state in the redox couple and the unoccupied state (photoholes in the valence band) in the TiO_2 photoanode seems improbable. Therefore, the result shown in Fig. 4 might indicate the participation of some surface energy level in the charge transfer process between the TiO_2 photoanode and redox agents, as has recently been suggested by Frank and Bard.[6]

In conclusion, we could prove the usefulness of the RRDE measurement technique for the investigation of photoelectrochemical processes at the semiconductor/electrolyte interface. Further application of this method to various problems in this field is now being undertaken.

References

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