



Fabrication of a visible-light-responsive photocatalytic antibacterial coating on titanium through anodic oxidation in a nitrate/ethylene glycol electrolyte

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ARTICLE INFO

Article history:

Received 4 August 2014

Accepted in revised form 8 December 2014

Available online 16 December 2014

Keywords:

Anodic oxidation

Nitrate electrolyte

Visible-light response

Photocatalytic TiO₂

Antibacterial coating

ABSTRACT

To provide semi-permanent antibacterial function for titanium medical implements, such as micro-tweezers, hemostatic forceps, and needle holders, a visible-light responsive nitrogen-doped titanium dioxide (TiO₂) layer that strongly adheres to Ti materials was fabricated through anodization in an electrolyte comprising ammonium nitrate in ethylene glycol, followed by heating at 723 K in air. The predominant structure of the oxide layer was TiO₂ with a rutile structure that contained ca. 1 at.% of incorporated nitrogen. The outward appearance of the oxide layer was quite smooth, and the topographic microstructure was a flat surface that included small pores. The thickness of the surface layer was approximately 10 μm, and the layer strongly adhered to Ti substrates. This fabricated anodic layer acted as a photocatalyst both under UV-light and visible-light illumination, and showed excellent antibacterial performance under both types of illumination. Anodic oxidation in a nitrate/ethylene glycol electrolyte is an innovative surface modification technique that can be used to simply form visible-light responsive photocatalytic antibacterial coatings on biomedical Ti materials.

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1. Introduction

In recent years, titanium (Ti) materials have been used instead of stainless steel for various medical implements, such as micro-tweezers, hemostatic forceps, and needle holders, because of the good mechanical strength and excellent corrosion resistance of Ti. The use of Ti materials is beneficial for the reduction of inflammations and allergic reactions arising from the release of toxic metallic ions [1–3]. However, Ti materials themselves cannot remove microbial contaminants such as bacteria and fungi. Sterilization procedures, such as autoclave sterilization using steam at high temperature and pressure, are therefore indispensable before using these materials in surgical procedures. However, the risk of microbial contaminants cannot be excluded completely during the post-sterilization process because such infections can also occur during the surgical procedure itself. This risk often threatens the life of a patient; accordingly, antibacterial materials, which show continuous antibacterial activity, are required in medical settings.

Formation of a surface layer that releases antibiotic agents is a common technique for fabrication of antibacterial devices, and many experimental investigations have focused on antibacterial surface layers based on degradable materials such as polylactic acid, silica sol-gel, and chitosan [4–8]. However, the effect of the antibiotics in these devices is diminished with increasing usage time and hence, this

method is not useful when the medical implements are repeatedly used. Titanium dioxide (TiO₂) is a common photocatalyst that shows strong photo-oxidation performance when illuminated [9–11]. This oxidation effect can decompose microorganisms and persists permanently without deterioration of its performance over time [12–15]. Owing to these characteristics, the formation of a photocatalytic TiO₂ layer is likely to be an appropriate method for fabricating antibacterial devices that are repeatedly used in medical settings [16,17]. However, when proposing the use of TiO₂-coated Ti in medical settings, high adhesion strength between the TiO₂ layer and substrate is indispensable because peeling of this layer could cause serious clinical problems. Popular TiO₂ coating processes such as the sol-gel procedure and sputtering deposition are therefore inappropriate because their adhesion strengths are comparatively low. Furthermore, bare TiO₂ only acts as a photocatalyst under ultraviolet (UV) light because the band gaps of TiO₂ (3.0 eV for the rutile phase and 3.2 eV for the anatase phase) are slightly higher than the energy corresponding to visible light. Ambient room lighting contains only a small portion of UV light and is not sufficient to utilize the antibacterial activity of bare TiO₂.

Anodic oxidation is a simple surface treatment technique that involves connecting Ti to the anode and then applying a direct current (DC) through the electrolyte. This technique has recently proven useful for producing a photocatalytic TiO₂ coating strongly adhered to a Ti substrate [18–23]. Another advantage of anodic oxidation is that specific elements from the electrolyte used are incorporated into the TiO₂ layer [22]. In 1986, Sato et al. demonstrated that a visible-light response was

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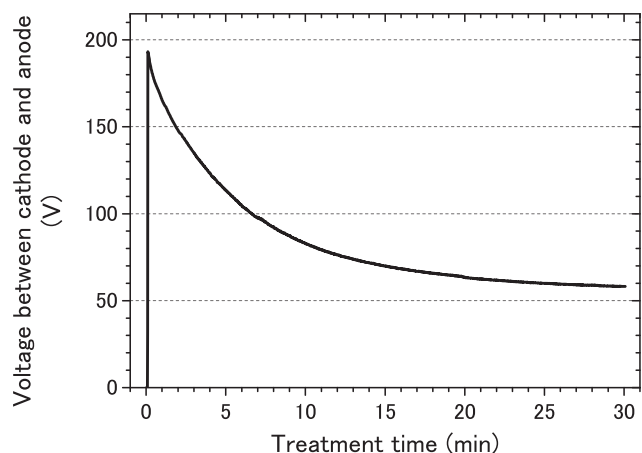


Fig. 1. Time transient analysis of the voltage between the cathode and the anode during the anodization.

obtained when TiO_2 was doped with NO_x [24]. Asahi et al. also reported that the band gap of TiO_2 decreased in response to the substitution of a portion of the oxygen atoms for nitrogen, resulting in the compound acting as a photocatalyst under visible light irradiation [25]. Based on these findings, anodic oxidation in an electrolyte including nitrate (NO_3^-) is likely to lead to the formation of a photocatalytic TiO_2 layer that is active when irradiated with visible light. However, it is well known that dielectric breakdown of the oxide layer is induced when anodization is carried out in HNO_3 aqueous solutions, leading to the formation of rough and inhomogeneous surfaces [26–28]. Nakahira et al. reported that when employing a 0.25 M HNO_3 aqueous solution as the electrolyte, precipitates were formed on the Ti substrate during anodizing owing to the dielectric breakdown. Subsequent analysis of these precipitates revealed that they consisted of nitrogen-doped TiO_2 , but they were completely removed from the surface through ultrasonic washing [26]. We previously attempted to fabricate a nitrogen-doped TiO_2 layer by anodizing a Ti substrate in HNO_3 with a concentration not exceeding 0.1 M. The layer fabricated demonstrated sufficient photocatalytic activity under visible-light illumination [27] and showed antibacterial performance [28]. However, similar to the work of Nakahira, the resultant layer was easily removed by wiping the surface gently. From these previous studies, it was concluded that anodization using NO_3^- aqueous solutions as the electrolyte is unsuitable for the formation of photocatalytic TiO_2 layers that strongly adhere to Ti substrates.

Raja et al. recently demonstrated that the anodization of a Ti substrate using fluoride containing polyhydric alcohols, such as ethylene glycol, as an electrolyte results in the formation of TiO_2 arrays that include a small amount of F and has a smooth surface [29]. These results made us expect that comparatively smooth layers with sufficient adhesion strength could be formed using nitrate solutions if ethylene glycol is used as the solvent instead of water. Based on these considerations, in the present study, we fabricated an oxide layer on a Ti substrate through anodic oxidation in an electrolyte comprising ammonium nitrate (NH_4NO_3) and ethylene glycol. The surface structure, photocatalytic activity, and antibacterial performance of the fabricated layer were compared with an anodic layer on Ti formed using an aqueous nitrate solution or a TiO_2 layer fabricated by the dip-coating process with a commercially available reagent.

2. Experimental procedures

2.1. Anodic treatment of Ti substrate

The electrolyte used in the anodic treatment was a 0.1 M nitrate solution prepared by dissolving NH_4NO_3 in ethylene glycol. The aqueous electrolyte of 0.1 M NH_4NO_3 , prepared by dissolving NH_4NO_3 in distilled

water, was also used to produce the reference material. Ti plates (99.5%) with a dimension of $10 \times 20 \times 1 \text{ mm}^3$ were chemically polished using a colloidal silica suspension with an average particle size of 40 nm, after which the plates were thoroughly rinsed with ethanol in an ultrasonic cleaner. The Ti plate was used as the anode for the anodic oxidation process, and a Pt plate was used as the cathode. The galvanostatic direct current (DC) applied had a constant value of 400 mA, and the DC voltage varied accordingly. The duration of the anodization process was 30 min, after which the sample was thoroughly rinsed in distilled water using ultrasonic agitation, and then heated at 723 K for 5 h in air [22]. Fig. 1 shows the time transient of the applied voltage between the cathode and the anode during the anodization. At the beginning of the anodization, the voltage increased abruptly up to about 200 V. Thereafter, the voltage decreases exponentially until 30 min, whereupon its value reached about 50 V.

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 diffractometry patterns (XRD; New D8 Advance, Bruker AXS, Germany) were measured with Bragg–Brentano geometry using $\text{Cu K}\alpha$ radiation. X-ray photoelectron spectroscopy (XPS; PHI 5000 Versa Probe, Ulvac-Phi, Japan) was conducted using monochromatized $\text{Al K}\alpha$ radiation ($h\nu = 1486.6 \text{ eV}$) to evaluate the incorporated nitrogen. The diameter of the X-ray probe was about 100 μm , 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 of the samples. The adhesion strength of the oxide layer was estimated by measuring the scratch resistance with a nanolayer scratch tester (CSR-2000, Rhesca, Japan). A diamond tip stylus with a diameter of 5 μm was used at a $100 \text{ g}\cdot\text{mm}^{-1}$ spring rate to measure the critical scratch point of the layer. The amplitude, scratch speed, and load rate were 100 μm , $10 \mu\text{m}\cdot\text{s}^{-1}$, and $100 \text{ mN}\cdot\text{min}^{-1}$, respectively.

The photocatalytic activity was evaluated using a methylene blue (MB) degradation test. Before starting the degradation test, the specimen was irradiated with UV for 90 min at an intensity of ca. $6 \text{ mW}\cdot\text{cm}^{-2}$ to eliminate surface contaminants. The specimens were then immersed in $10 \text{ mg}\cdot\text{L}^{-1}$ 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 with wavelengths of 370 nm or 420 nm, respectively, were used to illuminate the vessel, and the radiation intensities were adjusted to $1 \text{ mW}\cdot\text{cm}^{-2}$. 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 degradation rate of MB was plotted against the illumination periods, and the reaction rates for MB degradation ($\text{min}^{-1}\cdot\text{mL}^{-1}$) were calculated from this plot.

2.3. Evaluation of the antibacterial activity

Antibacterial activity of the specimens was examined using *Escherichia coli* (*E. coli*) strain ATCC 6922. Prior to the antibacterial test, *E. coli* was cultured in nutrient broth at 37°C in a conical flask. The bacterial suspension was diluted to $2 \times 10^6 \text{ CFU mL}^{-1}$ with a one five-hundredths diluted nutrient broth, and was dropped on each test specimen. The specimens were then placed in a dark place for 4 h, or illuminated with a black light or a xenon (Xe) lamp (XFE-152S, Tokina, Japan) equipped with a UV cutoff filter, at a radiation intensity of $100 \mu\text{W}\cdot\text{cm}^{-2}$ or $1000 \mu\text{W}\cdot\text{cm}^{-2}$, respectively. The *E. coli* cultured on the specimen was washed into a broth of soybean-casein digest with lecithin and Polysorbate 80 (SCDLP). We confirmed by using SEM that the *E. coli* were detached completely from the surface. The

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