



# Surface structure and photocatalytic performance of an anodic oxide layer fabricated on titanium in a nitrate/ethylene glycol electrolyte with different treatment durations



Naofumi Ohtsu <sup>\*</sup>, Kento Yokoi

Instrumental Analysis Center, Kitami Institute of Technology, 165 Koen-cho, Kitami, Hokkaido 090–8507, Japan

## ARTICLE INFO

### Article history:

Received 1 May 2015

Revised 2 February 2016

Accepted in revised form 13 March 2016

Available online 18 March 2016

### Keywords:

Anodic oxidation

Nitrate electrolyte

Visible-light response

Photocatalytic TiO<sub>2</sub>

Anodization duration

## ABSTRACT

Anodic oxidation of titanium substrate in an electrolyte comprising ammonium nitrate in ethylene glycol is an innovative technique for fabricating a visible-light-responsive photocatalytic titanium dioxide (TiO<sub>2</sub>) layer. In this study, the effects of the duration of anodization on photocatalytic activity were investigated to improve its performance. Surface morphologies of the fabricated layer were comparatively flat for small durations of anodization, but small cracks were generated when anodizing for over 120 min. The thickness of the layer increased with treatment time up to 60 min, beyond which time no further increase in thickness was observed. The predominant structure of the oxide layer was TiO<sub>2</sub> with a rutile structure, and its amount increased with longer treatment duration. Nitrogen doping was observed in the layer regardless of the duration although its chemical state and photocatalytic activity varied depending on the duration. Under ultraviolet light irradiation, the change in activity was small, whereas the activity was drastically enhanced with longer treatment duration in the case of visible light irradiation. Based on these results, we concluded that the optimum duration of anodization is 60 min in the present setting because a TiO<sub>2</sub> layer showing good photocatalytic activity without any surface cracks could be formed.

© 2016 Published by Elsevier B.V.

## 1. Introduction

Anodic treatment of titanium (Ti) has recently gained attention as a fabrication process for photocatalytic titanium dioxide (TiO<sub>2</sub>) layer [1–6]. The technique is a simple process that involves connecting a target substrate to the anode in an electrolyte and applying voltage, resulting in the formation of a thin oxide layer on the target substrate. In the case of a Ti substrate, the oxide layer fabricated is generally TiO<sub>2</sub>. A characteristic feature of this process is the incorporation of the constituent elements of the electrolyte [7–10]. A semiquantitative model constructed by Wood et al. explained that the electrolyte anions adsorbed on the topmost surface are incorporated with growth of the oxide layer [10]. The elements incorporated in the oxide layer affect the layer characteristics such as crystallinity and surface morphology [7,11], and thus, this phenomenon often complicates the control of layer characteristics.

However, in the case of TiO<sub>2</sub> photocatalysis, this phenomenon is rather beneficial. In recent years, doping of specific elements into the TiO<sub>2</sub> layer has become a major technology for expanding its responsiveness to the visible light region [12,13]. Mizukoshi et al. fabricated a sulfur-doped TiO<sub>2</sub> layer on a Ti substrate using anodic treatment in

sulfuric acid, and then revealed that the fabricated layer could bleach methylene-blue dye under visible light irradiation [14]. Our research group has synthesized a visible light responsive nitrogen-doped TiO<sub>2</sub> layer through anodic treatment [15,16]. The use of nitric acid as an electrolyte resulted in the formation nitrogen-doped TiO<sub>2</sub> layer with visible light photocatalytic activity, whereas the resultant layer was easily removed by wiping the surface gently [15]. The problem of adhesion was drastically improved by changing the electrolyte solvent to ethylene glycol. We previously reported that the anodic layer fabricated in nitrate/ethylene glycol electrolyte acted as a photocatalyst both under UV-light and visible-light illumination and showed excellent antibacterial performance under both types of illumination [16]. We believe that the anodic treatment using a nitrate/ethylene glycol electrolyte is a promising method for fabricating antibacterial and environmental purification mediums applicable to industry.

In the previous study, only one set of treatment conditions was investigated [16]. Since the treatment conditions affect the layer characteristics and its photocatalytic activity, the parameters of the process should be optimized. Komiya et al. reported that the photocatalytic activity was drastically changed depending on the treatment time when anodizing the Ti substrate in an aqueous solution of a sulfuric salt [17]. Based on their findings, we chose the duration time as the investigating parameter. In the present study, therefore, we fabricated an anodic oxide layer on a Ti substrate in a nitrate/ethylene glycol electrolyte

<sup>\*</sup> Corresponding author.

E-mail address: [nohtsu@mail.kitami-it.ac.jp](mailto:nohtsu@mail.kitami-it.ac.jp) (N. Ohtsu).

with different durations of anodization. Thereafter, its surface characteristics and photocatalytic performances were investigated in detail. Together with these results, we determined the optimum treatment duration for fabricating a high-performance nitrogen-doped TiO<sub>2</sub> layer that can be used in industry.

## 2. Experimental methods

### 2.1. Anodic treatment of Ti substrate

The anodic treatment was performed in a 0.1 M nitrate solution prepared by dissolving NH<sub>4</sub>NO<sub>3</sub> in industrial grade ethylene glycol (99%). Ti plates (99.5%, 10 × 20 × 1 mm<sup>3</sup>) were chemically polished using a colloidal silica suspension until they achieve a mirror-like surface. The plates were thoroughly rinsed with ethanol in an ultrasonic cleaner. The Ti plate without surface masking was connected to a Pt plate as the cathode, after which galvanostatic direct current (DC) was applied at a constant value of 100 mA cm<sup>-2</sup>. Here, the distance between the cathode and the anode was approximately 50 mm. The anodic treatment was performed in an ambient atmosphere; accordingly, the ethylene glycol solvent would contain trivial water from the atmosphere. The DC voltage varied accordingly. The temperature of the electrolyte was not controlled in this study because from our preliminary investigation, we obtained experimental evidence that the cooling of the electrolyte did not affect the performance. We prepared six anodized plates with different treatment times: 5, 15, 30, 60, 120, and 180 min. After the treatment, the sample was thoroughly rinsed in distilled water using ultrasonic agitation for ca. 600 s, and then heated at 723 K for 5 h in air.

### 2.2. Characterization of the surface

The surface morphologies of the specimens were observed by scanning electron microscopy (SEM; JCM-5000 Neo Scope, JEOL, Japan) using the secondary electron image mode, and the cross-sectional structures of the surfaces were observed using field-emission SEM (FE-SEM; JSM-6701F, JEOL, Japan). X-ray diffraction patterns (XRD; New D8 Advance, Bruker AXS, Germany) were measured in the Bragg-Brentano geometry using Cu K $\alpha$  radiation. Chemical state and concentration of the incorporated nitrogen were analyzed using X-ray photoelectron spectroscopy (XPS; PHI 5000 Versa Probe, Ulvac-Phi, Japan). A monochromatized Al K $\alpha$  radiation ( $h\nu = 1486.6$  eV) with the diameter of ca. 100  $\mu$ m was used for photoelectron excitation. The photoelectron take-off angle (TOA) was set at 45°.

### 2.3. Evaluation of the photocatalytic activity

The photocatalytic activity was evaluated by the bleaching rate of a methylene blue (MB) dye under UV and visible lights illumination. As a preliminary treatment, the specimen surfaces were irradiated with comparatively high-intensity UV light (ca. 6 mW cm<sup>-2</sup>) for 90 min to remove organic substances. Thereafter, the specimens were immersed in 10 mg L<sup>-1</sup> MB solution in a polypropylene vessel for 24 h to complete the adsorption of MB molecules onto the surface. The MB dye in the vessel was replaced to a new solution and then, UV and visible light from LED lamps with wavelengths of 370 nm or 420 nm, respectively, were illuminated onto the immersed specimen surface. A schematic illustration of the experimental setup is shown in Fig. 1. The radiation intensities were adjusted to 1 mW cm<sup>-2</sup>. The photocatalytic activity was evaluated by measuring the absorbance of MB at 664 nm during irradiation every 20 min for 180 min using a UV-vis spectrometer (UV-2400PC, Shimadzu, Japan). The bleaching rate of MB was plotted against the duration of radiation, and the reaction rates for MB bleaching (min<sup>-1</sup> · mL<sup>-1</sup>) were calculated from the slope of its linear plot.

## 3. Results and discussions

### 3.1. Changes in surface morphology and layer thickness with prolonged treatment time

The topological microstructures of the surfaces anodized in nitrate/ethylene glycol electrolyte for different treatment durations are shown in Fig. 2. The surface morphology is comparatively flat for samples treated for 5 and 15 min. Small pores appeared on the surface after 30 min, but disappeared again upon increasing the treatment duration beyond 60 min. Further treatment beyond 120 min results in the generation of small cracks, which grow larger upon prolonging the duration to 180 min.

The change of the layer thickness with an increase in the treatment duration is shown in Fig. 3(b). Here, the thickness of the layer is estimated from the cross-sectional SEM image of the surface (Fig. 3(a)). We calculated the average value of several points. The thickness increases exponentially with an increase in the treatment duration up to 60 min, whereas the rate of increase becomes constant beyond 120 min. The thickness value at 120 min is about 20  $\mu$ m.

To analyze the layer growth behavior further, we recorded the variations in the applied DC voltage during the anodization process (Fig. 4). At the beginning of the treatment, the DC voltage is abruptly raised to a maximum value, after which it decreases gradually up to about half of the maximum value. We confirmed that the electric conductivity of

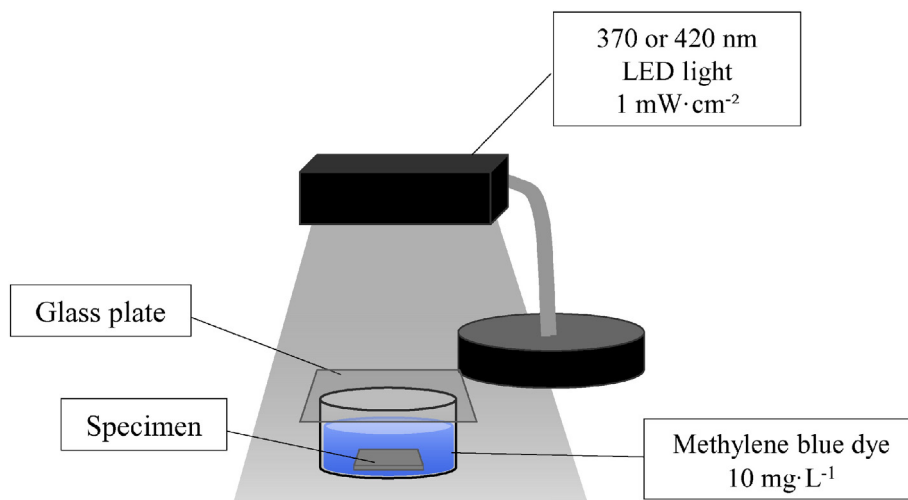


Fig. 1. A schematic illustration of methylene-blue bleaching experiment.

Download English Version:

<https://daneshyari.com/en/article/1656418>

Download Persian Version:

<https://daneshyari.com/article/1656418>

[Daneshyari.com](https://daneshyari.com)