Quartz Crystal Microbalance Study on Photoelectrochemical Deposition of Lead(IV) Oxide on Titanium(IV) Oxide Nanoparticulate Films

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Photoelectrochemical quartz crystal microbalance measurements were used for *in situ* monitoring of the photoelectrochemical deposition of PbO₂ onto a TiO₂ nanoparticulate film electrode. It was found that the photodeposition behavior of PbO₂ was influenced by pH of solution. At pH 3.8, the mass of the TiO₂ film electrode decreased in the initial stage of irradiation due to the desorption of Pb²⁺ from the TiO₂ surface and then linearly increased due to PbO₂ deposition with an increase in the charge flowing as a photocurrent, while the initial decrease of the mass was much smaller at pH 1.8.

Key Words : TiO₂ Nanoparticulate Film, Photodeposition, PbO₂, QCM

1 Introduction

TiO₂ nanoparticulate thin films have attracted much attention because of their potential applications for photovoltaic devices^{1, 2)} and photocatalysts.^{3, 4)} The behavior of electrons in the conduction band of a TiO₂ film, which are generated by direct photoexcitation of TiO₂ or injected from a photoexcited dye adsorbed on the TiO₂ film, has been intensively investigated by using various techniques, such as laser pulse-induced transient photocurrent measurements^{5–8)} and intensity-modulated photocurrent spectroscopy,^{9–11)} and the mechanism of electron transport in a TiO₂ film has been clarified. On the other hand, reactions of positive holes with redox species in solution are also important, especially for clarification of the mechanism of photocurrent generation with band-gap excitation of TiO₂. Furthermore, it has been reported that these reactions can be utilized for photocatalytic degradation of organic pollutants.^{3, 4)} However, little is known about the details of reactions of photogenerated holes in a TiO₂ nanoparticulate film surface.

The quartz crystal microbalance (QCM) technique enables measurement of mass changes with a precision of the order of nanograms, and a combination of the QCM technique with electrochemical measurements provides a powerful tool for clarifying the interfacial processes, such as deposition/dissolution of mono- and multi-layers, mass transport in modified layers, and adsorption kinetics.¹²⁾ The QCM technique has also been employed for *in situ* monitoring of mass transfer in photoelectrochemical processes, such as photochemical intercalation of protons in TiO₂ particles under accumulation conditions,¹³⁾ photocorrosion of CdSe electrodes,¹⁴⁾ and photoreduction behavior of polyaniline films containing TiO₂ particles.¹⁵⁾ Since it has been reported that the irradiation of TiO₂

films in the presence of Pb²⁺ in solution caused the deposition of PbO₂ particles on the film surface,¹⁶⁾ the photoelectrochemical QCM technique may also be a promising method for investigation of the reactions of photogenerated positive holes in TiO₂ films with Pb²⁺ in solution. To the best of our knowledge, however, such analyses of oxidative photodeposition of a metal oxide on a semiconductor surface have never been reported.

In this study, photoelectrochemical QCM measurements were used for *in situ* monitoring of the photodeposition of PbO₂ onto a TiO₂ nanoparticulate film electrode, and the pH dependence of its growth rate was clarified.

2 Experimental Section

Commercially available TiO₂ colloid aqueous solution (TiO₂ content: 0.85 wt%) (TO sol, Mitsui Mining Material Co., Ltd) was used in this study. TiO₂ particles had the anatase crystalline phase, and the average size of the particles was 10 nm. AT-cut, 5-MHz circular quartz crystal wafers with a diameter of 1.3 cm were used for the substrate, onto which 100 nm of titanium and 200 nm of gold were successively deposited by a vacuum evaporation. The area of gold electrode was 0.59 cm². After the original TiO₂ colloid has been diluted five times with water, a 20 mm³ portion of the resulting solution was cast onto the gold film on one side of the quartz crystal, followed by drying in air. By repeating these procedures, a film having 170 μg cm⁻² TiO₂ was prepared, the amount of immobilized TiO₂ particles being determined from the frequency difference in the quartz crystal between before and after preparation of the TiO₂ film. The films were finally calcined at 500°C for 1 h.

A quartz crystal was mounted in a QCM detector head connected to a home-made oscillator in a copper Faradic

cabin to avoid surrounding electromagnetic noise. The frequency was monitored with a universal frequency counter (Hewlett-Packard, HP53131A). Frequency data were analyzed on the basis of Sauerbrey's equation.¹⁷⁾ Since a 5-MHz quartz crystal was used, a frequency decrease of 1 Hz corresponded to an increase in the mass of 17.7 ng cm^{-2} , which was calibrated by electrochemical deposition of silver on the crystal. The TiO_2 -coated gold electrode on the quartz crystal and a platinum foil were used as a working electrode and a counter electrode, respectively. A real hydrogen electrode was used as a reference electrode. Potentials in this paper are referred to an Ag/AgCl electrode. The potential was controlled by a Hokuto Denko HA-301 potentiostat, and photocurrent responses were recorded on a Graphtec WX1200 X-Y-t recorder. Irradiation of the TiO_2 film electrode was performed by chopping light with a wavelength of $350 \pm 30 \text{ nm}$ at 100 Hz, which was obtained by passing light from a 300 W xenon lamp through a band-pass filter. The irradiation light intensity was 0.19 mW cm^{-2} . All measurements were performed under argon atmosphere. The pH in an electrolyte solution was adjusted with HClO_4 to the value lower than 4, because at the higher pH the precipitation of $\text{Pb}(\text{OH})_2$ occurred.

3 Results and Discussion

By adding a $\text{Pb}(\text{ClO}_4)_2$ solution into the electrolyte and stirring for several seconds, the frequency rapidly decreased and then reached a constant value after the system was left to stand for about 30 min. Figure 1a shows the frequency change of QCM crystal (Δf) as a function of $\text{Pb}(\text{ClO}_4)_2$ concentration in the electrolyte. The fre-

Fig. 1 (a) Frequency change of a TiO_2 -coated QCM electrode as a function of the concentration of $\text{Pb}(\text{ClO}_4)_2$ in a solution (pH 3.8) containing 0.10 mol dm^{-3} NaClO_4 . (b) Dependence of the frequency change on pH of a solution containing 0.10 mol dm^{-3} $\text{Pb}(\text{ClO}_4)_2$ and 0.10 mol dm^{-3} NaClO_4 .

quency decreased with an increase in the concentration of Pb^{2+} and finally gave the saturated value. No obvious change in the frequency was observed when NaClO_4 solution was introduced in the similar way. These facts indicated that the frequency decrease in TiO_2 films was caused by the adsorption of Pb^{2+} on TiO_2 surface, which enhanced with an increase of the solution concentration of Pb^{2+} . The frequency of the QCM crystal in a solution containing Pb^{2+} ion was also influenced by the pH of the solution as shown in Fig. 1b; the frequency decreased drastically with increase in pH. Since TiO_2 has the point of zero charge at 6.9,¹⁸⁾ the surface hydroxyls of TiO_2 were protonated, the degree of which was enhanced at lower pH. The pH-dependent frequency response must be caused by the decrease in the amount of Pb^{2+} adsorption due to the electrostatic repulsion between Pb^{2+} ions and the positively charged TiO_2 surfaces. Similar pH dependence has been reported for the adsorption of Ag^+ on TiO_2 particles.¹⁸⁾

Figure 2 shows photocurrent and frequency responses observed with UV light irradiation under potential application at 0.83 V vs. Ag/AgCl. In order to obtain the efficient charge separation of photogenerated charge carriers in TiO_2 electrodes, the potential more positive than the flat band potential of anatase TiO_2 ($-0.58 \text{ V vs. Ag/AgCl}$ at pH 3.8¹⁹⁾) was applied. No appreciable current or frequency change was observed without the UV irradiation. An anodic photocurrent was observed during the UV irradiation, regardless of the presence of Pb^{2+} in the solution, and their magnitude decreased rapidly in an early stage of irradiation and then gave the constant value. The anodic photocurrent would be generated by scavenging positive holes photogenerated in TiO_2 parti-

Fig. 2 Time course of photocurrent (a) and frequency change (b) during UV irradiation of a TiO_2 film under the potential application of 0.83 V vs. Ag/AgCl. The electrolyte solutions used were 0.10 mol dm^{-3} NaClO_4 aqueous solution (pH 3.8) with (●) and without (○) 0.10 mol dm^{-3} $\text{Pb}(\text{ClO}_4)_2$.

cles, according to eq.1 and both eqs. 1 and 2 in the absence and presence of Pb^{2+} in aqueous solutions, respectively.

It should be noted that the magnitude of photocurrent observed became small with addition of Pb^{2+} in the solution. Since Pb^{2+} ions were strongly adsorbed on the TiO_2 surface as shown in Fig. 1, this result might be caused by the formation of recombination sites of photogenerated electrons and holes at the TiO_2 surface with the Pb^{2+} adsorption. Figure 2b shows the frequency change with UV irradiation. No significant frequency change was observed in the absence of Pb^{2+} in solution, indicating that the reaction of eq. 1 caused by UV irradiation could not influence the frequency of QCM crystals under the conditions used in this study. On the other hand, it is expected in the presence of Pb^{2+} that the deposition of PbO_2 occurs during UV irradiation; the frequency of QCM decreases monotonically with irradiation. As shown in Fig. 2b, however, the observed behavior of frequency changes was different than that expected: in the initial stage of irradiation, the frequency increased up to a maximum value (*ca.* 13 Hz) (stage I) and then decreased with time (stage II). As shown in Fig. 3, when the irradiation was interrupted during stage I, the frequency quickly decreased and finally became a constant value, which was smaller than that before the irradiation. The repetition of this procedure caused a similar rapid decrease in the frequency. This frequency decrease due to short-time irradiation indicates that PbO_2 had been already deposited in stage I, while an increase in frequency was observed during the irradiation. It should be noted that the reactions in both eqs. 1 and 2 released H^+ into the solution and then decreased pH near the TiO_2 film surface. Considering the pH dependence of Pb^{2+} adsorption on a TiO_2 surface and the frequency change in

Fig. 3 Frequency change of a TiO_2 -coated QCM electrode observed with interruption of irradiation. The electrode potential was 0.83 V vs. Ag/AgCl. The electrolyte solution used was 0.10 mol dm^{-3} NaClO_4 aqueous solution (pH 3.8) containing 0.10 mol dm^{-3} $\text{Pb}(\text{ClO}_4)_2$.

Fig. 4 Frequency change of a TiO_2 -coated QCM electrode under the potential application of 0.83 V vs. Ag/AgCl in solutions with pH 1.8 (solid circles) and 3.8 (open circles) as a function of the charges flowing as an anodic photocurrent. The electrolyte solutions used were aqueous solutions containing 0.10 mol dm^{-3} NaClO_4 and 0.10 mol dm^{-3} $\text{Pb}(\text{ClO}_4)_2$.

stage I, much smaller than that caused by Pb^{2+} adsorption at pH 3.8, *ca.* -1700 Hz, the local pH change would cause desorption of a part of the adsorbed Pb^{2+} , and then the mass of the TiO_2 film would decrease with irradiation until the mass change with Pb^{2+} desorption is smaller than that with PbO_2 deposition. Thus, the decrease in frequency observed with the interruption of irradiation shown in Fig. 3 is attributable to the re-adsorption of Pb^{2+} due to recovery of the local pH value to the value before irradiation.

This view is supported by the frequency responses of a TiO_2 -coated QCM electrode during UV light irradiation in solution at pH 1.8. Figure 4 shows the frequency changes obtained under the potential application of 0.83 V vs. Ag/AgCl in the solutions at pH 1.8 and 3.8 as a function of amount of charges flowing as an anodic photocurrent. At pH 1.8, the initial increase in frequency was much smaller than that at pH 3.8, indicating that a smaller amount of Pb^{2+} was desorbed. These facts could be accounted for by the smaller amount of adsorbed Pb^{2+} on TiO_2 at pH 1.8 than at pH 3.8, as shown in Fig. 1b, and by the relatively small changes in local pH with the reactions of eqs. 1 and 2 owing to the higher H^+ concentration. Furthermore, it should be noted that a linear relation was observed between the frequency change and the charge flowing as photocurrent in stage II as shown in Fig. 4, regardless of the pH in the solutions. This fact indicated that the constant fraction of the photocurrent, at least in stage II, was consumed for the deposition of PbO_2 on the TiO_2 surface. The adsorbed mass change per mole of electrons (mpe) can be calculated from the linear relations, and the values of 27.8 and 79.5 $\text{g mol}(\text{e}^-)^{-1}$ were obtained for pH 1.8 and 3.8, respectively. When the electrochemical deposition of PbO_2 on a gold electrode was performed in an aqueous solution containing $\text{Pb}(\text{ClO}_4)_2$ at pH 3.8 under the potential application at 1.10 V vs. Ag/AgCl, which is more positive than the equilibrium potential of $\text{PbO}_2/\text{Pb}^{2+}$ (0.80 V vs. Ag/

AgCl),²⁰⁾ an mpe value of $121 \text{ g mol(e}^{-})^{-1}$ was obtained, which is in good agreement with that expected from eq. 2 ($120 \text{ g mol(e}^{-})^{-1}$). Based on the assumption that PbO_2 deposition caused the observed frequency decrease and positive holes photogenerated in TiO_2 particles were competitively consumed by the water and Pb^{2+} oxidation, the photocurrent efficiencies of the PbO_2 deposition were determined to be 23.3 and 66.5% at pH 1.8 and 3.8, respectively. Since the amount of adsorbed Pb^{2+} decreased with a decrease in pH in solution as shown in Fig. 1b, the observed pH dependence in the efficiencies of the PbO_2 photodeposition was probably due to the change in the surface concentration of Pb^{2+} available for scavenging positive holes photogenerated in TiO_2 films.

In conclusion, it has been revealed by photoelectrochemical QCM measurements that photogenerated holes react with surface-adsorbed Pb^{2+} and/or water to desorb Pb^{2+} and that the current efficiency of photodeposition of PbO_2 is governed by pH-dependent Pb^{2+} adsorption.

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