Electrochimica Acta 78 (2012) 236–243

Contents lists available at SciVerse ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Hydrothermal crystallization and modification of surface hydroxyl groups of anodized TiO_2 nanotube-arrays for more efficient photoenergy conversion

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ARTICLE INFO

Article history:
Received 20 February 2012
Received in revised form 15 April 2012
Accepted 29 May 2012
Available online 18 June 2012

Keywords:
TiO_2 nanotube
Hydrothermal
Crystallization
Dye-sensitized solar cells
Hydroxyl group

ABSTRACT

This paper describes a crystallization method for anodized TiO_2 nanotube-array using a hydrothermal process. Pre-sintered TiO_2 nanotube-array could further crystallize without experiencing a collapse of the nanotubes under the hydrothermal environment. Applying the hydrothermal crystallization method, the transition of surface bonds of nanotube from Ti–O to Ti–OH/Ti–OH_2 can be controlled by acidic hydrothermal pH levels. Dissolution and structural transformation of nanotubes was easily induced if the hydrothermal environment became basic. These effects depicted great influence on the anchoring of carboxylate groups on the surface of TiO_2 nanotubes and affected the performance of the dye-sensitized solar cell utilizing the hydrothermally crystallized TiO_2 nanotubes as the photoelectrode. The photoenergy conversion efficiency increased from 6.40% for thermally annealed nanotubes to 7.13% for hydrothermally crystallized ones under illumination of 100 mW cm^{-2}.

1. Introduction

TiO_2 nanotubes have been widely researched in recent years for many advanced applications in photocatalytic functions, sensing technology, solar cells and photoelectrolysis [1–4]. Various methods have been proposed to prepare the TiO_2 nanotubes including template assisted deposition, the sol–gel process, the hydrothermal method and anodic oxidation [5–8]. Usually, synthetic methods, such as the sol–gel or hydrothermal method, result in randomly oriented nanotubes, while deposition with a template or anodic oxidation can fabricate one dimensionally well aligned nanotube-arrays. For anodic oxidation, the geometrical properties, such as pore diameter and the tube length of the anodized nanotubes can be easily controlled by the electrochemical conditions [9,10]. Because of the advantages of the highly ordered structure, the high surface-to-volume ratio and the ease of fabrication, there has been a lot of research focused on the photovoltaic application of anodized TiO_2 nanotubes [10–15].

However, the as-anodized TiO_2 nanotubes are amorphous. It is obviously necessary to improve the crystallinty of TiO_2 nanotubes and, among the available techniques, thermal annealing is the most commonly used method for nanotube crystallization. After being subjected to 450–500 °C thermal annealing, the nanotubes will be in pure anatase phase, which is favorable in applications of catalytic and photo energy harvesting [4,16,17]. After thermal annealing, nanotubes are in polycrystalline form with a crystallite size of 20–30 nm. To further enhance the crystallinity, Yu et al. have examined the influences on the nature of crystallization of the anodized nanotubes by hydrothermal and vapor thermal methods [18]. They have found that the surface properties and photocatalytic activities of the TiO_2 nanotubes are dependent on the method used for crystallization. Both techniques could substantially increase the TiO_2 crystallite sizes [19–21]. Nevertheless, severe collapse of the nanotubes would be simultaneously induced during the hydrothermal process, thus making hydrothermal methods an inapplicable method for improving the crystallinity of nanotubes.

Herein, we found the hydrothermally induced collapse problem can be prevented by employing a pre-sintering technique. The crystallinity of the hydrothermally crystallized nanotubes was better than those crystallized by thermal annealing. Besides, great influence of the hydrothermal pH level on the resulting surface hydroxyl groups and on the structure of the hydrothermally crystallized nanotubes were identified. Different bonding types on the surface did affect the adsorption of carboxylate groups of bipyridyl dyes on the nanotube and greatly impact the photovoltaic performance of the fabricated solar cells.

2. Experimental

2.1. Preparation of the free-standing nanotube-array

To fabricate TiO_2 nanotube-arrays, anodization of Ti foil (0.25 mm, Alfa Aesar) was carried out at 50 V, 40 °C in solution

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http://dx.doi.org/10.1016/j.electacta.2012.05.157

containing 0.3 wt% NH_4F and 2 vol% H_2O in ethylene glycol with Pt serving as the counter electrode. The bias was provided by a DC power supply, and the temperature of the overall reaction was controlled by a temperature-static tank. Before the anodization, the Ti foil was first cleaned by sonication in de-ionized water and in isopropanol, and a preliminary anodizaiton of the cleaned Ti foil was firstly applied for 30 min at 10 °C. After the first anodization, the firstly anodized TiO_2 layer was removed by sonication in water so that the surface of the Ti foil was textured to enhance the ordering of the TiO_2 nanotubes formed afterward. Then, the TiO_2 nanotube-array was fabricated by anodization for 1–2 h at 40 °C.

After the anodization, the TiO_2 nanotube-array was sintered at 400 °C for 1 h under atmospheric ambient. Next, the pre-sintered sample of TiO_2 nanotubes was set in a 23 ml autoclave, and 10–14 ml solution was filled into the Teflon aligner of the autoclave. The autoclave was heated to 240 °C in an oven using a heating rate of 6 °C min^{-1} for the hydrothermal reaction. After the hydrothermal reaction process proceeded for 2 h, the autoclave was allowed to cool to room temperature naturally. Then, the sample was moved out and the surface of the nanotubes was cleaned using CF_4/CHF_3 plasma to remove disoriented nanotubes. The sample was finally anodized again at 50 V for 30 min to cause detachment of the nanotube-array. Next, the third anodized layer was dissolved in 2 M HCl solution, and the TiO_2 nanotube-array was separated from the Ti substrate to be a free standing membrane.

2.2. Fabrication and measurement of solar cells

The detached nanotube membrane was bonded to fluorine doped tin oxide (FTO, $12\,\Omega\,\square^{-1}$) glass. The sol of titanium isopropoxide in acetic acid mixed with polyethylene glycol was used to bond the closed ends of the TiO_2 nanotubes to the FTO glass. The nanotube-array bonded on FTO was annealed at 400 °C 1 h for sintering of the bonding sol and the removal of residual solution. The peripheral edges of the nanotube region were cleaned by tape to remove additional TiO_2 particles formed by the sol. The nanotube-array was then immersed into 3×10^{-4} M N3 (cis-di(thiocyanato)-bis(2,2′-bipyridyl-4,4′-dicarboxylic acid)-ruthenium(II)) or N719 (bis(tetrabutylammonium)[cis-di(thiocyanato)-bis(2,2′-bipyridul-4-carboxylate-4′-carboxylic acid)-ruthenium(II)]) solution for 12 h. To measure the amount of the dye adsorbed by the nanotubes, the dye was desorbed into 5 mM KOH aqueous solution, and the concentration of the desorbed solution was measured by UV–Visible spectroscopy.

To fabricate the solar cell, the dye loaded nanotube-array was used as one electrode, and Pt sputtered FTO was used as the counter electrode. The two electrodes were spaced by a 60 μm thermoplastic film, and an electrolyte containing 0.05 M I_2, 0.1 M LiI, 0.5 M 4-tert-butylpyridine and 0.6 M 1-propyl-3-methylimidazolium in 3-methoxypropionitrile, was filled into the space. The photovoltaic characteristic of the fabricated cell was measured by an electrical sourcemeter (Keithley 2400) with the cell illuminated by a solar simulator (Oriel 96000) with a global AM 1.5 filter. The illumination power density was modified to be 100 mW cm^{-2} by a power meter (840-C, Newport).

The internal charge recombination rates of the fabricated cells were measured by electrical impedance spectroscopy (EIS) using a potentiostat (EG&G 273A) equipped with a frequency response analyzer. DC bias ranged from 0.5 V to 0.7 V with AC signal of 5 mV amplitude was applied and the recorded frequency range was 10^5 to $10^{-2}\,s^{-1}$.

2.3. Characterizations of nanotubes

The prepared free-standing nanotube-array was bonded onto the glass substrate in order to characterize the crystalline properties by measuring the grazing incidence X-ray diffraction (GIXRD) using a PANalytical X'Pert Pro diffractometer with Cu Kα radiation. In order to analyze the surface bonding modes of the dye molecules on the surface of the hydrothermally treated nanotubes, the nanotube-array was bonded to the intrinsic silicon wafer for measurement of the Fourier transformed infrared spectroscopy (FTIR) using a QS-300 FT-IR spectrometer (BIO-RAD). The measurement of X-ray photoelectron spectroscopy (XPS) was performed using a VG Scientific Microlab 310F system with an Mg Kα source, and the XPS binding energies were calibrated using an additionally deposited Pt pad on the substrate.

2.4. The first-principles calculations of the nanotubes

The first-principles calculations of the anatase nanotubes are performed in the framework of density functional theory (DFT) with the Perdew–Burke–Ernzerhof (PBE) exchange correlation functional and the projector augmented wave (PAW) basis, as implemented in the Vienna Ab-initio Simulation Package (VASP). The plane-wave energy cutoff is taken to be 400 eV. The anatase nanotubes follow the same crystal geometries proposed by Bandura and Evarestov [22]. One first takes an infinitely long belt of a single anatase sheet with its length and width in the (1 0 1) and (0 1 0) directions, respectively, and then the sheet is rolled along (0 1 0) to form a tube. This tube structure is then relaxed by DFT calculations.

3. Results and discussion

3.1. Effects of pre-sintering temperature and hydrothermal solution volume

To sustain the high pressure environment in the hydrothermal process, the as-anodized TiO_2 nanotubes have to be pre-sintered. First, we tested different pre-sintering temperature followed by a hydrothermal treatment at 240 °C in water. With pre-sintering temperature below 350 °C, most of the TiO_2 nanotubes were destroyed during the hydrothermal process. This caused a 70% shortening of tube length, and an additional nanoparticle-like structure was formed on the sidewall of remaining nanotubes. The collapse of the anodized nanotubes after hydrothermal treatment was found to be avoidable when the pre-sintering temperature was raised to 400 °C. The pre-sintered nanotubes were observed to maintain their tubular structure even after the hydrothermal process reached a temperature of 240 °C, which was higher than the reported hydrothermally induced collapse temperature of 180 °C [18].

Fig. 1 shows the XRD results of the pre-sintered nanotubes before and after the hydrothermal process of various conditions. A pure anatase phase was identified for the nanotubes after pre-sintering and hydrothermal treatment. Fig. 1a depicts the comparison of XRD of nanotubes of different pre-sintering temperature followed by the same hydrothermal condition in 10 ml water. The enhancement of crystallinity properties was clearly observed when comparing the (1 0 1) X-ray diffraction intensities of the 400 °C pre-sintered nanotubes before and after the hydrothermal process. Even lowering the pre-sintering temperature to 350 °C, followed by a hydrothermal treatment, demonstrates nanotubes with higher crystallinity properties than the 400 °C sintered sample. When the pre-sintering temperature was over 450 °C, later hydrothermal treatment in 10 ml water seemed insufficient to induce further crystallization of the nanotubes. On the other hand, Fig. 1b shows a comparison of XRD peaks of nanotubes that were pre-sintered at the same 400 °C with varying amounts of water used in the hydrothermal process. The data show a strong dependence of the