

Vanishing of Current-Doubling Effect in Photooxidation of 2-Propanol on TiO₂ in Solutions Containing Fe(III) Ions

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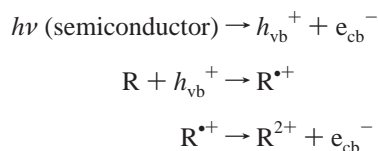
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When organic compounds such as 2-propanol are in aqueous solutions and are photooxidized on the surface of semiconductor electrodes, the current quantum efficiency can reach close to 200% (current-doubling effect). However, we found that the current-doubling effect in the photooxidation of 2-propanol on TiO₂ electrodes disappeared in solutions containing Fe(III) ions. From the analyses of the products, we found that acetone was produced in quantitative correlation to the photocurrent, and that practically no Fe(II) ions were generated in the solution. We also found that Fe(II) ions were not oxidized at a TiO₂ photoanode in a solution containing Fe(III) ions, while they were oxidized in quantitative correlation to the photocurrent in the solution without Fe(III) ions. These results refuted the possibility that Fe(III) ions accepted electrons from the oxidation intermediates of 2-propanol. The plausible reason for the disappearance of the current-doubling effect is that 2-propanol is oxidized by two holes on the Fe(III)-adsorbed TiO₂ surface.

Introduction

Current-doubling effects are sometimes observed when organic compounds are photooxidized on semiconductor electrodes.^{1–14} These effects are attributed to the simultaneous oxidation of the reaction intermediates, which occurs by the release of electrons into the conduction band. The oxidation intermediates of inorganic compounds also sometimes inject electrons, and a current-quadrupling effect is observed for the photocorrosion of Si electrodes in HF solutions.^{15,16}

On photoirradiated semiconductors, photooxidation of organic compounds, such as alcohols, aldehydes, or formate, proceeds successively as follows:



After releasing two protons, the R²⁺ form of alcohols generates ketones or aldehydes. As a result, one photon produces two electrons in the conduction band, leading to a 200% quantum efficiency.

On TiO₂ photocatalysts, oxidative decomposition of various organic compounds has been extensively studied.^{17–19} The mechanism of photocatalytic reactions is considered to be similar to that of semiconductor photoelectrodes.^{20,21} To understand the efficiency of photocatalytic reactions, a discussion of the current-doubling effect is necessary. Since the current cannot be monitored in the particulate system, the information obtained with the electrode system is very useful.

For the efficient photocatalytic oxidation of various compounds, the choice of electron acceptors to be added to the reaction system is very important. Fe(III) ions show great capacity to act as electron acceptors.^{22,23} In solutions containing Fe(III) ions, even water can be oxidized to molecular oxygen

with high efficiency using rutile TiO₂ powder.²⁴ The usefulness of Fe(III) ions as electron acceptors for the photocatalytic oxidation of organic compounds has been discussed previously in the literature.^{22,23}

Here, we report that the current-doubling phenomena for the photooxidation of 2-propanol on TiO₂ electrodes disappears with the addition of Fe(III) ions to solution. The finding is especially important as regards the efficiency of photocatalytic reactions.

Experimental Section

Materials. TiO₂ single crystals having the rutile crystalline form were obtained from Earth Chemical Co. Anion-exchange membrane was obtained from Tokuyama Co. Guaranteed-grade Fe(III) nitrate and Fe(II) nitrate were obtained from Wako Pure Chemicals. For colorimetry of Fe(II) ions, 2,4,6-tris(2-pyridyl)-s-triazine (TPTZ) obtained from Dojindo Laboratories was used as the complexing reagent. All other chemicals used in the experiments were purchased from commercial sources as guaranteed-grade reagents and used without further purification.

Preparation of TiO₂ Single-Crystal Electrode and Electrochemical Experiments. Rutile TiO₂ single crystals were heated in a stream of hydrogen at 650 °C for 1 h so as to gain the electrical conductivity. The electrodes for photoelectrochemistry were fabricated by connecting copper wire to the back surface of the TiO₂ crystals via a Ga–In alloy.

The electrochemical measurements were carried out in 0.1 mol dm^{−3} H₂SO₄ aqueous solutions (50 mL) under potentiostatic conditions using a potentiostat (Nikkokeisoku, NPOT-2501) and an Ag/AgCl electrode as a reference electrode. A platinum plate was used as a counter electrode. For observation of current doubling, 2-propanol (25% in volume) was added to the aqueous solutions. The effect of Fe(III) ions was investigated by adding Fe(III) ions to the solutions at various concentrations. A 500 W high-pressure mercury lamp (Wacom, BMO-500DY) was used as a light source. The light beam was passed through a copper sulfate solution to cut off infrared radiation and a U-360 band-pass filter to take out the 365 nm light.

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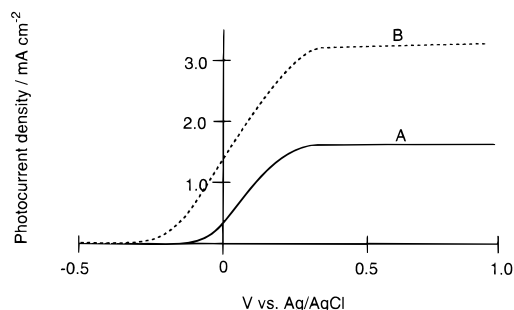


Figure 1. Photocurrent–voltage characteristics of a TiO_2 electrode measured in 0.1 M H_2SO_4 (A) and in 0.1 M H_2SO_4 containing 2-propanol (25% in volume) (B).

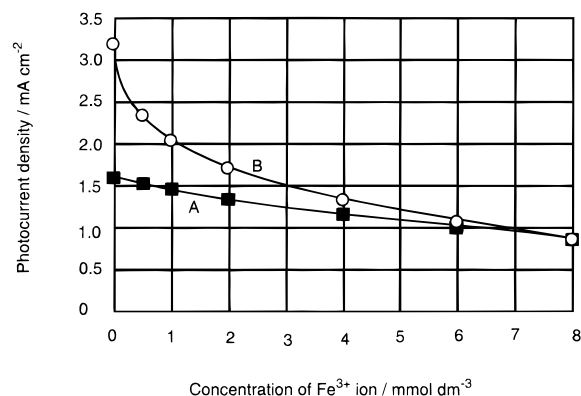


Figure 2. Saturated value of photocurrent vs concentration of Fe(III) ions measured in 0.1 M H_2SO_4 (A), and in 0.1 M H_2SO_4 containing 2-propanol (25% in volume) (B). Photocurrents were measured at 1.0 V vs Ag/AgCl .

For the analyses of the reaction products, we used an H-type cell in which the products generated on TiO_2 electrode were separated by anion-exchange membrane from the compartment of the counter electrode. Acetone generated by photocatalytic reactions was analyzed by gas–liquid chromatography. Concentrations of Fe(II) ions and Fe(III) ions in the solutions were determined from UV–vis absorption spectra, which were measured with a Shimadzu UV-2500PC spectrophotometer. Before the spectroscopic measurements, Fe(II) ions were colored by complexing with TPTZ in solutions at pH 4.6, and Fe(III) ions by complexing with chloride ions in solutions of 6 mol dm^{-3} hydrochloric acid.

Results and Discussion

Photocurrents of TiO_2 Single-Crystal Electrodes in Solutions with and without 2-Propanol. Figure 1 shows the typical photocurrent–voltage characteristics of a TiO_2 electrode in 0.1 mol dm^{-3} H_2SO_4 solution with and without 2-propanol. When 2-propanol is included in the solution, the saturated photocurrent density is doubled; this represents the typical current-doubling effect. In addition, with 2-propanol in the solution, the onset of the photocurrent shifts toward a negative potential by about 0.2 V. This result is consistent with the fact that 2-propanol is more likely to be oxidized on TiO_2 than water.²⁵

The saturated current density observed in solution containing 2-propanol was found to be lowered by the addition of Fe(III) ions to the solution, as seen in Figure 2. A decrease in the saturated current density was also observed in solutions prepared without 2-propanol, where water is oxidized to oxygen. This decrease can be attributed to the filter effect of Fe(III) ions present in the solution. Compared with this profile, the saturation current observed in the solution containing 2-propanol was

TABLE 1: Experimental Results and Expected Production of Acetone and Fe(II) Ion and the Current Multiplication Effect from Three Possible Reaction Routes

	acetone/electron	Fe^{2+} /electron	current multiplication
exptl results	0.50	0.0	1.0 ^a
exptl results ^b	0.52		2.0 ^a
route 1	0.50	0	2
route 2	0	0	1
route 3	1	1	1

^a Ratio of photocurrent observed at 1.0 V vs Ag/AgCl in solution with 2-propanol compared with that in solution without 2-propanol.

^b Results obtained in solution without Fe(III) ions.

drastically lowered by the addition of Fe(III) ions. The addition of 8×10^{-3} mol dm^{-3} Fe(III) ions caused the current-doubling effect to vanish completely.

If 2-propanol is photooxidized by the current doubling mechanism (route 1), one photon gives one acetone molecule and two electrons (or current doubling). However, experimental results have shown that the current-doubling effect disappeared in the presence of Fe(III) ions in the solution. A possible explanation for the disappearance of the current-doubling effect by the addition of Fe(III) ions is that instead of 2-propanol, water becomes photooxidized on TiO_2 (route 2). By this mechanism, no acetone can be produced. In contrast to this expectation, from the analyses of the reaction products, we found that quantitative amounts of acetone were produced. For example, after passing 11.5 C (119.2 μmol of electrons) of photocurrent through the solution, 59.5 μmol of acetone was produced. This observation means that two electrons flow for generation of one acetone molecule and it excludes the possibility of the oxidation of water.

Another possible explanation for the disappearance of the current-doubling effect is that the electron released from the oxidation intermediate of 2-propanol is captured by Fe(III) ions (route 3). This mechanism has been proposed for the quenching of the current-doubling effect at a ZnO electrode by the addition of Cu(II) ions.² In our case, the mechanism leads to the generation of one acetone molecule and one Fe(II) ion by one photon. However, we found that no Fe(II) ions are produced in the solution after passing photocurrents through it. Reoxidation of Fe(II) ions at the TiO_2 electrode is ruled out by the fact that water is effectively oxidized on photoirradiated TiO_2 in solution containing both Fe(II) and Fe(III) ions. More precisely, from the analysis of the concentrations of Fe(II) and Fe(III) ions, we found that only 0.57 μmol of Fe(II) ions were oxidized at a TiO_2 anode in the solution of 8×10^{-3} mol dm^{-3} Fe(II) ions containing 4×10^{-3} mol dm^{-3} Fe(III) ions after passing 2.29 C (23.8 μmol of electrons), while 138 μmol of Fe(II) ions were oxidized in a solution of 8×10^{-3} mol dm^{-3} Fe(II) ions without Fe(III) ions after passing 13.4 C (139 μmol of electrons) of photocurrent. These results are consistent with the efficient photooxidation of water on TiO_2 particles in the solution containing Fe(III) ions.²⁴

Table 1 summarizes the experimental results as well as the expected production of acetone and Fe(II) ions and the current-doubling effect for the above three routes. All of these three routes are inconsistent with the experimental results. After rejecting these possibilities, we can only account for the results of the present study by assuming that when Fe(III) ions are added to the solution, 2-propanol is oxidized by two holes on the surface of TiO_2 .

In a previous report, we discussed the specific affinity of Fe(III) ions to TiO_2 surfaces in aqueous solutions.²⁴ In solutions

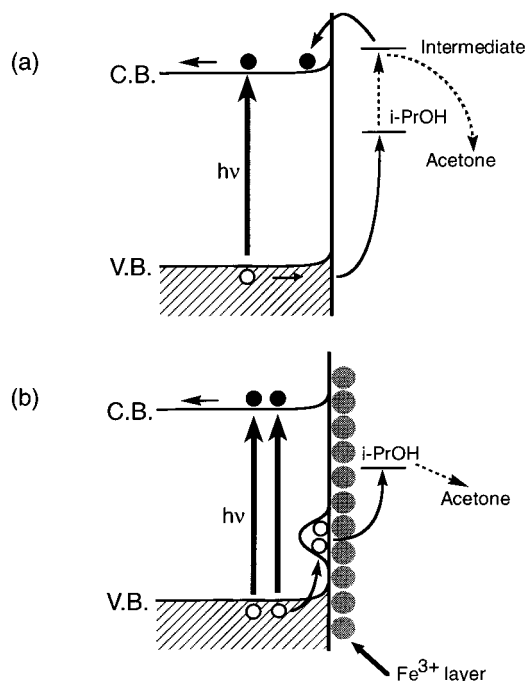


Figure 3. Mechanisms for the oxidation of 2-propanol on photoirradiated TiO_2 in aqueous solutions without Fe(III) ions (a) and with Fe(III) ions (b).

containing Fe(III) ions at concentrations higher than $2.0 \times 10^{-3} \text{ mol dm}^{-3}$, the whole TiO_2 surface was mono-molecularly covered with Fe(III) ions. Furthermore, we found that the TiO_2 electrodes, on which Fe(III) ions are adsorbed, have improved ability to photooxidize water.²⁴ Although we do not know the details of the mechanism of the improved photooxidation of water by Fe(III) ions, we can assume that the Fe(III) ions that are adsorbed on the TiO_2 surface stabilize the oxidation intermediates or trapped holes on the surface. The accumulation of the intermediates (or surface trapped holes) is considered to lead to the oxidation of 2-propanol by two holes. The proposed reaction mechanisms for the oxidation of 2-propanol in solutions with and without Fe(III) ions are illustrated in Figure 3.

Conclusion

The current-doubling effect has long been known in the field of semiconductor photoelectrochemistry. This phenomenon is

found to be important to discussions of the efficiency of photocatalytic reactions on semiconductor photocatalysts. The disappearance of the current-doubling effect on TiO_2 electrodes by the addition of Fe(III) ions is of note because Fe(III) ions are often added to photocatalytic reaction systems.

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