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Full Length Article

Effect of heat treatment on surface hydrophilicity-retaining ability of titanium dioxide nanotubes

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ABSTRACT

The aim of this study is to investigate the effect of different annealing temperature and atmosphere on the surface wettability retaining properties of titania nanotubes (TNs) fabricated by anodization. The TNs morphology, crystal phase composition and surface elemental composition and water contact angle (WCA) were investigated by scanning electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy and contact angle instrument, respectively. After the samples annealed at 200 °C, 450 °C, 850 °C have been stored in air for 28 days, the WCAs increase to 31.7°, 21.1° and 110.5°, respectively. The results indicate that crystal phase composition of TNs plays an important role in surface wettability. Compared with the WCA (21.1°) of the samples annealed in air after 28 days, the WCA of samples annealed in oxygen-deficient atmosphere is lower, suggesting the contribution of oxygen vacancy in the enhanced hydrophilicity-retaining ability. Our study demonstrates that the surface hydrophilicity-retaining ability of TNs is related to the ordered nanotubular structure, crystal structure, the amount of surface hydroxyl group and oxygen vacancy defects.

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1. Introduction

Titania nanotubes (TNs) can be used for photocatalysis [1,2], solar cells [3], water splitting [4] and drug delivery [5] owing to the orderly and controllable surface morphology [6–8], excellent thermal-chemical stability, non-toxic and biocompatibility. As a kind of surface wetting material, TNs exhibit great potential for applications in many fields, such as surface self-cleaning [9], oil-water separation [10] and biomaterials [11,12].

For biological systems, especially, the hydrophilicity of biomaterial surface plays a crucial role in affecting protein adsorption and cellular adhesion [13–15]. Therefore, surface wettability is regarded as one of the most important properties of biomaterials and can be quantified by contact angle [16]. Some literatures have reported that surface wettability is governed by surface chemistry, free energy and morphology [17,18]. Many methods were used to improve or control TNs surface hydrophilicity, such as two-step anodization method[19], the increase of the tube diameter [20], the change of the crystal structure or thickness [21,22], and biological or chemical modification [23,24]. In addition, annealing treatment at various temperature can remove superficial organic contaminants of TNs to improve their surface hydrophilicity [25]. However, a lot of researches have demonstrated that TNs hydrophilic surface would became more hydrophobic after being exposed and aged in air, which may be attributed to alkane contamination and organic contaminants in the atmospheric storage [26]. Hence, in order to achieve non-aging hydrophilic surfaces, some methods were developed [27–29]. Reports have demonstrated that hydrophobic TNs surfaces could turn to hydrophilic surfaces with UV irridiation [27,28]. Hamlekhan et al. demonstrated that nanotubes annealed at 600 °C could maintain their surface hydrophilicity significantly longer than nanotubes annealed at 300 °C [29]. Despite of these achievements, the reason and strategy for the anti-aging ability of TNs need to be further studied.

In this study, we focus on the obtaining high hydrophilicity-retaining ability of TNs surface by changing annealing temperature and atmosphere. The effects of the annealing treatment on the microstructure, crystal phase composition, surface characteristics and wettability of TNs are also analyzed.

2. Experimental procedure

2.1. TNs samples fabrication

Commercially bare titanium (TA2, 10 × 10 × 1 mm^3) was carefully polished with No.400, 600, 800 and 1000 metallographic abrasive paper. After being degreased by sonicating in pure

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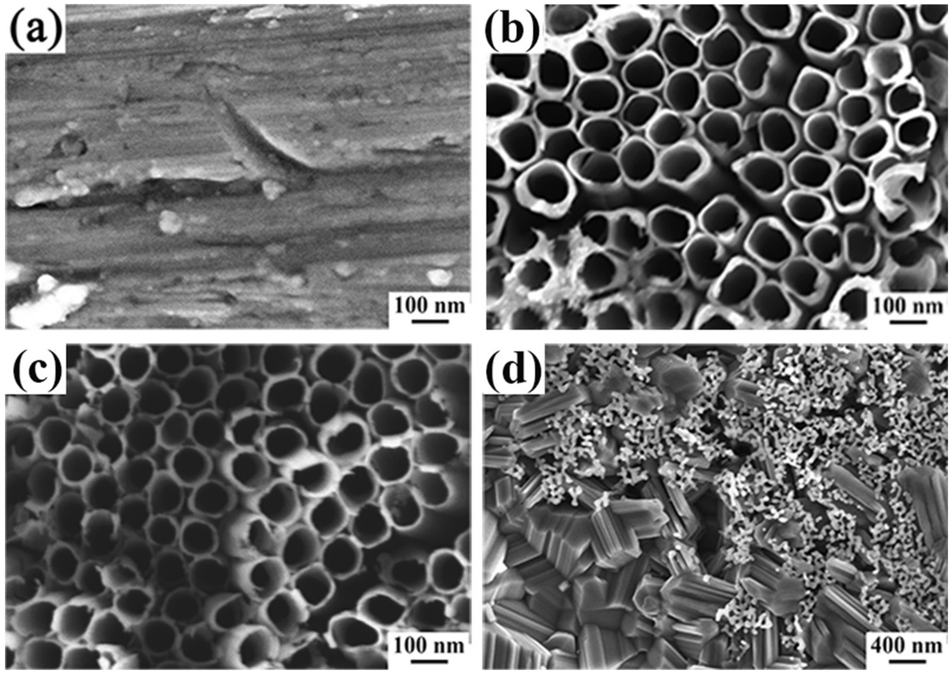

Fig. 1. SEM images of samples (a) Bare Ti (b) TN-unannealed (c) TN-450 and (d) TN-850.

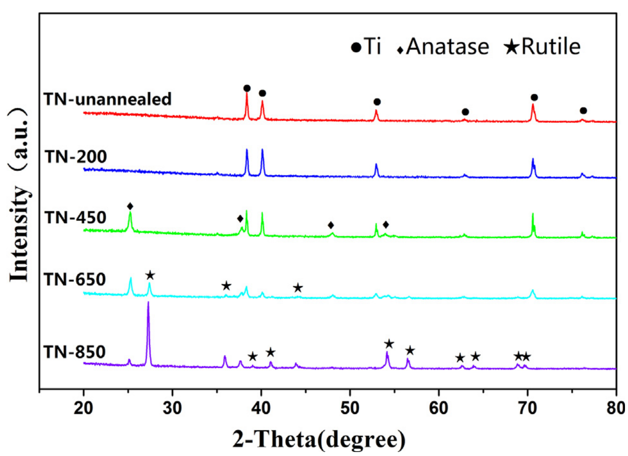

Fig. 2. XRD patterns of samples annealed at different temperature in air atmosphere.

acetone (Analytic Reagent, AR, KeLong Chemical, Chengdu), ethanol (AR, KeLong Chemical, Chengdu), and distilled water for 10 min, respectively, the titanium sheets were dried at 60 °C in air atmosphere. The titanium dioxide nanotubes (TNs) samples were prepared by anodization process in electrolytes based on ethylene glycol (AR, KeLong Chemical, Chengdu) containing 0.3 wt.% NH_4F (Analytic Reagent, AR, KeLong Chemical, Chengdu) and 6 vol.% distilled water. Anodization was performed in a two-electrode cell with bare titanium sheet sample as an anode and the titanium plate as a cathode under a constant 50 V anodic potential for 40 min at room temperature. The obtained samples were named as TN-unannealed.

In order to get different phase composition of TNs, samples were annealed in air at different temperatures (200 °C, 450 °C, 650 °C and 850 °C) for 2 h in a muffle furnace. The annealed samples were denoted as TN-200, TN-450, TN-650 and TN-850, respectively. At the same time, TNs samples were also annealed at 450 °C in different atmosphere, including air, argon, nitrogen and mixture atmosphere (95 vol.% argon and 5 vol.% hydrogen), and the corresponding products were denoted as TN-Air, TN-Ar, TN-N_2 and TN-Mix, respectively.

Table 1
Effect of annealing temperatures on phase structures of TNs.

Temperature (°C)	200	450	650	850
Percentages of crystallinity (%)[a]	100.0(T)	82.2(T) 17.8(A)	60.5(T) 20.3(A) 19.1(R)	 21.7(A) 78.3(R)

[a] T, A and R denote titanium, anatase and rutile, respectively.

2.2. Materials characterization and electrochemical measurements

Scanning electron microscopy (SEM, Hitachi S4800, Japan) was used to observe the surface morphology of the fabricated TNs samples. X-ray diffraction (XRD, X'Pert Pro MPD, Holland) was used to analyze the crystal structure of the obtained TNs using Cu-Kα radiation (λ = 1.54059 Å). All X-ray photoelectron spectroscopy (XPS, Thermo Escalab 250xi, America) were recorded with monochromatic Al Kα radiation ($h\upsilon$ = 1361 eV). Electrochemical properties of the TNs were measured in a 1 M Na_2SO_4 aqueous solution with an electrochemical workstation (CHI660E, China). Cyclic voltammetry (CV) tests were conducted over a potential voltage range from 0 to 0.9 V (vs Ag/AgCl) at a scan rate of 20 mV s^{-1}. The surface contact angles of water droplet on TNs surface were measured by the contact angle instrument (JC2000C1, China). All the contact angle measurements were conducted in sextuple.

All values were presented as means ± standard deviation (SD), and commercial statistical software SPSS was used for statistical analysis. $P < 0.05$ was considered to indicate statistical significance.

3. Results and discussion

3.1. The effect of annealing temperature on TNs

Fig. 1 presents the SEM images of bare Ti, TN-unannealed and the sample annealed at 450 °C, 850 °C for 2 h, respectively.

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