



Full Length Article

Bi-functional anodic TiO₂ oxide: Nanotubes for wettability control and barrier oxide for uniform coloring



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ABSTRACT

A uniformly colored TiO₂, on which the surface is functionalized with nanotubes to control wettability, was prepared by a two-step anodization; the first anodization was carried out to prepare nanotubes for a super-hydrophilic or -hydrophobic surface and the second anodization was performed to fabricate a thin film barrier oxide to ensure uniform coloring. The effect of the nanotubes on barrier oxide coloring was examined by spectrophotometry and UV-vis-IR spectroscopy. We found four different regimes governing the color changes in terms of anodization voltage, indicating that the color of the duplex TiO₂ was primarily determined by the thickness of the barrier oxide layer formed during the second anodization step. The surface wettability, as confirmed by the water contact angle, revealed that the single barrier TiO₂ yielded 74.6° ± 2.1, whereas the nanotubes on the barrier oxide imparted super-hydrophilic properties as a result of increasing surface roughness as well as imparting a higher hydrophobicity after organic acid treatment.

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1. Introduction

Nanostructured titanium oxide has been studied for use in several areas including coating technology [1–3], energy conversion [4–6], and biomedical devices [7–11] because of its unique physical properties, such as high chemical inertness, excellent corrosion resistance, and photocatalytic effects. Among various preparation methods, anodization is the most widely-used method for producing decorative oxide on a Ti substrate since a uniform film with a targeted color and fairly good adhesion can be realized over a large surface area [12–15]. Color of the anodic TiO₂ film can be delicately tuned by adjusting the thickness of the barrier oxide, which can be precisely controlled in terms of anodic voltage with a proportionality constant of approximately 2.5–2.7 nm/V (the so called anodizing ratio) in acidic media, such as sulfuric or phosphoric acid [16–18]. However, the barrier film of TiO₂ is typically hydrophilic as well as oleophilic, which often leads to a degradation of film color due to the absorption of contaminants while the TiO₂ films are in use [19,20]. Thus, there is a continued demand for the development of colored TiO₂ films with hydrophobic (or oleophobic) properties in order to maintain the original film color for long-term usage [21–31].

In general, the color of anodic TiO₂ films originates from the constructive/destructive interference of light, which is reflected from the interface between air and the TiO₂ film and the interface between the TiO₂ film and the Ti metal [32,33]. Thus, if the surface roughness of TiO₂ is modified to form microstructures in order to manipulate hydrophilicity/hydrophobicity, the surface color cannot be maintained in its original state. One of the methods for preserving film color while imparting different surface wettability properties is to use a nanoscale surface on the colored barrier oxide. If the surface morphology in the barrier film is changed to nanotubes, different contact angles can be obtained [34–36]. In addition, if the size of nanotubes is small enough, it will not disturb the propagating light and it is possible to avoid color alteration by not deviating from its original barrier oxide thickness. It is a well-defined technology that tubular TiO₂ oxide films can be prepared by anodization in the electrolyte containing F⁻ ions [37–39]. When nanotubular TiO₂ is post-treated in an organic acid, the surface property becomes hydrophobic with low wettability [23,40].

In this work, nanotubes on barrier TiO₂ are prepared by two-successive anodization steps; the first anodization is carried out to form nanotubes to control wettability and the second is the growth of the barrier oxide, which typically determines the color. We expect that this is applicable over certain voltage ranges. These findings are valuable regarding the design of decorative films with modified wettability. Additionally, we expect that these bi-functional structures can be used for other potential applications,

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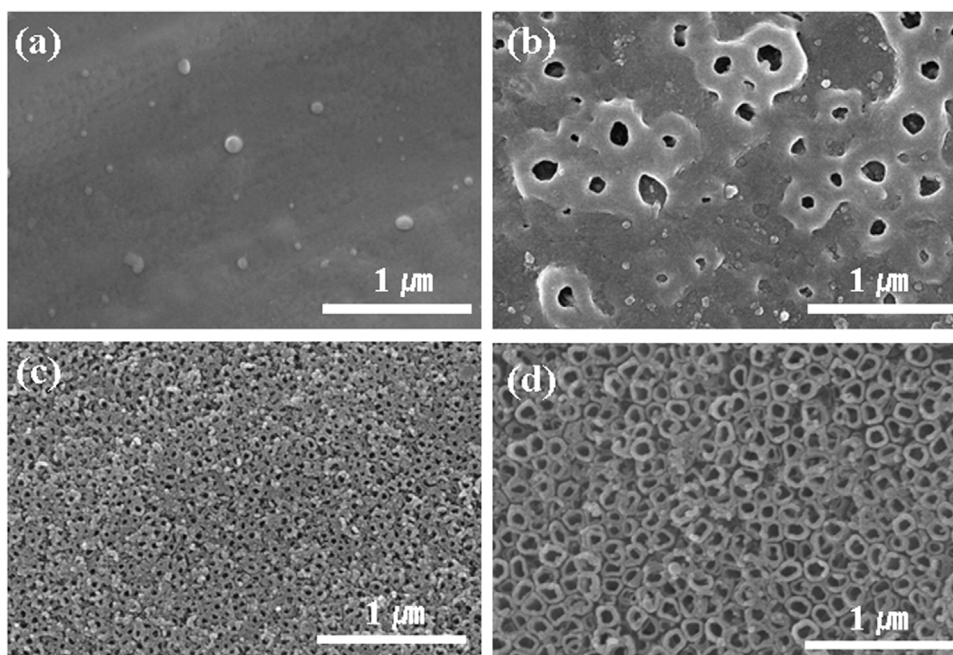


Fig. 1. SEM images of anodic TiO₂ films. (a, b) barrier TiO₂ was prepared in a 0.5 M H₂SO₄ solution for 1 min at (a) 50 V and (b) 110 V. (c, d) Nanotubes were prepared in a mixture solution of 1 M H₃PO₄, 1 M NaOH, and 0.3 wt% HF for 3 h at (c) 10 V and (d) 20 V.

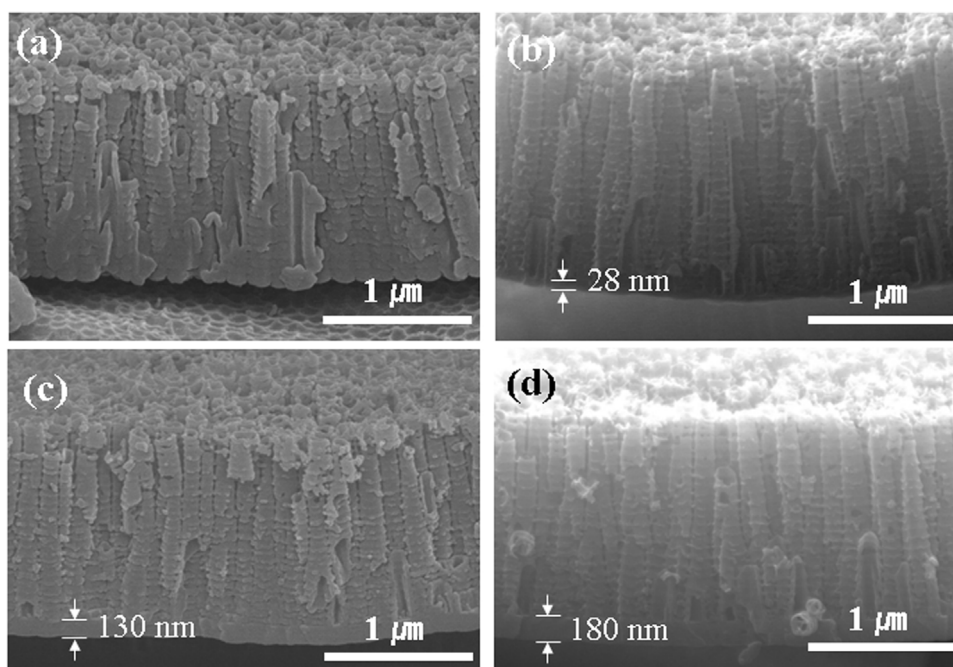


Fig. 2. Cross-sectional SEM images of TiO₂ nanotubes prepared at an anodization voltage of (a) 20 V (electrochemical conditions explained in Fig. 1(d)). (b–d) cross-sectional SEM images of nanotubes on barrier oxides prepared by a 2-step anodization method; (b) nanotubes and the barrier oxide were both prepared at 20 V (NT₂₀B₂₀). (c) NT₂₀B₅₀ (d) NT₂₀B₆₀.

such as anti-wetting & self-cleaning device, electrochromic device, displays, and humidity sensors, etc.

2. Experimental

Titanium foil was degreased and cleaned by sonication in acetone, ethanol, and deionized (DI) water for 15 min each, successively, and then dried with a nitrogen stream. A two-electrode cell consisting of titanium as the anode and platinum as the cathode was used for the anodization. Nanotubular TiO₂ was grown

in a mixture solution of 1 M H₃PO₄, 1 M NaOH and 0.3 wt% HF (denoted as NT_x, x = applying voltage, 10 or 20) for 3 h, which was chosen among many receipts for fabrication of TiO₂ nanotubes due to that it produced clear mouth of nanotubes without formation of any nanograss, and barrier TiO₂ was prepared by the anodization of Ti in an electrolyte of 0.5 M sulfuric acid at different voltages (denoted as B_y, y = applying voltage, from 10 to 120). For example, B₃₀ designates a barrier oxide anodized at 30 V) for a total of 1 min. In order to determine the effect of the nanotubular structure on the barrier oxide, TiO₂ nanotubes were fabricated on the barrier

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