

A review on the Fabrication and material properties of TiO₂ nanotube arrays by anodization

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ABSTRACT

We review the fabrication and properties of TiO₂ nanotube arrays made by anodic oxidation of titanium in fluoride-based electrolytes. The material architecture has proven to be of great interest for use in water photoelectrolysis and photocatalysis.. We examine the ability to fabricate nanotube arrays of different shape (cylindrical, tapered), pore size, length, and wall thickness by varying anodization parameters including electrolyte concentration, pH, voltage, and bath temperature, with fabrication and crystallization variables discussed in reference to a nanotube array growth model. We review efforts to lower the band gap of the titania nanotubes by anionic doping. The article concludes by examining various practical applications of the remarkable material architecture, including its use for water photoelectrolysis.

Keywords: Nanotube array, TiO₂, Titania, Photoelectrolysis, Water photolysis

INTRODUCTION

Nanotubes are of great interest due to their high surface-to-volume ratios and sizedependent properties. The discovery of carbon nanotubes with their variety of interesting properties have stimulated the quest for the synthesis of nanotubular structures of other substances and chemical compounds[1].

Several recent studies have indicated that titania nanotubes have improved properties compared to any other form of titania for application in photocatalysis [2,3], sensing [4], photoelectrolysis [5], and photovoltaics [6]. Titania nanotubes, and nanotube arrays, have been produced by a variety of methods including deposition into a nanoporous alumina template [7], sol-gel transcription using organo-gelators as

templates [8,9], seeded growth [10], and hydrothermal processes [11]. However, of these nanotube fabrication routes, the architecture demonstrating by far the most remarkable properties are highly ordered nanotube arrays made by anodization of titanium in fluoride-based baths [12,13] the dimensions of which can be precisely controlled. Uniform titania nanotube arrays of various pore sizes (22–110 nm), lengths (200–6000 nm), and wall thicknesses (7–34 nm) are easily grown by tailoring electrochemical conditions. A variety of reports in the literature give evidence of the unique properties this material architecture possesses, making it of considerable scientific interest as well as practical importance[14].

In 1991, Zwilling and co-workers [15] reported the porous surface of titania films electrochemically formed in fluorinated electrolyte by titanium anodization. A decade later Grimes and co-workers [12] first reported formation of uniform titania nanotube arrays via anodic oxidation of titanium in an hydrofluoric (HF) electrolyte. Varying pH and electrolyte concentration, this same research group achieved a 6.4 mm long nanotube array using a fluoride solution of pH 5.5 [16]. Recently, Schmuki and co-workers [17,18] also reported the formation of long nanotubes

during anodization of titanium in neutral fluoride solutions.

FABRICATION OF TITANIA NANOTUBE ARRAYS BY ANODIZATION

Fabrication of titania nanotube arrays via anodic oxidation of titanium foil in a fluoride-based solution were first reported in 2001 by Grimes and co-workers [12]. Further studies focused on precise control and extension of the nanotube morphology [19], length and pore size [16], and wall thickness[20]. Electrolyte composition plays a critical, and as of yet essentially unexplored role in determining the resultant nanotube array nano architecture and potentially, its chemical composition.

Electrolyte composition and its pH, determines both the rate of nanotube array formation, as well as the rate at which the resultant oxide is dissolved. In all cases, a fluoride ion containing electrolyte is needed for nanotube array formation. In an effort to shift the band gap of the titania nanotube arrays so that they more fully respond to full spectrum light various doping strategies have been pursued [13,21,22] including the use of an organic anodization bath, and incorporation of anionic species during the anodization process. Anodization of titanium foils and thin films are conducted using a

two-electrode electrochemical cell with a platinum foil as cathode at a constant potential [23], see Fig. 1.

Anodization experiments are commonly conducted with magnetic agitation of the electrolyte which reduces the thickness of the double layer at the metal/electrolyte interface, and ensures uniform local current density and temperature over the Ti electrode surface [23].

Foils were anodized at different anodizing voltages and in HF aqueous solution at room temperature.

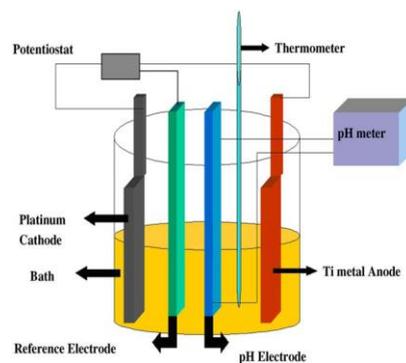


Figure 1
drawing of a three-electrode electrochemical cell in which the Ti samples are anodized.

Fabrication variables include temperature, voltage, pH and electrolyte composition.

In the growth of nanotubes via anodic oxidation of titanium, chemical dissolution and electrochemical etching process are two crucial factors in the

growth of nanotubes. Varying the electrolyte bath temperature can change the rate of both etching process [24].

Fig. 2 shows FE-SEM images of the morphology of titania nanotubes fabricated by anodization at 10V at (a) 5°C and (b) 50 °C.

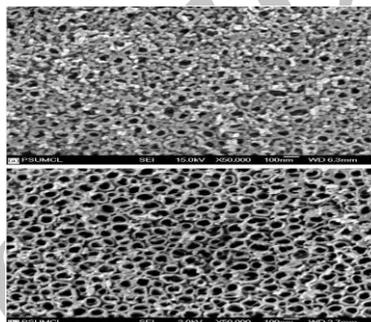
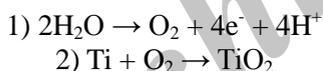


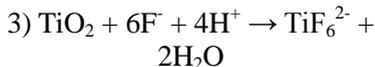
Figure 2
FE-SEM images of 10V nanotube arrays anodized at: (a) 5 °C and (b) 50 °C.

Anodization of single-layer titanium films was not successful as the metal layer in contact with the electrolyte surface was rapidly etched away, thus breaking electrical contact with the submerged portion of the film undergoing anodization before nanotubes could be formed. It appears that the non-uniform electric field distribution at the metal–air–electrolyte interface enhances the rate of chemical etching relative to the field-assisted oxidation of the metal. Therefore, a bilayer-film

scheme was adopted for thin film deposition and anodization. The first layer, of required thickness, was deposited over the entire substrate; a second layer of at least 400nm thickness was deposited atop the first layer over half the substrate area. Anodization to form the nanotube arrays was successfully accomplished by keeping the single layer region completely immersed in the electrolyte, while having the double-layer region in contact with the electrolyte surface. The higher thickness of the film in contact with the electrolyte surface ensured the sustained anodization of the submerged single layer region to the desired specifications. To help understand the process of nanotube formation, The overall reactions for anodic oxidation of titanium can be represented as:



In the initial stages of the anodization process field-assisted dissolution dominates chemical dissolution due to the relatively large electric field across the thin oxide layer [25]. Small pits formed due to the localized dissolution of the oxide, represented by the following reaction, act as pore forming centers:



Then, these pits convert into bigger pores and the pore density increases. After that, the pores spread uniformly over the surface. The pore growth occurs due to the inward movement of the oxide layer at the pore bottom (barrier layer) due to processes (1)–(3) [26,27].

The Ti^{4+} ions migrating from the metal to the oxide/electrolyte interface dissolve in the HF electrolyte [25,26,28]. The rate of oxide growth at the metal/oxide interface and the rate of oxide dissolution at the pore-bottom/electrolyte interface ultimately become equal, thereafter the thickness of the barrier layer remains unchanged although it moves further into the metal making the pore deeper.

MATERIAL PROPERTIES

The properties of titania depend on the crystallinity and isomorph type. Anatase phase is preferred in charge separation devices such as dye-sensitized solar cells, while rutile is used predominately in gas sensors and as dielectric layers. Rutile has minimum free energy in comparison to other titania polymorphs hence given the necessary activation energy all other polymorphs including anatase transform into rutile

through first-order phase transformation.

However, the temperature at which metastable anatase to stable rutile transformation takes place depends upon several factors, including impurities present in the anatase, primary particle size, texture and strain in the structure. Hence, porosity and/or surface area reduction occur due to the sintering effects associated with nucleation-growth type of phase transformations [29,30].

APPLICATIONS OF TITANIA NANOTUBE ARRAYS

- Photoelectrochemical and water photolysis properties
- Application to dye-sensitized solar cells
- Hydrogen sensing
- Self-cleaning sensors
- Biological Properties

CONCLUSIONS

In this work we have reviewed the fabrication, properties and selected applications of titania nanotube arrays made by anodization of a titanium foil or thin film. For crystallization the as-anodized amorphous nanotubes are typically annealed in an oxygen ambient, at elevated temperatures, for several hours. The temperature at which samples crystallized without disturbance

of the nanotubular structure is found to be a function of the nanotube length.

In summary, although only a few years have passed since their discovery [12], the photolysis, charge transport, photocatalytic, and gas-sensing properties of the described titania nanotube arrays are nothing short of remarkable. As such, we believe the material architecture warrants extended and in-depth study, comparable to the efforts that have been spent investigating the properties of carbon nanotubes. Certainly, the work has only just begun in exploring the science and engineering applications of this remarkable material platform.

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