Synthesis and Characterization of Anodized Titanium Oxide Nanotubes Arrays


*Chemical Engineering Department, Prairie View A & M University, P.O. Box 519 MS 2505, Prairie View, TX 77446. USA, jgabitto@aol.com
** Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

ABSTRACT

Anodized titanium oxide containing highly ordered, vertically oriented TiO_2 nanotube arrays is a nanomaterial architecture that shows promise for diverse applications. In this paper, an anodization synthesis using HF-free aqueous solutions is described. The anodized TiO_2 film samples (amorphous, anatase, and rutile) on titanium foils were characterized using scanning electron microscopy, X-ray diffraction, and Raman spectroscopy. Additional testing was performed using an electrochemical cell to study the photoelectrochemical splitting of water. Results were analyzed in terms of the efficiency of current generated, defined as the ratio of the difference between the electrical energy output and the electrical energy input divided by the input radiation energy. It was determined that the anatase crystalline structure is a better photocatalytic material for hydrogen production via photoelectrochemical splitting of water.

Keywords: TiO_2, anodization, nanostructures, anatase, water splitting.

1 INTRODUCTION

Anodized titanium oxide (ATO) containing highly ordered, vertically oriented TiO_2 nanotube arrays has been considered as an important nanomaterial platform for various applications, including solar cells, sensors, catalysts, and devices for the generation of hydrogen by water photoelectrolysis [1]. The nanoporous nature of ATO offers a large internal surface area without concomitant decrease in geometrical and structural order. The orientation of crystalline nanotube arrays provides excellent electron percolation pathways for vectoral charge transfer between interfaces.

Hydrogen has been produced from water using sunlight as the energy source, but efficiencies are small. A target hydrogen production efficiency of 10% is required for water-splitting technology to be commercially viable [2]. This goal is based on current fuel and infrastructure costs and is likely to change depending on future economic and political conditions. The pioneering work of Fujishima and Honda [3] showed that water splitting was possible by illuminating a TiO_2 electrode in an electrochemical cell with sunlight. Titanium dioxide is a popular photocatalyst as it is less toxic, stable, and inexpensive. The anatase and rutile phases of TiO_2 have a bandgap of 3.2 and 3.0 eV, respectively. Since only 2.7% of the solar photon flux has energy greater than 3.0 eV, the light-harvesting ability of TiO_2 is very limited.

The principal impetus toward fabricating nanodimensional materials lies in the promise of achieving unique properties and superior performance due to their inherent nano-architectures. Titanium dioxide nanotubes fabricated by anodization are highly ordered, high-aspect-ratio structures with nanocrystalline walls oriented perpendicular to the substrate. The nanotubes have a well-defined and controllable pore size, wall thickness, and tube length. TiO_2 exists in three different crystalline structures: anatase, rutile, and brookite. The anatase structure has attracted much attention over the last few decades for its technological applications. Titanium dioxide in the anatase phase exhibits a high photocatalytic activity, which is promising for many applications.

Highly ordered nanotube arrays, in place of porous or nonporous structures, are formed at relatively low potentials (e.g., 10 V) as a result of the competition between the electrochemical etching and the chemical dissolution [4]. These arrays were reported to be obtained only in either fluoride-containing acids [5] or in a mixture of fluoride-containing acids and other acids [4]. Since the high rate of chemical dissolution of the oxide in electrolytes containing hydrofluoric acid - is the factor directly limiting the nanotube length, our efforts have focused on controlling the dissolution rate by adjusting the pH of the electrolyte through additives and by using different fluoride-containing salts, such as KF and NaF instead of HF.

In this paper, films that contain TiO_2 nanotube arrays on titanium foils were synthesized by anodization in HF-free solutions; anatase and rutile phases were obtained by annealing under controlled temperatures. Analyses by scanning electron microscopy (SEM), X-ray diffraction (XRD), and Raman spectroscopy were conducted on the various synthesized and annealed ATO samples. Then studies on photoelectrochemical water splitting were carried out with various phases of anodized TiO_2 for potential application in photocatalytic hydrogen production.
2 EXPERIMENTAL

2.1 Preparation of TiO$_2$ Nanotube Arrays

The synthesis parameters that affect the anodization include applied voltage, initial current, voltage sweep rate (i.e., the rate to increase voltage from zero to the target voltage), and the concentration of $F^-$, the temperature, and the anodization time. A typical anodization procedure involves the following steps: (1) the Ti foil and Pt plate are ultrasonically cleaned with acetone, isopropanol, ethanol, and deionized water; (2) after the Ti foil and Pt plate are dried, they are clipped onto the electrodes of a power supply and positioned in parallel with an interspacing of $\sim 2$ cm; (3) a Teflon container is filled with 50 mL of electrolyte solution, and the parallel Ti foil and Pt plate are submerged in the solution without stirring; (4) target anodization potential and initial current are set to 20 V and 0.020 A, respectively; (5) the power supply is turned on, and the anodization is carried out at room temperature ($\sim 22^\circ$C); (6) anodization continues for 6 h, usually, (during anodization, the Ti foil surface turns colorful and dark with time); (7) at the end of the anodization process, the Ti foil surface is rinsed several times with deionized water; and (8) the unwanted surface deposits or leftover particles are removed by ultrasonication in deionized water for about 1 min, and then the samples are dried in air. For SEM imaging, a small slice of the ATO foil was cut off and glued onto the SEM sample holder with conductive carbon paste.

2.2 Electrochemical Measurements

The water-splitting efficiency of a photocatalytic electrode can be experimentally measured using a three-electrode electrochemical cell. This electrochemical cell consists of a working electrode, a platinum counter electrode, and a reference electrode. The electrodes are immersed in an electrolyte solution (1 M Na$_2$ SO$_4$) contained in a cell fitted with a quartz window. An Ag/AgCl reference electrode in saturated KCl (Metrohm AG) was employed for electrochemical measurements in this work. According to the manufacturer’s calibration, this reference electrode has a potential of $+197$ mV vs. a normal hydrogen electrode (NHE) at 25 $^\circ$C. Three square film samples composed of amorphous, anatase, and rutile phases, were used as the anode electrode in these photoelectrochemical studies. Square shaped film samples, $1”$ by $1”$ in size with active area approximately 4 cm$^2$ were used in all the measurements. Photoelectrochemical measurements were obtained for both dark and under illumination conditions. UV sunlight was simulated by using an Oriel 6271 mercury lamp. A nominal characterization of the light intensity can be done by setting the voltage and intensity of the lamp to constant values. The power density of the incident light ($I_o$) corresponding to given nominal values was determined using a light meter placed inside the electrochemical cell at the anode position without the electrolyte.

The system showed evidence of hysteresis. Therefore, it was important to obtain two sets of measurements: one in the direction of increasing applied potential (anodic scan) and another in the direction of decreasing applied potential (cathodic scan). In these experiments, it was easier to reach steady-state conditions using decreasing scans rather than increasing scans. The two sets of data showed significant differences sometimes. Steady-state data normally agree regardless of the scan direction. However, it took more time to reach steady state in the case of continuously increasing potential than in the case of continuously decreasing potential. A good discussion about such observations can be found in Torres et al. [6].

The efficiency, $\eta$, of the water-splitting reaction was determined using the equations proposed by Khan et al. [7]. The photoconversion efficiency ($\eta$) of light energy to chemical energy in the presence of an externally applied potential ($E_{app}$) can be expressed as,

$\eta = \{ \text{total power output} \ - \ \text{electrical power input} \} / \text{light power input}$

(1), or

$\eta = \{ J_p [1.23 \ \text{V} - E_{app}] \} / I_o \}$

(2).

Where $J_p$ is the photocurrent density, defined as the measured current density under illumination minus the dark current at the same applied voltage; 1.23 V is the potential corresponding to the Gibbs free energy change per electron for water-splitting reaction; $E_{app} = E_{mea} - E_{aoc}$. $E_{mea}$ is the working electrode potential relative to the reference electrode under illumination; $E_{aoc}$ is the electrode potential at open circuit condition in the same electrolyte solution and under the same illumination of light at which was measured; and $I_o$ is the flux of incoming radiation experimentally measured [7].

3 RESULTS AND DISCUSSIONS

3.1 Experimental Analysis results

The surface morphology of the nanostructures was studied using Scanning Electron Microscopy technique (SEM). SEM results are shown in figure 1. The anodized TiO$_2$ film shows good arrays of nanotubes ($80 \ \text{nm}$ in diameter and $\sim 0.5 \ \mu \text{m}$ in thickness, figures 1a, and 1b). After annealing at 500$^\circ$C in flowing of Ar gas at 1 atm for 30 min, the morphology of the nanotubes was still maintained. However, after annealing at 800$^\circ$C in Ar for 30 min, the nanotube array structure had been transformed into crystalline pores with random orientation.

Nucleation and growth was studied using in situ high-temperature XRD (HTXRD). The structure of the anodized film of TiO$_2$ nanotube arrays is amorphous. Post-annealing of the amorphous films at different temperatures
under controlled atmospheres produced crystalline phases of anatase and rutile. The nucleation of anatase TiO$_2$ starts at 400°C and remains the same up to 700°C, when the rutile phase starts to nucleate in the presence of the anatase phase. With an increase in the temperature, the rutile phase becomes dominant over the anatase phase. When the TiO$_2$ sample was heat-treated directly at 500°C, the nucleation of the anatase phase was instantaneous, and the intensity saturation occurred within five min. With an increase in the heat treatment time, the anatase phase remained stable without the formation of any other secondary phases.

### 3.2 Electrochemical Results

The variation of measured current with increasing applied voltages for different films under UV illumination is shown in Figure 2. The photocurrent density values determined with anode illumination (photocurrent) showed only a slight increase with respect to the values measured without illumination (dark current) for the amorphous material. The photocurrent values increased as the applied potential increased for all the materials. Anatase films showed the highest current increase at all applied voltages, followed by the rutile films, the amorphous films showed only a small increase.

Figure 3 shows the efficiency calculated using Eq. (2) for anatase films under different light intensities. The efficiency curves show a maximum for all the light intensity values. The value of the efficiency increases as the incident photon energy increases. The maximum values determined for the anatase phase were approximately 5.9%. In the case of rutile, the maximum efficiency value was determined to be 3.8%.
The efficiency values shown in figure 3 are below the values reported in literature by Khan et al. [7]. In this work light scattering through the walls of the electrochemical cell could provoke a smaller ‘effective’ light intensity on the electrode.

4 CONCLUSIONS

Titanium oxide nanotube arrays in the form of films on the surface of titanium have been synthesized by anodization of titanium metal foil in HF-free aqueous solutions. An as-prepared ATO film is amorphous; however, it becomes anatase with maintained nanotube array morphology after being annealed at 500°C in an argon atmosphere. At 800°C, a pure rutile crystalline phase can be obtained, but with the loss of nanotube array morphology. Application of UV light produced a significant increase in the measured photocurrent values for both the anatase and the rutile films. Anatase films showed the highest increase in photocurrent generation. These films also showed the highest efficiency of all the tested materials, about 5.9%. Rutile films showed a maximum value of 3.8%. These results demonstrate that one can use light to generate photocurrent and produce hydrogen by water splitting.

ACKNOWLEDGEMENTS

This work was supported by the Department of Energy, Office of Basic Energy Sciences, Department of Materials Science and Engineering Program and by the Laboratory Directed Research and Development (LDRD) program of ORNL. ORNL is managed by UT-Battelle, LLC, for the U.S. Department of Energy, under contract No. DE-AC05-00OR22725. NSF-DOE support for J. F. Gabitto under the Faculty-Students Teams program (FAST) is kindly acknowledged.

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