

# Effect of electrolysis conditions on photocatalytic activities of the anodized TiO<sub>2</sub> films

Kinji Onoda, Susumu Yoshikawa\*

*Institute of Advanced Energy, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan*

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## Abstract

Photocatalytic activities of anodized TiO<sub>2</sub> films for decomposition of gaseous acetaldehyde were investigated. The anodized TiO<sub>2</sub> films were fabricated by galvanostatic anodization in a mixed electrolyte composed of H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, and H<sub>2</sub>O<sub>2</sub>. Pre-nitridation treatment effectively enhanced the photocatalytic activity of the anodized TiO<sub>2</sub> films. The electrolysis parameters such as anodization time, current density, electrolyte temperature, and electrolyte composition significantly affected the photocatalytic activity of the anodized TiO<sub>2</sub> films. The improvement of photocatalytic activity of the anodized films is attributed to increase in surface areas of the anodized specimens.  
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**Keywords:** TiO<sub>2</sub>; Anodization; Nitridation; Photocatalyst; Acetaldehyde

## 1. Introduction

TiO<sub>2</sub> photocatalysts have attracted much research attention due to their numerous advantages such as their high photocatalytic activity, low cost, safety, and stability. In relation to these merits, TiO<sub>2</sub> photocatalysts have been widely utilized in environmental purifications [1–4]. The most forms of TiO<sub>2</sub> photocatalysts are fine particles of nanometer in size, leading to obtaining extremely high surface area. For preparing the commercial photocatalytic products, the coating procedures using binder chemicals must be employed. For using an organic binder to coat TiO<sub>2</sub> fine particle on the substrate, the organic binders can be decomposed by TiO<sub>2</sub> photocatalyst, thus only inorganic chemicals, such as silica, can be used as the binders to avoid the photodegradation.

On the other hand, TiO<sub>2</sub> films can be easily formed on metallic titanium by anodization. It was reported that the galvanostatically anodization of metallic titanium induces crystalline TiO<sub>2</sub> phase under an electrolytic breakdown of the anodized TiO<sub>2</sub> films [5,6]. Among the forms of crystalline TiO<sub>2</sub>, anatase TiO<sub>2</sub> has received much attention

because it has a higher photocatalytic activity than rutile TiO<sub>2</sub> [7,8]. Inagaki et al. [9] reported that the activity of TiO<sub>2</sub> photocatalyst depended on a high crystallinity in anatase phase. Habasaki et al. [6] reported that anatase TiO<sub>2</sub> was formed in the inner region of the anodized specimen and the amorphous TiO<sub>2</sub> was formed on the surface of the anodized specimens by anodization processes. Since the photocatalytic reaction can occur at the surface of the specimens, the anatase TiO<sub>2</sub> fabricated in the inner region of the anodized specimens cannot work as a photocatalyst. Some researchers have investigated the fabrication of photocatalytic TiO<sub>2</sub> films by anodization. For instance, Nakahira et al. [10] fabricated the anatase TiO<sub>2</sub> films by anodization in 0.25 M H<sub>3</sub>PO<sub>4</sub> at a high applied voltage such as 250–350 V, but XRD patterns of the films showed a broad peak to be almost amorphous films. Kuraki et al. [11] also fabricated the anatase TiO<sub>2</sub> film by anodization at a high applied voltage such as 150–200 V in acidic electrolyte composed of 1.5 M H<sub>2</sub>SO<sub>4</sub>, 0.3 M H<sub>3</sub>PO<sub>4</sub>, and 0.3 M H<sub>2</sub>O<sub>2</sub>, but the films hardly showed any photocatalytic activity due to the existence of low valence oxide phases such as TiO and Ti<sub>2</sub>O<sub>3</sub>, which retarded the photocatalytic activity. They demonstrated that the photocatalytic anodized TiO<sub>2</sub> films could be prepared by re-anodization in mixture of NH<sub>4</sub>HF<sub>2</sub> and

\*Corresponding author. Fax: 81 774 38 3508.

E-mail address: [s-yoshi@iae.kyoto-u.ac.jp](mailto:s-yoshi@iae.kyoto-u.ac.jp) (S. Yoshikawa).

H<sub>2</sub>O<sub>2</sub>, which effectively removed the low valence oxide phases created as byproducts in the anodization process. As mentioned above, the anatase TiO<sub>2</sub> films were obtained by anodization processes at a high voltage. However, the obtained anodized films hardly showed the photocatalytic activity due to an existence of amorphous TiO<sub>2</sub> and low valence titanium oxide phase.

The authors reported that the high-performance photocatalytic anatase TiO<sub>2</sub> films were successfully prepared by the combination treatment of pre-nitridation and potentiostatic anodization in an acidic electrolyte composed of 1.5 M H<sub>2</sub>SO<sub>4</sub>, 0.3 M H<sub>3</sub>PO<sub>4</sub>, and 0.3 M H<sub>2</sub>O<sub>2</sub> [12]. The pre-nitridation treatment had significant effects not only on the formation of anatase TiO<sub>2</sub> films but also on the photocatalytic activity of the anodized TiO<sub>2</sub> films for a photooxidation of iodide anion.

In this paper, to obtain the high-performance photocatalytic galvanostatically anodized TiO<sub>2</sub> films, the effects of electrolysis parameters on the photocatalytic activity of the galvanostatically anodized TiO<sub>2</sub> films were investigated. The photocatalytic activity of the anodized TiO<sub>2</sub> films was evaluated from a decomposition of gaseous acetaldehyde. The relation between the photocatalytic activity and the electrolysis parameters such as anodization time, current density, electrolyte temperature, and electrolyte composition was also discussed.

## 2. Experimental procedures

### 2.1. Preparation of TiO<sub>2</sub> films by galvanostatic anodization

Commercially pure Ti plates of purity greater than 99.5% (Nippon Steel Corporation) were electrolytic degreased in the aqueous solution of a commercially available degreasing chemicals (C. Uyemura & Co., Ltd.) at 50 °C for 5 min. Afterward, Ti plates were etched in 5% HF aqueous solution for 2 min at room temperature. The Ti plates were annealed under atmospheric nitrogen of 0.1 MPa at 950 °C for 6 h in a furnace (GR-6156-15-S, Koyo Thermo System Co., Ltd.). Ti plates with and without a pre-nitridation were galvanostatically anodized using a DC power supply (PU-300-5, Kenwood Corporation). The electrolyte temperature was controlled by using a water bath equipped with a chiller. The electrolyte was composed of H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, and H<sub>2</sub>O<sub>2</sub>.

### 2.2. Characterization of the anodized TiO<sub>2</sub> films

X-ray diffraction (XRD) patterns of the anodized TiO<sub>2</sub> films were obtained with an X-ray diffractometer (M18X-CE, Bruker AXS, CuK $\alpha$  radiation, operated at 40 kV and 100 mA). The degree of anatase TiO<sub>2</sub> film formation was evaluated by monitoring the integrated XRD intensity of 101 reflection in which  $2\theta$  is 25.4°. The morphologies of anodized films were observed by using a scanning electron microscope (S-2380, Hitachi High-Technologies Corpora-

tion). The surface area of the anodized TiO<sub>2</sub> films was also evaluated by measuring the amount of chemisorbed dye. The anodized TiO<sub>2</sub> films were immersed into the dye solution composed of 0.3 mM of N719 (Solaronix) in *t*-butanol/acetonitrile (1:1 in volume fraction) at 40 °C for 3 days. Afterward, the amount of adsorbed dye on the anodized TiO<sub>2</sub> films was determined from a concentration of dye desorbed from the surface of the anodized TiO<sub>2</sub> films into a mixed solution of 0.1 M NaOH and ethanol (1:1 in volume fraction) by using UV-vis spectrometer (UVmini 1240, Shimadzu). Since the desorbed dye solution has absorption maximum of 308 nm, the surface area of the anodized TiO<sub>2</sub> films was evaluated from monitoring the absorbance of the desorbed dye solution at a wavelength of 308 nm.

### 2.3. Evaluation of photocatalytic activities of anodized TiO<sub>2</sub> films

TiO<sub>2</sub> photocatalytic activity is usually evaluated from photodecomposition of gaseous acetaldehyde [13–16]. The photocatalytic activities of the obtained anodized TiO<sub>2</sub> films were evaluated by monitoring decomposition of gaseous acetaldehyde. The reaction container (Tedlar bag) containing 3 dm<sup>3</sup> of 100 ppm of gaseous acetaldehyde and the anodized specimens (surface area = 1 dm<sup>2</sup>) was irradiated from a top side. The gaseous acetaldehyde was prepared by diluting acetaldehyde (Wako Chemicals, purity greater than 90%) with air. A fluorescent lamp emitting in the near-UV region (Blacklight FL40S BLB-A, Toshiba Lighting & Technology Corporation, maximum emission wavelength: 365 nm) was used in this study. An excitation light intensity of approximately 2 mW/cm<sup>2</sup> was obtained at the surface of the anodized specimens. The concentration of gaseous acetaldehyde was measured by using Gastec standard detector tube system (gas sampling pump GV-100, acetaldehyde detection tube no. 92M or 92L) [17].

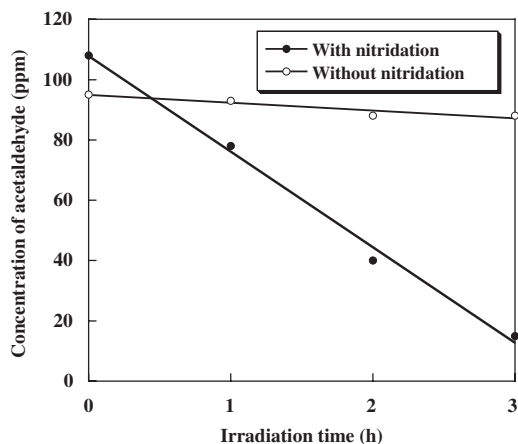


Fig. 1. Photocatalytic decomposition of acetaldehyde by anodized TiO<sub>2</sub> films with and without a pre-nitridation.

### 3. Results and discussions

#### 3.1. Effect of pre-nitridation on photocatalytic activity

Fig. 1 illustrates the photocatalytic decomposition of acetaldehyde by anodized TiO<sub>2</sub> films with and without pre-nitridation. The Ti plates were anodized in an acidic electrolyte composed of 1.5 M H<sub>2</sub>SO<sub>4</sub>, 0.1 M H<sub>3</sub>PO<sub>4</sub>, and 0.3 M H<sub>2</sub>O<sub>2</sub>. An electrolyte temperature and a current density were set at 20 °C and 1.0 A/dm<sup>2</sup>, respectively. It is clearly seen that a pre-nitridation treatment has an accelerating effect on the photocatalytic activity of the galvanostatically anodized TiO<sub>2</sub> film. Fig. 2 shows the formation of anatase TiO<sub>2</sub> film by anodization with and without a pre-nitridation from the evaluation of integrated anatase TiO<sub>2</sub> XRD intensity. The anodized film with a pre-nitridation has higher formation of anatase TiO<sub>2</sub> than that without a pre-nitridation. The anatase TiO<sub>2</sub> can be formed by anodization without a pre-nitridation. The poor

photocatalytic activity of the anodized TiO<sub>2</sub> films without a pre-nitridation can be observed. It is considered that the reasons for the poor photocatalytic activity of the anodized TiO<sub>2</sub> films without a pre-nitridation is resulted from not only an existence of low valence oxide [11] but also an existence of obtained anatase TiO<sub>2</sub> in the inner region of the anodized specimens [6]. On the other hand, the anodized film with a pre-nitridation exhibits the significant high photocatalytic activity for a decomposition of acetaldehyde. The obtained TiN films on surface of a Ti metal can be directly converted to the high-performance anatase TiO<sub>2</sub> films. The high-performance anatase TiO<sub>2</sub> films on the surface of Ti substrate can induce the high photocatalytic activity. It is well known that metallic titanium is high corrosion resistant because bare Ti surface is oxidized easily and a compact oxide film is subsequently formed. Even if the oxide film is broken, a protective

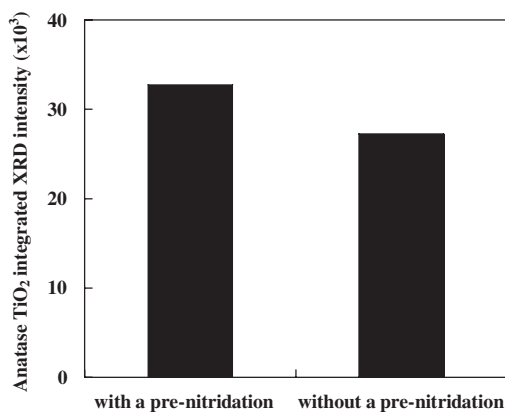


Fig. 2. Formation of anatase TiO<sub>2</sub> film fabricated by anodization with and without a pre-nitridation. The formation of anatase TiO<sub>2</sub> was evaluated from the integrated XRD intensity of 101 reflection.

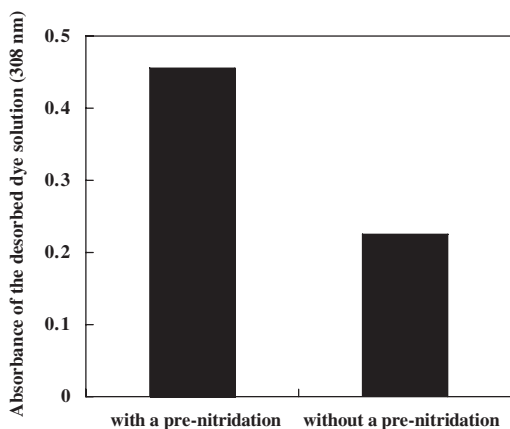


Fig. 3. Surface areas of the anodized TiO<sub>2</sub> films with and without a pre-nitridation. The surface areas of anodized films were evaluated from the concentration of the desorbed dye solution.

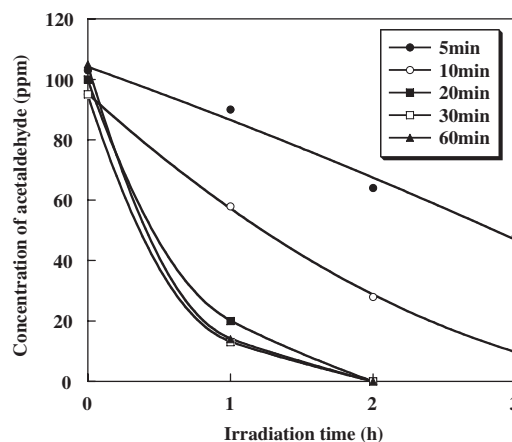


Fig. 4. Time-course of the photodecomposition of acetaldehyde by anodized TiO<sub>2</sub> films fabricated with various anodization times after a pre-nitridation.

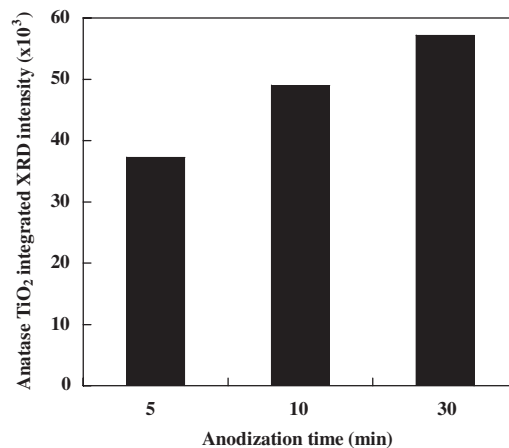


Fig. 5. Formation of anatase TiO<sub>2</sub> film fabricated with various anodization times after a pre-nitridation. The formation of anatase TiO<sub>2</sub> was evaluated from the integrated XRD intensity of 101 reflection.

passive film is immediately renewed on the Ti substrate due to high re-passivation capability of Ti [18]. The TiN surface was also covered with an oxide layer. However, the TiN film does not provide a good barrier against anodization, due to its lack of re-passivation capability, compared with metallic titanium [18]. From considering the crystal structures, Ti has a hexagonal closed structure, whereas TiN has a cubic structure. Oxygen atoms might be able to migrate easily into the TiN crystal due to the difference in crystal structure [19]. Fig. 3 shows the surface area of the anodized films with and without a pre-nitridation from the evaluation of the concentration of desorbed dye solution. It is clearly seen that the anodized film with a pre-nitridation has higher surface area than that without a pre-nitridation. Thus, it is considered that the pre-nitridation treatment effectively accelerates the photocatalytic activity of the galvanostatically anodized TiO<sub>2</sub> films.

### 3.2. Effect of anodization conditions on photocatalytic activity

Fig. 4 shows time-course of the photodecomposition of acetaldehyde by anodized TiO<sub>2</sub> films fabricated with various anodization times after a pre-nitridation. Anodization times were varied from 5 to 60 min. A Ti plate with a pre-nitridation was anodized in an electrolyte composed of 1.5 M H<sub>2</sub>SO<sub>4</sub>, 0.1 M H<sub>3</sub>PO<sub>4</sub>, and 0.3 M H<sub>2</sub>O<sub>2</sub>. An electrolyte temperature and a current density were controlled at 20 °C and 4.0 A/dm<sup>2</sup>, respectively. It is clearly seen that the photocatalytic activity of the anodized TiO<sub>2</sub> films initially increased with anodization by 30 min, while it did not increase anymore afterwards. Fig. 5 shows the formation of anatase TiO<sub>2</sub> of the anodized films fabricated with various anodization times after a pre-

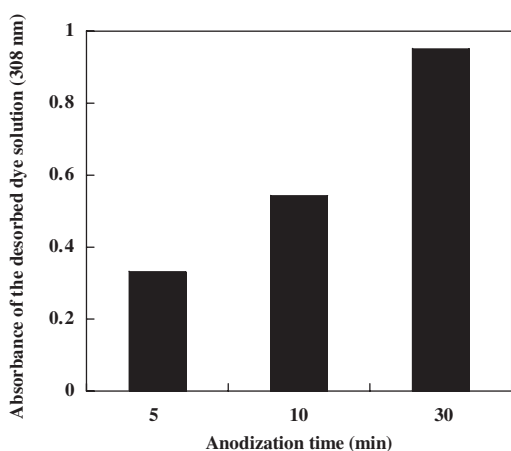


Fig. 6. Surface areas of the anodized TiO<sub>2</sub> films fabricated with various anodization times after a pre-nitridation. The surface areas of anodized films were evaluated from the concentration of the desorbed dye solution.

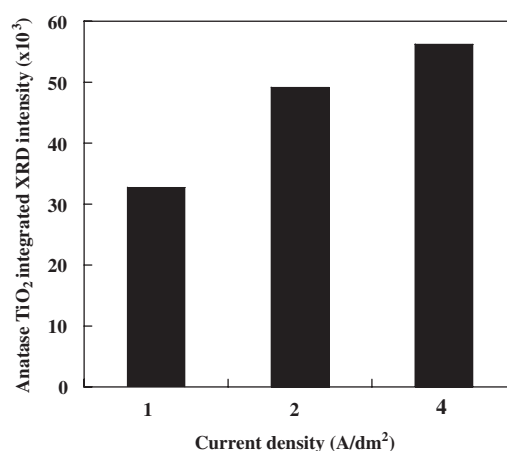


Fig. 8. Formation of anatase TiO<sub>2</sub> film fabricated with various current densities after a pre-nitridation. The formation of anatase TiO<sub>2</sub> was evaluated from the integrated XRD intensity of 101 reflection.

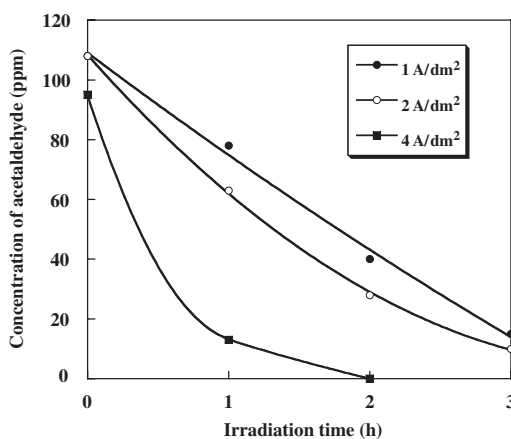


Fig. 7. Time-course of the photodecomposition of acetaldehyde by anodized TiO<sub>2</sub> fabricated with various current densities after a pre-nitridation.

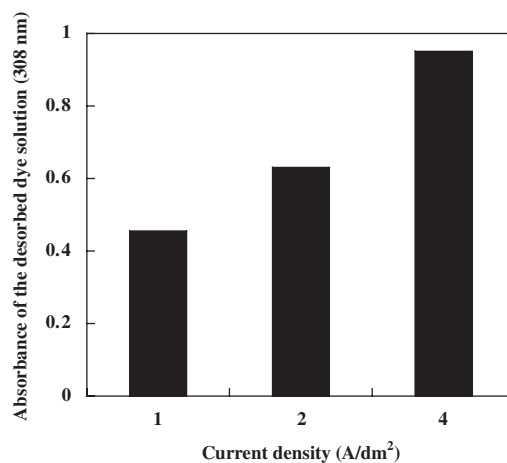


Fig. 9. Surface areas of the anodized TiO<sub>2</sub> films fabricated with various current densities after a pre-nitridation. The surface areas of anodized films were evaluated from the concentration of the desorbed dye solution.

nitridation from the evaluation of integrated anatase  $\text{TiO}_2$  XRD intensity. It is clearly seen that the formation of anatase  $\text{TiO}_2$  films increases with increase in anodization times. Fig. 6 shows the surface area of the anodized films fabricated with various anodization times after a pre-nitridation from the evaluation of the concentration of desorbed dye solution. It is also clearly seen that the surface area of the anodized specimen increases with increase in anodization time. In comparison of results in Figs. 5 and 6, the degree of increase in surface area is higher than the degree of increase in formation of anatase  $\text{TiO}_2$  films. The increasing photocatalytic activity is mainly attributed to the increase in surface areas of the anodized specimens with increase in anodization times. Oh et al. [20] reported that the diameters of the pores are smaller and distributions are more scattered at an early stage of anodization. The photocatalytic activities depend on the total surface area of photocatalytic  $\text{TiO}_2$ . It is considered that the surface area of anodized specimens increased with increase in anodization time at the initial stage of less than 30 min, but that of anodized specimens did not increase with increase in anodization time at more than 30 min.

Fig. 7 shows time-course of the photodecomposition of acetaldehyde by anodized  $\text{TiO}_2$  films fabricated at various current densities after a pre-nitridation. A current density was varied from 1.0 to 4.0  $\text{A}/\text{dm}^2$ . A Ti plate with a pre-nitridation was also anodized in an electrolyte composed of 1.5 M  $\text{H}_2\text{SO}_4$ , 0.1 M  $\text{H}_3\text{PO}_4$ , and 0.3 M  $\text{H}_2\text{O}_2$ . An electrolyte temperature and an anodization time were set at 20 °C and 30 min, respectively. It is clearly seen that the photocatalytic activity of the anodized  $\text{TiO}_2$  films increases with increase in current density. Fig. 8 also shows the formation of anatase  $\text{TiO}_2$  of the anodized films fabricated with various current densities after a pre-nitridation from the evaluation of integrated anatase  $\text{TiO}_2$  XRD intensity. The formation of anatase  $\text{TiO}_2$  films increased with increase in anodization current density. Diamanti and Pedefferri [21] reported that the

higher anodization current density accelerated the formation of anatase  $\text{TiO}_2$  film by anodization using an electrolyte composed of  $\text{H}_2\text{SO}_4$ . It is considered that the anodization current density affects the photocatalytic activity of the galvanostatically anodized  $\text{TiO}_2$  films, resulting from increase in formation of anatase  $\text{TiO}_2$  films with increase in anodization current density. Fig. 9 also shows the surface area of the anodized films fabricated with various current densities after a pre-nitridation from the evaluation of the concentration of desorbed dye solution. It is clearly seen that the surface area of the anodized films increases with increase in current density. Fig. 10 shows the top view of SEM images of the anodized  $\text{TiO}_2$  films with various current densities after a pre-nitridation. From the SEM observations of the anodized specimens, it can be seen that the surface areas of the anodized specimens also increase with increase in current density. The amount of adsorbed dye on the anodized films is considered to be closely related to SEM observations

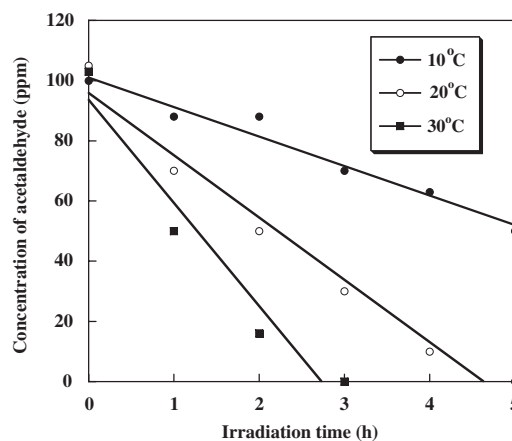


Fig. 11. Time-course of the photodecomposition of acetaldehyde by anodized  $\text{TiO}_2$  fabricated with various temperatures after a pre-nitridation.

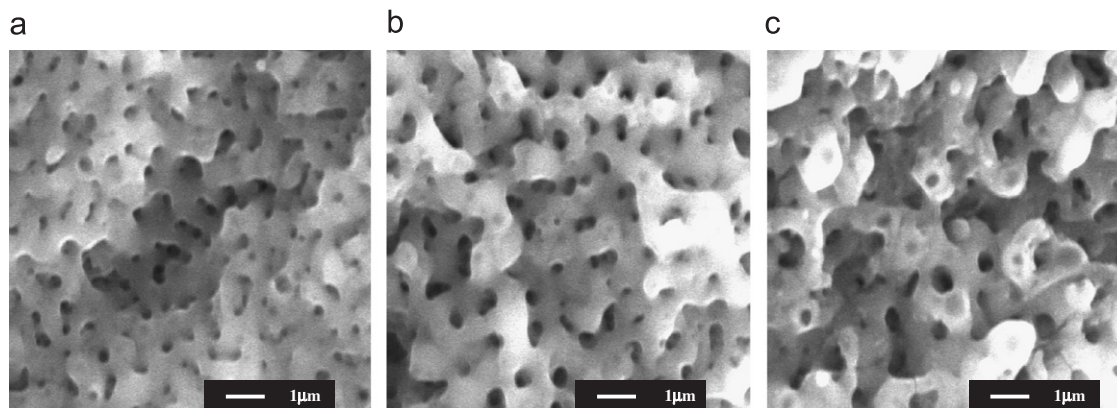


Fig. 10. Top view of SEM images of the anodized  $\text{TiO}_2$  films fabricated by anodization with various current densities after a pre-nitridation. The current density was set at (a) 1  $\text{A}/\text{dm}^2$ , (b) 2  $\text{A}/\text{dm}^2$ , and (c) 4  $\text{A}/\text{dm}^2$ , respectively.



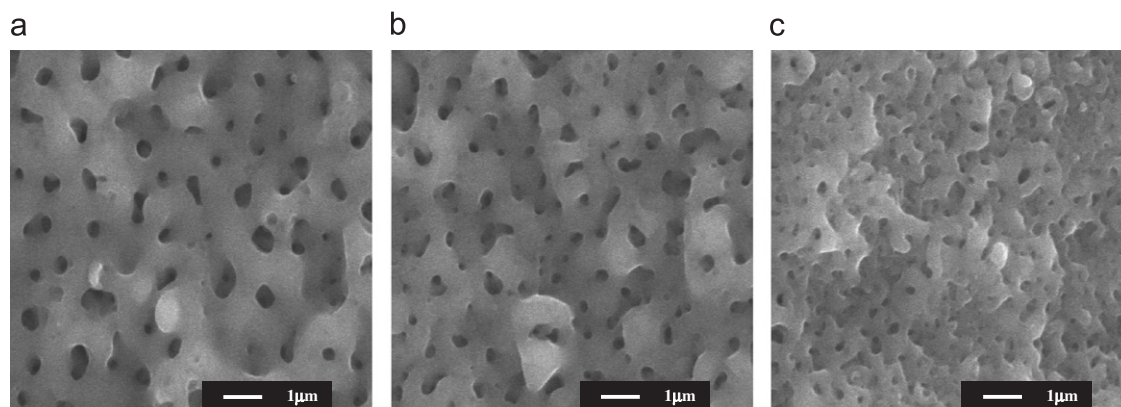


Fig. 12. Top view of SEM images of the anodized TiO<sub>2</sub> films fabricated by anodization with various electrolyte temperature. The electrolyte temperature was set at (a) 10 °C, (b) 20 °C, and (c) 30 °C, respectively.

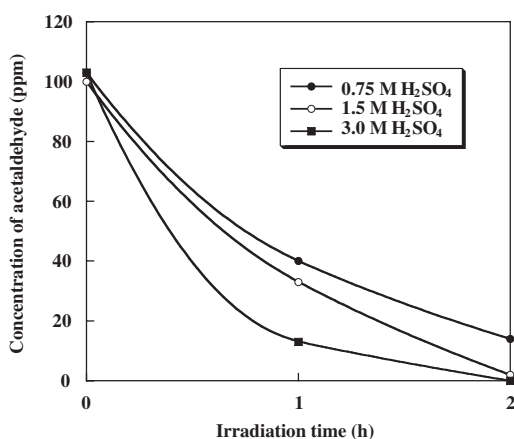


Fig. 13. Effect of concentrations of H<sub>2</sub>SO<sub>4</sub> on the photocatalytic activity of the anodized TiO<sub>2</sub> film with a pre-nitridation for decomposition of acetaldehyde.

of the anodized TiO<sub>2</sub> films fabricated with various current densities. In comparison of the XRD results (Fig. 8) and evaluation of surface area of the anodized specimens (Figs. 9 and 10), the increasing photocatalytic activity is also mainly attributed to the increase in surface areas of the anodized specimens with increase in current density.

Fig. 11 shows the time-course of the photodecomposition of acetaldehyde by anodized TiO<sub>2</sub> films fabricated at various electrolyte temperatures after a pre-nitridation. An electrolyte temperature was varied from 10 to 30 °C. A Ti plate with a pre-nitridation was also anodized in an electrolyte composed of 1.5 M H<sub>2</sub>SO<sub>4</sub>, 0.1 M H<sub>3</sub>PO<sub>4</sub>, and 0.3 M H<sub>2</sub>O<sub>2</sub>. An anodization time and a current density were set at 30 min and 1.0 A/dm<sup>2</sup>, respectively. It is clearly seen that the photocatalytic activity of anodized TiO<sub>2</sub> films increases with increase in

electrolyte temperature. A higher electrolyte temperature induces the higher reactivity against a Ti metal in the electrolyte containing H<sub>2</sub>SO<sub>4</sub>. It is considered that the higher reactivity against a Ti metal leads to the formation of high-performance photocatalytic TiO<sub>2</sub> films. Fig. 12 illustrates the top view of SEM images of the anodized TiO<sub>2</sub> films fabricated with varying the electrolyte temperature after a pre-nitridation. From the SEM observations of the anodized specimens, it can be seen that the surface areas of the anodized specimens also increase with increase in electrolyte temperature.

In the study of anodization parameters such as anodization time, current density, and electrolyte temperature on the photocatalytic activity of the anodized TiO<sub>2</sub> films, these parameters strongly depended on the formation of the high-performance photocatalytic TiO<sub>2</sub> films. From the SEM observations of the anodized TiO<sub>2</sub> films, the improvement of the photocatalytic activity of the anodized TiO<sub>2</sub> films is attributed to the obtained high surface area of the anodized specimens.

### 3.3. Effect of electrolyte compositions on photocatalytic activity

For obtaining the higher photocatalytic activities of the anodized TiO<sub>2</sub> films, optimization of electrolyte compositions was also investigated. The most commonly used electrolytes in anodization of titanium were H<sub>3</sub>PO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub>. It was believed that the electrolyte compositions affected the morphology and the crystallinity of the anodized TiO<sub>2</sub> films [22,23]. The effect of concentrations of H<sub>2</sub>SO<sub>4</sub> on the photocatalytic activities was investigated. A Ti plate with a pre-nitridation was anodized in electrolytes composed of 0.1 M H<sub>3</sub>PO<sub>4</sub> and 0.3 M H<sub>2</sub>O<sub>2</sub> with varying H<sub>2</sub>SO<sub>4</sub> concentrations in the range from 0.75 to 3.0 M. An electrolyte temperature, an anodization time, and current density were set at 20 °C, 30 min, and 4.0 A/dm<sup>2</sup>, respectively. Fig. 13 shows the effect of

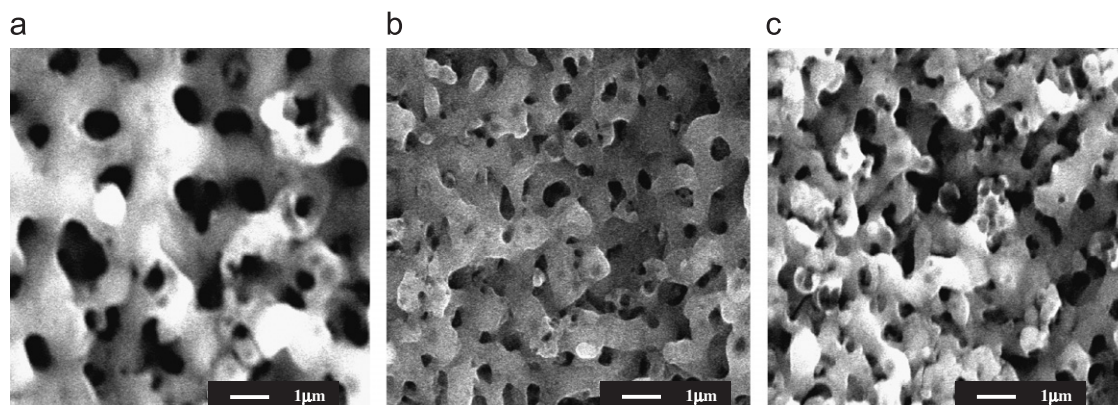


Fig. 14. Top view of SEM images of the anodized  $\text{TiO}_2$  films with a pre-nitridation by anodization in electrolytes composed of 0.1 M  $\text{H}_3\text{PO}_4$  and 0.3 M  $\text{H}_2\text{O}_2$  with varying  $\text{H}_2\text{SO}_4$  concentrations in the range from 0.75 to 3.0 M. The concentration of  $\text{H}_2\text{SO}_4$  was set at (a) 0.75 M, (b) 1.5 M, and (c) 3.0 M, respectively.

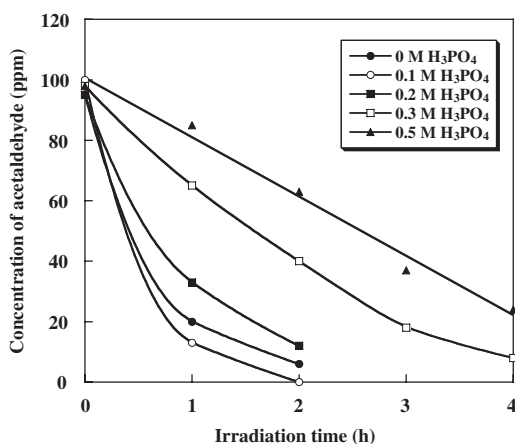


Fig. 15. Effect of concentrations of  $\text{H}_3\text{PO}_4$  on the photocatalytic activity of the anodized  $\text{TiO}_2$  films with a pre-nitridation for a decomposition of acetaldehyde.

concentrations of  $\text{H}_2\text{SO}_4$  on the photocatalytic activity of the anodized  $\text{TiO}_2$  film for a decomposition of acetaldehyde. It is clearly seen that the photocatalytic activity of the anodized  $\text{TiO}_2$  films increases with increase in concentration of  $\text{H}_2\text{SO}_4$ . It is considered that the higher concentration of  $\text{H}_2\text{SO}_4$  can induce a higher reactivity against a Ti metal, leading to obtaining of high surface areas of the anodized specimens. Fig. 14 shows the top view of SEM images of the anodized  $\text{TiO}_2$  films by anodization in electrolytes composed of 0.1 M  $\text{H}_3\text{PO}_4$  and 0.3 M  $\text{H}_2\text{O}_2$  with varying  $\text{H}_2\text{SO}_4$  concentrations in the range from 0.75 to 3.0 M. From the SEM observations of the anodized films, it can be seen that the surface area of the anodized specimens increases with increase in concentration of  $\text{H}_2\text{SO}_4$ . The increasing photocatalytic activity with increase in concentration of  $\text{H}_2\text{SO}_4$  can be

explained by increase of surface areas of the anodized specimens.

By examining the effect of concentrations of  $\text{H}_3\text{PO}_4$  on the photocatalytic activity, a Ti plate with a pre-nitridation was anodized in electrolytes composed of 1.5 M  $\text{H}_2\text{SO}_4$  and 0.3 M  $\text{H}_2\text{O}_2$  with varying  $\text{H}_3\text{PO}_4$  concentrations in the range from 0 to 0.5 M. Fig. 15 shows the effect of concentrations of  $\text{H}_3\text{PO}_4$  on the photocatalytic activity of the anodized  $\text{TiO}_2$  films for a decomposition of acetaldehyde. It is clearly seen that the photocatalytic activity decreased with increase in concentration of  $\text{H}_3\text{PO}_4$  in the range from 0.1 to 0.5 M. The highest photocatalytic activity was obtained at  $\text{H}_3\text{PO}_4$  concentration of 0.1 M. Kern and Zinger [24] reported that  $\text{H}_3\text{PO}_4$  acted as an inhibitor against the anodization process because the anodization current in the mixed electrolyte composed of  $\text{H}_2\text{SO}_4$  and  $\text{H}_3\text{PO}_4$  was lower than that in the electrolyte composed of only  $\text{H}_2\text{SO}_4$ . The decrease in the photocatalytic activity of the anodized  $\text{TiO}_2$  films with increase in  $\text{H}_3\text{PO}_4$  concentration could be explained from the inhibiting effect of  $\text{H}_3\text{PO}_4$  on anodization process. Xie and Li [25] reported that an anodization of Ti metal in an acidic electrolyte creates a competition between an oxidation to form  $\text{TiO}_2$  films and a dissolution to release Ti ion from  $\text{TiO}_2$ -electrolyte interface into an electrolyte. The existence of  $\text{H}_2\text{SO}_4$  in an electrolyte can accelerate the above-competed reaction to form the crystalline  $\text{TiO}_2$  films. However, the electrolyte composed of pure  $\text{H}_2\text{SO}_4$  can induce the low photocatalytic rutile  $\text{TiO}_2$  phase through the formation of high photocatalytic anatase  $\text{TiO}_2$  phase. It is considered that the addition of 0.1 M of  $\text{H}_3\text{PO}_4$  as the inhibitor into  $\text{H}_2\text{SO}_4$  as a promoter showed the best balance to form high-performance photocatalytic  $\text{TiO}_2$  films. Fig. 16 shows the top view of SEM images of the anodized  $\text{TiO}_2$  films by anodization in electrolytes composed of 1.5 M  $\text{H}_2\text{SO}_4$  and 0.3 M  $\text{H}_2\text{O}_2$  with varying  $\text{H}_3\text{PO}_4$  concentrations in the range from 0.1 to 0.5 M. From these SEM observations, it

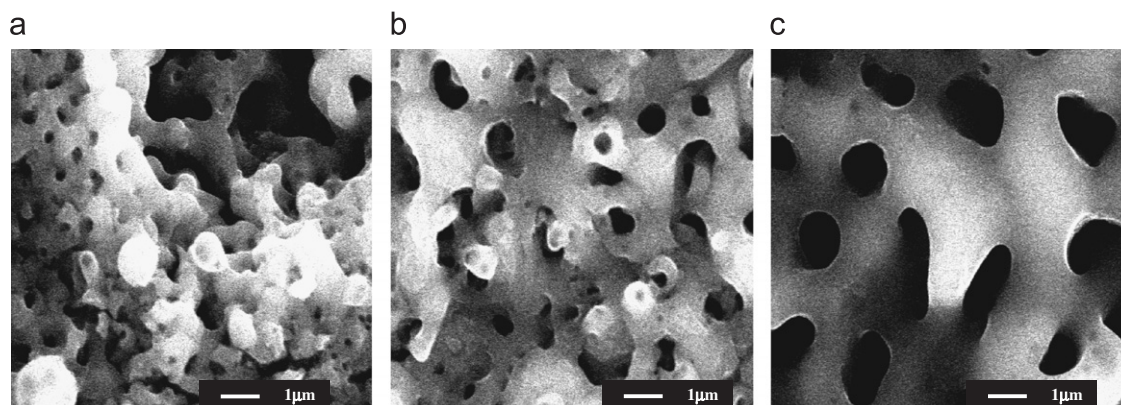


Fig. 16. Top view of SEM images of the anodized TiO<sub>2</sub> films by anodization in electrolytes composed of 1.5 M H<sub>2</sub>SO<sub>4</sub> and 0.3 M H<sub>2</sub>O<sub>2</sub> with varying H<sub>3</sub>PO<sub>4</sub> concentrations in the range from 0.1 to 0.5 M. The concentration of H<sub>3</sub>PO<sub>4</sub> was set at (a) 0.1 M, (b) 0.3 M, and (c) 0.5 M, respectively.

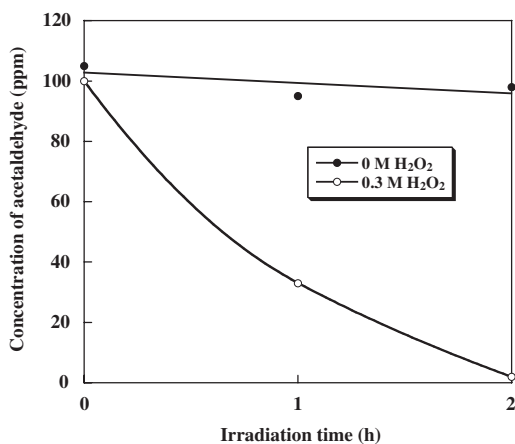


Fig. 17. Effect of concentrations of H<sub>2</sub>O<sub>2</sub> on the photocatalytic activity of the anodized TiO<sub>2</sub> films with a pre-nitridation for a decomposition of acetaldehyde.

can be seen that the surface area of the anodized specimens decreased with increase in concentration of H<sub>3</sub>PO<sub>4</sub>. The decreasing photocatalytic activity with increase in H<sub>3</sub>PO<sub>4</sub> concentrations in the range from 0.1 to 0.5 M could be explained by decrease in surface areas of the anodized specimens.

To investigate the effect of H<sub>2</sub>O<sub>2</sub> concentrations on the photocatalytic activity, the Ti plate with a pre-nitridation was anodized in electrolytes composed of 1.5 M H<sub>2</sub>SO<sub>4</sub> and 0.1 M H<sub>3</sub>PO<sub>4</sub> with varying H<sub>2</sub>O<sub>2</sub> concentrations. Fig. 17 shows the effect of concentrations of H<sub>2</sub>O<sub>2</sub> on the photocatalytic activity of the anodized TiO<sub>2</sub> films for a decomposition of acetaldehyde. It is clearly seen that the anodized TiO<sub>2</sub> film fabricated by anodization using electrolyte without H<sub>2</sub>O<sub>2</sub> has the poor photocatalytic activity for a photodecomposition of acetaldehyde. The photocatalytic activity of the anodized TiO<sub>2</sub> films strongly

depends upon the concentration of H<sub>2</sub>O<sub>2</sub>. Xie [26] reported that anodization using electrolyte containing H<sub>2</sub>O<sub>2</sub> can significantly accelerate the oxidation reaction to produce TiO<sub>2</sub>. The photocatalytic activity of anodized TiO<sub>2</sub> film using electrolyte containing H<sub>2</sub>O<sub>2</sub> is also thought to be resulted from the acceleration of oxidation reaction. Fig. 18 shows the top view of SEM images of the anodized TiO<sub>2</sub> films by anodization in electrolytes 1.5 M H<sub>3</sub>PO<sub>4</sub> and 0.1 M H<sub>3</sub>PO<sub>4</sub> with varying H<sub>2</sub>O<sub>2</sub> concentrations. From the SEM observations of the anodized specimens, it can be seen that the surface area of the anodized specimens also depends on the concentration of H<sub>2</sub>O<sub>2</sub>.

In the study of the effect of electrolyte compositions, the concentration of H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, and H<sub>2</sub>O<sub>2</sub> affected the photocatalytic activity of the anodized TiO<sub>2</sub> films for a decomposition of acetaldehyde, respectively. The improvement of photocatalytic activity of the anodized films is thought to be closely related to increase in surface areas of the anodized specimens.

#### 4. Conclusions

The high-performance photocatalytic TiO<sub>2</sub> films were obtained by combined treatment of pre-nitridation and galvanostatic anodization in the acidic electrolyte composed of H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, and H<sub>2</sub>O<sub>2</sub>. The photocatalytic activities of anodized TiO<sub>2</sub> films were determined by the photoinduced decomposition of gaseous acetaldehyde. The pre-nitridation treatment was affected on the photocatalytic activity of the anodized TiO<sub>2</sub> films. The anodization parameters such as anodization time, current density, electrolyte temperature, and electrolyte composition, were also affected on the photocatalytic activity. It is considered that the photocatalytic activity of the anodized TiO<sub>2</sub> films is improved by increasing the surface areas of the anodized specimens.



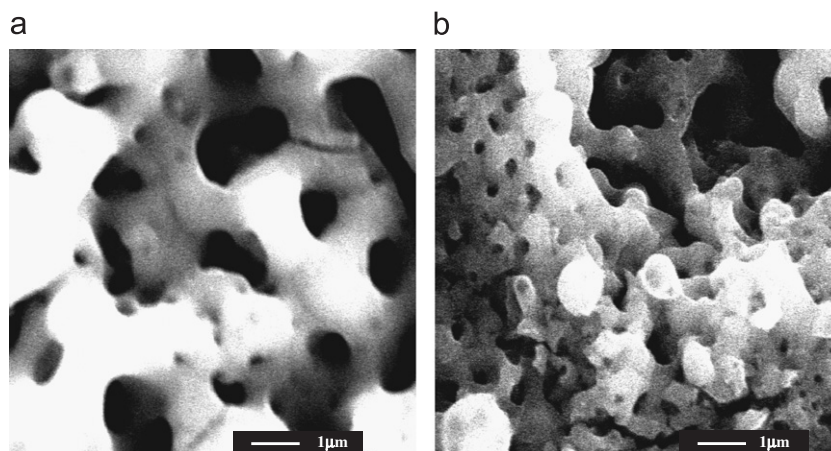


Fig. 18. Top view of SEM images of the anodized TiO<sub>2</sub> films with a pre-nitridation by anodization in electrolytes 1.5 M H<sub>2</sub>SO<sub>4</sub> and 0.1 M H<sub>3</sub>PO<sub>4</sub> with varying H<sub>2</sub>O<sub>2</sub> concentrations. The concentration of H<sub>2</sub>O<sub>2</sub> was set at (a) 0 M and (b) 0.3 M, respectively.

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