Preparation of titanium(IV) oxide film on a hard alumite substrate

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TiO₂ was deposited onto hard alumite (Al/Al₂O₃/TiO₂) by alternating current electrolysis and precipitation in (NH₄)₂[TiO(C₂O₄)₂] solution at various temperatures, where the hard alumite was prepared by the anodic oxidation of aluminum in sulfuric acid (Al/Al₂O₃). The TiO₂ electrodeposition mainly occurred at temperatures lower than about 50 °C, while the TiO₂ deposition due to TiO(C₂O₄)₂²⁻ adsorption onto alumina predominantly occurred at temperatures higher than about 50 °C. The amount of deposited TiO₂ increased with the increase in the deposition temperature, leading to high photocatalytic activity. The deposited TiO₂ at 90 °C followed by heat-treatment at 550 °C had an anatase structure and showed a high photocatalytic activity for the decomposition of acetaldehyde even under fluorescent lamp illumination. The Al/Al₂O₃/TiO₂ prepared at 50 °C was optimal for practical use, because of a relatively high activity and the sufficient adhesion strength between the TiO₂ and the Al/Al₂O₃ substrate due to the presence of the deposited TiO₂ in the pores of the alumina film.

I. INTRODUCTION

 TiO_2 is a promising material as a photocatalyst for photodecomposition reactions such as the photolysis of water¹⁻⁶ and decomposition of some chemical compounds^{7–15} under illumination. Various preparation and fixation methods for the TiO₂ photocatalyst have already been reported.^{14,16–28} The sol-gel or a similar method is most important^{11–14,18–22} because the prepared TiO₂ has a small size and therefore a high specific surface area. This is preferable for a catalyst,^{20–29} although the cost for preparation of these types of TiO₂ is generally high. Consequently, a low-cost preparation and fixation of the TiO₂ photocatalyst with nano-sized particles is necessary for practical use.

Aluminum is widely used as a building material because it is relatively cheap and light. Generally, aluminum is electrochemically oxidized to produce an alumite (aluminum with a porous alumina film, denoted by Al/ Al_2O_3), which protects against corrosion.^{30,31} It is well known that the alumite prepared by anodic oxidation in sulfuric and phosphoric acids has self-organized and nano-sized pores.^{30–33} Some metal and metal oxides can be deposited in the pores of the alumina film by alternating current (ac) and/or direct current (dc) electrolysis, and some metal deposited alumite is used as "colored alumite."^{30,34} Alumite will be useful as a substrate for the TiO₂ photocatalyst film because the alumite has nano-sized pores and may act as a carrier of the catalyst.

We developed new low-cost electrochemical methods for directly depositing the TiO₂ photocatalyst onto an Al/Al₂O₃ substrate (denoted by Al/Al₂O₃/TiO₂). In these cases, the electrodeposition was made by two-step³⁵ or onestep³⁶ electrolysis. In the former case, the as-deposited TiO₂ consisted of mixtures of the anatase, rutile, and amorphous phases, and showed high photocatalytic activity. However, the adhesion strength between the TiO_2 and the Al/Al₂O₃ substrate was insufficient for practical use. On the other hand, in the latter case, although the deposited TiO₂ showed low photocatalytic activity compared with that deposited by the two-step electrolysis because of its relatively small amount, an improvement in the adhesion between the deposited TiO_2 and the Al/Al₂O₃ substrate was accomplished. In this study, it is demonstrated that the Al/Al₂O₃ (hard alumite)/TiO₂ prepared by the one-step electrolysis showed high photocatalytic activity due to the increase in its amount by the temperature control of the electrolyte. Moreover, the most optimal preparation conditions were determined for the Al/Al₂O₃/TiO₂ from a comparison of the photocatalytic activity and adhesion strength between the TiO₂ and the Al/Al₂O₃ substrate.



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II. EXPERIMENTAL

An aluminum plate ($60 \times 50 \times 1$ mm thick) was etched by immersion in alkaline solution and then electrochemically oxidized at 20 mA cm⁻² in H₂SO₄ solution (2.5 M) for 45 min at 2 °C to prepare the porous hard alumite on its surface (Al/Al₂O₃). TiO₂ was electrodeposited by alternative electrolysis (60 Hz) or precipitated into the pores of the alumina film prepared by the previous method (Al/Al₂O₃/TiO₂). The TiO₂ deposition was carried out in a mixed aqueous solution consisting of 10^{-2} M (NH₄)₂[TiO(C₂O₄)₂] and 2.5 × 10⁻³ M (COOH)₂ adjusted to pH 4 by titration with NH₄OH for 10 min at various temperatures. A graphite plate ($50 \times 60 \times 10$ mm thick) was used as the counter electrode, and the distance between the counter and working electrode was fixed at 50 mm.

The morphology and elemental distribution of the prepared Al/Al₂O₃/TiO₂ were observed using electron probe microanalysis (EPMA). The amount of the deposited TiO₂ was analyzed by inductively coupled plasma (ICP) spectroscopy, where the sample was dissolved in 1.2 M H₂SO₄ and then the solution was analyzed. The ultraviolet (UV) and visible (vis) absorption spectrum of the Al/Al₂O₃/TiO₂, anatase (99.9%, Wako, Ltd., Osaka, Japan), and rutile TiO₂ (99.9% Wako, Ltd.) were measured with a UV-vis spectrophotometer. The structure of the TiO₂ films after the heat treatment was examined by x-ray diffraction analysis (XRD) using monochromatic Cu K_α radiation.

The photocatalytic activity of the prepared Al/Al₂O₃/TiO₂ was measured for the photodecomposition of acetaldehyde. A small amount of acetaldehyde gas was injected into a 1000-ml cylindrical quartz cell ($62.5 \text{ cm}^2 \times 16 \text{ cm}$), in which the Al/Al₂O₃/TiO₂ was previously fixed, and then illuminated. A 500-W xenon lamp (200 mW cm⁻²) and a 24-W fluorescent lamp (rareearth lamp, Mitsubishi-BS3601B, Tokyo, Japan, 10 mW cm⁻²) were used as the light sources.

III. RESULTS AND DISCUSSION

A. Deposition of TiO₂

Figure 1 shows the amount of TiO₂ deposited on the Al/Al₂O₃ substrate under various temperatures as a function of the applied maximum ac voltage. Most of the voltage was applied to the alumite side because the resistance of the electrolyte is very low (14.57 mS cm⁻¹). The amount of TiO₂ in the Al/Al₂O₃/TiO₂ was about 0.5×10^{-5} g cm⁻² in the voltage region less than about 8 V at 20 °C. However, this amount increased with the increase in the voltage region higher than about 9 V. In the electrolysis above 9 V brings about the reduction of H⁺ and/or H₂O, leading to deposition of TiO₂ due to the pH increase in the pores of the alumina film.

It should be noted that the amount of deposited TiO_2 remarkably increased with the increase in the electrolyte temperature. The amount of deposited TiO_2 did not depend on the ac voltage, and the deposition occurred even under no bias. Figure 2 shows an Arrhenius plot of the amount of the deposited TiO_2 as a function of temperature. For the nonapplied voltage [Fig. 2(b)], the log (amount of deposited TiO_2) increased linearly with K^{-1} , but not for the applied ac 12 V [Fig. 2(a)], where two regions are observed in the temperature dependence. The amount of the deposited TiO_2 depends on the applied ac voltage at 20 °C as shown in Figs. 1 and 2



FIG. 1. Amount of deposited TiO_2 as a function of the applied maximum ac voltage at various temperatures.



FIG. 2. Arrhenius plot of the amount of deposited TiO_2 for the (a) applied at 12 V and (b) nonapplied at voltage.

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when the voltage is higher than about 9 V. Consequently, the electrodeposition of TiO₂ predominantly occurs in the region of less than about 50 °C, while chemical deposition predominantly occurs at temperatures higher than about 50 °C. The activation energy of the chemical deposition was estimated to about 48.6 kJ mol⁻¹ from the slope in Fig. 2. Under a nonapplied ac voltage, the TiO₂ chemical deposition mainly occurred on the Al/Al₂O₃ substrate according to the Fig. 2 analysis since TiO(C₂O₄)₂²⁻ existing in the (NH₄)₂[TiO(C₂O₄)₂] solution at pH 4 will strongly adsorb on alumina surfaces whose pH value at point of zero charge (PZC) is about 8.^{37,38} The chemical deposition of the TiO₂ under a nonapplied ac voltage will occur on the surface of alumina as follows:

$$(NH_4)_2[TiO(C_2O_4)_2] \rightarrow TiO(C_2O_4)_2^{2-} + 2NH_4^+$$
, (1)

$$2\text{AIOH}_{2}^{+}_{\text{surf}} + \text{TiO}(\text{C}_{2}\text{O}_{4})_{2}^{2^{-}} + \text{H}_{2}\text{O} \rightarrow \\ \text{Al}_{2}\text{O}_{2}\text{TiO}(\text{H}_{2}\text{O})_{\text{surf}} + 2(\text{C}_{2}\text{O}_{4})^{2^{-}} + 4\text{H}^{+} \quad .$$
(2)

 $(NH_4)_2[TiO(C_2O_4)_2]$ will dissolve and then dissociate into $TiO(C_2O_4)_2^{2-}$ and ammonium ions (Eq. 1) in aqueous solution. The protonated surface of alumina at pH 4 will adsorb the $TiO(C_2O_4)_2^{2-}$, leading to the formation of Al–O–Ti and the deposition of TiO_2 , which will be hydrated (Eq. 2).

B. UV absorption spectra of the deposited TiO_2

Some absorption spectra of the present TiO_2 deposited on the Al/Al₂O₃ substrate and other TiO_2 samples (anatase and rutile powders: 0.3 μ m average particle size) are shown in Fig. 3. The deposited TiO₂ at (a) 20 °C and (b) 50 °C showed absorption in the wavelength region shorter than about 350 nm. Thus, the deposited TiO₂ at



FIG. 3. Absorption spectra of Al/Al₂O₃/TiO₂ prepared at ac 12 V for various temperatures and other TiO₂: (a) 20 °C, (b) 50 °C, (c) 90 °C, (d) anatase powder (0.3 μ m), and (e) rutile powder (0.3 μ m).

20 and 50 °C showed a blue shift compared with the (d) anatase and (e) rutile samples. The blue shift in these TiO₂ will be due to the quantized TiO₂ particle and/or highly dispersed state of the nano-sized TiO₂ in the pores of the alumina film,^{39–41} because the TiO₂ was roughly estimated to be deposited from a monolayer to ten layers, as discussed in Ref 36. On the other hand, the deposited TiO₂ at 90 °C was similar to (d) the anatase powder. This suggests that the deposited TiO₂ at 90 °C was in the form of bulk particles.

C. Photocatalytic activity of the Al/Al₂O₃/TiO₂

Figure 4 shows the concentration (C) of acetaldehyde as a function of the illumination time. In Fig. 4(a), a 500-W xenon lamp was used as the light source for the Al/Al₂O₃/TiO₂ prepared at 12 V at various temperatures, where the initial concentration (C₀) of acetaldehyde was



FIG. 4. C (concentration)/ C_0 [initial concentration, (a) ~30 ppm, (b) ~10 ppm] as a function of the illumination time, irradiated (a) by the xenon lamp and (b) and by the F-lamp.

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FIG. 5. XRD patterns of the Al/Al₂O₃/TiO₂ heated at various temperatures, which were prepared at lower than 12 V and 90 $^{\circ}$ C.

30 ppm. The concentration gradually decreased with illumination for all the samples, indicating that the deposited TiO_2 on the Al/Al₂O₃ substrate has photocatalytic activity. The apparent photocatalytic activity increased with an increase in the temperature of the electrolyte because the amount of the deposited TiO_2 increased with the temperature of the electrolyte. The catalytic activity of the TiO_2 hardly depended on the applied voltage when the electrolysis was done at temperatures higher than about 50 °C. Consequently, the photocatalytic activity of the prepared Al/Al₂O₃/TiO₂ mainly depends on the amount of the deposited TiO_2 .

In Fig. 4(b), a 24-W fluorescent lamp (F-lamp) was used as the light source for the Al/Al₂O₃/TiO₂ prepared at 90 °C, where the initial concentration of acetaldehyde was 10 ppm. The Al/Al₂O₃/TiO₂ (as-deposited at 90 °C) showed only a slight activity, while the Al/Al₂O₃/TiO₂ heat treated at 550 °C for 1 h showed high activity even under fluorescent lamp illumination. Figure 5 shows the XRD patterns of the Al/Al₂O₃/TiO₂ prepared at 12 V and 90 °C. From the XRD patterns of the Al/Al₂O₃/TiO₂ heat treated at temperatures higher than 450 °C, only anatase is produced by the heat treatment. Thus, the heat treatment temperature higher than 450 °C causes the crystallization to anatase, bringing about the high photocatalytic



FIG. 6. Line profile of EPMA elemental distribution in a cross section of the $Al/Al_2O_3/TiO_2$ at ac 12 V and various temperatures: (a) 20 °C, (b) 50 °C, (c) 90 °C, and each model (d), (e), (f), respectively.

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activity, as shown in Fig. 4(b). The activity of the Al/ Al_2O_3/TiO_2 heat treated at 450 °C for 1 h was similar to that at 550 °C.

D. Morphology of the Al/Al₂O₃/TiO₂

Figures 6(a)-6(c) and 6(d)-6(f) show the line profile of the EPMA elemental distribution in the cross section of the Al/Al₂O₃ with TiO₂ electrodeposited at 12 V under various temperatures and their models. The section where Al overlaps with O in the distribution corresponds to the alumina film formed on the Al. The thickness of the alumina film was estimated to be about $25-30 \ \mu\text{m}$. Ti was mainly deposited in the bottom portion of the pores of the alumina film at 20 °C [Figs. 6(a) and 6(d)]. On the other hand, the distribution of Ti was shifted to the surface of the alumina film with the temperature of the electrolyte as shown in Figs. 6(b), 6(c), 6(e), and 6(f). According to the x-ray photoelectron spectroscopy (XPS) measurement of the surface of the $Al/Al_2O_3/TiO_2$, TiO₂ on surface of the Al/Al₂O₃ substrate was detected for the deposition at 70 and 90 °C, but not at 50 °C. Most likely, the hydration of alumina (denoted as $Al_2O_3 \cdot nH_2O$ might be formed at the bottom of the pores of the alumina film by immersion in the hightemperature aqueous solution. Therefore, the pores of the alumina film were sealed with the produced hydrated alumina at high temperatures, leading to the change in the deposited TiO_2 location as shown in Fig. 6(f). For the precipitation at 20 °C, Ti was not detected because the amount of the deposited TiO_2 was quite low. The differences in the Ti distribution were not observed at 50 and 90 °C, whether the electrolysis was carried out or not.

In a previous paper,³⁶ an improvement in the adhesion between the deposited TiO_2 and the $\text{Al/Al}_2\text{O}_3$ substrate was accomplished by the presence of the deposited TiO_2 in the pores of the alumina film. Consequently, the TiO_2 deposition in the pore of the alumina film at temperatures less than about 70 °C is also preferable for the strong adhesion between the TiO_2 and the $\text{Al/Al}_2\text{O}_3$ substrate. In practice, most of the TiO_2 deposited at temperatures higher than 70 °C was removed from the Al/ Al_2O_3 substrate, but not for that at 50 °C, based on a Scotch tape adhesion peel test.

In conclusion, an improvement in the photocatalytic activity of the Al/Al₂O₃/TiO₂ was accomplished by increasing the temperature of the TiO₂ deposition. However, the adhesion strength between the deposited TiO₂ and the Al/Al₂O₃ substrate was insufficient for the TiO₂ deposition at 90 °C because the deposited TiO₂ mainly existed on the surface of the Al/Al₂O₃ substrate. The Al/Al₂O₃/TiO₂ prepared at 50 °C, which showed a relatively high photocatalytic activity, was the most preferable for practical use because most of the deposited TiO₂ existed in pores of the alumina film.

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