Process of growth TiO$_2$ nanotubes by anodization in an organic media

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The aim of this chapter is to show the process for the growth of TiO$_2$ nanotube by anodizing and its features as surface. The Ti anodized nanotubes were obtained by anodizing Ti in organic medium. The process of formation of TiO$_2$ nanotubes on Ti surfaces was established *ex-situ* by Scanning Electron Microscopy (SEM). At first, the growth of the TiO$_2$ on the surface of the Ti plate occurs because of the interaction of the Ti with O$^-$ ions. Then, an early oxide layer is formed. These anions migrate through the oxide layer to the Ti/TiO$_2$ interface and then react with Ti. Meanwhile, the applied electric field ejects Ti$^{4+}$ cations from the Ti/TiO$_2$ interface and makes Ti$^{4+}$ move towards the TiO$_2$/electrolyte interface. The chemical dissolution occurs at the interface of TiO$_2$/electrolyte where TiO$_2$ is dissolved by F$^-$ with the help of H$^+$ and the field assisted dissolution occurs at the Ti/TiO$_2$ interface. Simultaneously, with the time of anodizing increased, the current density also increases to reach a maximum value. The increase in current density was caused by the formation of pits and enlargement of the pits on the oxide layer. Beyond this point, current density drops, indicating the growth of the nanotube structure. In this work, TiO$_2$ nanotubes with inner diameter between 90-110 nm and wall sizes of 15-20 nm, after 120 min of anodizing are shown. The presence of TiO$_2$ was confirmed with Energy Dispersive X-ray Spectroscopy (EDS) results. Tests of roughness, and surface energy were carried out too.

**Keywords:** Anodizing; nanotubes; contact angle; surface energy

1. Introduction

The TiO$_2$ (titanium dioxide or titania) is a compound widely investigated and there are reports of multiple applications including: degradation of organic compounds and bacteria in both water and air, electric energy generation, application prosthetic, among others. The main features of this compound are: its high oxidizing capacity, superhydrophilicity, chemical stability, high durability, transparency to visible light, corrosion resistant and non-toxicity, making it friendly with the environment and with the interaction with the human beings.

The titanium dioxide does not absorb light in the visible region (400-700 nm) but disperse it very efficiently. This is the most broadly commercially used characteristic as white basis for paints, toothpastes, cosmetic products, plastics, etc.

However, TiO$_2$ absorbs UV (ultra violet radiation, 100-400 nm). This absorption causes the generation of the electron-hole pair (charge carriers), which cause chemical reactions on surfaces. Its photochemical properties have been extensively investigated but not widely used at commercial level. So, the titanium oxide semiconductor or titania (TiO$_2$) is one of the most important photoactive compounds, mainly for its characteristic stability and band gap energy with potential applications, such as: photovoltaic cells, batteries, sensors, optical emitters, photonic crystals, catalysis and photocatalysis, selective adsorption, ion exchange, ultraviolet blocking, smart surface coatings and as smart functional filling material in fabrics, paints, cosmetics, among others.

This kind of compound has been synthesized both with micro- and nano- sizes. However, the latter scale has been predominantly the millstone for research, especially by the acquired properties which differ from those of bulk materials. Among the various forms of achieved morphologies, there are: spheres, rods, sheets, fibers and tubes.

2. Background

2.1 Features of TiO$_2$ nanotubes.

It is proposed for the tubular TiO$_2$ semiconductor nanostructures that could be less recombination of charge carriers electron-hole (e$^-$ – h$^+$) caused by shorter necessary diffusion distance towards the target compounds to decompose. Nanotubes have been obtained by different methods, among which are: hydrothermal, sol- gel, assisted electrochemical methods with templates and anodizing methods.

The anodizing of Ti is among the most used methods for obtaining nanotubes. It has the lower inconveniences whenever carrying out the process. The main interest in this kind of structure in particular is because it has proved been efficient in photocatalytic applications.

The photoconversion efficiency in nanotubular titania surfaces is influence by various causes, among others, may be the manufacturing method, in which the factors are: the current, the electrolyte, concentration, impurities, processing temperature, dissolved oxygen, experimental setup, etc.

For the preparation of this compound, the most frequently used methods are the templates and the hydrothermal, which usually obtain a product in powder form. However, thin films and coatings with oriented nanostructure are more
desirable because it is possible to implement in applications, such as: catalysis, filtration, sensing, photovoltaic cells and electrodes with large surface area [1]-[12]. It is well known that the functional properties of the materials depend on their microstructure. Many types of nano-dimensional materials have been studied extensively [3-5], such as: nanowires, nanoneedles, nanofibers and nanotubes.

2.2 Some methods for obtaining TiO$_2$ nanotubes.
The TiO$_2$ films have been obtained with different morphologies, such as: nanorods [13]-[17], nanowires [18]-[20], and nanotubes [21]-[27]. These arrangements are of great interest since they have optical and electronic properties considered unique. There are different methods for preparing TiO$_2$ nanotubes layers, such as: the sol-gel method using gels as templates [28], hydrothermal predeposits of TiO$_2$ [29], [30], microwave-assisted hydrothermal method [31], sonochemical [28], microemulsion [32], solvothermal [33], atomic layer deposition (ALD) growth method without template, ionic liquids [34], anodized Ti [35], [36], among others.

3. Anodizing of Ti

3.1 Some aspects of anodizing of Ti.
No method used for obtaining TiO$_2$ nanotubes offers much control over the dimensions of these as does the anodized titanium (Ti) in fluorine-based electrolytes [37]-[39].

In 2001, Gong et al.[40] first developed titania nanotube arrays self-organized on a Ti substrate by potentiostatic anodic oxidation using a solution of HF as electrolyte and pure Ti plates as substrates, which led to the rise of research of TiO$_2$ nanotube arrangements. Their special nano-architecture provides a large internal surface without decrease in geometric and structural order [25,26].

The orientation of these nanostructures make them excellent electron percolation pathways for charge transfer between the interfaces, and offers better properties for applications in fields, such as: solar cells, catalysis, photolysis of water, hydrogen sensors, among others.

The anodizing process of Ti have influence during the growth of TiO$_2$ nanotubes the following main parameters: electrolyte composition, voltage, and time. Grimes et al. [17] reported the development of pores and holes in the surface of the titanium plates in the formation of nanotubes process. They proposed that the tube structure was the result of the depth and spread of small pores. Schmuki et al. [41] found that the low acidity in the bottom of the pore helps sculpting the pore into a tubular structure. However, it is not clear the detailed process of how the small pores become large pores and eventually evolve into a tubular structure.

The relationship between the pore diameter, the wall thickness and the anodizing voltage is related to a process of forming the array of TiO$_2$ nanotubes in the titanium surface [42], [43].

3.2 Electrolytic bath
The anodizing of titanium was carried out in a two-electrode cell with a capacity of one liter. The solution was prepared with technical and analytical grade reagents. All experiments were performed at a controlled temperature of 25 °C ±1°C and an atmospheric pressure of about 1 atm (Fig. 1).

![Thermographic image of electrolytic bath used for anodizing Ti plates.](image)

The medium used in this experiment was organic, composed of ethylene glycol 98% v/v (Karal, technical grade), deionized water 2% v/v, and NH$_4$F was added with 0.3 wt % (Alfa Aesar, 96%). The cathode and anode plates were industrial titanium. Anodizing duration varied using different times: 2, 4, 6 and 7 h. At the beginning of the experiment, a ramp 6 V/min was used to reach and fix the applied voltage at 60 V.
3.3 Roughness in the Ti plates.

The Ti plates used for producing nanotubes were industrial grade, which had 98 wt% of Ti. These plates were pretreated by sandblasting technique. Roughness was measured by optical profilometry in order to analyze the surface texture and topography of the samples. Figure 1 shows the topographic image of a sample with Ti sandblasting treatment with an average roughness (Ra) of $1.8 \pm 0.15 \mu m$. Figure 2 shows the surface topography of anodized Ti with TiO$_2$ nanotubes with an average roughness (Ra) of $1.7 \pm 0.18 \mu m$. The roughness did not show a signifying change with the anodizing process but the TiO$_2$ nanotubes shown a better mechanical strength avoiding the treated layer detachment.

![Fig. 2 Optical profilometry of Ti with sandblasting.](image1)

![Fig. 3 Optical profilometry of TiO$_2$ nanotubes.](image2)

3.4 Growth mechanism of TiO$_2$ nanotubes.

1. In a first stage, the formation of a compact layer of amorphous titanium dioxide occurs. It was formed due to interaction of the metal with $O^{2-}$ or OH- ions under influence of the electric field (reactions 1 and 2). Figure 4 show changes with a crust form at microscopic level.

\[
\begin{align*}
\text{Ti} & \rightarrow \text{Ti}^{4+} + 4\text{e}^- \\
\text{Ti}^{4+} + 2\text{H}_2\text{O} & \rightarrow \text{TiO}_2 + 4\text{H}^+
\end{align*}
\]

![Fig. 4 First step in the formation of TiO$_2$ nanotubes, TiO$_2$ layer.](image3)

2. Once formed the TiO$_2$ layer on the anode, it reacts with fluorine ions with the help of the electric field forming the [TiF$_6$]$^{2-}$ complex, resulting in fractures on the metal surface.

\[
\text{TiO}_2 + 6\text{F}^- + 4\text{H}^+ \rightarrow \text{TiF}_6^{2-} + 2\text{H}_2\text{O}
\]

![Fig. 5 Formation of pits in the TiO$_2$ layer, indicated with circle.](image4)

3. The fractures become larger pores and pore density increases. Subsequently, the pores spread evenly over the surface (Fig. 5).

4. As soon as the oxide growth rate on the metal-oxide interface and the ratio of oxide dissolution at the interface oxid-solution are finally equal, the thickness of the barrier layer remains unchanged, at the same time that it displaces deeper into the metal with the growth of the length of the pore.
5. The nanotube length increases until the rate of electrochemical oxidation is equal to the rate of chemical dissolution in the upper surface of the nanotubes. Thus, a self-organized porous layer was obtained. In the case, that a sandblasting was used as pretreatment, an uneven distribution of the nanotubes layer was obtained (Fig. 6).

![Fig. 6](image1.png) The last step consists in the spreading of pores and formation of TiO$_2$ nanotubes.

![Fig. 7](image2.png) Voltage ramp used and density current. The formation of TiO$_2$ is limited by the chemical oxidation.

At the time that the anodizing time increases, the current density proportionally increases, reaching a maximum value of 23mA/cm$^2$ (Fig. 7). The increased current density is caused by the formation of pits and holes extending into the oxide layer. Following this, the current density decreases, which indicate the growth of the TiO$_2$ nanotubes structures, which were formed after 120 min of anodizing. The inner diameter reached was between 90-110 nm in size and walls were around 15 to 20 nm (Fig. 6) in thickness.

Analysis of Energy Dispersive Spectroscopy X-ray (EDX) (Fig. 8) shows the presence of F. The presence of Al is attributable to sandblast. Cl, K, and Si are discarded in these analyses. This analysis confirms the formation of TiO$_2$.

![Fig. 8](image3.png) EDX analysis shows the presence of F in the nanostructures.

3.5 Wettability in TiO$_2$ nanotubes.

Table 1 shows the data obtained for the contact angles measurements. The TiO$_2$ nanotubes generated on Ti surfaces were shown to be hydrophilic. It can be seen that by measuring the contact angle with distilled water, the surface of Ti metal alone has a contact angle of 85.3°, while after anodizing, this result changes dramatically, showing a value of 9.8°. Also, the measurements done included assessment with canola oil, where it is possible to observe that the TiO$_2$ tubular nanostructures remarkably change the contact angle. The purpose of measuring with canola oil was to extend the study for including the surface energy measurements. Results about surface energy are shown in the table 1, this results was determined by Zisman method [44]. The Ti plates anodized are highly hydrophilic and have higher level of wettability, which is clearly defined by the surface free energy.
4. Conclusions

The TiO₂ nanotubes were obtained by using pretreated Ti surfaces through the sandblasting technique. These rough surfaces were anodized into an organic bath. Whenever sandblasting was used as pretreatment, an uneven distribution of the nanotubes layer was obtained. The roughness did not show a signifying change with the anodizing process but the TiO₂ nanotubes shown a better mechanical strength avoiding the treated layer detachment.

Through SEM imaging, the steps that occur during the anodizing process, forming a first layer of titanium oxide on the surface of Ti, then under influence of the electric field and the presence of fluorine chemical attack occurs is established, which causes fractures and pores subsequently grow into nanotubes by the effect of the electric field. It was also possible to establish the influence of the current during this process. It was observed that the increase in current density generated by the formation of pores and widening of these in the layer oxide. Following this, the low current density and is stable, indicating the growth of TiO₂ nanotube structure.

Acknowledgements The authors gratefully acknowledge the financial support from the Mexican Council for Science and Technology (CONACyT, Grant CB-2009-01 133157). Also, the first author acknowledges CONACyT for his graduate fellowship. Especial thanks to José Eleazar Urbina Alvarez for his valuable help in obtaining the SEM images, and Dr. Francisco Espinoza for his assistance in obtaining the images of optical profilometry.

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