



Titania nanotubes from weak organic acid electrolyte: Fabrication, characterization and oxide film properties



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ABSTRACT

In this study, TiO₂ nanotubes were fabricated using anodic oxidation in fluoride containing weak organic acid for different durations (0.5 h, 1 h, 2 h and 3 h). Scanning electron microscope (SEM) micrographs reveal that the morphology of titanium oxide varies with anodization time. Raman spectroscopy and X-ray diffraction (XRD) results indicate that the as-formed oxide nanotubes were amorphous in nature, yet transform into crystalline phases (anatase and rutile) upon annealing at 600 °C. Wettability measurements show that both as-formed and annealed nanotubes exhibited hydrophilic behavior. The electrochemical behavior was ascertained by DC polarization and AC electrochemical impedance spectroscopy (EIS) measurements in 0.9% NaCl solution. The results suggest that the annealed nanotubes showed higher impedance (10⁵–10⁶ Ω cm²) and lower passive current density (10^{−7} A cm^{−2}) than the as-formed nanotubes. In addition, we investigated the influence of post heat treatment on the semiconducting properties of the oxides by capacitance measurements. In vitro bioactivity test in simulated body fluid (SBF) showed that precipitation of Ca/P is easier in crystallized nanotubes than the amorphous structure. Our study uses a simple strategy to prepare nano-structured titania films and hints the feasibility of tailoring the oxide properties by thermal treatment, producing surfaces with better bioactivity.

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1. Introduction

The synthesis of nanostructured titanium oxide through anodic oxidation for biomedical applications has been investigated by many authors owing to their interesting features like large surface area, biocompatibility/bioactive properties, non-toxicity, corrosion resistance and adequate mechanical properties [1,2]. This method can control the titanium oxide formation to nanoscale dimensions. Over the years, four generations of fluoride containing electrolytes – aqueous solution of acidic pH [3], aqueous solution of neutral pH [4], organic [5,6] and chloride in both aqueous [7] and organic [8] based electrolytes have been utilized to develop nanotubes of varied dimensions. TiO₂ nanotubes grown on titanium render increased surface area, which accelerates bone growth in orthopedic and dental implants [9]. Such a surface layer enhances cell adhesion, cell proliferation and protein adsorption [10,11]. Hydroxyapatite formation, which is considered to be an essential step for the bone-binding ability of biomaterials, is enhanced in porous surfaces as compared to flat compact surface [9,12]. Controlling the size and arrangement of pores helps bone growth and this promotes the use of titania nanotubes for biomedical applications. A mixed crystalline nanotube (anatase + rutile) structure showed better biocompatibility than the amorphous nanotubes [12]. Various researchers focused on the effect of anodization time and voltage on

the surface morphology and studied the film properties [5,13]. The passive film behavior of titanium and its alloys plays a crucial role for its suitability as an implant material. The kinetics of corrosion process can be reduced by the passive film which blocks the diffusion of aggressive ions present in the body fluids to the substrate metal [14]. It has been shown that the blood compatibility of heart valve materials is influenced by the semi-conducting nature of non-stoichiometric titanium oxide films [15]. Hence, the rate of active dissolution of ions strongly depends on the chemical composition and defective nature of the oxide layer.

Though few studies have reported on the passive film and semiconducting properties of the titanium oxide in a biomedical perspective [15–17], there is no report which provides an overall picture on the synthesis and on the variation of semiconducting properties of titania nanotubes subjected to thermal treatments (annealing). In this respect, we experimentally investigated and compared the as-formed and annealed nanotubes and an attempt is being made to characterize the variation in the morphology and passive film properties of the oxide nanotubes in saline solution.

2. Experimental procedure

2.1. Sample preparation and anodization

High purity titanium sheets (Grade 2, 99.99%) of dimension 20 × 10 × 1 mm³ were employed in this work. The sheets were

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metallographically prepared, ultrasonically cleaned with acetone and then rinsed in distilled water. The electrolyte used in this work was 0.1 M citric acid with 0.5 wt.% NaF at an initial pH 4. Before anodizing, the polished titanium surfaces were etched in a solution containing 1:4:5 ratio of HF:HNO₃:H₂O. All solutions were prepared from reagent grade chemicals and distilled water. A surface area of 2 cm² was exposed to the electrolyte. Oxide films were grown by anodizing in a two electrode electrochemical cell with titanium as working electrode and graphite rod as counter electrode. The experiments were performed at room temperature and a constant potential of 20 V was applied for varying time durations of 0.5, 1, 2 and 3 h, respectively. After anodization, the samples were rinsed with distilled water and dried. Another set of samples were heat treated at 600 °C by holding them for 3 h and subsequently furnace cooled.

2.2. Surface characterization

The surface morphology and cross sectional features of anodized surfaces were examined using field emission scanning electron microscopy (FE-SEM FEI Quanta FEG 400). Energy-dispersive X-ray spectroscopy (EDS) fitted to SEM was used to analyze the composition of the oxide films. Surface roughness of the anodic oxide layers were measured using 3D noncontact surface optical profiler (Bruker ContourGT Inmotion). Image analysis and processing was performed using computer-aided software analysis (vision analysis). X-ray diffraction (XRD) measurements (X'Pert PRO, PANalytical) were carried out using a incident Cu K α radiation ($\lambda = 1.54 \text{ \AA}$), tube voltage 30 kV at a scan speed of 5°/min. Raman spectrum was recorded using a micro Raman Spectroscopy (Horiba Jobin Yvon, model HR800UV) instrument with He-Ne laser (632.81 nm) and analyzed with grating of 600 lines/in. The acquisition time of 5 and 30 s were used in the analysis with 10 mW incident power.

Contact angle measurements were carried out on the as-formed and annealed surfaces using a contact angle detect system (Easy Drop, KRUSS, Germany) with distilled water. Water droplet (0.5 μ l) was dispensed onto the surface with a syringe and the digital images of the droplet silhouette were captured with a CCD camera (KB-1380) within 10 s after wetting. All data reported here are expressed as mean \pm standard error, and analyzed statistically by appropriate t-test. A value of $p < 0.05$ was considered significant.

2.3. Electrochemical characterization

Potentiodynamic polarization and impedance spectroscopy were performed using a Gamry Potentiostat (Reference 600–14083) controlled by a personal computer and softwares (Gamry Framework and Gamry Echem Analyst). A conventional three electrode cell was used for all the electrochemical measurements. A saturated calomel electrode (SCE) was used as the reference electrode, graphite rod as counter electrode and titanium as the working electrode. All experiments were carried out at room temperature in an electrolyte of 0.9% NaCl at pH 7.2. The working electrode was pressed against an O-ring sealing from outside of the cell exposing an area of 0.5 cm². All potentials reported in this paper are with reference to SCE.

Before the electrochemical tests, all samples were immersed in electrolyte for a time period of 3 h in order to attain a stable open circuit potential (OCP). Potentiodynamic polarization measurements were performed from $-0.5 V_{SCE}$ to $+1 V_{SCE}$ at a scan rate of 1 mV s⁻¹. Electrochemical impedance measurements were performed under open circuit conditions in the frequency range of 0.1 MHz–10 mHz with an excitation voltage of 10 mV (peak-to-peak). The measured spectra were fitted with an equivalent circuit using Gamry Echem Analyst software. The space charge capacitance measurement was carried out using the Mott Schottky analysis at a frequency of 1 kHz by sweeping the potential in the negative direction from 0.6 V_{SCE} to $-0.5 V_{SCE}$ at a scan rate

of 50 mV s⁻¹. The electrochemical measurements were performed at least three times to confirm reproducibility.

2.4. Evaluation of apatite inducing ability

As-formed and annealed samples were immersed in simulated body fluid (SBF) with pH 7.4, whose ion concentrations (Na⁺ 142.0, K⁺ 5.0, Mg²⁺ 1.5, Ca²⁺ 2.5, Cl⁻ 147.8, HCO₃⁻ 4.2, HPO₄²⁻ 1.0, SO₄²⁻ 0.5 mM) are nearly equal to those of human blood plasma at 36.5 °C [18]. The SBF was prepared by dissolving reagent grade chemicals of NaCl, NaHCO₃, KCl, K₂HPO₄·3H₂O, MgCl₂·6H₂O, CaCl₂ and Na₂SO₄ in distilled water and buffered at pH 7.4 with tris(hydroxymethyl)aminomethane and 1 M HCl at 37 °C. 30 mL of SBF was added to the beaker to maintain a ratio of the specimen surface area per volume (SA/V) of 0.1 cm⁻¹ [18]. After soaking in this medium for 5 days, the samples were removed, washed with distilled water and then dried.

3. Results and discussion

3.1. Morphological characteristics of TiO₂ nanotubes

Fig. 1a–d shows the surface morphology of the samples anodized for different time durations (0.5, 1, 2 and 3 h) in 0.1 M citric acid containing 0.5 wt.% of NaF electrolyte. In order to convert amorphous oxides into crystalline, all samples were annealed at 600 °C for 3 h. The SEM micrographs of the annealed samples are shown in Fig. 2b. The average inner and outer pore diameters (D_i and D_o), interpore distance (w), wall thickness (t) and tube length (L) were obtained using image J software. In pore diameter calculations, pore shapes were assumed to be perfect circles. The total surface area of the nanotube (A), pore density (n), porosity of the lattice (P), specific surface area (A_s) can be estimated from the following expression [19,20],

$$A = 2\pi(D_o^2 \sim D_i^2) + 2\pi L(D_o + D_i) \quad (1)$$

$$n = \frac{10^{14}}{(3)^{0.5} \cdot D_o^2} \quad (2)$$

$$P = 0.90 \left(\frac{D_i}{D_o}\right)^2 \quad (3)$$

$$A_s = n \cdot A. \quad (4)$$

The morphological parameters of anodized titanium grown at different time intervals are presented in Table 1. Tube length does not vary with anodization time even when the specimens were anodized for 2 h, whereas the other dimensions vary. The levels of porosity measured were in the range of 35–50%. After annealing the as-formed nanotubes, the wall thickness and porosity decreases and this will be explained in later sections. Standard deviations of the values are reported and the difference observed is insignificant. Further, BET measurements would be helpful in comparing the total surface area of the fabricated nanotubes with the existing calculations.

The cross-section and bottom views of TiO₂ nanotubes are shown in Fig. 2a. Variation in wall thickness is attributed to the current oscillations which arise due to the change in pH at the pore tip and thereby transitory increase in the dissolution rate [21]. The obtained nanotubes are straight and hollow with wrinkled walls. Increased water content in the electrolyte is responsible for the formation of ripples in the tube walls. From the bottom view, it is clear that the semispherical tubes generate dimple structures on the titanium surface underneath and closed with a barrier oxide layer. Hence the bonding strength between these interfaces can be improved due to the 'cup- and cone-like' structure formation. Also, it was observed that nanotube arrays maintain highly ordered structures when the film is removed from the substrate.

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