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Article

Improved growth rate of anodized TiO₂ nanotube arrays under reduced pressure field and light illuminationShuyao Huo^{a,b,c,1}, Zhen Xu^{a,1}, Min Yin^a, Dongliang Yu^a, Xiaoyuan Chen^a, Hui Wang^{a,*}, Li Tian^a, Dongdong Li^{a,*}^a Shanghai Advanced Research Institute, Chinese Academy of Sciences, Shanghai 201210, China^b University of Chinese Academy of Sciences, Beijing 100039, China^c ShanghaiTech University, Shanghai 201210, China

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ABSTRACT

The one-dimensional titanium oxide (TiO₂) nanotubes (TONT) can be rationally fabricated in the fluoride-containing electrolyte by electrochemical anodization. The high-speed growth of TONT for elongated nanotubes is highly desirable because the undesirable chemical etching will induce “nanograss” on the top of nanotubes and restrain the continued elongation of nanotubes. Herein, the external fields were employed to accelerate the growth of TONTs and obtain the elongated TONT arrays. A growth rate up to 18 μm/h was achieved under the presence of reduced pressure (0.07 MPa) and UV light (365 nm) stimulation. The generation of longer nanotube arrays could be attributed to the applied fields, which facilitate timely gas pumping out and induce chemical equilibrium shift forward. The TONT films obtained under different parameters were subsequently employed as anodes for photoelectrochemical (PEC) water splitting. The photocurrent (at 0 V vs Ag/AgCl) of TONT electrode obtained under external fields represented a 50% enhancement compared with the photoanode produced by the conventional method.

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1. Introduction

Titanium dioxide (TiO₂), has shown great potential of application in various fields, such as solar cells [1,2], photocatalysis [3,4], electrochemical switching [5,6], environmental monitoring and sensing [7–9], energy storage [10,11], due to its abundance, high oxidation efficiency, nontoxicity and stability. The one-dimensional anodic TiO₂ nanotubes (TONTs) provide a large specific surface area and a direct pathway for charge separation and transport [3], thus demonstrate superior capabilities in light harvesting, charge separation and transport. The synthesis of TONT has been extensively studied with a variety of electrolytes [12,13], additives [14,15] under different temperatures [16], applied potential [16] or current [17], etc. In addition, some external fields, such as ultrasonic oscillation [18], light illumination [19], and magnetic field [20] have been imposed on the formation of TONT with tunable geometries [18,19] and even crystalline structure [21].

Longer nanotubes with higher aspect ratio count for a more active area for (photo-) electrochemical applications. However, longer nanotubes generally need extended anodizing time, which often leads to an irreversible transformation from nanotubes to nanograss, due to the intrinsic etching effect of TiO₂ in fluoride-based electrolyte [22,23]. The formation of nanograss at the top end of nanotubes will restrain the infiltration of electrolyte, and in turn depress the charge transport dynamics in TONT based devices [24,25]. Therefore, the rapid growth of TONT is of great importance in getting the long nanotube without the tube tops being etched into nanograss.

The controllable synthesis of TONT largely relies on the understanding of the underlying growth mechanism of TONT. The formation of TONT are generally explained by the field-assisted dissolution model (i.e. an equilibrium between the oxide-growth current and chemical-dissolution at the tubes bottom where the electric field is stronger), or field-assisted plastic flow model (i.e. a constant upward displacement of the oxide to form the NTs). The field-assisted ejection of the Ti⁴⁺ ions (i.e. ions are ejected into the electrolyte without oxide formation) [26,27] was also proposed as referring the growth of anodic aluminum oxide films [28,29]. According to the proposed mechanisms, researchers usually focus on manipulating the reaction parameters at the anode to achieve

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the longer TONT, such as lowering the water content [23] of the anodization solution to reduce dissolution rate and imposing high electric field without the local dielectric breakdown by adding specific additives [14].

It is worth noting that the anodic current includes the ionic current and electron current, where the latter one is responsible for the formation of oxygen gas at the anode [30]. Meanwhile, a side reaction, the hydrogen evolution reaction (HER) with a copious amount of hydrogen released, also exists at the cathode. Considering constant gas evolution during anodization, it is expected that controlling the ambient pressure would affect the growth process of the nanotube and leave the influence on the geometry of the nanotube. It has been reported that the reduced pressure could affect the growth process during the Al foil anodization due to the improved gas removal [30]. It is expected that the similar trend could happen on the Ti anodization process. On the other hand, TiO₂ is the photoactive material, where the conduction band electrons and valence band holes will be generated as the titania surface is illuminated with energy greater than the band gap. The growth process and the surface morphology during the anodization process will be influenced as the electrons and holes participate in the anodization processes.

In this work, we report the synthesis of TONT under various ambient pressures and UV light (365 nm) stimulation during the anodization. It was found that a combination of reduced pressure (0.07 MPa) and UV illumination delivered a growth rate of 18 μm per hour, which outweighs the growth rate under the conventional condition for one-fold. Bamboo like TONT films was also obtained under voltage and pressure pulsed cycles in order to understand the effect of ambient pressure on the faster growth of TONT. Moreover, the elongated TONT shows much enhanced photoelectrochemical performance under simulated air mass (AM) 1.5 G irradiation. The present results may not only help people understand the formation process of TONT, but also would motivate researchers to adapt other fields into the materials synthesis process.

2. Materials and methods

Ti foils (99.7%, 0.2 mm thickness) were chemically polished in a mixed solution consisting of H₂O, HF and nitric acid (HNO₃) in a ratio of 1:1:2 by volume. Then it was rinsed with deionized water and dried in nitrogen. TONT films were synthesized by anodization in ethylene glycol electrolyte containing 0.3 wt% NH₄F and 2 vol% H₂O under ambient pressures of 0.11, 0.1, 0.09, 0.07 to 0.05 MPa at room temperature. All experiments were performed at 60 V for 1 h according to our previous work [31]. Additionally, TONT arrays were also prepared with UV light illumination (5.8 mW/cm² at 365 nm) under pressures of 0.07 and 0.1 MPa. In order to rule out the influence of moisture on the water content while pumping out air, the experiments imposing the pressure pulses during the further anodization process. The as-prepared TONT samples were all crystallized in ambient air at 450 °C for 2 h with a heating rate of 2 °C/min for the following photoelectrochemical (PEC) water splitting characterization.

A depiction of the experimental setup for anodization under different pressure and UV light irradiation is shown in Fig. 1, mainly consisting of a DC power supply, vacuum pump with a vacuum gauge, a sealed glass container on a stirrer controller and a UV light source. Ti sheet (3 mm × 2 mm × 0.2 mm) serves as an anode, a graphite sheet (3 mm × 4 mm × 0.5 mm) as the cathode electrode. The distance between the anode and cathode is maintained at about 40 mm. By controlling the triple valve, variable pressures above the electrolyte can be obtained. When needed to increase pressure, the vacuum pump is replaced by a peristaltic pump to

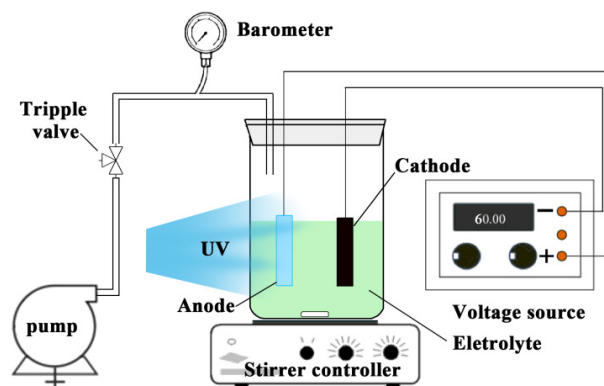


Fig. 1. (Color online) Depiction of the experimental setup used for anodization in the presences of variable pressure and UV light irradiation.

maintain the pressure at 0.11 MPa. UV light irradiation on the Ti substrates during anodization is supplied by a portable UV lamp.

The morphologies of nanotube films were characterized by field-emission scanning electron microscope (FESEM, FEI Quanta 600). The PEC water splitting performances of the TONT films were evaluated by AUTOLAB (PGSTAT302N/FRA2) using a three-electrode configuration with a Ag/AgCl (3 mol/L KCl) electrode as the reference electrode, a platinum foil as the counter electrode and the TONT films (1 × 1 cm²) as the working electrodes. During the measurements, the entire back surface and edges of the working electrodes were coated with insulating epoxy resin with an exposed area of 1 cm². The supporting electrolyte was 1 mol/L potassium hydroxide (KOH, pH = 13.8). The PEC performances were measured under simulated solar irradiation (100 mW/cm²) with a Xe lamp (Newport No. 94063A) coupled with an AM 1.5 G filter.

3. Results and discussion

3.1 Morphology analysis

The ambient pressure dependent TONT morphology evolution is shown in Fig. 2. It can be seen that the nanotube becomes longer from 9.13 to 11.5 and further to 14.1 μm as the pressure above the electrolyte decreases from 0.1 to 0.09 and further to 0.07 MPa. The influence of ambient pressure on the length almost comes to a plateau when the pressure is reduced down to 0.07 MPa as indicated in Fig. 2f. Further decreasing the pressure to 0.05 MPa brings a little enhancement in the length of TONT (14.3 μm as shown in Fig. 2e). While increasing the pressure to 0.11 MPa by pumping air into the system would result in shorter TiO₂ nanotube (about 7.75 μm). The inner/outer diameter variation shows a similar trend as the pressure changes, with the biggest inner/outer diameter at the pressure of 0.07 MPa. In the past reported studies, it has been reported that the pore structure of porous anodic alumina (PAA) during Al foil anodization could be changed by reducing the pressure [30]. In the surface of PAA, it exists an anion-contaminated alumina layer. In the case of the reduced pressure, the rate of oxygen release is great enough to clean up partially the anion-contaminated alumina layer located in the pore wall, resulting in an increase of the pore size. During our anodization of Ti foil, the similar trend of pore size increase was observed under the reduced pressure form 0.11 to 0.07 MPa due to the oxygen removal. However, a little increase of inner/outer diameter was observed as the pressure reduced to 0.05 MPa. The anodized titanium films are more complicated than anodized aluminum. At the bottom of the pits, both chemical dissolution and electrochemical etching take place, making the barrier

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