Effect of Water Content in Ethylene Glycol as Electrolyte for Fabrication of Anodic Titania Nanotubes: Synchrotron XRD Characterization

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Nanodimensional materials are the promise of achieving unique physical, optical, and electrical properties and superior performance due to their inherent nanoarchitectures. One-dimensional architectures are particularly versatile materials for use in sensing, solar cells, water photolysis, fuel cells, and environmental remediation. Among them, nanotube arrays have a higher surface area than nanowires due to the additional surface area enclosed inside the hollow structure. In the case with a given pore diameter and wall thickness, the internal surface area increases almost linearly with nanotube length. As initially reported by Gong and co-workers[1] in 2001, the first generation titania nanotube arrays fabricated by anodization using an aqueous HF-based electrolyte could be grown to a length of about 0.5 m. Subsequently, the length was increased to ~ 7 m by controlling the anodization electrolyte pH into a higher value. Now, we are fabricating a new generation of anodic growth of highly ordered titania nanotube arrays to 270 m,[2] well over 2 order of magnitude increase in length, by the use of nonaqueous electrolytes, which is expected further improvements in technical applications.

In this study, the starting Ti foil (0.3 mm thick) was washing in turn with water and isopropyl alcohol followed by being sonicated in acetone for 5 min. Anodization was carried out using a two-electrode configuration. The electrolytes were 0.25 wt.% NH_4F in ethylene glycol with variable water addition of 2, 4, 7 and 10 wt%. The anode was Ti foil with 1 x 1 cm^2, coupled with a Pt foil acting as a cathode. The distance between the anode and the cathode was maintained at 3 cm. A DC power supplier was applied at 80 V for anodization period of 24 hours. The as-grown TiO_2 nanotube arrays (TiNTs) was then immersed in 33 wt% $H_2O_{2(aq)}$ for 30 seconds so that the TiNTs could be flaked off from the titanium foil. The freestanding TiNTs can be easily ground into powder, named AO-TiO_2-*x*% which refers to water content.

The morphology of the as-prepared AO-TiO_2-*x*% exhibited both spherical and tube-like shapes with a size distribution ranged from 50 to 100 nm. The Brunauer-Emmett-Teller (BET) surface area of AO-TiO_2 was about 20 m^2/g, as determined from N_2 sorption isotherms at 77 K. Before heating, AO-TiO_2-*x*% were amorphous.

The phase transformation of AO-TiO_2-*x*% during heating in oxygen flow was measured using synchrotron X-ray diffraction (BL17A1). 0.1 g of AO-TiO_2-*x*% was filled at the center of quartz capillary (inner diameter = 1.0 mm and wall thickness = 0.01 mm) and flowed with oxygen at 25 mL/min. The programmed temperature was finely controlled by a gas-flow heater as following: hold at 200 ^{0}C for 10 min. and then heated to 600 ^{0}C at the rate of 5 ^{0}C/min.

The resulting XRD patterns of AO-TiO_2-*x*% using *in-situ* synchrotron X-ray diffraction with of 1.32633 nm were shown in Fig.1. The annealing temperature of the initially amorphous phase transformed to anatase phase were 289, 289, 355 and 400 ^{0}C for AO-TiO_2-*2*%, AO-TiO_2-*4*%, AO-TiO_2-*7*% and AO-TiO_2-*10*%, respectively. The fact is that the increase in the temperature of initial crystallization increased with the water content of ethylene glycol electrolyte whereas the rate of crystallization decreased with increasing water content. With further heating to 600 ^{0}C, only anatase phase was observed without subsequently transforming to the rutile phase. The properties of the phase transformation affecting the photocatalytic performance of these AO-TiO_2-*x*% will be further identified. This will be the objective of our future work.

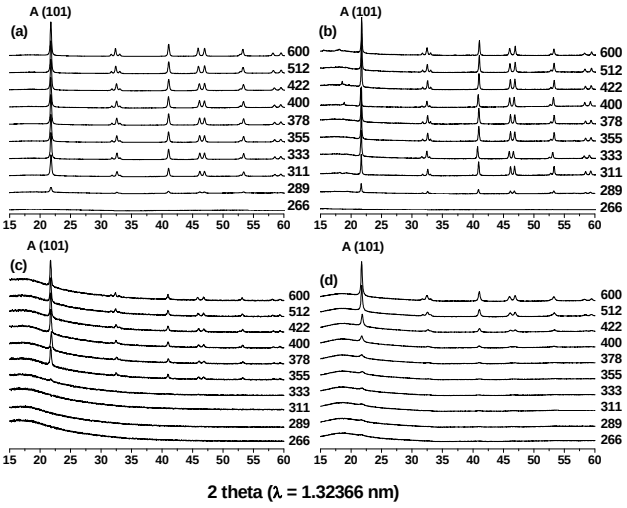

Figure 1. The XRD spectra of AO-TiO_2-*2*% (a), AO-TiO_2-*4*% (b), AO-TiO_2-*7*% (c) and AO-TiO_2-*10*% (d) at the temperatures of 266 to 600 ^{0}C.

References:

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[2] C. J. Lin, W. Y. Yu, and S. H. Chien, Appl. Phys. Lett. **91**, 233120 (2007).