



Self-ordered Nanotubular TiO₂ Multilayers for High-Performance Photocatalysts and Supercapacitors



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ARTICLE INFO

Article history:

Received 17 February 2016

Received in revised form 22 March 2016

Accepted 9 April 2016

Available online 12 April 2016

Keywords:

Titania nanotubes
photocatalysts
supercapacitors
multilayers
anodization

ABSTRACT

Arrays of multilayered TiO₂ nanotubes are successfully fabricated by anodizing commercial Ti foils with multi-pulsed voltage waveforms. The fabricated structures feature an interesting multilayered morphology with each layer consisting of self-ordered TiO₂ nanotubes (diameter of tens of nanometers and length of several hundred nanometers) aligned vertically to the Ti substrate, and the possible growth mechanism is proposed. The novel multilayered TiO₂ nanotubes exhibit significantly enhanced photocatalytic efficiency than the conventional TiO₂ nanotubes and the multilayered nanoporous TiO₂ structures previously reported by our group. Moreover, the multilayered TiO₂ nanotubes are for the first time investigated for supercapacitor applications, enabling superior capacitance and good cycling stability: the specific capacitance of the C-modified multilayered TiO₂ nanotubes is ~60 times higher than the pristine multilayered TiO₂ nanotubes, and ~1.6 times of the C-modified single-layered TiO₂ nanotubes.

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1. Introduction

Since the first report on the light-induced water splitting on TiO₂ surfaces by Fujishima and Honda in 1972 [1], TiO₂ has been extensively studied as an important photocatalyst owing to its long-term stability, low-cost fabrication, and strong photocatalytic ability [2–5]. Among the numerous synthetic strategies, anodization, based on a simple electrochemical oxidizing treatment of Ti metals, represents a most elegant and convenient approach to grow highly oriented TiO₂ nanotubes with different tube morphologies (e.g., different tube diameters or packing density) [5–9]. Anodic TiO₂ nanostructures have attracted much interest for wide-ranging applications, such as water photo-splitting devices [10–12], pollutant cleansers [4,13], lithium ion batteries [14,15],

biomedical devices [16,17], solar cells [18–22] and supercapacitors [23–26].

Different anodization techniques have been explored to fabricate TiO₂ nanostructures with various morphologies for improved device performance. For example, Schmuki and coworkers [27] fabricated bamboo-typed TiO₂ nanotubes that feature well-aligned vertical nanotubes running through the horizontal TiO₂ thin layers. The fabricated bamboo-typed TiO₂ was demonstrated an attractive electrode material for dye-sensitized solar cells, owing to the much increased dye-loading around the bamboo rings [28]. Furthermore, anodic TiO₂ with structural periodicity has been fabricated with good successful results [29]. Most of the anodic TiO₂ with structural periodicity reported to date take the form of self-ordered nanotubes with evenly spaced notches along the tubes. Recently, our group reported a facile “multi-pulse” anodization method to fabricate an exotic type of nanoporous TiO₂ multilayer by anodizing commercial Ti metals with high imperfection levels. The films thus obtained feature tens of well-defined porous layers with long-range structural periodicities and vivid film colors [30]. Furthermore, these films have a higher capability to uptake H⁺ ions than the conventional

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self-ordered TiO₂ nanotubes; therefore, are better suited for the electrochromic applications. In spite of these advances, there is generally a lack of investigation in applying the anodic TiO₂ with structural periodicity in applications such as supercapacitor electrodes and photocatalysts.

From literature, the specific capacitance of TiO₂ nanotube arrays was ~100–911 $\mu\text{F cm}^{-2}$ [31–34]. Their relatively low capacitance was ascribed to the low electrochemical activity and poor electrical conductivity of TiO₂ [35,36]. Doping with various foreign non-metal elements (e.g., carbon or nitrogen) is found to be an effective and promising solution to address these limitations [5,11,37–39]. For example, R. Hahn et al. reported the anodic TiO₂ nanotubes heated in acetylene at high temperatures (e.g., 850 °C) exhibited higher electrical conductivity and significantly enhanced catalytic activity for methanol oxidation by 700% [40]. According to our previous study [41], greatly enhanced capacitance (~33 fold higher) with good cycling stability can be achieved on the C-modified TiO₂ nanotubes by a facile thermal treatment at lower temperatures (e.g., 300–600 °C).

Herein, we utilized the “multi-pulse” anodization method to fabricate novel multilayered TiO₂ nanotube arrays. These arrays feature multiple layers with each layer comprised of a self-ordered nanotube array that is several hundreds of nanometers (~500 nm) thick. The possible growth mechanism is proposed based on the current-time characteristics. The novel multilayered TiO₂ nanotube array displays significantly higher photocatalytic efficiency than the previously reported nanoporous multilayered TiO₂ structures and the conventional self-ordered TiO₂ nanotubes, mainly due to its high surface area and clean top surface. Moreover, the electrochemical performance as supercapacitors is here reported for the first time on these multilayered TiO₂ arrays. Furthermore, a very thin layer of amorphous carbon coating on multilayered TiO₂ is found to greatly enhance its specific capacitance by ~60 times.

2. Experimental

2.1. Preparation of Anodic TiO₂

The titanium foils (99.6% purity, 0.20 mm thick, shining surface finish, Baoji Yirun Co., Ltd) were ultrasonically cleaned in acetone, ethanol and deionized water successively, and then dried in a nitrogen stream before anodization. Anodic TiO₂ films were generated in a two-electrode electrochemical cell, with Pt gauze as the counter electrode and a Ti foil as the working anode. The Ti working anode was pressed together with an Al foil against an O-ring, defining a working area of 1.2 cm². An ethylene glycol (99%+, Sigma-Aldrich) solution of 0.27 wt% NH₄F (98%+, Sigma-Aldrich) was used as the electrolyte. A computer controlled Keithley 2400 Sourcemeter was used to apply the anodization voltage and record the anodization current simultaneously.

Multi-pulsed voltage waveforms with four voltage steps per period (successively at voltages 60 V, –4 V, 40 V, and –4 V for t_1 , 20 s, t_2 , and 20 s, respectively) were used to generate TiO₂ multilayers (denoted as Sample ML). Typically, $t_1 = 1.5$ min; $t_2 = 10$ min. For comparison, single-layered TiO₂ nanotubes (denoted as Sample SL) were fabricated using single-pulsed voltage waveforms with each period consisting of two voltage steps (at 60 V for 3 min and then at –4 V for 75 sec, 20 periods). Another structure for comparison is the exotic type of nanoporous multilayers previously reported by us, fabricated by similar multi-pulsed voltage waveform but with $t_1 = 5$ min and $t_2 = 3$ min. All the anodization experiments were performed at room temperature. After anodization, the sample was washed with ethanol and then dried in a nitrogen stream. To obtain the anatase TiO₂ nanotubes, the as-anodized samples were thermally treated at 450 °C in air for 3 hrs.

2.2. Thermal carbon modification

For carbon modification, the as-annealed anatase TiO₂ nanotubes were put in a 1.5 kW ASTeX microwave plasma chemical vapor deposition (MWCVD) system, and heated to 600 °C (temperature measured by a thermal couple in contact with the substrate holder). Hydrogen plasma was then generated at a microwave power of 400 W for 10 min under a total pressure of 30 Torr with the hydrogen and methane flow rate of 270 sccm and 30 sccm, respectively. After that, the sample was cooled down naturally to room temperature. The carbon modification was performed on both single-layered TiO₂ nanotubes and multilayered nanotubes (denoted as Samples SL/C and ML/C, respectively).

2.3. Characterization

Sample morphologies were characterized using a Philips XL30 field-emission scanning electron microscopy (SEM) and a transmission electron microscope (TEM) (JEOL-2100F). X-ray diffraction patterns were collected on a Bruker diffractometer with D2 Phaser using Cu K α radiation ($\lambda = 1.5405 \text{ \AA}$). Surface chemical analysis was carried out using an X-ray photoelectron spectrometer (XPS) (VG ESCALAB 220i-XL). Raman spectroscopy (Renishaw 2000, Raman microscope with 633 nm argon ion laser) was employed to verify chemical bonding characteristics.

2.4. Photocatalytic Degradation Test

All the anodic TiO₂ films used in the photocatalytic study were heated beforehand in air at 450 °C for 3 hrs. The efficiency of the fabricated anodic TiO₂ films to degrade methyl red (MR) was measured and used as an indicator of the photocatalytic ability of these TiO₂ films. The fabricated anodic TiO₂ film was immersed in an aqueous solution of MR (2.5 ml, 2.6×10^{-5} M). The working area of the anodic TiO₂ film was fixed to be 0.6 cm \times 0.7 cm. A high-pressure mercury lamp with maximum output wavelength at 365 nm was used as the illumination source. The illumination intensity was 20 mW/cm², measured using a UVX digital radiometer at the sample surface. The concentration of MR was monitored as a function of reaction time using a UV-vis spectrometer (Lambda 2S). The concentration of MR was calculated from the absorption maxima located at 526 nm.

2.5. Electrochemical measurements

Electrochemical measurements were performed at room temperature on a potentiostat (PAR Verstat 3) using a three-electrode configuration including a saturated calomel reference electrode (SCE), a platinum sheet (2 cm \times 3 cm) as the counter electrode, and the sample as the working electrode. The electrolyte used was an aqueous solution of 0.5 M Na₂SO₄. The cyclic voltammetry curves were measured between 0 (vs. SCE) and 0.8 V (vs. SCE) with a scan rate of 100 mV/s. The charge/discharge profiles were measured at a current density of 50, 100, 150, and 200 $\mu\text{A/cm}^2$. Cycling stability was tested with a charge/discharge current density of 100 $\mu\text{A/cm}^2$ for 1000 cycles. Electrochemical impedance spectroscopy (EIS) measurements were carried out on an electrochemical work station (IM6) with a two-electrode system in a frequency range of 1 Hz to 100 kHz.

3. Results and Discussion

3.1. Morphology and Current Study

The multi-pulsed voltage waveforms with four voltage steps per period were used to anodize Ti foils, following our previous

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