



Fabrication of visible-light-responsive titanium dioxide layer on titanium using anodic oxidization in nitric acid

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ARTICLE INFO

Article history:

Received 23 October 2012

Received in revised form 12 January 2013

Accepted 13 January 2013

Available online 23 January 2013

Keywords:

Photocatalysis

Titanium dioxide

Nitrogen-doping

Anodic oxidation

Visible-light response

ABSTRACT

A visible-light-responsive titanium dioxide (TiO₂) layer was fabricated by anodizing a Ti plate in aqueous nitric acid (HNO₃) solutions, followed by annealing at 723 K for 5 h in air. The predominant structure of the oxide layer was TiO₂ with an anatase structure that contained ca. 1 at% of incorporated nitrogen. The crystallite size of the anatase TiO₂ was enlarged as anodizing voltage increased, but the atomic ratio of the incorporated nitrogen was almost constant. The TiO₂ layers could degrade methylene blue (MB) solution under an UV light at 370 nm, exhibiting photocatalytic activity. The activity increased monotonically as the crystallite size of the oxide increased. The TiO₂ layers with their crystallite size exceeding a specific value showed excellent response under visible light at 420, 450, and 505 nm. Overall, the results of this study showed that anodic oxidization of Ti in HNO₃ solution is a promising technique for fabrication of a visible-light-responsive TiO₂ layer.

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1. Introduction

Titanium dioxide (TiO₂) is one of the most prominent photocatalytic oxides owing to its high photocatalytic activity, low cost, nontoxicity, and environmentally friendly nature [1]. These characteristics have resulted in TiO₂ attracting widespread attention for use in environmental purification media [2,3] and antibacterial coatings [4–7], which have been utilized as air purifiers and in biomedical products. However, TiO₂ is a semiconductor with wide band gaps of 3.0 eV in its rutile phase and 3.2 eV in its anatase phase; accordingly, it only acts as a photocatalyst under ultraviolet (UV) light. Natural solar light is the most powerful light source, whereas UV light accounts for only a small portion of the total energy in light. As a result, the band gap must be adjusted to the visible-light region to utilize solar light effectively for activation of TiO₂ photocatalysis instead of an artificial light source.

In 1986, Sato demonstrated that a visible-light response appeared in response to doping TiO₂ with NO_x [8]. Asahi et al. also reported that the band gap of TiO₂ decreased in response to substitution of a portion of oxygen for nitrogen, resulting in the compound acting as a photocatalyst under visible light [9]. Based on these findings, researchers have employed various methods to incorporate nitrogen into TiO₂. These methods have been

based on methods such as sol-gel synthesis [8,10–12], heating in a nitrogen-containing atmosphere [13,14,16,17] and oxidation of titanium nitride [15], or on physical processes such as ion implantation [18,19] and magnetron sputtering deposition [20,21]. The products fabricated by these methods have often shown somewhat different photocatalytic activities. It is believed that these differences originated from the location of nitrogen doping (N-doping) in the TiO₂ structure; however, no general consensus has yet been reached regarding the location of nitrogen involved in photocatalytic activity. Alternative fabrication techniques might produce a N-doped TiO₂ with novel photocatalytic properties [22].

Anodic oxidation is an industrial technique developed for production of a metallic oxide layer on a metallic substrate. This technique has recently also been shown to be useful for synthesis of TiO₂ coatings on titanium (Ti) substrate. For example, Nakahira et al. fabricated a TiO₂ coating with an anatase-type structure by anodizing Ti substrate in H₃PO₄ electrolyte [23]. Similarly, Onoda et al. reported that a photocatalytic TiO₂ coating with photocatalytic activity could be prepared by anodizing pre-nitrided Ti substrate in a mixed electrolyte composed of H₂SO₄, H₃PO₄, and H₂O₂ [24]. The process of growing an anodic oxide layer can be explained using basic electrochemistry principles. The oxide growth is initiated by the penetration of oxygen and the production of a cation, the transport is explained by electric field-supported hopping. The electric field also attracts the anions contained in the electrolyte, which then react with the surface of the substrate. Therefore, anodic oxidization is advantageous because the oxide coating strongly adheres to the substrate and anions can be

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easily incorporated into the coating by adding target anions in an electrolyte. By focusing on the latter advantage, anodic oxidation can be used to easily synthesize anion doped-TiO₂ coatings via a single-step process. Mizukoshi et al. reported that sulfur-doped TiO₂ coatings having rutile-type structures could be synthesized by anodizing Ti substrate in a highly concentrated sulfuric acid electrolyte [25]. The efficient photocatalytic activity of such coatings could bleach methylene blue (MB) aqueous solution under visible-light illumination at wavelengths greater than 413 nm. Based on these findings, it seems feasible that anodic oxidation in nitric acid (HNO₃) can produce N-doped TiO₂ coatings with visible-light response. However, HNO₃ acts as an oxidizing agent, thereby leading to dielectric breakdown of the TiO₂ layer during anodizing. Nakahira et al. reported that, when employing 0.25-M HNO₃ as an electrolyte, precipitates were produced during anodizing in exchange for degradation of the Ti plate owing to the dielectric breakdown [26]. Subsequent analysis of these precipitates revealed that they consisted of N-doped TiO₂. These findings indicate that suppression of the oxidizability of nitrate may enable the synthesis of a N-doped TiO₂ layer as an alternative to TiO₂ powder.

In the present study, we attempted to fabricate a N-doped TiO₂ coating by anodizing a Ti substrate in HNO₃ with a concentration not exceeding 0.1 M. In addition, we investigated the photocatalytic activity under UV and visible-light regions from 370 nm to 505 nm. The effects of nitrogen doping and crystal structure on the photocatalytic properties were explored through careful analysis using X-ray diffractometry (XRD) and X-ray photoelectron spectroscopy (XPS).

2. Experimental procedures

A pure titanium plate (99.9%) with dimensions of 20 mm × 10 mm × 1 mm was chemically polished using a colloidal silica suspension with an average particle size of 40 nm. This plate was used as a substrate. The substrate and a platinum electrode with dimensions of 20 mm × 10 mm × 1 mm were connected to the anode and cathode, respectively, after which direct current (DC) at 200 mA was supplied for 30 min in aqueous HNO₃ solutions with concentrations of 1 mM, 10 mM, and 100 mM, respectively. Under this restricted current setting, the DC voltage could not be applied beyond a specific value owing to the dielectric breakdown of the oxide layer. The maximum voltages are actually 183 V, 40 V, and 22 V for 1 mM, 10 mM, and 100 mM, respectively. After the oxidation process was completed, the specimen was ultrasonically rinsed in distilled water and then annealed at 723 K for 5 h in the air.

The surface morphology of the specimen was observed by scanning electron microscopy (SEM; JCM-5000 Neo Scope, JEOL) using secondary electron image mode at an acceleration voltage of 10 kV. The cross-sectional structure of the layer was observed by conventional transmission electron microscopy (TEM; JEM-2100, JEOL). The TEM specimens were prepared using an ion slicer (EM-09100IS, JEOL). X-ray diffractometry patterns (XRD; New D8 Advance, Bruker AXS) were measured with Bragg-Brentano geometry using Cu K α radiation. X-ray photoelectron spectroscopy (XPS; PHI 5000 Versa Probe, Ulvac-Phi) was conducted using monochromatized Al K α radiation ($h\nu = 1486.6$ eV) to evaluate the incorporated nitrogen. The diameter of the X-ray probe was about 100 μ m, and the photoelectron take-off angle (TOA) was set at 65°, where TOA denotes the angle between the substrate surface and the spectrometer slit. An Ar-ion gun was used to analyze the nitrogen incorporated in the inner region.

The photocatalytic activity was evaluated by a methylene blue (MB) degradation test. Before starting the degradation test, UV light was applied to the specimen for 90 min at an intensity of

ca. 6 mW cm⁻² to eliminate the surface contaminants, after which the specimens were immersed in 10 mg L⁻¹ of MB solution in a polypropylene vessel for 24 h to complete the adsorption of MB molecules onto the surface. UV and visible light from LED lamps consisted of 100 LEDs with wavelengths of 370 nm, 420 nm, 450 nm, or 505 nm were used to illuminate the vessel, and their radiation intensities were adjusted to 1 mW cm⁻². The photocatalytic activity was evaluated by measuring the absorbance of MB at 664 nm using the UV-vis spectrometer (UV-2400PC, Shimadzu) every 20 min during illumination for 180 min. The degradation rate of the MB was linearly plotted against the illumination periods, and reaction rate for MB degradation (μ mol L⁻¹ min⁻¹) were calculated from this plot.

3. Results and discussion

3.1. Morphology, structure and chemical state of the oxide layer anodized in HNO₃ solution

SEM images of Ti substrate anodized in 100-mM HNO₃ with applied voltages of 15, 20, and 22 V are shown in Fig. 1. The image of non-treated Ti substrate is also shown in the figure. On the surface treated with 15 V, square-shaped pores on the micrometer scale with swelling at their boundaries were observed. When the voltage was increased to 20 V, the swelling disappeared and large hollows of ca. 100 μ m in size appeared on the surface. A collapsed surface containing winding and crossed grooves was formed when treated with 22 V. We consider that the NO₃⁻ in the electrolyte facilitates the oxidization of Ti, thereby inducing dielectric breakdown of the oxide layer when applying the voltage beyond a specific value [27]. The hollows on the surface would be caused by the dielectric breakdown, and the collapsed surface containing grooves might be formed by continuing the breakdown during anodizing.

To confirm our assumptions, we recorded the change in electric current between Ti substrate and the Pt electrode (Fig. 2). In the case of 15 V, the electric current decreased to near zero immediately after starting the oxidation, indicating that no dielectric breakdown occurred. In contrast, at 20 V, the current decreased slightly after starting, after which current with a specific value continued to flow during treatment. It is likely that the flowing current during the treatment is due to the dielectric breakdown in the oxide. Decreased current was not observed in the case of 22 V, implying that the intense dielectric breakdown occurs continuously. These changes in the electric current are direct evidence that the distinct morphology is related to dielectric breakdown occurring in the HNO₃ solution. Furthermore, it should be noted that small precipitates were often found in the electrolytes after the oxidation process was completed. The precipitates were probably TiO₂ produced via dielectric breakdown of the oxide layer, which was also reported by Nakahira et al. [26].

Fig. 3 shows a cross-sectional TEM image of the surface of the anodized Ti substrate corresponding to the Fig. 1(a). The TEM image shows that about 2- μ m thick oxide layer containing the grooves is formed upon the collapsed surface part of a Ti substrate. This indicates that the dielectric breakdown is most likely to induce the formation of the TiO₂ layer.

The XRD patterns of Ti substrate anodized in 100-mM HNO₃ aqueous solution with various applied voltages are shown in Fig. 4. The peak observed at 25.4° is attributed to TiO₂ with an anatase structure, indicating that the predominant phase in the oxide is anatase-type TiO₂. The peaks attributed to Ti with an hcp structure originated from the substrate. The peak intensity corresponding to the anatase TiO₂ increased with increasing voltage. A similar trend in the XRD patterns was also observed on the surface anodized in 1- and 10-mM HNO₃ aqueous solutions with various applied voltages.

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