

# Formation mechanism of anodic TiO<sub>2</sub> nanotubes

Hang Shi

University of Science & Technology Beijing, Beijing, China

hangshi\_ustb@163.com

## Abstract

The present review gives an overview of the highlights of more than 10 years of research on formation mechanism of ordered oxide structures (nanotube layers, hexagonal pore arrangements) that are formed by self-organizing anodization of metals. In particular, we address the questions after the critical factors that lead to the spectacular self-ordering during the growth of anodic oxides that finally yield morphologies such as highly ordered TiO<sub>2</sub> nanotube arrays and similar structures. Why are tubes and pores formed—what are the key parameters controlling these processes?

**Keywords:** nanoporous materials; anodization; electrolyte; formation mechanism

## 1. Introduction

Titanium dioxide (TiO<sub>2</sub>) is an n-type semiconductor material with wide bandgap, it has a stable physical and chemical properties, low cost, easy synthesis, and non-toxic and other excellent properties [1], which is favored by many researchers. With the development of nanotechnology, the use of physical or chemical methods of titanium dioxide into one-dimensional, two-dimensional, three-dimensional ordered structure has become the focus of the study. Compared with other nanostructures, one-dimensional titanium dioxide nanotubes have greater specific surface area, higher mechanical strength, stronger adsorption capacity, higher photoelectric conversion efficiency and photocatalytic activity, have good biocompatibility and the advantages of biological non-toxic. Thus it is widely used in the solar cells, photocatalytic degradation of organic matter, photolysis of water preparation of hydrogen, lithium-ion batteries, sensors, biomedical and other aspects.

At present, the general synthesis of TiO<sub>2</sub> nanotubes is template method, sol-gel method, hydrothermal method and anodic oxidation method [3]. Compared with the previous methods, the anodic oxidation method has the advantages of no template, simple and fast, low cost, easy recovery of products and easy control. TiO<sub>2</sub> nanotube synthesized by anodic oxidation method began in 1991, Zwillig et al. [4] found that the anodized-titanium film has a porous surface in the fluorine-containing electrolyte. Grin et al. [5] reported the successful synthesis of highly ordered anodic TiO<sub>2</sub> nanotubes (ATNTs) by electrochemical anodic oxidation. Since then, the research on synthesis and properties of one-dimensional tubular arrays have been widely studied. A lot of work is doing for modification of ATNTs to improve its electrical properties, optical properties, catalytic performance, biocompatibility. The main methods of modification are heat treatment, metal or non-metallic doping, composite and surface modification [6].

## 2. Formation process and related reaction of titanium dioxide nanotubes

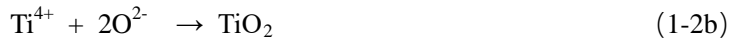
### 2.1 Initial stage of oxidation

The image of current-time transient and X-ray photoelectron spectroscopy (XPS) allow the development of chemical model of the growth process. The reaction at the anode is the oxidation of the metal, releasing Ti<sup>4+</sup> and electrons (formula (1-1)):



The Ti<sup>4+</sup> are then recombined with OH<sup>-</sup> and O<sup>2-</sup> provided by water. The dissociation of water is electric field assisted (high electric field is conducive to water molecules break chain), so the high electric field conducive to the formation of oxides. This leads to the formation of hydrated oxides, which will take several steps, and can be simply summarized as a single process (formula (1-2a)) with the formation of oxides (formula (1-2b)).

Subsequently, the oxidation is further oxidized into the hydrated anode layer by the condensation reaction to release water (formula (1-3)):



These reactions (formulas (1-1) - (1-3)) represent field-assisted oxidation processes. At the cathode, there is hydrogen release (formula (1-4)):



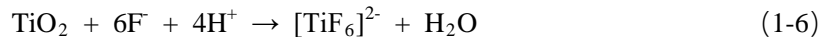
The reaction of the above (the formulas (1-1) to (1-4)) is summarized, and the formation process of the oxide can be expressed as:



This is the initial stage of oxidation; it will form a dense high-resistance initial oxide film (barrier layer) on the anode surface (Figure 1 [7] (a)).

### 2.2 Formation of porous oxide film

The fluoride ions present in the electrolyte are chemically dissolved in the hydrated layer or oxide (compounds of formulas (1-6) and (1-7)), or reacted with  $\text{Ti}^{4+}$  (formula (1-8)). Fluoride binding (chemical dissolution) and electric field will weaken the bond between the adjacent Ti and O (field assisted dissolve). Actually, the fluoride in the electrolyte may form a fluorine complex, the most stable one is  $[\text{TiF}_6]^{2-}$ . The formation of the fluorine complex also benefited from the application of the voltage, which drives the fluoride ion ( $\text{F}^-$ ) to move towards the metal while the  $\text{Ti}^{4+}$  moves towards the electrolyte. These processes can be visually described by the following chemical equations:



The distribution of  $\text{F}^-$  is uneven in the solution, and it will aggregate in the surface of the oxide film with strongly energy and dissolved the oxide. The surface of the oxide film becomes uneven; the thinner the oxide film is, the higher the electric field strength is, and the oxide film easily dissolves (Figure 1.1 (b)), and the pore core is expanded into micropores due to the ongoing field and chemical dissolution processes (Fig. 1.1 (c)) to form a porous oxide film structure [8].

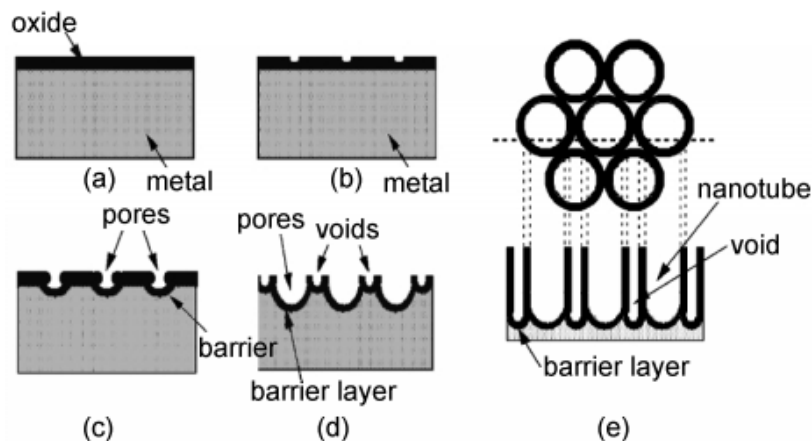


Fig.1 Formation mechanism of  $\text{TiO}_2$  nanotubes [7] (a) The formation of initial oxide layer (b) The formation of pits (c) The formation of voids (d) The formation of voids between holes (e) The formation of titanium dioxide nanotubes

### 2.3 Stable growth of oxidation film

With the growth of micropores, the metal that is not oxidized between the holes is raised upward, forming a peak shape, causing the power line to concentrate and enhance the electric field, so that the top of the oxide film accelerates the dissolution, resulting in small cavities (Fig. 1 (d)-voids); The small cavities are gradually deepened and the continuous pores are separated to form an orderly independent nanotube structure (Fig. 1 (e)). When the rate of formation of the oxides (equations (1-2) and (1-3)) and the dissolution rates (equations (1-6) - (1-8)) are equal (the equilibrium is balanced), the length will not increase, and this balance depends primarily on the voltage applied by the anodic oxidation. In addition, the overlooked ring is the precipitation of oxygen at the anode (Equation (1-9)) [9], which is the side reaction that occurs during the titanium anodic oxidation process, as discussed later, which affects the morphology of the anode layer.



Oxygen is generally more pronounced in aqueous solutions and can also be observed in organic media containing a small amount of water (up to 5 vol%), and it affects the growth efficiency of nanotubes.

### 3. Effect of anodic oxidation parameters on nanotube size

There are many factors that affect the morphology and size of nanotubes, such as the types of electrolytes and electrolytes and the pH and aging, anodic oxidation voltage, current, voltage application, anodic oxidation time, oxidation temperature and so on, in which the electrolyte is the greatest impact.

#### 3.1 The effect of electrolyte

The electrolyte is divided into fluorine and fluorine-free. Fluorine-free electrolyte, generally refers to chloride ions, perchlorate ions, bromide or nitrate solution. In most cases, a very long (tens of millimeters) and non-self-organized nanotubes may be obtained with a very short anodic oxidation treatment time (several seconds or several minutes). The formation of ordered nanotubes in organic media containing chloride ions has also been reported.

Fluorine electrolytes have two main categories: aqueous electrolyte (mixed solution of HF solution or HF with other acids) and organic electrolyte (mixed solution of HF with ethylene glycol, glycerol, dimethyl sulfoxide). According to the composition of the electrolyte, the development of TiO<sub>2</sub> nanotubes by anodic oxidation has gone through four generations. Early use of HF-containing aqueous solution, nanotubes can only grow to 0.5µm long [5,10] due to the high chemical dissolution of TiO<sub>2</sub> in acidic electrolytes. By reducing the acidity of the electrolyte and the use of aqueous solutions containing fluorinated salts rather than HF aqueous solutions, the chemical solubility of titanium dioxide is reduced to produce longer nanotubes up to 2-4 µm long [11]. And Macak et al. [12] found that the use of Na<sub>2</sub>SO<sub>4</sub> / NaF or (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> / NH<sub>4</sub>F aqueous solution is possible to produce nanotubes, and the Cs<sub>2</sub>SO<sub>4</sub> / CsF or K<sub>2</sub>SO<sub>4</sub> / KF aqueous solution will lead to high precipitation and dissolution of TiO<sub>2</sub>. These experimental results show that it is extremely important to select the appropriate cation to optimize the growth of the nanotubes.

In the organic electrolyte, the contribution of oxygen to the anodic oxidation process is quite difficult because the oxygen ions are strongly bonded to carbon, either by a single bond (C-OH) or a double bond (C = O). In most anodizing processes, the growth and oxidation of titanium dioxide nanotubes are generally completed by the addition of a small amount of water or an aging electrolyte that will absorb environmental moisture.

#### 3.2 The effect of anodic voltage

Most experiments are carried out under constant potential conditions, which have constant potential applications and the anodic oxidation current is monitoring. In contrast, constant current growth has not been used, because the shape of the anodic nanotubes under the constant current is difficult to control. The applied potential determines the electric field strength across the oxide, which in turn affects the migration of the ions and ultimately determines the size of the nanotubes. The results show that the length of nanotubes is proportional to

the oxidation voltage in a certain oxidation time. With the increase of the number of  $Ti^{4+}$  in the bottom of the nanotubes and the amount of  $O^{2-}$  in the medium, the average tube diameter, thickness, and length are increased.

#### **4. Conclusion**

In this paper, the formation process of titanium dioxide nanotubes is analyzed in detail from the research background of the anodic titanium nanotubes, three stages of nanotube formation, the effects of the formation of nanotubes. The effect of different oxidation parameters on the morphology of nanotubes was studied in detail, but the formation mechanism of nanotubes cannot be characterized by in-situ characterization. Therefore, the formation mechanism of nanotube structure, self-organizational processes are urgently needed to be studied.

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