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Template assisted fabrication of TiO_2 and WO_3 nanotubes

Chien Chon Chen[a], Chin-Hua Cheng[b], Chung-Kwei Lin[c,*]

[a]Department of Energy Engineering, National United University, Miaoli 36003, Taiwan
[b]Department of Materials Science and Engineering, Feng Chia University, Taichung 40724, Taiwan
[c]School of Dental Technology, College of Oral Medicine, Taipei Medical University, Taipei 11031, Taiwan

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Abstract

Anodic aluminum oxide (AAO) templates with diameters of 200–500 nm were generated by anodizing a commercial aluminum (Al) substrate (99.7%) in 1 vol% phosphoric acid (H_3PO_4), with an applied voltage of 195 V. Titania and tungsten oxide nanotubes (NTs) were successfully grown on AAO template by the sol–gel process. Thermal gravimetric analyzer (TGA) curves showed that gel can be transfered to nanocrystalline particles after 19% weight loss of water molecule by evaporation. The results showed that the nanocrystalline TiO_2 NTs presented at 200 °C, and grains grew as temperature increased. At a temperature of 550 °C, the (101), (103), (004), (112), (200), (105), and (211) planes of anatase TiO_2 were detected clearly, whereas tungsten oxide NTs are amorphous after heat treatment at 200 °C or 300 °C. But the (110), (111), (002), (022), (222), and (004) planes of γ-WO_3 phase can be observed obviously after the heat treatment at 400 °C.

Keywords: A. Sol–gel; Titania; Tungsten oxide; Nanotube; AAO

1. Introduction

Many nanostructures have very interesting properties. For example, titania has been used in various applications such as environment [1], catalysis [2], dielectrics [3], optoelectronics [4], sensors [5], and solar cells [6–8]. Also, WO_3 nanopores show excellent ion intercalation properties (electrochromic devices, charge storage) [9–13]. The oxides have varied stable phases. For example, titanium dioxide has three stable phases: anatase, brookite, and rutile [14]. Tungsten oxide has four: α-WO_3 (tetragonal, 1010–1170 °C), β-WO_3 (orthorhombic, 600–1170 °C), γ-WO_3 (monoclinic, 290–600 °C), and δ-WO_3 (triclinic, 230–290 °C) [15]. The transformation of those phases depends on the annealing temperature at a constant oxygen pressure, as in an air furnace.

It is also interesting that in the case of titanium alloys, small amounts of the alloying element can drastically affect the properties, while the unique nano-tubular morphology is completely retained. For example, TiW (0.2 at%) alloys show a strongly enhanced electrochromic response and improved photocatalytic properties [16]. Yang et al. [17] doped WO_3 into TiO_2 NT to enhance the photo-catalysis property. Smith and Zhao [18] produced a TiO_2/WO_3 core/shell structure that enhances the separation rate of electrons and holes. Xiao et al. [19] coated WO_3 particles on TiO_2 NT; this nano-composite material can reduce the recombination rate of electrons and holes. Schmuki made TiO_2–WO_3 composite nanotubes by TiW alloy anodization; such nanotubes have an excellent dye-absorbance ability [20].

AAO has characteristics of being light and transparent, with large surface, good mechanical strength, and flexibility, making it a candidate material for the template. In this work, AAO template was made by anodization; TiO_2 and WO_3 NTs were made by the sol–gel deposition on AAO. We also examined the morphology and crystallization characteristics in the above nano-materials. The effects of post heat-treatment on the morphology and phase transformation of TiO_2 NT and WO_3 NT were examined by SEM, TEM, EDS, XRD, XAS, XPS, TGA, and FTIR analysis.

*Corresponding author. Tel.: +8862 2736 1661x5115.
E-mail address: chungkwei@tmu.edu.tw (C.-K. Lin).

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2. Experimental procedures

2.1. AAO template fabrication

Anodic aluminum oxide (AAO, Al_2O_3) templates with a pore size of 10–500 nm were generated by a two-step anodizing process on a commercial aluminum (Al) substrate (99.7%) in acid solutions of sulfuric acid (H_2SO_4), oxalic acid $(COOH)_2$, or phosphoric acid (H_3PO_4). The Al substrate was first ground to # 1000 by SiC waterproof paper. Then the residual stress of the Al substrate was released by annealing at 550 °C for 1 h in an air furnace. After annealing, the sample was electro-polished in a bath consisting of 15 vol% perchloric acid ($HClO_4$, 70%), 70 vol% ethanol (C_2H_6O, 99.5%), and 15 vol% monobutylether (($CH_3(CH_2)_3OCH_2$-CH_2OH), 85%) with 42 V (DC) applied for 10 min and titanium foil used as a counter. AAO templates with diameters of 200–500 nm were generated by anodizing a commercial aluminum (Al) substrate (99.7%) in 1 vol% phosphoric acid (H_3PO_4), with applied voltages of 195 V and pore widening using 5 vol% H_3PO_4 for 0.5–4 h. A more detailed description of the AAO process can be found in our previous study [21–23].

2.2. TiO_2 NT formation in AAO

The TiO_2 NT was prepared by immersing the Al_2O_3 template in 0.02 M titanium fluoride (TiF_4) solution. The immersion steps were as follows: (1) adjust pH value of DI-water to 1.0–1.3 using hydrochloric acid (HCl); (2) add TiF_4 into DI-water; (3) immerse sample into TiF_4 solution for 10 min; (4) adjust pH value of TiF_4 solution to 3.0–3.3 using NH_4OH (ammonium hydroxide); and (5) immerse sample into TiF_4 solution for 120 min. After the immersion steps, the sample was annealed at 200, 300, 400, and 550 °C for 1–3 h to obtain anatase TiO_2 NT on the Al_2O_3 template.

2.3. WO_3 NT formation in AAO

The WO_3 NT was prepared by immersing Al_2O_3 template into tungsten (VI) chloride (WCl_6) containing sol–gel as follows: (1) make tungsten precursor in ethanol (C_2H_5OH) solvent with 10 wt% WCl_6 and 2 h stirring; (2) add 20 vol% surface-active agent of 2,4-pentanedione ($C_5H_8O_2$) to the solution with 2 h stirring again to form tungsten-containing sol; (3) add 0.15 vol% DI-water to the solution with 12 h stirring to form tungsten-containing sol–gel; (4) immerse sample in tungsten (VI) chloride (WCl_6) containing sol–gel for 1 h and (5) after the immersion steps, the sample was annealed at 550 °C for 1 h to obtain γ-phase (monoclinic) WO_3 NT on the Al_2O_3 template.

2.4. TiO_2/WO_3 NTs formation in AAO

The TiO_2 NT was first formed on the AAO template by TiF_4 solution, and then the sample was immersed in 10 wt% sodium tungstate dihydrate ($Na_2WO_4 \cdot 2H_2O$)

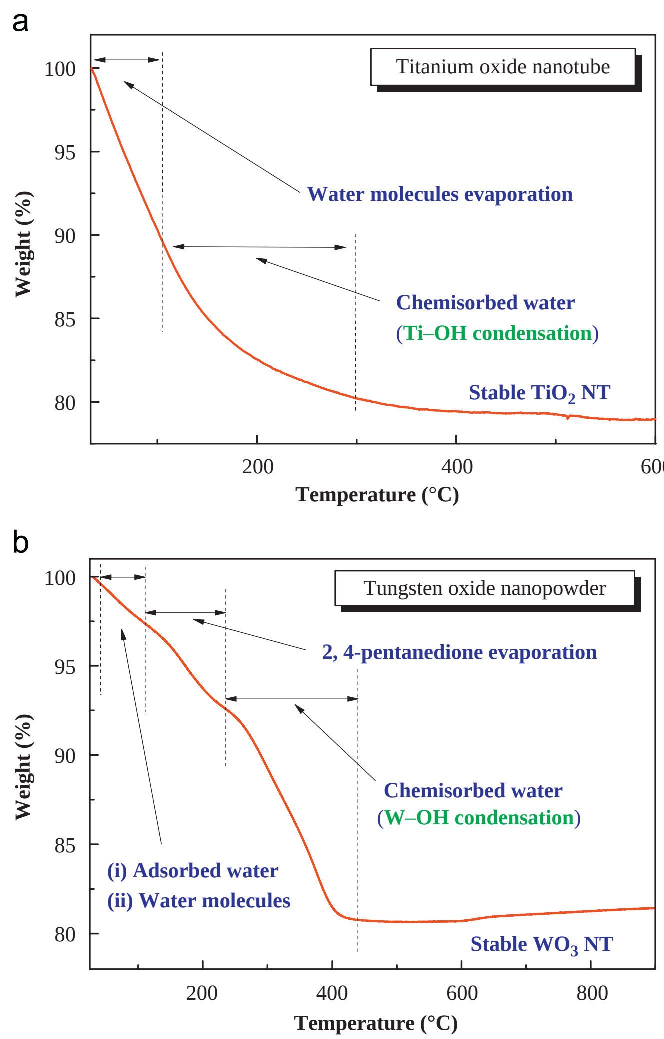

Fig. 1. TGA curves of (a) TiO_2 NT between 25 and 600 °C and (b) WO_3 NT between 25 and 900 °C.

Table 1
Summary of the experimental procedures of methods, solution, and heat treatment temperature.

Materials	Fabrication method	Crystallization
AAO	1 vol% H_3PO_4, 195 V anodization and 5 vol% H_3PO_4 pore widening for 0.5–4 h	Amorphous
TiO_2 NT	Sol–gel: 0.02 M TiF_4 (pH:3.0–3.3) for 2 h	550 °C for anatase phase
WO_3 NT	Sol–gel: 10 wt% WCl_6,20 vol% $C_5H_8O_2$ and 15 vol% C_2H_5OH for 17 h	400 °C for γ-phase