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Photoelectrochemical and structural properties of TiO_2 nanotubes and nanorods grown on FTO substrate: Comparative study between electrochemical anodization and hydrothermal method used for the nanostructures fabrication

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ABSTRACT

Titanium dioxide in the form of one-dimensional (1D) nanostructure arrays represent widely studied morphological arrangement for light harvesting and charge transfer applications such as photocatalysis and photoelectrochemistry (PEC). Here we report a comparative structural and PEC study of variously grown 1D TiO_2 nanostructures including i) nanorod arrays prepared by a hydrothermal method (TNR), ii) nanotube arrays fabricated by a two-step hydrothermal method using a ZnO nanorod array film as a template (THNT) and finally iii) nanotubes grown by self-organized electrochemical anodization of Ti films deposited on the FTO substrate (TNT). These nanostructures are assumed to be utilized as photoanodes in PEC water splitting devices. Field-emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), TEM images and UV–vis absorption spectra were used to characterize TiO_2 nanostructures. The SEM and TEM morphology images revealed that the main difference among the nanostructures grown on the FTO are the shape and diameter of the individual nanotubes/nanorods and also the array's density in the range of TNR > THNT > TNT and the degree of organization in the range of TNT > TNR > THNT. The obtained photocurrents at 0 V vs. Ag/AgCl increased in the order of THNT (110 $\mu A\,cm^{-2}$) < TNT (185 $\mu A\,cm^{-2}$) < TNR (630 $\mu A\,cm^{-2}$). Extended electron lifetime and light absorption shifted to the longer wavelengths were attributed to the enhanced PEC performance of TNR.

1. Introduction

Titanium dioxide (TiO_2) has been dominantly used as a core material in several modern solar energy conversion approaches involving predominantly dye sensitized solar cells (DSSC) [1,2], more recently perovskite solar cells [3,4], and photoelectrochemical water splitting (PEC-WS) [5,6]. The latest represents one of the most widely investigated approach for a sustainable and environmentally friendly production of hydrogen, considered the most significant renewable energy source of the future [7]. TiO_2 has been widely studied as the photoanode material for PEC-WS since the pioneering work by Fujishima and Honda [8] due to its highly beneficial properties such as nontoxicity, high chemical stability, resistance to photocorrosion, abundance, and low production cost [9]. However, conventional TiO_2 film photoanodes provide an insufficient surface area and electron collection efficiency, which are crucial parameters for an optimized PEC performance. Nanostructuring of photocatalysts and photoelectrodes has been recognized as a powerful strategy to dramatically improve overall solar-to-fuel conversion efficiencies [10]. In view of geometry recently 1D TiO_2 nanostructures, such as nanotubes (NTs) [11–14], nanorods (NRs) [15–17], nanowires (NWs) [18–21], etc. attracted wide interest because they provide a significant enlargement of the material surface area (simultaneously increase the number of catalytically

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active sites and improves the light harvesting), facilitate the electrical transport, and suppress the negative effect of short diffusion length of holes and the recombination losses. Furthermore 1D nanostructures features a number of other characteristics (e.g., size confinement, atomically curved surface, extended surface-to-volume ratio, preferential percolation pathway for enhanced charge separation/transport/collection) that are highly beneficial for aforementioned photo-electrocatalytic applications. As a direct consequence, the nanoscale effects give rise to 50%-90% PEC efficiency gain [6]. The efficiency of TiO_2 photoanodes has been even more enhanced by adding impurities to improve their electronic properties [22–24] as well as by a combination with heterogeneous partners [25,26], quantum dots [27–29], and plasmonic materials [19,30] to optically sensitize the large-band gap TiO_2. However, a research study directly comparing the performance of various unmodified 1D TiO_2 nanostructure for PECs water splitting is still missing although the high activity of pristine TiO_2 photoelectrode is the essential prerequisite for a high-performance of whole PEC-WS device. Here, we present a systematic comparing study of directly grown 1D TiO_2 nanostructures based on nanotube and nanorod arrays using two principally different fabrication methods; namely electrochemical anodization and hydrothermal procedure. Self-organizing electrochemical anodization of a metal substrate (here Ti film deposited onto FTO substrate), is often referred to as the simplest, low-cost and straightforward approach leading 1D highly-ordered NTs [31]. Under a specific set of experimental conditions (e.g., applied voltage, anodization time, electrolytic solution), nanotubular properties, such as the degree of self-organization, tube length and diameter, electronic and ionic properties can be easily controlled [32]. Similarly in case of more commonly applied hydrothermal approach the properties of 1D nanostructures (e.g. crystalline structure, morphology, length, density, and array ordering) grown can be influenced and controlled by the synthetic conditions such as concentration of the precursor solution, hydrothermal growth temperature, and reaction times [33–35]. This work refers on three different approaches to grow 1D nanostructured TiO_2 photoanodes including electrochemically anodized nanotubes and hydrothermally grown nanorods as well as nanotubes. The three nanostructured TiO_2 photoanodes were judged on the basis of physical properties such as crystalline structure, optical absorption, and surface topography. The functional properties were investigated under simulated photoelectrochemical (PEC) water splitting conditions.

2. Experimental

2.1. Preparation of 1D nanostructured TiO_2 photoanode

Chemicals: Titanium *n*-butoxide (Sigma-Aldrich, 97%) and hydrochloric acid (HCl, 37%) were used for photocatalyst preparation. Sodium hydroxide (NaOH) was used as an electrolyte. All solutions were prepared using distilled water. All the three types of TiO_2 1D nanostructures were grown on fluorine doped tin oxide glass substrate (FTO, TCO22-7, surface resistivity: 7 Ω/sq Solaronix). Prior to the depositions the FTO substrates were ultrasonically cleaned using a mixture of acetone, isopropyl alcohol and distilled water in volume ratio of 1:1:1, respectively. After the sonication the FTO substrates were washed by DI water and dried by nitrogen flow.

2.1.1. Preparation of TiO_2 nanorod arrays by hydrothermal method (TNR)

TiO_2 nanorod arrays were prepared by hydrothermal method described by Liu et al. [36] In typical experiment, 15 mL of hydrochloric acid and 15 mL of distilled water was mixed for five minutes. Then, 0.5 mL of titanium *n*-butoxide was added dropwise under vigorous stirring for another five minutes. Then, the as prepared clear solution and FTO substrate were placed into Teflon-liner stainless steel autoclave (50 mL) while the conductive side of FTO substrate was facing down. The hydrothermal reaction was conducted at 150 °C for 20 h. Then, the autoclave was cooled down under flowing water. The FTO substrate was rinsed with distilled water and air dried. Afterwards, the as prepared TiO_2 nanorods were annealed in air at 500 °C for 1 h with heating rate of 5 °C/min.

2.1.2. Preparation of TiO_2 nanotube arrays by hydrothermal method (THNT)

A thin ZnO seed layer was prepared on FTO glass by spin coating method with 0.02 M zinc acetate dihydrate solution at 4000 rpm for 35 s. Arrays of ZnO nanorods, which serve as sacrificial templates for the nanotubes, were grown on the seed layer by hydrothermal method at 85 °C for 10 h. 0.025 M zinc nitrate hexahydrate and 0.025 M hexamethylentetramine were used as precursor chemicals. The synthesized ZnO nanorod arrays on the FTO were immersed in aqueous solution containing 0.075 M ammonium hexafluorotitanate and 0.2 M boric acid at room temperature for 0.5 h. In this solution, ammonium hexafluorotitanate hydrolyzed to TiO_2 on the individual ZnO nanorod while ZnO dissolved simultaneously in the solution with acids produced by ammonium hexafluorotitanate hydrolysis. Subsequently, the resulting TiO_2 nanotube arrays were immersed in a 0.5 M boric acid solution for 1 h to remove the residual ZnO inside the tubes. The arrays were finally rinsed with DI water and calcined at 500 °C for 1 h to increase crystallinity.

2.1.3. Preparation of anodized TiO_2 nanotube arrays (TNT)

Self-organized highly ordered TiO_2 nanotubes were grown by electrochemical anodization of titanium films deposited directly on FTO substrate by pulsed magnetron sputtering of pure titanium target (99.995%, Lesker). The depositions were carried out under a constant operating pressure of 0.2 Pa. The duty cycle of the pulse was 90%, the frequency was 50 kHz, and the deposition rate was 30.0 nm/min. Prior to the deposition an advanced plasma cleaning and activation of FTO substrate was performed in order to attain sufficient adhesion of the titanium film to the substrate. For this purpose the substrate holder the FTO glass substrate were treated by radio-frequency (RF) plasma using O_2/Ar working gas mixture with the pressure 10 Pa in the reactor chamber. The substrate holder worked as a RF electrode connected to the RF power supply working at frequency 13.6 MHz. The deposition process followed immediately after RF plasma treatment without interruption of vacuum in the reactor chamber. In the following procedure the magnetron sputtered titanium films on FTO glass were washed with ethanol before electrochemical anodization. TiO_2 nanotubes were grown at 50 V using a power source STATRON 3253.3 under self-organization conditions using a two-electrode configuration with the Ti films acting as the working electrode and a counter electrode made of platinum. As the electrolyte the solution of 0.2 M NH_4F + 4 M H_2O in ethylene glycol was used. The as deposited TiO_2 nanotube photoanodes were heat treated at 500 °C for 1 h in air (cylindrical furnace-Clasic CLARE 4.0) to ensure proper crystallization.

2.2. Physical characterization

X-ray diffraction was performed at two instruments-Rigaku SmartLab difractometer and Siefert XRD7 diffractometer. The Rigaku SmartLab diffractometer is equipped with 9 kW rotation X-ray tube. The Johansson monochromator was used in primary beam in order to obtain only CuKα1 radiation. Soller slit 2.5°, 5 mm incident slit and 5 mm beam mask were placed in primary beam. Soller slits of 2.5°, 20 mm receiving slits and lin-

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