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Anodized TiO$_2$ Nanotubes: Synthesis, Growth Mechanism and Applications

Junye Dong

Abstract

TiO$_2$ nanotubes synthesized by Ti anodization have attracted significant and continually increasing research interest over the past years with the high potential for technological applications. TiO$_2$ nanotubes provide a unique combination of wide band gap semiconductor properties with a large surface area and precisely controlled morphologies, making them promising candidates for solar cells, water splitting, environment remedies, sensors, sterilization, surface wettability control, and more. In order to optimize the properties for different applications, the microstructures of anodized TiO$_2$ should ideally be designed and tailored at the nanoscale. A crucial step toward this goal is a developed understanding of the formation mechanisms and morphology evolution.

The dynamic competitions between oxidation and chemical dissolution during Ti anodization have been identified in this thesis. This demonstrates experimentally that the inside diameter of nanotubes gradually increases towards the tube apex, due to the longer period of dissolution of the inside tube-wall. When the dynamic balance between oxidation and chemical dissolution is reached, nanowires can be synthesized at the top region. The morphology evolution of anodized TiO$_2$ has been investigated and discussed. It reveals that the applied voltage determines the pattern of etching pits, which in turn governs the anodized TiO$_2$, including the tube diameter and hexagonal features. With this developed understanding, several novel hierarchical morphologies are synthesized. The obtained microstructures provide a convenient case to evaluate the influence of morphology on surface wettability, proving that surface morphology acts as an amplifier for surface wettability. By tailoring the microstructures and organic modification, the surface wettability of anodized TiO$_2$ can be well tuned from superhydrophilicity to super-hydrophobicity, with the maximum water contact angle up to 172°. The potential application for aquatic devices is also explored on a treated Ti mesh, which shows strong floating stability.
The formation of anodized TiO$_2$ is a dynamic process involving the oxidation process at the interface between oxide layer and Ti substrate, which suffers from the insufficient supply of oxygen. Ti anodization is thus applied to synthesise defective TiO$_{2-x}$ with controllable oxygen vacancy. The obtained black TiO$_{2-x}$ shows ultrahigh absorbance over the visible light region (400-800 nm), doubling the highest absorbance previously reported on hydrogenated TiO$_2$. Electron paramagnetic resonance analysis shows the controllable levels of oxygen vacancies, and transmission electron microscopy reveals its partial crystallised structure - both of which can be easily controlled by post-annealing. The preliminary works have shown its high photocatalytic activity under visible light, and further revealed its ability to absorb microwave energy. This research on defective black TiO$_{2-x}$, although preliminary, has shown tremendous potential of this material, pointing out a new direction that crystal defects might be the key to developing visible-light sensitive and microwave-absorbing materials.
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Extent of contribution by PhD candidate (%)
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CHAPTER 1

Introduction
In 1991, the successful synthesis of carbon nanotubes by S. Iijima et al. marked a milestone in Materials Science and Engineering [1]. By using a simple arc discharge reaction, carbon nanotubes of several micrometers length and only a few nanometers diameter were formed. These nanotubes exhibited high physical strength and hardness, electrical conductivity, and other superior properties [2]. This excellent work thus triggered many studies on one-dimensional nanomaterials. A number of transition metal oxides have been reported to form nano-tubular structures using various methods in the past, and have stimulated immense research interests with more than 120,000 papers published on the “smart materials” [3-7].

Aside from scientific curiosity, the main reason for nanotubes research is the anticipated economic and social impacts of their promising applications. Among them, the techniques to synthesize titanium dioxide (TiO$_2$) in the form of nanotubes immediately attracted numerous attention due to the perspective of applying TO$_2$ nanotubes for developing photocatalysis, solar cells, semiconductors and other fields [8, 9]. The meaningful applications thus made TiO$_2$ nanotubes one of the most studied functional materials in the past decade.

<table>
<thead>
<tr>
<th>Crystal Form</th>
<th>Crystal System</th>
<th>Space Group</th>
<th>a / nm</th>
<th>b / nm</th>
<th>c / nm</th>
<th>Band-gap</th>
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<tbody>
<tr>
<td>Anatase</td>
<td>tetragonal</td>
<td>I41/amd</td>
<td>0.379</td>
<td>0.379</td>
<td>0.951</td>
<td>-3.2</td>
</tr>
<tr>
<td>Rutile</td>
<td>tetragonal</td>
<td>P42/mnm</td>
<td>0.459</td>
<td>0.459</td>
<td>0.296</td>
<td>-3.0</td>
</tr>
<tr>
<td>Brookite</td>
<td>orthorhombic</td>
<td>Pbca</td>
<td>0.918</td>
<td>0.545</td>
<td>0.515</td>
<td>-3.14</td>
</tr>
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</table>

Figure 1.1 Structural parameters (a) and crystal structures (b) of anatase, rutile and brookite [11].

### 1.1 TiO$_2$ semiconductor

TiO$_2$ is normally seen in three crystalline polymorphs: anatase, rutile, and brookite. Tetragonal rutile can be easily synthesized at higher temperatures, and the other two are more easily obtained at lower temperatures [10]. Their different structural parameters are listed in
Figure 1.1, which contribute to different physical and chemical properties. All three types of \( \text{TiO}_2 \) consist of \( \text{TiO}_6 \) octahedra, but differ in the distortion of the octahedron units, and share edges and corners in different manners. Bulk anatase, rutile and brookite have band gaps of 3.2 eV, 3.0 eV, and 3.14 eV, meaning they only absorb photons of wavelength smaller than 387 nm, 431 nm, and 395 nm, respectively. The difference in the band gap and absorption onset is naturally attributed to the crystal structure difference in the lattice, which causes different orbital coupling between the oxygen 2p and titanium 3d orbitals [11].

![Synthesis Scheme](image)

<table>
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<tr>
<th>Synthesis Scheme</th>
<th>Typical Morphology</th>
<th>Features</th>
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| Hydrothermal     | ![Image](image)   | - Single tubes or loose agglomerates of tubes and bundles  
|                  |                   | - Small diameter: 2-20nm  
|                  |                   | - Thin tube-wall: few atomic layers  
|                  |                   | - Length of up to several micrometres  
|                  |                   | - Open-ended  
| Template         | ![Image](image)   | - Tube arrays or loose agglomerates  
|                  |                   | - Template filling by sol-gel, ALD, PVD or electrochemical techniques  
|                  |                   | - Length: a few nm to several micrometres  
|                  |                   | - Diameter: 10 nm - 500 nm  
| Anodisation      | ![Image](image)   | - Aligned TiO\(_2\) nanotube arrays  
|                  |                   | - Length from 100nm to 1000\(\mu\)m  
|                  |                   | - Diameter: 15\(\mu\)m - 800\(\mu\)m  
|                  |                   | - Directly attached to the metal  
|                  |                   | - Blind-ended  

Figure 1.2 TiO\(_2\) nanotubes synthesized by hydrothermal [12], template [13] and anodization methods [14], including the synthesis processes, typical morphologies and general features [15].

1.2 Growth techniques of TiO\(_2\) nanotubes

A number of techniques have been developed to produce TiO\(_2\) nanotubes, mainly using template, hydrothermal and anodized techniques. These techniques synthesize different features of TiO\(_2\) nanotubes with typical morphology and properties, as illustrated in Figure 1.2.

In 1998, T. Kasuga et al. first reported TiO\(_2\) nanotubes by the hydrothermal reaction [16], based on the alkaline treatment of TiO\(_2\) precursors. TiO\(_2\) nanotubes are obtained after heating oxide powders in alkaline solution at high pressure and temperatures after 1-2 days. Hydrothermal TiO\(_2\) nanotubes consist of rolled atomic planes with monomolecular layer thickness. They can be regarded as “true” nanotubes, since the effects of quantum size and dimensionality are significant on the physical and chemical properties [12].

The first effort to form TiO\(_2\) nanotubes by the template method was carried out by P.
Hoyer et al. in 1996 [17], by electrochemically filling the anodized alumina template in order to produce ordered TiO$_2$ nanotubes. Now, several filling methods have been developed and employed, such as the sol–gel technique, atomic layer deposition, and physical vapour deposition [13]. For practical applications, the porous template can be used with the deposited oxide, or selectively removed to result in free nanotubes.

Electrochemical Ti anodization is a simple method to fabricate self-organized TiO$_2$ nanotubes. V. Zwilling et al. synthesized TiO$_2$ nanotubes by Ti anodization in 1999 [18], and immediately triggered many studies on this technique, mostly using fluoride (F$^-$) based aqueous electrolytes. The synthesized TiO$_2$ nanotubes were inhomogeneous in the first few years [19], severely limiting the potential of anodized TiO$_2$ to tune its structures to achieve desired properties. The morphology was far from perfect until the introduction of non-aqueous electrolytes in 2005 by C. Grimes et al. [20]. The following work showed a very high adjustability of TiO$_2$ nanotubes’ geometry [21], which has promoted Ti anodization to be the most investigated technique to form TiO$_2$ nanotubes in the past decade. Because of this, we will emphasize the self-organized TiO$_2$ nanotubes synthesized by Ti anodization, and give more information on the formation mechanisms and experimental factors in the following section.

![Figure 1.3 Schematic diagrams for the current versus time curve, nanotubes formation process, and the dynamic adjustment between oxide formation and chemical dissolution.](image)

**1.3 Ti anodization for synthesizing TiO$_2$ nanotubes**

Electrochemical anodization has been intensively studied for synthesizing TiO$_2$ nanotubes due to the lower cost, simple operation and adjustable morphology. These TiO$_2$ nanotubes also have good mechanical adhesion on substrate and electrical conductivity, which is important for practical applications.

1.3.1 Formation Mechanism

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In Ti anodization, the formation of TiO$_2$ nanotubes is a dynamic process competing between chemical dissolution, field-assisted dissolution and oxidation reaction: (1) TiO$_2$ forms at the interface of metal and oxide for the interaction of Ti with H$_2$O; (2) Ti$^{4+}$ ions migrate from the metal substrate towards the oxide and electrolyte interface due to the force of the electric field; (3) TiO$_2$ is dissolved by fluorine ions (F$^-$) [22]. The TiO$_2$ nanotubes are the completed result of these three processes.

When the reaction starts, surface Ti atoms are oxidized with water molecules from the electrolyte, forming a passive oxide film spreading across the surface.

At the Ti anode, the reaction happens as:

$$Ti + H_2O = TiO_2 + 2H^+ + 4e^- \quad \text{Eq. 1.1}$$

While hydrogen evolution occurs at the cathode:

$$8H^+ + 8e^- \rightarrow 4H_2 \quad \text{Eq. 1.2}$$

The whole process can be described as Eq. 1.3:

$$Ti + 2H_2O \rightarrow TiO_2 + 2H_2 \quad \text{Eq. 1.3}$$

Due to the positive potential, fluorine ions (F$^-$) are attracted towards the Ti anode and react with the formed oxide layer and diffused Ti$^{4+}$ ions, resulting in etching pits. The chemical dissolutions are:

$$TiO_2 + 6F^- + 4H^+ \rightarrow TiF_6^{2-} + 2H_2O \quad \text{Eq. 1.4}$$

$$Ti^{4+} + 6F^- \rightarrow TiF_6^{2-} \quad \text{Eq. 1.5}$$

With the ongoing reaction, the unevenly distributed etching-pits develop to pores, which interfere with each other and compete for the limited current. This competition leads to a situation in which the pores equally share the available current. Self-ordering under steady-state conditions is eventually established, forming the ordered nanotubes. Oxide generates from the interface between the Ti metal and oxide layer, while the chemical dissolution occurs at the interface between oxide and electrolyte. The upper part of TiO$_2$ nanotubes suffer more chemical etching due to the longer time exposure to the electrolyte, and finally are consumed. When the rate of oxide generation is equal to chemical dissolution, the length of the nanotubes (or the thickness of the oxide layer) stops growing and remains constant [23].

The typical curve of current versus time can illustrate the formation process of anodized TiO$_2$ nanotubes (Figure 1.3) [24]. The curve is divided to three stages. In the first stage, the current decreases exponentially due to the formation of passive oxide film, which significantly increases electric resistance. In stage 2, etching-pits appear and penetrate the passive film, which exposes the Ti substrate underneath. This morphology helps to reduce the electric resistance, which in turn increases the current intensity. The tubular oxide continuously grows
in stage 3, resulting in a gradually reduced current. At the end, a constant current density is achieved after a certain period of reaction time, reflecting the establishment of a dynamic balance between chemical dissolution and oxide formation.

Figure 1.4 Different morphologies formed in Ti anodization, depending on (a) applied voltage and water concentration in electrolyte [25], and (b) applied voltage, hydrodynamic parameters (RPM), and NH4F concentration in electrolyte [26].

1.3.2 Experimental factors

The formation of perfect nanotubes depends on several important factors, including applied voltage, electrolyte composition, reaction temperature, pre-treatment of Ti substrate, and post-annealing. Figure 1.4 shows the formation of nanotubes versus other morphologies at different experimental parameters. It generally indicates that the high water content, hydrodynamic flow in the electrolyte, and applied voltage favour the transition of nanotubes to a sponge structure, while low water content and high NH4F concentration will change Ti anodization to a kind of electrochemical polishing treatment [25, 26].

Under optimized conditions, nanotube diameter is determined by the applied voltage. Oxide thickness can be easily adjusted by controlling reaction time within a range, until the competing balance is reached between oxide generation and chemical dissolution. The electrolytes can also affect the oxide thickness and nanotube diameter. Nanotubes with a diameter below 100 nm are typically obtained in aqueous electrolytes, while larger diameters can be synthesized in nonaqueous electrolytes. A diameter up to 800 nm has been achieved in dimethyl sulfoxide with 2 wt.% HF [27]. Aqueous solution exhibits strong chemical etching; and the dynamic balance between oxide generation and chemical dissolution is reached within a short time. Thus, TiO2 nanotubes only grow up to a few micrometres in aqueous electrolytes. In contrast, TiO2 nanotubes over 1000 μm in length have been synthesized in ethylene glycol containing 0.5 wt.% NH4F [28].

Nevertheless, the thickness of the tube-wall is affected by chemical dissolution. The tube-
wall at the upper segment is thinner than the bottom root due to the longer time exposure. The inner pore appears like a “V” shaped pattern [29]. After ample time for reaction, a needle-like morphology (or nanowires) is presented at the top of the nanotubes [23].

Temperature is another critical factor. TiO$_2$ nanotubes transform into hexagonally nano-columns in a cold environment [30], and change to a sponge topography at sufficiently high temperatures [31]. The post-annealing temperature affects the architectures as well. Relatively low temperatures have little influence on oxide morphology, while the formed nanotubes start to collapse from 600°C, and is completely destroyed at 800°C due to the phase transformation [32].

1.4 Functional applications

Anodized TiO$_2$ is a highly functional nanomaterial that has attracted tremendous attention in the past decade. In addition to its specific properties mentioned previously, its utilization is also highly desirable due to the high chemical and mechanical stability, non-toxic nature and low-cost preparation. The main applications of anodized TiO$_2$ are outlined here.

1.4.1 Energy harvest and storage

TiO$_2$ nanotubes have been intensively studied for solar cell applications due to their suitable electronic band structure [33], which provides a superior platform for building up ordered hetero-junctions for enhanced charge separation and electron transportation. Their microstructure can be finely tailored, allowing the optimization of device fabrication for different types of solar cells. With TiO$_2$ nanotubes, solar energy can also be converted and contained as H$_2$ gas [34]. This is the intensively studied water-splitting reaction.

One of the most promising applications of nanostructured TiO$_2$ is used in dye-sensitized solar cells (DSSCs). TiO$_2$ layer plays the role of electron-transporting-medium, and the electron transport rate significantly affects the overall DSSCs efficiency. In order to achieve a fast electron pathway, the vertically oriented TiO$_2$ nanotubes synthesized by anodization have been widely studied as one of the most promising approaches. In 2005, Macak et al reported the first attempt of using this material for DSSCs. It showed only 3.3% photo-energy-conversion efficiency, due to the unsuitable aspect ratio and type of nanotubes (100 nm diameter and 500 nm length). Over the past time, anodized TiO$_2$ nanotubes have been intensively investigated, and achieved many drastically enhanced performances in DSSCs.

Some important discoveries have been found in TiO$_2$ nanotubes and nanoparticles - based DSSCs. For instance, Zhu et al. found the electron transport times in TiO$_2$ nanoparticles and nanotubes are similar due to a similar average crystal size. However, TiO$_2$ nanoparticles showed
10-times faster recombination than that of TiO$_2$ nanotubes. It explained the 25% higher charge collection efficiency of TiO$_2$ nanotube when compared with TiO$_2$ nanoparticles. Another meaningful finding is the estimated electron diffusion length is about 100 μm, which was based on the measured electron diffusion coefficients and lifetimes on a 20 μm thick TiO$_2$ nanotubes. It indicated that thicker TiO$_2$ nanotubes could be applied to enlarge the surface areas for optimized DSSCs.

TiO$_2$ annealing history is another key factor that strongly affects the DSSCs performances. As-anodized TiO$_2$ is amorphous and must be annealed to show good electron conductivity for DSSCs. Generally, higher annealing temperature results at higher conversion efficiency. It is because the formation of anatase with an increased crystallinity that finally leads to improved electron diffusion coefficients and lifetimes. Morphology effects, including nanotubes length, diameter, and wall thickness, have also received great attention, as the geometry features can affect TiO$_2$ surface area, dye loading, light reflection, electrolyte diffusion, etc.

Another highly promising application is to use TiO$_2$ nanotubes as a super-capacitor for future energy storage. In 2012, X. Lu et al. reported that hydrogenated TiO$_2$ nanotubes yielded 3.24 mF/cm$^2$ specific capacitance at a scan rate of 100 mV/s [35]. Notably, the novel material had remarkable rate capability with 68% areal capacitance retained when the scan rate increases from 10 to 1000 mV/s. It also showed outstanding long-term cycling stability.

1.4.2 Environmental Remedy

TiO$_2$ is one of the most active materials for the photo-degradation of organic pollutants due to its special electronic band structures [36]. Several reactive species can be generated from the surrounding water by charge exchange at TiO$_2$ valence and conduction bands, including H$_2$O + h$^+$→ OH· and O$_2$ + e$^-$ → O$_2^{}$. The radical half-life of OH· radical is $\sim$ 10$^{-9}$ sec, and that of O$_2^{}$ is very short and depends on the reactive substrates. These radicals and peroxide ions are able to virtually oxidize most organic materials to CO$_2$ and H$_2$O.

CO$_2$ atmospheric level rose from 270 ppm in the preindustrial era to nearly 400 ppm nowadays, which has caused serious climate and environmental problems. Another meaningful reaction based on TiO$_2$ nanotubes is the photo-electrochemical reduction of CO$_2$ to chemical fuels, including formaldehyde, methyl alcohol, and methane [37].

1.4.3 Other Applications

TiO$_2$ nanotubes have been explored for sensing applications. Particularly for H$_2$ sensing, its relative change of electric resistivity or sensitivity is superior to other widely studied materials [38]. The geometry of the nanotubes indicates that they might be used as a drug-delivery capsule. N. Shrestha et al. already presented that TiO$_2$ nanotubes filled with magnetic
Fe$_3$O$_4$ nanoparticles may be magnetically guided to some desired locations [39]. Another interesting application is in biomedical fields. Today, 40% of biomedical implant materials are based on titanium or titanium alloys. The anodized morphology of Ti is ideal for studying and applying size effects with living matter or biologically relevant species [40].

1.5 Research objectives

The numerous applications of anodized TiO$_2$ nanotube arrays grown from a Ti metal have attracted wide scientific and technological interest. Their microstructures should ideally be tailored at the nanoscale to optimize the properties for various applications. While a number of excellent works focus on their growth conditions and exploiting applications, relatively little work deals with the questions for the origin of morphology evolution in Ti anodization, including:

(i) The formation mechanism for the hexagonal structures;
(ii) The reasons of the effect of applied voltage on the anodized Ti oxide;
(iii) How to better tailor the microstructures and properties of anodized TiO$_2$.

The research described in this thesis will first focus on the growth mechanisms for anodized TiO$_2$ nanotubes and tailoring of the microstructures. Armed with the developed understanding, the next aim of this thesis is to explore their various applications, including:

(1) Ti metal has been widely used in biocompatible materials, aeronautical materials, and in many other important applications for its superior physical and chemical properties. Therefore, alteration and control of its wetting property is of great interest for its applications as smart surface materials. It is known that surface wettability is a function of surface morphology and roughness [41]. The designed microstructures of anodized TiO$_2$ can provide a convenient case to evaluate the influence of morphology on surface wettability.

(2) TiO$_2$-based materials have wide applications for solar cells, H$_2$ generation, and pollutants destruction using UV radiation. Low absorbance of visible light severely limits its efficiency using solar energy. The introduction of lattice defects into TiO$_2$ might generate a new electronic band and expand its light absorbance into the visible light region [42]. Here, it is hypothesized that oxygen defects can be ‘planted’ into anodized TiO$_2$ via Ti anodization under an oxygen-deficient environment. The aim is to propose a new method to producing defective TiO$_2$, and achieve a breakthrough on visible-light driven TiO$_2$ photocatalysis.

(3) Microwave absorbing materials (MAMs) are widely used in civil and military applications for absorbing unwanted electromagnetic radiation. While TiO$_2$ has been intensively studied in harvesting solar light, which is also a type of electromagnetic energy, it has rarely been considered as a MAM candidate. To break this ‘barrier’, we plan to synthesize
a partial crystallized TiO$_2$ for absorbing microwave energy, based on the interface electric field theory [43].

1.6 Thesis framework

In this thesis, the work is presented following the outline as below:

Chapter 1 presents the state of the art anodized TiO$_2$ nanotubes. Current understanding on the formation mechanism and main applications are presented in this chapter, followed by a detailed thesis outline.

In Chapter 2, hierarchically structured TiO$_2$ synthesized via Ti anodization is shown. Based on the dynamic relations between oxidation reaction and chemical dissolution, a physical model is developed for the growth mechanism of anodized TiO$_2$, which can evaluate the effects of several experimental parameters [23].

Chapter 3 describes the process to make a super-hydrophobic surface on Ti substrate. After applying Ti anodization, a hierarchical structure with disordered nanowires on top of regular nanotubes is fabricated. After organic modification, this material shows a very high water contact angle of 172 degrees. The potential application for aquatic devices is explored on a treated Ti mesh, which shows strong floating stability [44].

Material wettability is significantly affected by surface morphology. Chapter 4 shows an in-depth study on the wettability of anodized TiO$_2$, which is tailored from super-hydrophilicity to super-hydrophobicity [45]. This chapter also addresses some important questions for the morphology evolution of Ti anodization, and displays several novel hierarchical structures.

Chapter 5 describes black oxygen-deficient TiO$_{2-x}$ synthesized by anodization technique for the first time [46]. The obtained oxide exhibits ultrahigh visible-light absorption and photocatalytic activity under visible light. This finding may indicate a potential breakthrough in defective TiO$_{2-x}$ synthesis and TiO$_2$-based photocatalysis.

TiO$_2$ is not a conventional microwave absorbing material due to its poor absorption of electromagnetic energy. In Chapter 6, amorphous TiO$_{2-x}$ synthesized via Ti anodization is partially crystalized, which displays strong microwave absorption [47]. Interfacial electric field forms at the boundary of crystalline-amorphous phases due to the uneven oxygen-vacancy distributions in the two phases, which amplifies the absorption of microwave.

Chapter 7 summarizes the results in this thesis and their contributions to Ti anodization and the related applications. Planned work for the future development of this study is also displayed in this chapter.
CHAPTER 2

Nanostructured TiO$_2$ Synthesized by Anodization

CHAPTER ABSTRACT

TiO$_2$ nanotubes have wide applications due to their large surface area and special material properties. A comprehensive understanding of the Ti anodization process is required to precisely tailor the oxide nanostructure for specific applications. In the present work, the gradually decreasing thickness of nanotube-wall was displayed, and the evolution of nanotubes during the anodization process was investigated. With the extended time of anodization, the top part of the nanotubes was chemically corroded to thin walls and broke down to fine nanowires, which is the result of dynamic competition between oxidation and chemical dissolution. A simple physical model of Ti anodization was proposed for understanding the nanostructure of anodized TiO$_2$.

Graphical Abstract

2.1 Introduction

Self-organized oxide layers formed by metal anodization have recently attracted considerable interest in materials science and technology. Particularly, highly ordered TiO$_2$ nanotubes formed under optimized electrochemical treatment show good mechanical adhesion and electrical conductivity. The dimensions of nanotubes can be controlled by the anodization conditions. Due to the large surface area and special electrical and chemical properties, TiO$_2$ nanotube arrays are considered to have wide applications such as water-splitting, photo-degradation, sterilization, membranes, and solar cells.

As the morphology is essential to its properties, TiO$_2$ structures with controllable length and diameters have been extensively investigated [48]. However, little research has been carried out on the decreasing thickness of tube-wall and the evolution of the anodized nanostructure. A better understanding of the anodization mechanism is needed to control the morphology and properties of anodized nanostructures.

In this chapter, we presented a facile method for generating TiO$_2$ hybrid nanostructures of nanotube-nanowire via anodization technique with ample reaction time. A physical model is
also proposed for the observed gradual evolution of TiO$_2$ nanotubes into nanowires, based on the dynamic equilibrium between the oxidation of Ti metal and dissolution of Ti oxide during anodization.

### 2.2 Experimental section

Titanium (Ti) sheets (99.6% purity) with a 0.5 mm thickness were prepared as the substrate. The surface of the Ti samples was mechanically ground and polished to a mirror-smooth surface by 3 micro diamond powder suspension. After degreasing ultrasonically in acetone, ethanol and distilled water, the anodization process was performed in a two-electrode electrochemical cell. The prepared substrate was used as the anode, and a platinum (Pt) foil served as the cathode. The substrate with a rectangle-shaped 1 cm$^2$ surface area was exposed to electrolyte, and the distance between the anode and cathode was kept at 2 cm.

The anodizing process was carried out under a voltage of 60 V for 20 hours in electrolyte of 150 ml ethylene glycol containing 0.25 wt.% NH$_4$F and 2 vol.% distilled water. In order to avoid cracks in the oxide layer, the anodized samples were immersed in ethanol at 30°C for 48 hours to remove the organic electrolyte and to release the possible inner stress due to the volume expansion from the formation of oxide. The samples were then cleaned ultrasonically in a clean ethanol solution for 2 minutes [49]. For comparison, some samples were cleaned gently with ethanol, not by ultrasonic cleaner. Microstructure and morphology observations of specimens were performed on a field-emission scanning electron microscope (FEI Quanta 200F ESEM).

### 2.3 Results and discussions

The evolution of anodized TiO$_2$ nanostructure is schematically shown in Figure 2.1a. The middle part of the structure are highly arrayed nanotubes (Figure 2.1b), showing the ordered nanotubes changing to the disordered nanowires as the top layer (Figure 2.1c). Figures 2.1d-e illustrate the top views of surface morphologies before and after ultrasonic cleaning, respectively. Before the ultrasonication, a layer of randomly oriented nanowires was retained on the top surface of the anodized sample (Figure 2.1d). After the ultrasonic cleaning and the layer of nanowires removed, a highly oriented nanotubes array with open top appeared (Figure 2.1e), indicating that a long-time anodization produced a hybrid nanostructure with nanowires on the top and nanotubes at the bottom.

It is known that the formation of oxide products during anodization is a dynamic process of competition between oxidation of metal and dissolution of oxide. The three essential processes along anodization are:

(i) Field-assisted oxidation at the metal/oxide interface;
(ii) Metal ion migration from metal to metal/oxide interface;

(iii) Field-assisted dissolution of oxide at the barrier layer/electrolyte interface.

Figure 2.1 Schematic diagram (a) for the growth of anodized TiO2; SEM images for the cross-section views of anodized oxide layer at the middle (b) and up (c) parts; Top views of anodized oxide layer before (d) and after (e) ultrasonic cleaning.

As anodization starts, oxidation takes place at the metal/electrolyte interface, forming an oxide barrier layer (Eq. 2.1) [50]. Corrosion pits occur and then develop into the uniform porous structure, due to the combined effects of oxidation, field-assisted reaction and chemical dissolution. As the pits grow, nanotubes are formed and exposed to the electrolyte containing $F^-$ ions. Negatively charged $F^-$ ions are attracted and accumulate around the anode due to the positive electric field. These mobile $F^-$ ions attack and interact with the oxide (Eq.2.2).

$$\text{Ti} + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2 + 2\text{H}_2 \quad \text{Eq.2.1}$$

$$\text{TiO}_2 + 6F^- + 4H^+ \rightarrow \text{TiF}_6^{2-} + 2\text{H}_2 \quad \text{Eq.2.2}$$

After a long time exposure to electrolyte, these nanotubes were corroded gradually into nanowires, and finally dissolved into the electrolyte. Nanotubes are compactly packed, and only the inside walls were exposed to the electrolyte. Hence the inside tube-walls are chemically dissolved. The inside diameter of tubes gradually increases towards the apex, due to the longer
time exposure of the inside tube-wall to electrolyte, as illustrated in Figure 2.2a.

Figure 2.2 Schematic diagram for the gradual decrease of tube-wall thickness along nanotube’s axis (a); the different positions for the fine nanowires at the tip (b), regular nanotubes at the middle (c) and bottom (d) parts of the hybrid nanostructure.

This assumption was verified by images at different positions of nanotubes. At the apex region, nanotubes were corroded into the fine nanowires (Figure 2.2b). After removing the nanowires, nanotubes were displayed with an inside diameter of around 125 nm (Figure 2.2c). The bottom of the nanotubes was shown after nanotubes were rived, where the inside diameter decreased to around 70 nm (Figure 2.2d). However, the outside diameters of the tubes remained the same, approximately 150 nm, indicating that the chemical dissolution of oxide only takes place at the inside tube-wall. Therefore the inside diameters of tubes increased gradually towards apex of nanotubes.

During the anodizing process, metal is corroded, with oxide growing into the metal substrate. For the Ti anodization process, oxidation occurs at the metal/oxide interface, and the chemical dissolution of oxide takes place at the nanotubes/electrolyte interface. Taking one single nanotube for example, the upper region of the tube has been exposed to the electrolyte for a longer time than the lower parts, and the bottom of the nanotubes is just produced, and suffers little chemical corrosion. Hence the thickness of tube-wall at the top is the thinnest. With ample time of anodization, the top parts of the nanotubes are corroded into thin walls, break down to fine nanowires, and finally consumed, at which point the nanotubes stop growing.
Figure 2.3 Dimensions of nanotubes generated under different voltages, including outside diameters and thickness of the tube-wall (a), schematic diagram for the proposed physical model of the relationship among the chemical dissolution rate \( r_{\text{oxid}} \), the corrosion rate \( r_{\text{corr}} \) as well as the maximum length \( L_{\text{max}} \) and thickness \( d \) (b).

Nanotubes morphology is a function of applied voltage [51], with TiO\(_2\) nanotubes generated via anodization for 2 hours verifying the effect of voltage. The outside diameter of the anodized tubes increased with increasing applied voltage. The thickness of the tube-wall at the top of the nanotubes remained almost same, at approximately 12 nm (Figure 2.3a), indicating that the chemical dissolution in the electrolyte is not affected by the applied voltage or the growth rate of the anodizing products. There is a maximum length of nanotubes for each applied voltage as the oxidation and dissolution processes can reach a balance, where further exposure does not have a significant difference.

Nanotubes are formed due to the dynamic competition between oxidation and chemical dissolution. The oxide generated at the metal/oxide interface finally moves to the apex of nanotubes (Figure 2.3b), and the duration time \( t \) for this process can be expressed as:

\[
t = L_{\text{max}}/r_{\text{oxid}}
\]

Eq. 2.3

Oxide exposed to the corrosive electrolyte is completely dissolved at the top. Ignoring the thickness of the barrier layer, the relationship between the corrosion rate \( r_{\text{corr}} \) and duration time is:

\[
d = t r_{\text{corr}}
\]

Eq. 2.4

These two relationships can be combined as Eq.1.5, where \( d \) is the thickness of the newly generated tube-wall, \( r_{\text{oxid}} \) is the rate of oxidation at the metal/oxide interface, and \( r_{\text{corr}} \) is the rate of chemical dissolution. \( d \) is decided by temperature [52], \( r_{\text{oxid}} \) and the outside diameter are correlated with the applied voltage, and \( r_{\text{corr}} \) depends on the composition of the electrolyte. Overall, the maximum length of the nanotube is determined by the relationship of the temperature, applied voltage and electrolyte.

\[
L_{\text{max}} = (d r_{\text{oxid}})/(r_{\text{corr}})
\]

Eq.2.5
2.4 Conclusions

This chapter studies the anodization process of Ti metal. It demonstrates experimentally that the inside diameter of nanotubes gradually increases towards the tube apex due to the longer time dissolution of the inside tube-wall. When the dynamic balance between oxidation and chemical dissolution is reached, nanowires form at the top region. The physical model for the formation of TiO$_2$ nanowires and the changing thickness of tube-wall has been proposed, which may also explain the relationship of the maximum length of nanotubes with the anodization processing parameters.
CHAPTER 3

Superhydrophobic Surface of Nanostructured TiO$_2$

CHAPTER ABSTRACT

Superhydrophobic properties of solid surfaces have attracted considerable interest due to its scientific and technological significance. This work studies the formation of a superhydrophobic surface by Ti anodization. A hierarchical structure of TiO$_2$ with disordered nanowires on top of regular nanotubes was fabricated. With organic monolayers, this morphology showed stronger superhydrophobic properties than regular nanotubes. After partially removing the dense nanowires, the surface roughness was increased, resulting in a water contact angle of 172°. The potential application for aquatic devices was explored by a treated Ti mesh, which showed strong and long-time floating stability.

3.1 Introduction

Wettability is one of the most important properties of a solid surface, which is ascribed to the cooperation of surface structures and chemistry [53]. This property is conventionally quantified by a liquid contact angle (CA) by the Young equation. Recently, superhydrophobic surfaces have generated considerable interest in the scientific and technological fields of nanotechnology. With a water CA greater than 150°, superhydrophobic surfaces play an important role in biological systems, chemical industries, military applications and other fields. Superhydrophobic surfaces are commonly fabricated by modifying surface energy and adjusting surface microstructures, such as those on lotus leaves [54]. Several approaches using organic monolayers have already been proposed to tailor the wettability of solid materials.

Titanium (Ti) has been widely used in biocompatible materials, aeronautical materials, chemical equipment, and in many other niche applications for its superior physical and chemical...
performance. Therefore, alteration and control of the surface topography and wetting property of Ti is of great interest for many applications as smart surface materials [55]. In 2005, P. Schmuki et al. first modified the anodized TiO$_2$ with organic molecules, and showed the superhydrophobic properties [56]. He also presented that the wetting properties can be adjusted up to 159°C by increasing the nanotubes’ diameter [57].

According to our previous results involving TiO$_2$ nanotube evolution, tubular TiO$_2$ formed on a Ti substrate and the tip region was etched to disordered nanowires, forming a hierarchical structure with a vast surface area and toughness [23]. This hybrid topography is similar to water striders’ legs covered with superhydrophobic setae, which enable them to stand effortlessly and move quickly on the surface of water. It is known that surface roughness can act as an amplifier for surface wettability and non-wettability. In this work, we have investigated the hydrophobic properties of the hierarchical structure of TiO$_2$ modified with organic self-assembled monolayers, and explore the potential application of this TiO$_2$ topography in the aquatic area.

### 3.2 Experimental section

#### 3.2.1 Anodization processes for material preparation

To fabricate hierarchically nanostructured TiO$_2$, Ti substrates were electrochemically anodized under specified conditions for 10 hours. Ti foils (1 mm thickness, 99.96% purity) were first mechanically ground and polished, ultrasonically cleaned in acetone, methanol, and deionized water, followed by drying in a nitrogen stream. The prepared substrates were used as the anode, and a platinum foil served as the cathode with a distance of 2 cm from the anode. Square-shaped Ti foils (1 × 1 cm) were exposed to the electrolyte. The anodizing reaction was performed in a two-electrode electrochemical cell under a voltage of 60 V for 10 hours in an electrolyte of 150 ml ethylene glycol (95%, ECP Ltd) containing 0.25 wt.% NH$_4$F (98%, Sigma-Aldrich) and 2 vol.% distilled water. To avoid cavities in the TiO$_2$, the as-prepared samples were kept in ethanol at 30°C for 48 hours to clean the organic electrolyte and eliminate inner stress caused by the generation of oxide. Thermal annealing was performed in ambient air up to 450°C for 2 hours under a heating and cooling rate of 20 K/min.

#### 3.2.2 Surface organic modification

Before modifying porous oxide layers with organic molecules, specimens were exposed to UV light for 1 hour for surface cleaning. Following the procedures in previous investigations [56, 57], each sample was placed in a beaker with a 20 ml solution of an organic surface modifier, which is a toluene solution (99.6%, Scharlau) containing 50 µM octadecylphosphonic acid (C$_{18}$H$_{37}$PO(OH)$_2$) (97%, Sigma-Aldrich). Upon putting samples into the solution, the
beakers were kept in the dark at room temperature for 48 hours for the formation of an organic monolayer on the oxide surface. Specimens were then taken out and washed with toluene, acetone, and distilled water. Finally, they were dried under a nitrogen gas flow and kept in an oven at 70°C overnight.

3.2.3 Characterization of material properties

The surface morphology was studied by a field emission scanning electron microscope (FEI Quanta 200F ESEM). To investigate the wetting properties of the specimens, water contact angles were measured on a goniometer (KSV CAM-101) at room temperature with 3.5 μl water droplets and analyzed by the built-in program.

![Figure 3.1 Morphologies of nanotubes at the upper (a) and lower (b) positions; disordered nanowires (NW) (c); collapsed nanotubes (NWNT) (d); ordered nanotubes (NT) (e); the contact angles of oxide layers with different topographies after modified by organic monolayers (f).](image)

3.3 Results and discussions

It is known that the formation of TiO$_2$ nanotubes during anodization is a dynamic process involving two competing reactions, i.e. metal oxidation at the interface of the oxide/metal and chemical dissolution of the oxide at the oxide/electrolyte interface. When the reaction started, oxidation took place at the Ti surface and formed an oxide layer. Corrosion pits occurred and gradually evolved to compactly packed nanotubes, leaving the inside tube-wall exposed to the corrosive electrolyte. The upper region of nanotubes was exposed to the electrolyte for a longer
time than the lower parts, and the root of the generated nanotubes only contact the electrolyte for a short time with little chemical dissolution. Therefore, the thickness of tubes-wall was thinner at the upper part, and the inside diameter gradually increased towards the tip (Figures 3.1a and 3.1b). With ample time exposure to the electrolyte, the top parts of nanotubes were corroded into thin walls, broken down to fine nanowires, and then consumed entirely, at which point the nanotubes stopped growing.

Hierarchical TiO$_2$ nanostructure was fabricated by Ti anodization. In order to optimize the hydrophobic performance after organic modification, the resulting oxide was sintered at 450°C for 2 hours to transform to anatase from the amorphous phase. With controlled ultrasonic treatment, the top layer of disordered nanowires (NW) (Figure 3.1c) was completely removed, and the regular-shaped nanotubes were exposed from underneath (NT) (Figure 3.1e).

Water contact experiments indicated that without applying any organic monolayer, compact TiO$_2$ film is generally hydrophilic with a water contact angle ranging from 0° to 54°, depending on the dark/UV treatment [58]. In our case, all specimens of different morphologies were extremely hydrophilic. The water contact angle of porous TiO$_2$ remained at near-zero even without UV treatment, due to the high surface energy and increased surface roughness. The wettability was significantly enhanced for the porous layer due to the increase in contact area between water and TiO$_2$. The lower part of tubular structure could also further enhance its wettability by the capillary effect, which pulled water into the pores.

In order to alter the surface properties, octadecylphosphonic acid was used to the prepared TiO$_2$ to lower the surface energy while maintaining the surface microstructure. After surface modification with octadecylphosphonic acid, phosphonic acid molecules form on TiO$_2$ surface. It has an unpolar organic hydrophobic alkyl chain, which can change TiO$_2$ surface wettability. Its wettability changed remarkably with the self-assembled monolayer. Its original hydrophilic surfaces became superhydrophobic. As a reference, compact TiO$_2$ film prepared by sintering the polished Ti sheet at 450°C showed a water contact angle of 88.5 ± 1.3° after organic modification. Disordered nanowires displayed a water contact angle of 167 ± 1.3°, and for tubular TiO$_2$, it was 163 ± 1.3° (Figure 3.1e). It is believed that the anodized TiO$_2$ nanostructures predominantly contributed to the high surface hydrophobicity.

Another interesting result was seen after the specimens with hierarchical TiO$_2$ nanostructures were treated gently with ultrasonic waves in distilled water, causing the collapsed TiO$_2$ nanotubes to be exposed (NWNT) (Figure 3.1d), with its CA further increased to 172.4 ± 1.3°. However, continued ultrasonic treatment depressed its CA to 168 ± 1.3°, and finally to 163 ± 1.3°, the same CA level as the regular nanotubes. On the other hand, ultrasonic
treatment had no significant effect on the CA of the modified compact TiO$_2$ film.

Figure 3.2 Topographies of anodized TiO$_2$: before (a, c) and after (b) controlled ultrasonic treatment; tubular structure (d); structure transformation from NW to NWNT, and finally to NT (e).

The gradual changes of CA (Figure 3.1e) revealed that with a given surface energy, the surface wettability of hierarchical TiO$_2$ is affected by their topographies. A scheme was proposed to illustrate the CA change due to the TiO$_2$ topographies adjusted by ultrasonic treatment. Compared with hierarchical structures, the surface roughness of tubular oxide (Figure 3.2d) may be insufficient due to the tubular morphology. The additional nanowires on the nanotubes can also increase its surface area and roughness.

It can be seen that there was a compact nanowire layer covering the collapsed nanotubes of the lower part (Figures 3.2a and 3.2c). With gentle ultrasonic treatment, the compact nanowire layer was removed, revealing the lower collapsed nanotubes (Figure 3.2b). More air was trapped inside the porous structure, which reduced the actual contact area between water and TiO$_2$. Therefore, the surface exhibited higher hydrophobicity.

With organic molecule modification, TiO$_2$ nanotubes showed superhydrophobic behaviour, and its water contact angle generally increased with an increasing pore size [57]. In this work, our above results illustrated that hierarchical structure with additional nanowires
formed at the tip segment of tubular oxide displayed stronger hydrophobicity, and its hydrophobicity was further enhanced by removing the dense nanowire layer.

Figure 3. Ti mesh in water: the modified Ti mesh holding water drops (a) and floating in water (b); the mesh floating stably with some parts being forced into water (c), and keeping dry under water (d); poured water permeating down directly (e); and water drop kept on the floating mesh (f). The inserts are schematics showing the water-air positions.

Surface hydrophobicity is an important property for many practical applications, including reaction containers and pipelines, surfaces of electronic and optical devices, the surface of glasses and building materials, and water-floating devices. For instance, the maximum floating force grows continuously with increasing surface hydrophobicity. Because the ions generated during the anodizing process can diffuse freely to any direction, the present method is applicable to any materials regardless of shape or size.

Following the experimental procedures shown above, a Ti mesh (3×1.5 mm cavity size, 3 mm thickness) was used to explore the potential application of this technology as a floating unit in aquatic field. Without modification, the Ti mesh was highly wettable, and it sunk
instantly into water. After anodizing treatment and organic modification, the original wettable surface transformed to a superhydrophobic surface. Due to water surface tension and the superhydrophobic surface, water can be held by the mesh (Figure 3.3a). Because of the low flow resistance between water and mesh surface, water drops aggregated immediately on the Ti mesh driven by the tendency of surface energy minimization.

As shown in Figure 3.3, we tested the superhydrophobic Ti mesh with water. With the mesh floating on water, the water surface behaved like an elastic film with indentations caused by the mesh’s edges (Figure 3.3b). The floating capacity comes from water surface tension surrounding the mesh, and the maximum supporting force for floating specimens depends on the volume of the water dimple [59]. The mesh kept floating even with some parts being immersed in water (Figure 3.3c). Entrapped air was observed around the immersed part, which contributed to its floating stability (Figure 3.3d). After removing the pressing force, it recovered to the original state without any wetted area.

In another test, water was poured on the mesh from above, and it directly permeated downwards through the cavities of the Ti mesh (Figure 3.3e). This is due to the impact of poured water from a certain height exceeding the critical pressure. With a reduced pouring height, the mesh could stop water from flowing downward, and air was trapped in the mesh between the upper and lower water layers (Figure 3.3f).

Assuming the cavity is in a cylindrical shape, the minimum pressure intensity (P_{min}) to push water into the hole is:

\[ P_{\text{min}} = \frac{2a \cos(\pi - \theta)}{r} \]  
\[ \text{Eq.3.1} \]

where \( a \) is surface tension, \( r \) is radius, and \( \theta \) is contact angle.

In Figure 3.3e, the force of poured water exceeded \( P_{\text{min}} \), thus water passed through the mesh. When water was poured from a lower level, the mesh stopped water flowing downward. The critical pouring height \( h \) is:

\[ h = \frac{P_{\text{min}}}{\rho g} \]  
\[ \text{Eq.3.2} \]

where \( \rho \) is water density, and \( g \) is gravity constant.

The modified mesh displayed the above floating performances again after two months of fabrication. The Ti mesh treated by this method exhibited good floating stability due to the superhydrophobic surface and mesh structure.

3.4 Conclusions

TiO_{2} hierarchical nanostructures fabricated by electrochemical anodization exhibited superhydrophobic properties after being modified with organic molecules. The nanowires layer
on the top of the tubular structure could strengthen its non-wetting performance. With a controlled treatment to remove the compact nanowires, more air can be trapped inside the hybrid structure, resulting in enhanced superhydrophobic properties.

The potential application of this technology in aquatic devices was demonstrated by the modified Ti mesh, which showed striking floating stability on water. Moreover, the air entrapped around the mesh contributed to its floating stability, and can also reduce the fluidic drag force and fluid resistance.
CHAPTER 4

Morphology Evolution of TiO$_2$ Nanotubes, and Tailoring the Surface Wettability

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CHAPTER ABSTRACT

Alteration of anodized TiO$_2$ topography is of great interest for their applications as smart materials. While a number of excellent works focus on their growth conditions and exploiting applications, relatively little work deals with questions about the origin of morphology evolution in Ti anodization. This work revealed that anodized voltage actually determined the pattern of etching pits, which in turn governed the nanotube diameter and hexagonal features. Novel hierarchical topographies with controlled nanopores underneath the hexagonal porous layer were obtained by two-step anodization. With these designed microstructures, the surface wettability of anodized TiO$_2$ was well tuned from superhydrophilicity to superhydrophobicity.

![Graphical Abstract](image)

4.1 Introduction

Over the past decade, vertically oriented TiO$_2$ nanotubes synthesized by Ti anodization have attracted wide scientific and technological interest due to the potential applications in energy conversion and storage, photocatalysis, membranes, and sensors. Ti anodization as a surface treatment technique can also improve surface biocompatibility and control wettability. The properties are profoundly affected by microstructures and morphologies [60, 61]. Alteration of anodized TiO$_2$ topography and properties is of great interest for their applications as smart materials.

The microstructures of anodized TiO$_2$ should ideally be tailored at the nanoscale to optimize properties to suit various applications. A crucial step toward this goal is a better understanding of the formation mechanisms and how to control the morphology evolution. While a number of excellent works focus on growth conditions and exploiting applications,
relatively little work deals with the questions about the origin of morphology evolution in Ti anodization, including: (1) the reason for the applied voltage dictating the tube diameter is still unclear; (2) the formation mechanism for the hexagonal nanotubes is still unclear; and (3) how to better tailor the microstructures of anodized TiO$_2$ via Ti anodization.

It is thus the goal of this work to address these points. We revealed that anodized voltage actually determined the pattern of etching pits, which in turn governed the nanotube diameter and hexagonal features. Novel hierarchical topographies with controlled nanopores underneath the hexagonal porous layer were obtained by two-step anodization. With these designed microstructures, the surface wettability of anodized TiO$_2$ was well tuned from superhydrophilicity to superhydrophobicity.

4.2 Experimental Section

4.2.1 Anodization Processes for Material Preparation

Titanium sheets (99.96%, 0.5 mm thick) were ground and polished to remove the oxide film. After ultrasonically degreased in acetone, methanol, and deionized water, the Ti substrates were dried in nitrogen, and used as the anode. A platinum foil served as the cathode with a distance of 2 cm from the anode. Square-shaped Ti foils (1 x 1 cm) were exposed to the electrolyte. Anodization was performed in 150 ml ethylene glycol (99.8%, Sigma-Aldrich) containing 0.25 wt.% NH$_4$F (98%, Sigma-Aldrich) and 2 vol.% deionized water at a voltage under 60 V with controlled time intervals. To avoid cavities in TiO$_2$, the as-prepared samples were kept in ethanol at 30°C for 48 hours to remove the organic electrolyte and eliminate inner stress caused by the generation of oxide. The resultant oxide was rinsed with methanol and dried in air. To fabricate the hierarchically topographies, the as-anodized specimens were ultrasonically cleaned to strip off the oxide layer, and then subjected to a second anodization under 20 V, 30 V, 40 V and 50 V for 30 min.

4.2.2 Surface organic modification

Specimens were annealed in ambient air at 450°C for 1 hour with a 20 K/min heating rate. As a reference, the compact TiO$_2$ film was prepared by sintering the polished Ti sheet at 450°C for 1 hour. Before modifying the oxide layers with organic molecules, specimens were exposed to UV light for 1 hour for surface cleaning. Each sample was placed in a beaker with a 20 ml solution of an organic surface modifier which is a toluene solution (99.6%, Scharlau) containing 50 µM octadecylphosphonic acid (C$_{18}$H$_{37}$PO(OH)$_2$) (97%, Sigma-Aldrich). Upon putting samples into the solution, the beakers were kept in dark at room temperature for 48 hours. Specimens were then taken out, and washed with toluene, acetone, and distilled water. Finally, they were dried under a nitrogen gas flow and kept in an oven at 70°C overnight.
4.2.3 Characterization of Material properties

Morphological analyses of specimens were performed on a field-emission scanning electron microscope (FEI Quanta 200F ESEM). The cross-sectional morphologies of nanotubes along their depth were viewed at the fracture part. The transmission electron microscopy (HRTEM) was taken on the Tecnai TF20 TEM. TiO$_2$ nanotubes were dispersed in ethanol by ultrasound treatment, and then loaded by copper discs for TEM characterization. The elemental composition was measured by Kratos Axis UltraDLD X-ray Photoelectron Spectrometer (XPS). To test the wetting properties, equilibrium contact angles were measured on a goniometer (KSV CAM-101) at room temperature with 3.5 μL water droplets and analyzed by the built-in program.

![Figure 4.1](image)

Figure 4.1 Electrochemical etching pits (a-c), and morphology evolution with anodizing time (d-f).

4.3 Results and discussion

4.3.1 Microstructure evolution and mechanisms

Electrochemical etching pits were obtained after 5 minutes of anodization under different voltages. They all appeared as similar nanopores of ~10 nm (Figures 1a-c). However, the density of the etching pits gradually decreased from 20 to 60 V. This may be attributed to the
greater thickness of passive oxide film that initially formed on Ti substrate as the voltage was increased [62]. The thick passive film can depress the formation of penetrating etching pits, which exposes fresh Ti underneath to the electrolyte for further reactions. Hence, high voltages resulted in lower levels of etching pit formation.

Anodized TiO$_2$ fabricated under 60V was examined here to study the morphology evolution. After a 1.5 hour reaction, a porous surface with pore sizes in the range of 40–80 nm formed on the Ti substrate (Figure 4.1d). The porous oxide evolved into a hierarchical structure after 3.5 hours, with pore sizes increasing to 70–140 nm (Figure 4.1e) and cracks appearing on the porous layer with disordered nanowires underneath (Figure 4.1e inset). As the reaction time was prolonged to 6.5 hours, the porous layer became partially consumed by the electrolyte, and disordered nanowires were visible from the surface (Figure 4.1f). As shown in Figure 4.1f inset, these disordered nanowires were formed by collapsed nanotubes on the tip.

The observations related the different corrosion resistance of the passive-oxide-film formed in the initial stage of anodization versus the amorphous titanium oxide generated underneath (Figure 4.2) [63]. A passive oxide film was developed on the Ti substrate upon applied voltage, which had a high corrosion resistance. The passive film was then electrochemically etched and eventually penetrated through, forming the porous topography. The chemical dissolution continually progressed downward with the simultaneous generation of amorphous oxide at the metal/oxide interface [24]. The upper segment of the tubes were exposed to the corrosive electrolyte for a longer period of time compared to the newly formed oxide at the root segment. As a result, a higher degree of chemical dissolution occurred at the upper segment of the anodized tubular structure. Meanwhile, the passive oxide layer maintained its porous structure during the early stages of anodization. As the reaction progressed, the nanotubes underneath started to collapse and were gradually etched into disordered nanowires, forming the hierarchical structure as shown in Figure 4.1f.

After removing the disordered nanowires on top, circular-shaped nanotubes with ca. 10 nm wall thicknesses and ca. 140 nm inner diameters were exposed, which are typical at the upper part of these nanotubes (Figure 4.3a). The middle part was exposed after the nanotubes were sectioned. The wall thickness increased to ca. 40 nm and the inner diameter reduced to ca. 90 nm (Fig. 4.3b). The root segment showed compactly packed hexagonal nanotubes with the inner diameter further reduced to ca. 60 nm and an increased wall thickness of ca. 60 nm (Figure 4.3c). By stripping the nanotubes, Ti substrate was exposed which showed a hexagonal-dimpled morphology that matched with the bottom morphology of the nanotubes (Figure 4.3d and f). Interestingly, regular ridge-shaped morphology was visible on the outer walls of these
hexagonal nanotubes at the root segment (Figure 4.3e), while the circular-shaped nanotubes at the upper segment appeared to have relatively smooth walls (Figure 4.3e inset).

Figure 4.2 SEM (left) and HRTEM (right) images of amorphous oxide

Chemical dissolution accounted for the changing morphology of TiO$_2$ nanotubes along the depth direction. Newly generated nanotubes were closely packed, leaving their inner walls exposed to the corrosive electrolyte. The upper tubes were exposed to the electrolyte for a longer period, where tube walls suffered more etching. This is evidenced by the observation that the wall thickness of these nanotubes decreased from ca. 60 nm at the root region to ca. 10 nm at the tip region. Driven by the electrical force, negatively charged F$^-$ ions accumulated among the nanoridges, and smoothen the tubes into circular shapes.
Figure 4.3 Cross-sectional morphologies of TiO$_2$ nanotubes fabricated under 60 V along their depth (a-d); (e) Outer walls of TiO$_2$ nanotubes at root and upper segments; (f) Ti substrate after removing nanotubes; (g) Irregularities of the hexagonal bottom; TiO$_2$ nanotubes fabricated under 20 V (h) and 40 V (i).
Figure 4.4 Surface nanostructure of TiO$_2$ formed on the dimpled Ti substrates at controlled voltages.

The etching pits helped to explain the formation of hexagonal root of nanotubes. Upon starting anodization, etching pits formed randomly and developed until they encountered each other, forming the hexagonal boundaries. Negatively charged F$^-$ ions were attracted into the etching pits and etched downward into Ti substrate, forming the hexagonally tubular feature. This evolution mechanism also explained the irregularities seen on the hexagonal roots of TiO$_2$ nanotubes, owing to the uneven distributed etching pits (Figure 4.3g). The density of the etching pits approximately matched the nanotubes fabricated under different voltages (Figures 4.1a-c, 4.3a, h and i). This confirmed that anodizing voltage dictated the density of etching pits, which in turn governed the diameter of TiO$_2$ nanotubes.

With the above understanding on voltage, hexagonal-dimpled Ti substrates were subjected to electrochemical etching under 20V, 30V, 40V, and 50V for 30 minutes. Novel hierarchical topographies with controlled nanopores underneath the hexagonal porous layer were obtained (Figure 4.4). Under high voltage, sparse etching pits formed and developed larger and deeper inside the hexagonal dimples [64], which was in agreement with our above conclusions.
Figure 4.5 Left: Water contact angles measured on anodized TiO2 nanostructures. Right: Schematics for the nanostructures: Sample 1, Compact TiO2 film; Sample 2, Ti substrate after removing TiO2 nanotubes on top (Figure 2g); Samples 3–6, hierarchical TiO2 nanostructures (Figures 3a–3d); Sample 7, intact TiO2 nanotubes (Figure 1d); Sample 8, collapsed nanotubes (Figure 1c inset).

4.3.2 Tuning surface wettability

These designed microstructures provided a convenient case to evaluate the effect of surface morphology on wettability (Figure 4.5). With no organic modification, the compact TiO2 film was moderately hydrophilic with a 54° CA, and the dimpled Ti substrate displayed a similar CA of 44°. Surface wettability improved notably in hierarchical structures with larger and deeper inner nanopores, which displayed CAs from 22° to near-zero. Both the intact and collapsed TiO2 nanotubes displayed superhydrophilicity on their surfaces. Clearly the microstructures decided the surface hydrophilicity, which was significantly enhanced with the increasing contact area between the water and TiO2. The large porosity underneath further enhanced the wettability by capillary effects [57].

To lower surface energy, octadecylphosphonic acid monolayers were incorporated onto the oxide layer while maintaining the nanostructures. The modified compact TiO2 layer showed a CA of 88°, and the dimpled Ti substrate showed a CA of 115°. The surface hydrophobicity of the four hierarchical nanostructures fabricated increased steadily from 122° to 157°. Intact TiO2 nanotubes displayed a CA of 163°, and the collapsed nanotubes displayed the highest CA at 172° [44]. These microstructures are schemed in Figure 4.5, with increased roughness from Sample 1 to Samples 8. Surface roughness acted as an amplifier for surface non-wettability, which was quantified by the vertical deviations of the real surface from the ideal flat form [65-67].
4.4 Conclusions

In summary, we examined the morphology evolution of anodized TiO$_2$, and revealed that applied voltage determined the pattern of etching pits, which in turn governed the anodized TiO$_2$, including the tube diameter and hexagonal features. The chemical dissolution shaped the hexagonal root to circular tubes at the upper segment. Novel hierarchical topographies, with controlled nanopores inside the hexagonal dimples, were obtained by electrochemical etching the dimpled Ti substrates. The surface wettability was tuned from superhydrophilicity to superhydrophobicity by tailoring the microstructure.
CHAPTER 5
Defective Black TiO$_2$ for Visible Light Photocatalysis

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CHAPTER ABSTRACT

TiO$_2$ has been studied as one of the most promising technologies to address the energy and environmental challenges that we face today. A major hurdle in developing this technology is that TiO$_2$ only adsorbs UV light, which is approximately ~5% of solar radiation. In this part, black defective TiO$_{2-x}$ was synthesized via a facile anodization technique. Electron paramagnetic resonance provided evidence on the controllable levels of oxygen vacancy, which extended the photon-absorbance deeply into the visible light region. By stripping off the nanotubes on the top of anodized TiO$_2$ layer, a hexagonally dimpled layer of black TiO$_{2-x}$ was exposed and exhibited remarkable visible-light absorption and photocatalytic activity.

Graphical Abstract

5.1 Introduction

Self-organized titanium dioxide (TiO$_2$) layers formed by anodization has shown promising applications in water-splitting, photodegradation, sterilization, and solar cells; and has attracted substantial research interests for its robust mechanical adhesion and electrical conductivity. The shortcoming of TiO$_2$ is that it can only adsorb UV light, which is only ~5% of all solar radiation. Low absorbance of visible light severely limits its use of solar energy. In order to harvest more solar energy, there have been persistent efforts to alter anodized TiO$_2$ composition by doping elements to change its band gap, most notably, metal and non-metal doping [68-70]. An inherent limitation of this approach, however, is that the dopants introduced often act as charge carrier recombination centers, which compromise the photocatalytic activity of the materials [71]. Thus great attempts are being made to overcome this limitation by using other techniques.

Recently reported work has shown that, by introducing crystal defects into TiO$_2$, a new
vacancy band can be generated below its conduction band, expanding the photon-absorbance of TiO$_2$ into the visible light region without the recombination effect from doped impurities [72, 73]. Developing a simple and scalable anodization method for the synthesis of defective TiO$_2$ is therefore of particular interest [74, 75]. Herein we present a facile technique to synthesize oxygen vacancy (V$_{o}$)-doped TiO$_2$ with high visible-light-induced photocatalytic activity. Our experimental evidence highlights a layer of black, defective anodized TiO$_{2-x}$, which possesses remarkable capability to absorb energy of from full solar radiation spectrum. This process has not been reported in previous studies.

Figure 5.1 Experimental process and optical images of the stripped TiO$_2$ layer.

5.2 Experimental Section

5.2.1 Anodization Processes for Material Preparation

Titanium foils were ultrasonically degreased in acetone, ethanol, and distilled water, followed by drying in nitrogen stream. Using a two-step anodization method, an oxide layer was formed on the Ti foil. The first-stage anodization took 10 hours; and the as-anodized Ti foil was ultrasonically cleaned in distilled water to strip off the initial oxide layer. The foil was then subjected to a second stage of anodization for 10 h.

The anodizing reaction was performed in a two-electrode electrochemical cell. The anodized Ti foil was rinsed in ethanol and distilled water, dried at 150°C for completely removing organic species, and sintered at 450°C for 1 hour in an ambient atmosphere. The top oxide layer was removed from the bent sample. By the two-step anodization method, the anodized TiO$_2$ layer can be feasibly removed after sintering (Figure 5.1).
5.2.2 Characterization of Material properties

(1) The high-resolution transmission electron microscopy (HRTEM) was taken on FEI TF20 TEM.

(2) The X-ray diffraction spectra were acquired on a Bruker D2 Phaser X-ray diffractometer.

(3) Morphological analyses of specimens were performed on a field-emission scanning electron microscope (FEI Quanta 200F ESEM).

(4) Electron paramagnetic resonance spectra were recorded at room temperature on a Bruker ESP300e spectrometer under a microwave power of 6.36 mW with a frequency of 9.67 GHz. The magnetic field was calibrated using the g-value of Mn$^{2+}$ signal. Elemental data was collected using EDAX Phoenix EDS detector.

(5) Diffuse reflectance UV–Vis light spectra were measured on a JASCO V-650 UV-Vis Spectrophotometer equipped with a diffuse reflectance accessory kit.

(6) Fourier transform infrared spectroscopic (FTIR) analysis was performed on a JASCO FT/IR-6100 FTIR spectrometer using KBr disks.

(7) Photocatalytic degradation experiments were conducted in 6 mL solution with 2 mg/L RhB. Samples have a size of 2 × 2 cm. The concentration of RhB in each degraded solution was monitored by UV-Vis spectroscopy.

5.3 Results & discussions

ESEM images showed the tubular microstructure of the stripped oxide layer on the anodized Ti foil. The internal diameter is estimated to be 150–180 nm at the tip region, which decreased along the depth direction (Figures 5.2a-d). The homogeneous structure transformed to double-shelled tubes at the root segment after annealing, with the inner shell composed of nanoparticles (Figure 5.2e). These nanotubes are approximately 115 µm in length, giving a draw ratio of more than 660 (Figures 5.2f). The bottom of these nanotubes exhibit a hexagonal topography. Detailed topographies of the root segment are shown in the insets of Figure 4.3g. By removing these nanotubes on the top of the TiO$_2$ layer, a black oxide layer was exposed which covered the Ti substrate with a hexagonally dimpled morphology [76].

HRTEM micrograph and X-ray diffraction showed that the anodized TiO$_2$ was in pure anatase phase (Figures 5.3a), and exhibited a nano-crystal structure with the characteristic disorder surface layer (Figure 5.3b). The electron paramagnetic resonance (EPR) spectrum recorded at room temperature confirmed the significant presence of V$_o$ in the black TiO$_2$, with a strong signal at g = 2.003 induced by electrons trapped on V$_o$ (Figures 5.4a-d) [77-79]. Such
a signal was not observed in the EPR spectrum of commercial P25 TiO$_2$ (Figure 5.4e). The EPR spectra also indicated that there was no Ti$^{3+}$ present in the black TiO$_2$, as characterized by the absence of the signal at $g = 1.975$ [74].

Figure 5.2 Microstructures of as-anodized TiO$_2$ at different positions (a-d), and cross sections of the sintered TiO$_2$ nanotubes (e-f).
Figure 5.3 TEM images and XRD analysis of anodized TiO$_2$ after 450°C sintering.

Figure 5.4 EPR spectra of the anodized TiO$_{2-x}$ with different heat treatments: (a) before / after sintering; (b) sintering by putting sample in a pre-heated furnace / cold furnace which was heated from room temperature; (c) sintering in a cold furnace with 3K/20K heating speeds; (d) sintering in a pre-heated furnace for 30min / 60 min; (e) EPR spectra of commercial P25 TiO$_2$ and the anodized black TiO$_{2-x}$ before sintering.

Approximately 73% V$_o$ in anodized TiO$_{2-x}$ was consumed after directly sintering in a pre-heated furnace (Figure 4.3a). More V$_o$ was consumed after sintering in a cold furnace, which was heated from room temperature to 450°C (Figure 4.3b). It was interesting to find that the concentration of oxygen-vacancy C(V$_o$) stayed constant when annealing at different times or at different heating speeds (Figure 4.3c-d). This may be ascribed to the presence of an initially formed crystalline layer outside, which prevented the inside V$_o$ from oxidation by O$_2$ in the air.
The presence of $V_{o}$ in anodized TiO$_{2-x}$ can be explained by the oxide formation mechanisms. During anodization, the formation of TiO$_2$ is a dynamic process involving oxidation at the oxide/metal interface and chemical dissolution at the oxide/electrolyte interface. In the oxidation process, water molecules from the electrolyte solution acted as the oxygen source. The diffusion of electroneutral water molecules was relatively difficult, hindered by the large draw ratio of the nanotubes grown on top [21, 49]. As a result, the oxidation process suffered from the insufficient supply of oxygen. $V_{o}$ and Ti$^{3+}$ may be produced simultaneously at the oxide/metal interface. At the same time, negatively charged $F^-$ ions were attracted to the anode by the electric field, and consumed the generated Ti$^{3+}$ ions as they were more active and vulnerable to chemical dissolution. Also, $F^-$ ions were found in all prepared samples. It was thus proved that there were sufficient $F^-$ ions to consume Ti$^{3+}$ ions. Therefore, a defective, non-
stoichiometric titanium oxide (TiO$_{2-x}$) layer was formed on the Ti substrate with rich oxygen vacancies.

Infrared spectroscopy analysis shows no difference in the anodized TiO$_{2-x}$ chemical structure compared to the intact TiO$_2$ (Figure 5.5). However, the diffuse reflectance UV-Vis spectrum of TiO$_{2-x}$ exhibited ultrahigh absorbance over the full visible light region (400-800 nm), twice as much absorbance of the previously reported TiO$_{2-x}$, which was reduced by H$_2$ (HP-TiO$_{2-x}$) (Figure 5.6) [73, 80]. A steep increase in light absorbance is observed in all samples at wavelengths below 400 nm, and the photon absorbance of TiO$_{2-x}$ significantly extends into longer wavelengths, maintaining a high level of absorbance throughout the entire visible light region. The black TiO$_{2-x}$ layer also showed dramatically higher visible-light absorbance than the tubular TiO$_2$ grown on top.

Photocatalytic activity of the anodized black TiO$_{2-x}$ was assessed by monitoring the degradation of Rhodamine B (RhB, a model organic dye) in water under blue light irradiation (400–500 nm) (Figure 5.7). TiO$_{2-x}$, which sintered in a pre-heated furnace containing high C(V$\text{O}$), initiated rapid degradation of RhB in water, with ~80% RhB degraded after a 4 hour reaction. In contrast, TiO$_{2-x}$ of low C(V$\text{O}$) degraded ~60% RhB within 4 h. This shows that high C(V$\text{O}$) could strengthen the photocatalytic properties under visible light. The photocatalytic result indicated that the post-annealed TiO$_{2-x}$ failed to reduce RhB, which confirmed the above hypothesis: V$\text{O}$ was exposed after removing the top oxide layer and existed on the TiO$_2$ surface.

![Figure 5.7 Photocatalytic degradation of RhB under blue light (400-500 nm) irradiation.](image)

TiO$_2$ nanotubes, which have a larger surface area as shown in the ESEM images, showed a much slower degradation rate to the model dye. Due to its hexagonally dimpled morphology, the black TiO$_{2-x}$ has a relatively small surface area compared to the TiO$_2$ nanotubes. However, its remarkable photocatalytic activity proved it to be an excellent photocatalyst under visible light. However, it should be mentioned that there is still little knowledge on the desired or
optimized amount of oxygen vacancies, because it is extremely difficult to identify the amount of oxygen vacancies. Also, there is no effective method to control the amount of oxygen vacancies.

In addition, its robust nonporous structure and immobilized nature can be further exploited to overcome issues of photocatalyst recovery that prove to be difficult with fine particles or thin whiskers photocatalyst.

5.4 Conclusions

In conclusion, the present work demonstrates a facile anodization technique to synthesize defective black TiO$_2$ with controllable level of defects, which exhibited high photocatalytic activity under visible light. Mechanistic analysis and characterization results indicate that oxygen vacancies were formed in an oxygen-deficient environment during the anodization process, and account for the high photon-absorbance of the black TiO$_{2-x}$ throughout the visible light region. The synthesized black TiO$_{2-x}$ also exhibited remarkable visible-light absorption and photocatalytic activity.
CHAPTER 6

Partially Crystallized TiO$_2$ for Microwave Absorption

CHAPTER ABSTRACT

TiO$_2$ is not among the traditional microwave absorbing materials due to its poor absorption of electromagnetic energy. Here, amorphous TiO$_2$ synthesized via Ti anodization is partially crystalized to form the controlled coexistence of crystalline and amorphous phases. An interfacial electric field occurs across the boundaries of crystalline-amorphous phases due to the uneven distributions of positively charged oxygen vacancies, which amplify the absorption of electromagnetic energy. This study grants anodized TiO$_2$ a new potential application for absorbing microwaves, opens up the concept of partial crystallization of amorphous TiO$_2$, and may inspire further developments of other exciting functional materials.

6.1 Introduction

Microwave absorbing materials (MAMs) are widely used in civil and military applications for absorbing unwanted electromagnetic radiation, such as signal and data protection, noise reduction and stealth coating on aircrafts [81-83]. TiO$_2$ has been widely studied and used in energy harvesting and storage due to its low cost, chemical stability, nontoxicity, and high reactivity. However, TiO$_2$ is not a MAM candidate due to the poor absorption of electromagnetic energy.

In 2013, successful synthesis of the so-called black titania by Chen et al. marked a milestone in MAMs [43, 80]. By exposing TiO$_2$ nanocrystalline powders to 5.0 bar H$_2$ at 450°C,
reduced TiO\textsubscript{2} powders were obtained that exhibited high microwave absorption. These powders consisted of a crystalline core encapsulated by a thin amorphous layer [84]. Electrical charges accumulated at the boundaries of crystalline - amorphous phases, forming the interfacial electric field (IEF) that amplified the microwave absorption [85]. This work has attracted wide scientific and technological interest. However, a major obstacle impeding the further development lies in the highly specialized facilities and harsh synthesis conditions required. This method also does not have the effective capacity to control the TiO\textsubscript{2} amorphous part for tuning the IEF, as H\textsubscript{2}-induced reduction only happens at the oxide surface [84].

Ti anodization has recently emerged as a facial approach in synthesizing amorphous TiO\textsubscript{2} with rich oxygen vacancy (V\textsubscript{O}), which can be utilized for photocatalysis after controlled annealing [46]. As we present here, the amorphous TiO\textsubscript{2} synthesized by Ti anodization is partially crystallized to result in the controlled coexistence of crystalline - amorphous phases. The obtained material displays superior microwave absorbing properties to many extensively studied MAMs.

**6.2 Experimental**

6.2.1 Anodization Processes for Material Preparation

Titanium sheets (99.96%, 0.5 mm thick) were ground and polished to remove the oxide film. After ultrasonically degreased in acetone, methanol, and deionized water, the Ti substrates were dried in nitrogen, and used as the anode. A platinum foil served as the cathode with a distance of 2 cm from the anode. Square-shaped Ti foils (1 × 1 cm) were exposed to the electrolyte. Anodization was performed in 150 ml ethylene glycol (99.8%, Sigma-Aldrich) containing 0.25 wt.% NH\textsubscript{4}F (98%, Sigma-Aldrich) and 2 vol.% deionized water under voltages of 60 V for 10 hours. To avoid cavities in TiO\textsubscript{2}, the as-prepared samples were kept in ethanol at 30°C for 48 hours to remove the organic electrolyte and eliminate inner stress caused by the generation of the oxide. The resultant oxide was rinsed with methanol and dried in air. Abrupt annealing was carried out by directly putting the as-anodized TiO\textsubscript{2} into a pre-heated furnace of controlled temperatures for 1 hour.

6.2.2 Characterization of Material Properties

The following techniques have been used to characterize the properties of anodized TiO\textsubscript{2}:

(1) The X-ray diffraction spectra (XRD) were acquired on a Bruker D2 Phaser X-ray diffractometer.

(2) The Raman spectra were collected on a Renishaw RM1000 Research Laser Raman spectrometer.
(3) Morphological analyses of specimens were performed on a field-emission scanning electron microscope (FEI Quanta 200F ESEM). The cross-sectional morphologies of nanotubes along their depth were viewed at the fracture part.

(4) The transmission electron microscopy (HRTEM) was taken on Tecnai TF20 TEM.

(5) The elemental composition was measured by Kratos Axis UltraDLD X-ray Photoelectron Spectrometer (XPS).

(6) Electron spin resonance spectroscopy (ESR) was recorded at 300K and 100K temperatures on a JEOL - JES-FA200 Electron Spin Resonance Spectrometry.

(7) The complex permittivity and permeability of samples were measured in the frequency range of 2–18 GHz using a N5244A PNA-X Microwave Network Analyzer. The ground powders were dispersed in melting paraffin wax, and the mixture was cast into a ring mold with thickness of 2.0 mm, inner diameter of 3 mm, and outer diameter of 7 mm. The contents of TiO$_2$ nanocrystals were 40 wt%, 60 wt%, and 80 wt%, and the testing was performed at room temperature.

(8) Thermal diffusivity of anodized TiO$_2$ was measured using NETZSCH LFA 447 Nanoflash at room temperature. Stripped oxide films were ground into fine powders, and dispersed in melted paraffin at concentrations of 60 wt%, which was then made into a disk shape.

Figure 6.1 XRD spectra of anodized TiO$_2$ indicating the phase transformation from amorphous to anatase after annealing (The background XRD spectra was all removed).

6.3 Results & discussions
6.3.1 Crystal structures & chemical compositions

Anodized TiO$_2$ was first synthesized by Ti anodization. The as-anodized (RT) TiO$_2$ showed a tubular structure with amorphous phase, which crystallized into anatase phase after abrupt annealing at 300°C for 1 hour, as showed by X-ray diffraction (XRD) (Figure 6.1). Raman peaks at around 144, 201, 399, 520, and 643 cm$^{-1}$ verified the anatase phases of anodized TiO$_2$ after annealing (Figure 6.2) [86]. The XRD and Raman patterns also indicated that the grain size grew larger after annealing at 400°C and 500°C.

![Figure 6.2 Raman spectra of anodized TiO$_2$ after annealing at different temperatures.](image)

TEM images showed heterogeneous TiO$_2$ nanocrystals which were formed after crystallization (Figures 6.3a and b). While the oxide surface was fully crystallized (Figure 6.3c), the inner nanocrystals were well-defined lattice cores encapsulated by amorphous area (Figure 6.3d). As the annealing temperature ($T_a$) increased, the amorphous area reduced. The unique structures of anodized TiO$_2$ are the results of crystal nucleation and growth during the annealing process. Initially, heterogeneous nucleation occurred on the tube surface where lower activation energy was required, thus more nucleation sites were formed on the surface layer than inside the bulk material [87-89]. The nucleation cores then grew larger and formed a fully crystallized surface, with some amorphous areas still left inside. Thus, it was the partial crystallization of the inner amorphous oxide that formed the unique structures. As crystal growth requires the diffusion of Ti and O atoms to form an ordered lattice structure, which strongly depends on the annealing temperature $T_a$ [90], an elevated $T_a$ resulted in less amorphous area encapsulating the crystal cores.
Figure 6.3 Anodized TiO$_2$ characterized by TEM before (a) and after (b) annealing; HR-TEM images of annealed TiO$_2$ at oxide surface (c) and inner part (d).
Figure 6.4 XPS spectra of anodized TiO$_2$ before and after sintering at different temperatures.
Figure 6.5 Anodized TiO$_2$ characterized by ESR at 300 K (a) and 110 K (b) temperatures.

X-ray photoelectron spectroscopy (XPS) spectra appeared similar for all specimens, except that the fluorine ions detected in room temperature TiO$_2$ almost disappeared after annealing (Figure 6.4). Ti$_{2p}$ XPS spectra showed identical patterns for lattice Ti$^{4+}$ ions, with peaks centered at around 458.7, 464.3, and 472.2 eV [91]. The OH bands at 532.5 eV adjacent to the O$^2-$ peaks indicated higher OH contents in RT TiO$_2$, which originated from the electrolyte [92].

Since XPS is a surface analytical technique, electron spin resonance spectroscopy (ESR) was used as an additional means to characterize the anodized TiO$_2$ structure. ESR spectra recorded at 100 K and 300 K verified the presence of V$_{o}$ in anodized TiO$_2$. The signals at g = 2.00 were induced by electrons trapped in V$_{o}$ (Figure 6.5) [42]. The reduced intensities of ESR signals further showed that the V$_{o}$ content in anodized TiO$_2$ decreased to ca. 42%, 27%, and 13% after annealing at 300°C, 400°C and 500°C, respectively. Our previous work showed that
O₂ diffusion from air was negligible in this process [46]. The loss of V₀ can therefore be ascribed to the crystallization of amorphous TiO₂ during the annealing process. This is reasonable as amorphous TiO₂ only has short range orders at the atomic scale, which facilitates the formation of V₀ [93].

During the annealing process, disordered atoms transferred to latticed positions, eliminating crystal disorders including V₀. These positively charged V₀ mainly existed in the amorphous areas, and contributed to the IEF formation at the boundaries of crystalline/amorphous phases. The IEF is able to facilitate charge diffusion [94], and affect the electrical attributes. Schmuki et al. showed that electrical resistance of anodized TiO₂ decreased after crystallization at low Tₐ, and then gradually increased at higher Tₐ [95]. Thermal conductivity of anodized TiO₂ can also be affected by post-annealing, since phonon scattering is much greater in disordered structures [96]. Higher Tₐ annealing formed less amorphous phase and V₀, which in turn enhanced the thermal conductivity.

6.3.2 Microwave absorption properties

To evaluate the microwave absorbing properties, the complex permittivity (ε = ε' + ε'') and permeability (μ = μ' + μ'') of anodized TiO₂ were measured within the range of 2–18 GHz. Stripped oxide films were mechanically ground into fine powders, and dispersed in melted paraffin at concentrations of 40 wt.%, 60 wt.%, and 80 wt.%. The real (ε') part of complex permittivity of anodized TiO₂ increased sharply after 300°C annealing, then dropped steadily after 400°C and 500°C annealing (Figures 6.6a-c). Anodized TiO₂ showed relatively stable ε' in the microwave range of 2–18 GHz, with an average ε' value of 4.4 for 40 wt.%, 8.3 for 60 wt. %, and 15.7 for 80 wt.% on 300°C annealed TiO₂. The intrinsic ε' value of pure 300°C annealed TiO₂ was calculated to be around 27.7, which was higher than those annealed at 400°C (26.4), 500°C (15.3), and RT (10.8), demonstrating its superior property of electrical energy storage. The intrinsic ε' values of 300°C and 400°C annealed anodized TiO₂ were also higher than that of some extensively studied MAMs, including carbonyl-iron (9–24) [97, 98], carbon nanotubes (10–22) [98, 99], LiZn ferrites (10–26) [100], and hydrogenated TiO₂ (H-
Figure 6.6 Real and imaginary values of anodized TiO$_2$ complex permittivity and permeability.
The 300°C heat treatment also yielded the highest efficiency in dissipating electrical energy under an electromagnetic field, as shown by the imaginary ($\varepsilon''$) values (Figures 6.7d-f). The average $\varepsilon''$ values of 300°C annealed TiO$_2$ were 0.10 for 40 wt.%, 0.35 for 60 wt.%, and 1.06 for 80 wt.%, with a predicated intrinsic $\varepsilon''$ value of around 2.45. Permeability values were almost identical for all specimens, with $\mu' = \sim 1$ and $\mu'' = \sim 0$ for 40 wt.%, 60 wt.%, and 80 wt.% measurements (Figures 6.6g-l). It indicates that these samples are of no magnetism, and have the same efficiencies in storing and dissipating the magnetic energy of microwaves.

Figure 6.7 (a) Influence of material thickness on microwave absorption; (b) Influence of heat treatments on microwave absorption.

The reflection loss of 80 wt.% anodized TiO$_2$ with 20% paraffin was explored. As for thicker oxide layers, the positions of reflectivity peaks moved to a lower frequency (Figure 6.7a). With the given 4 mm thickness, 300°C annealed TiO$_2$ achieved a reflection loss below -10 dB (90% absorption) over 1.0 GHz in the range of 13.8 - 14.8 GHz, and the minimum value was -36.9 dB at 14.3 GHz. Samples annealed at 400°C absorbed more than 90% of microwaves in the range of 15.1–16.1 GHz, with the minimum value - 15.6 dB at 15.5 GHz (Figure 6.7b).
RT TiO2 and 500°C annealed TiO2 exhibited relatively lower absorptions, which was in agreement with our conclusions from the complex permittivity and permeability of anodized TiO2.

Figure 6.8 Real and imaginary values of the complex permittivity and permeability of intact TiO2 (60 wt.%), as-anodized TiO2 (60 wt.%) and pure paraffin.

Compared with H-TiO2 ($\mu' = \sim 0.9$, $\varepsilon'' = \sim 6$ and $\mu'' = \sim 0.2$), the higher intrinsic $\mu'$ value of anodized oxide indicated the superior capacity in magnetic energy storage. The relatively lower $\varepsilon''$ and $\mu''$ values of anodized oxide showed that less electrical and magnetic energy would be lost inside the material, which was transferred to heating [101]. This heating energy is very limited, and can always be ignored in practical applications. It should be noted that the robust structure and immobilized nature of the anodized oxide grew on the Ti substrate, allowing it to work independently, overcoming the difficulties of microwave absorbing materials in the forms of nanoparticles or fibers.

Figure 6.9 Schematic diagram of the interfacial electric field.

6.3.3 Mechanism for absorbing microwaves
V_o was unlikely to be responsible for the microwave absorption of anodized oxide. While RT TiO_2 contained higher V_o, it responded less to the electromagnetic field than annealed samples. RT TiO_2 even showed a similar absorption as the intact TiO_2 without any V_o (Figure 6.8). This therefore implies that the dipole-rotation mechanism in typical microwave absorption does not explain the microwave absorbing properties of these materials.

Here, we propose that the strong microwave absorption of anodized TiO_2 comes from the interfacial electric field (IEF), which occurs when there are uneven V_o distributions between two phases [102]. Anodized TiO_2 partially crystallized after low temperature annealing. The boundary of the crystalline - amorphous phases formed with more V_o left in the amorphous part. This unique structure caused the IEF formation, and enhanced the absorption of electromagnetic energy. After high temperature annealing, more amorphous areas were consumed, and the boundary and V_o-level diminished. There was thus less and weaker IEF in the material, which was illustrated in Figure 5.12. The microwave absorption gradually decreased after annealing at 300°C, 400°C, and 500°C. This hypothesis is verified by experimental results that the higher temperature annealing significantly reduced the microwave absorption of anodized TiO_2. Further studies are underway to investigate the detailed relations between the crystallization, annealing process, and electromagnetic energy absorption of anodized TiO_2.

6.4 Conclusions
In summary, amorphous TiO_2 synthesized via Ti anodization is partially crystalized to form the controlled microstructure of coexisting crystalline - amorphous phases. This material displays strong microwave absorbing capability. Mechanistic analysis and characterization results indicate that the interfacial electric field occurs across the boundaries of crystalline - amorphous phases, amplifying the microwave absorption. This study grants anodized TiO_2 a new potential application for absorbing microwaves. The concept of partial crystallization of amorphous TiO_2 may inspire further developments of other exciting functional materials.
CHAPTER 7

Conclusions and Future Work
7.1 Conclusion

This thesis aims to develop cutting-edge technology for the reliable fabrication of functional TiO$_2$ nanomaterials. The formation mechanisms, microstructure and various properties of the anodized Ti oxide have been investigated systematically. The main conclusions are drawn as follows:

(1) The microstructure of anodized TiO$_2$ nanotubes was carefully studied. It has been experimentally demonstrated that the inside diameter of nanotubes gradually increases towards the tube apex due to the longer time dissolution of the inside tube-wall. When the dynamic balance between oxidation and chemical dissolution is reached, nanowires can be synthesized at the upper part of the tubes. A physical model for the formation of TiO$_2$ nanowires and the changing thickness of the tube-wall has been proposed, which could explain the effects of experimental parameters on the maximum length of anodized Ti oxide nanotubes.

(2) Hierarchical nanostructures fabricated by electrochemical anodization exhibited superhydrophobic properties after being modified with organic molecules. The nanowire layer on the top of the tubular structure could strengthen its non-wetting performance. With a controlled treatment to remove the compact nanowires, more air is trapped inside the hybrid structure, resulting in enhanced superhydrophobic properties. The potential application of this technology in aquatic devices was demonstrated by the modified Ti metal mesh, which showed very strong floating stability on water. Moreover, the air entrapped around the mesh contributed to its floating stability, and may also reduce the fluidic drag force and fluid resistance.

(3) We examined the morphology evolution of anodized TiO$_2$, and revealed that applied voltage determined the pattern of etching pits, which in turn governed the anodized TiO$_2$, including the tube diameter and hexagonal features. Chemical dissolution shaped the hexagonal root to circular tubes at the upper segment. Novel hierarchical topographies, with controlled nano-sized pores inside the hexagonal dimples, were obtained by electrochemical etching the dimpled Ti substrates. The surface wettability was adjusted from superhydrophilicity to superhydrophobicity by tailoring the microstructure.

(4) We have developed a facile anodization technique to synthesize oxygen-deficient black TiO$_2$ with controllable level of defects, which exhibited high photocatalytic activity under visible light. Mechanistic analysis and characterization results indicated that oxygen vacancies were formed in an oxygen-deficient environment during the anodization process, and accounted for the high photon-absorbance of the black TiO$_2$.x throughout the visible light region.

(5) Amorphous TiO$_2$ synthesized via Ti anodization was partially crystalized to form the controlled coexistence of crystalline - amorphous phases. The obtained material displayed
strong microwave absorbing capability. Mechanistic analysis and characterization results indicate that interfacial electric field occurs across the boundaries of crystalline - amorphous phases, amplifying the microwave absorption property. This study grants anodized Ti oxide a new potential application for absorbing microwaves. The concept of partial crystallization of amorphous TiO₂ may inspire further developments of other exciting functional materials.

This work provides powerful approach to tailor the microstructures and properties of self-organized TiO₂ nanotubes, which may have far-reaching implications in the design of future nanoscale structures and advanced materials systems. The progress together with emerging methods for deterministic assembly leads to compelling opportunities for research, from basic studies of two-dimensional physics to the development of applications such as optoelectronic or photovoltaic devices, photocatalysis, nano-template, sensors, and more.

7.2 Suggestions for Future Work

The most promising and novel discovery in this thesis is the oxygen vacancies found in anodized black TiO₂, which provided significantly improved photocatalytic properties and microwave energy absorption. However, there are a number of questions that arise from this discovery:

(1) The critical factors in the Ti anodization process and formation mechanism of black TiO₂ₓ;

(2) Methods to control lattice defects and disorders in black TiO₂ₓ;

(3) Correlations between lattice defects and disorders and various properties of TiO₂ₓ.

Based on a good understanding of the above questions, we will be able to explain TiO₂ₓ formation during anodization, understand how to optimize the properties of TiO₂ₓ to suit different applications, and apply this simple method to create new oxide systems with controlled defective structure. The suggested future approaches are:

7.2.1 Understand the formation mechanism of defective TiO₂ₓ

This part is to answer the above questions (1). Our examination has confirmed the presence of Vₒ in anodized TiO₂, which has not been discovered in traditional metal anodization. Regarding the trapped Vₒ in anodized TiO₂, the chemical reactions and physical process of Ti anodization need to be further studied.

The anodization process is a dynamic competition between metal oxidation and oxide dissolution, which are affected by the applied voltage, electrolyte and temperature. It is suggested that quantification of the anodizing process can be achieved by using electrochemical measurements including EPR spectroscopy, scanning electron microscopy (SEM) and in situ synchrotron powder diffraction to characterise the oxide produced during the anodizing process.
This information is essential for understanding the formation process of defective TiO$_{2-x}$.

7.2.2 Investigate the effect of oxygen vacancies on TiO$_2$ structure

This part is to solve problem (2). Our current study indicated that the introduction of disorder led to a continuum extending to and overlapping with the conduction band edge, which enhanced the visible and infrared absorption. As well as this, the uneven distribution of positive charged V$_o$ formed the interfacial electric field (IEF) for enhancing the microwave absorption. While the band gap being engineered by crystal defects and immersed IEF has been noticed, the detailed effects of lattice disorders are much more complicated that no existing model can be used to explain. Our anodized TiO$_{2-x}$ provides a convenient case that can be designed to study the effect of defect-level on TiO$_2$ crystal/electronic structures.

We suggest the use of X-ray photoelectron spectroscopy (XPS) and UV–visible spectroscopy to quantify the relationship of TiO$_{2-x}$ bandgap and defect level. The crystal structure of TiO$_{2-x}$ can be evaluated by high-resolution TEM, Raman spectroscopy and synchrotron powder diffraction. The IEF phenomena should be indirectly studied by complex permittivity and permeability and other methods. Physical and mathematical models can then be established based on this research.

7.2.3 Optimise the properties and further development

This part of work is to address problem (3). The understanding of anodized TiO$_{2-x}$ formation mechanisms and physical/mathematical models established from the above work will give us the relationships between Ti anodization, defect level and TiO$_{2-x}$ structure. These models are powerful tools to optimize processing to obtain the designed properties of TiO$_{2-x}$. The fundamental investigation on anodized TiO$_{2-x}$ will help us use anodization to develop the anodization process for a wide range of other transition metals such as Zn, Zr, Al, V, and Mg to produce corresponding defected oxides. Properties of defective oxides, including photocatalysis and electric conductivity will be first studied. This work may lead to truly attractive developments in nanotechnology and materials science.
Reference