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TiO₂ Nanotube Arrays Prepared by Anodizing in Water-Glycerol Electrolyte and Their Photocatalytic Properties

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ABSTRACT

TiO₂ has attracted much attention in the last decades owing to its superior positions as biomaterials, in photocatalytic applications, and in dye-sensitized solar cells (DSSCs). For the photocatalytic application of TiO₂, the generation of electron–hole pairs and their oxidative nature provide manifold applications, such as decomposition of organic pollutants in water and air. The structure and morphology of TiO₂ have a considerable influence on the photocatalytic performance of TiO₂. Thus, over the past few years, considerable progress was made particularly in optimizing the nanoscale morphology of TiO₂.

Most recently, a novel 1D nanotube structure, TiO₂ nanotube array, has been shown to be highly competitive, and in many cases, favorable to achieve enhanced photocatalytic performance. The cheapest and most straightforward method that leads to ordered TiO₂ nanotube array is anodization technique. In particular, the anodization approach allows an easy control on dimensions of anodized TiO₂ nanotube arrays (such as layer thickness, pore diameter, interpore distance). Valuable properties of TiO₂ nanotube array, which include semiconductive behavior, photocatalytic and photoelectrochemical properties, can be enhanced by controlling its geometry. In ethylene glycol-containing electrolyte, by controlling the anodization conditions, many types of TiO₂ nanotubes (e.g., ripples free, double-wall) can be formed. However, detailed investigations about these special structures in glycerol-containing electrolyte have not been fully performed yet.

In this context, the preset thesis focuses on revealing the critical mechanisms and anodization conditions to form TiO₂ nanotube arrays with various nanostructures (for example, double-wall and ripples) in glycerol-based electrolytes. The annealing effect on the morphology, chemical composition and structure of double-wall TiO₂ nanotube array were further investigated by both *ex situ* and *in situ* annealing method. For the *ex situ* annealing, “fluoride-rich” layer was confirmed in between the double-wall

nanotubes. For the *in situ* annealing, oxygen gas can be introduced into the TEM column, the *in situ* sintering behavior of double-wall TiO₂ nanotubes was compared with and without oxygen gas at real-time by TEM observation. Furthermore, the photochemical activities of double- and single-wall TiO₂ nanotube arrays were compared, decoration of Pt nanoparticles inside both double- and single-wall TiO₂ nanotube arrays was also examined to enhance their photocatalytic activities.

CHAPTER 1

Introduction

1.1 Photocatalysis and semiconductor materials

The Sun, which locates at the center of solar system, supports nearly all the life on earth by irradiating solar light. For example, through the well-known photosynthesis process, plants and other organisms can convert the solar light energy to chemical energy (such as carbohydrate molecules).¹ This supplies all of the organic compounds and most of the energy which is necessary for life on earth. Nearly all the forms of energy (coal, oil, natural gas, etc.) are from solar energy. These abundant and economical energies greatly promoted the civilization of our human life. However, with the revolution and development of human society, energy consumption of rapidly increased and gave rise to energy crisis. At the meantime, environmental pollution and global warming are also the main problems in need to be solved for the sustainable development of our human society.

Displacement of the traditional energy by renewable, clean solar energy is necessary to solve the global problems discussed above. One important and potential technology related to this concept is using solar energy through photocatalysis. Through photocatalysis technology, water splitting is available to relieve the problem of energy crisis and global warming.² Meanwhile, photodegradation of organic pollutants is also available and benefit for the environment purification.³ So the research and development of photocatalysis have been the focus of considerable attention across a broad range of environmental and energy-related fields. Many photocatalysts are obtained and exhibit high photocatalytic activity. Especially, inorganic semiconductor materials are particular attractive for photocatalysis for their ability to absorb solar energy.⁴

Photosensitization by a semiconductor is a reaction system wherein a solid photocatalyst simultaneously sensitizes two heterogeneous redox reactions,⁵ it is

generally the so-called photocatalysis. This photocatalysis process can be carried out in many medias: gas phase, pure organic liquid phase and aqueous phase. Taking the liquid phase as an example, the overall process can be divided into five independent steps:⁶

1. Transfer of the reactants in fluid phase to the surface of photocatalysts.
2. Adsorption of the reactants.
3. Redox reaction in the adsorbed phase.
4. Desorption of the products.
5. Removal of the products from the interface region between liquid phase and photocatalysts.

The photocatalytic reaction takes place in the absorbed phases (step 3). When excited with light of wavelength equal to or greater than the band gap energy of semiconductor catalysts, mobile holes and electrons can be generated in valence and conduction band. The photogenerated electron-hole pairs can then facilitate the redox reactions during photocatalytic process. The sequence of reactions can be represented as below:

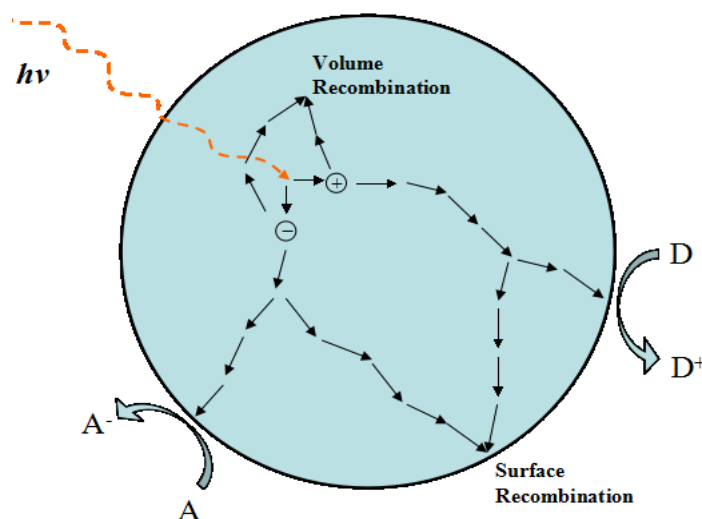
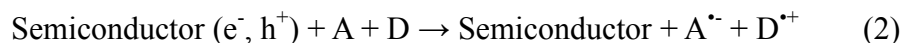
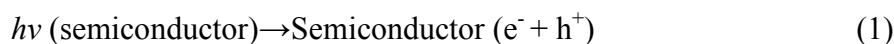


Figure 1.1 Schematic illustration of semiconductor excitation by ultraviolet light illumination leading to the creation of electron-hole pairs.

Primary ions will be produced through the electron exchange with donor and acceptor (D and A), subsequently, react to form the intermediates and final products. The absorption of the semiconductor catalysts, not the reactants, should be adapted to the photon energy. Moreover, according to reaction below, the electron-hole recombination can also happen and cause the loss of photo efficiency.



The employed semiconductor photocatalysts are common and typically classified into four groups: (1) d₀ metal (Ti⁴⁺, Zr⁴⁺, Nb⁵⁺, Ta⁵⁺, W⁶⁺, and Mo⁶⁺) oxide photocatalysts, (2) d₁₀ metal (In³⁺, Ga³⁺, Ge⁴⁺, Sn⁴⁺, and Sb⁵⁺) oxide photocatalysts, (3) f₀ metal (Ce⁴⁺) oxide photocatalysts, and (4) a small group of nonoxide photocatalysts.⁷ For these photocatalysts, many factors can affect their photocatalytic properties. Initially, the band gap E_g, which is the energy difference between the edges of conduction and valence bands, determines the minimum energy for the optical excitation of photocatalysts. Figure 1.2 illustrates the energies of some semiconductors in aqueous electrolyte. Wherein, anatase titania crystal phase has a band gap of 3.2 eV, it can only absorb light of wavelength shorter than 390 nm. While CdS has narrower band gaps (2.5 eV), making it sensitive to visible light. However, TiO₂ exhibits higher photocorrosion stability than CdS.

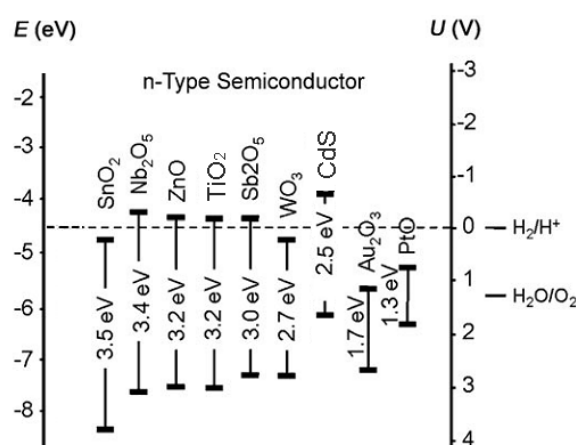


Figure 1.2 Banding positions of some semiconductors used as photocatalysts and their corresponding energy scales vs. the vacuum level and vs. the normal hydrogen electrode (NHE).

Impurities and defects can also affect the photocatalytic properties of semi-conductive materials. In the case of titania, its photocatalytic activity under visible light can be induced by the substitutional doping of nitrogen.⁸ Similar to the nitrogen-doped TiO₂, nitrogen-doping in Ta₂O₅ can also make the band gap narrowed.⁹ Recently, nitrogen-doped ZrO₂ and In₂O₃, carbon-doped In₂O₃ and Nb₂O₅ were also reported to show improved photocatalytic property for water splitting. Another important factor, which affects the photocatalytic property, is the specific surface area of semiconductor materials. Photocatalytic property of TiO₂ was greatly improved by increasing the surface area through supported zeolites.¹⁰

Many methods are now widely used for the characterization of semiconductor materials, including bulk and surface elemental analysis, X-ray powder diffraction, specific surface area measurement, diffuse reflectance spectroscopy, emission spectroscopy, and electron paramagnetic resonance and photoelectron-chemical experiment. Mobile charge carriers in semiconductor materials can be detected by either electron paramagnetic resonance spectroscopy or infrared spectroscopy.¹¹ A surface photovoltage method is reported to measure the lifetime of photogenerated charges. The obtained slow and fast components of photovoltage decay indicate the bulk and surface recombination respectively.¹² Bandgap value can be easily measured by diffuse reflectance spectroscopy. To obtain the band gap, Kubelka–Munk function is plotted as function of the energy of exciting light. The Kubelka–Munk function should be modified for an unambiguous conclusion.

1.2 TiO₂ nanomaterials and their photocatalytic applications

For photocatalysis application, titanium oxide is one of the most studied semiconductor materials, it has a unique set of features which include chemical stability, non-toxicity, low cost and transparency to visible light. This enables titanium oxide based materials have a superior position as photocatalysts. Moreover, with the development of the preparation method of nanomaterials, nano-TiO₂ with various morphologies can be obtained and promote its applications. For instance, fabrication of wettability patterns for the offset printing plate is reported to be a new application

of TiO_2 .¹³ The number of publications on titanium oxide is still increasing over years.

1.2.1 Structure and properties of TiO_2 materials

As a polymorphic material, TiO_2 has several crystal structures, they are anatase, brookite, rutile and TiO_2 (B), which is the less common phase. The property and application of TiO_2 depends on its crystal structures. Compared with anatase, rutile usually has minimum free energy and hence is most stable as bulk material. Anatase is preferred for photocatalytic application whereas rutile is widely accepted as gas sensing material. For many sol-gel or electrochemical methods, the as-formed TiO_2 is mainly amorphous material. Annealing is usually needed to convert the amorphous structure to crystal structures.

Unit cells for the three main phases of TiO_2 (anatase, brookite and rutile) are shown in Figure 1.3. These three structures can be described in terms of chains of TiO_6 octahedron, in which each Ti^{4+} is surrounded by six O^{2-} ions. But the assembly pattern of those chains and distortion of each octahedron are different for the three crystalline structures. For rutile, each octahedron is connected with ten neighboring octahedrons. However, each octahedron is in contact with eight neighboring octahedrons for anatase. For pure brookite phase, it has an orthorhombic structure with a unit cell described by the space group Pbca . However, pure brookite phase is rare, metastable and difficult to be prepared, its photocatalytic property has not been well studied.

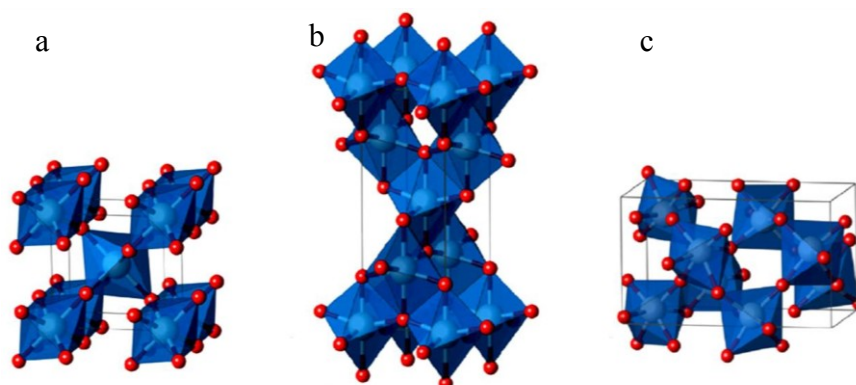


Figure 1.3 TiO_6 polyhedron for the rutile (a) anatase (b) and brookite (c) phases of TiO_2 .¹⁴

Recently, except for stoichiometric TiO_2 , there are also a wide range of suboxide phases which have very interesting properties. Magnéli phases are most remarkable and follow the formula $\text{Ti}_n\text{O}_{2n-1}$ ($4 \leq n \leq 10$), such as Ti_4O_7 , Ti_5O_9 , Ti_6O_{11} , Ti_7O_{13} , Ti_8O_{15} , Ti_9O_{17} .¹⁵ In magnéli phases, oxygen vacancies are ordered and lead to the slippage of crystallographic planes, new face-shared octahedron instead of corner or edge-shared TiO_6 octahedron can be formed. For titania oxides, such magnéli phases are highly conductive at room temperature and show high corrosion resistance in aqueous electrolyte. Under reductive high-temperature treatment in H_2 or H_2/N_2 , magnéli-phase titanium oxides can be formed.¹⁶

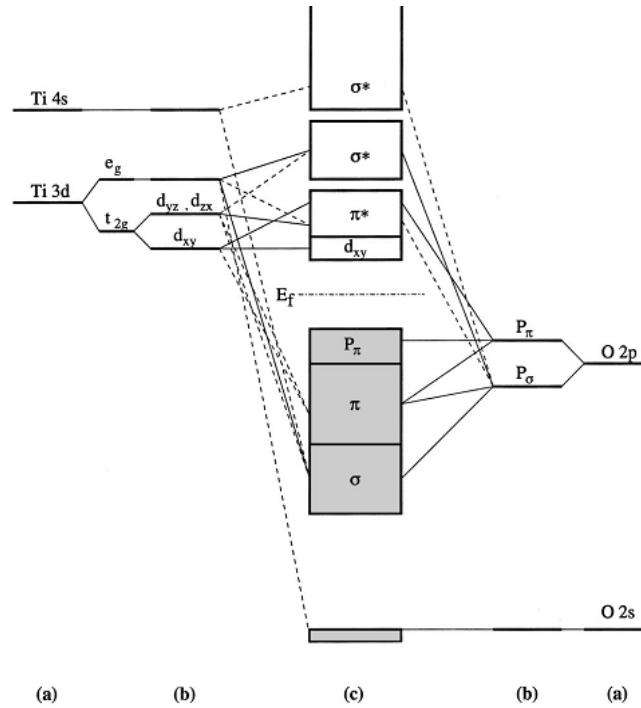


Figure 1.4 Molecular-orbital bonding structure of anatase TiO_2 . (a) atomic levels, (b) crystal-field split levels, and (c) final interaction states.¹⁷

As we all know, when atoms are brought together to form a compound, their atomic orbitals will combine and form molecular orbital. More molecular orbitals will be formed if more atoms are combined, so the energy levels of molecule will become increasing dense. The electronic band structure consists of two energy bands (valence and conduction band) and the band gap. The band gap is between the valence and conduction band. In semiconductor materials, the band gap is smaller than that in

insulators, electrons can be lifted from the valence band into the conduction band at room temperature. TiO_2 is a large band gap semiconductor, the band gap energy of indirect electron transition is 3.0 and 3.2 eV for rutile and anatase, respectively. For valence band, the top of the valence bands is mainly from the $\text{O}_{p\pi}$ orbitals. The lower valence bands, which located at about -17 eV, are mainly composed of O_{2s} character. The upper valence bands show strong hybridization between O_{2p} and Ti_{3d} electrons. For conductive bands, the bottom of conductive bands is predominated from the isolated Ti_{dxy} orbitals. The conductive bands below 8 eV consist mainly of Ti_{3d} states. The conductive above 8 eV has mainly s and p character. Although rutile phase has different crystal structure, its molecular-orbital bonding diagram is very similar to the anatase phase.

1.2.2 Synthesis of TiO_2 nanomaterials

After a lecture, which is called “There is a plenty of room at the bottom”, given by Feynman in 1959,¹⁸ nanotechnology has been greatly improved and facilitated the preparation of a wide range of nanomaterials. The size of nanomaterials is usually between 1–100 nm in at least one dimension. So nanomaterials can be classified into three categories with different dimensions in nanoscale range: (1) zero-dimensional nanomaterial (nanoparticle), (2) one-dimensional nanomaterial (nanotube, nanowire, nanorod, etc), (3) two-dimensional nanomaterial (nanofilm). With respect to the quantum effects, they are also called quantum dots, quantum wire and quantum well, respectively. For the extreme small size, nanomaterials show many special properties compared to bulk materials. For instance, nanoparticle, which is composed of a few atoms, has a large fraction of surface atoms. The average binding energy of per atom will be very high. So nanoparticles may hold a higher chemical reactivity than the bulk solid. As for nano-structural TiO_2 , it owns higher surface area than bulk TiO_2 , an improved photocatalytic property can also be achieved.¹⁹ Preparation of nano-structural TiO_2 materials plays an important role in the field of photocatalysis.

Many methods were conducted to prepare nanostructural TiO_2 . They can be divided into physical and chemical method. Physical method mainly contains molecular

beam epitaxy (MBE), pulsed laser deposition (PLD) and atomic layer deposition. These physical methods are very suitable to prepare TiO_2 nanofilms with high quality. However, equipment is usually high-cost, and industrial mass production is very difficult to be achieved for its small yields. Inversely, compared with physical method, chemical method has many advantages such as mild reaction conditions, low-cost and controllable morphology, etc. It is widely chosen to prepare nanostructural TiO_2 materials with different morphologies. As shown in Figure 1.5, by hydrothermal method, Xie et al. fabricated well-crystallized rutile TiO_2 hollow spheres, this sphere demonstrated a significantly improved photocatalytic performance.²⁰

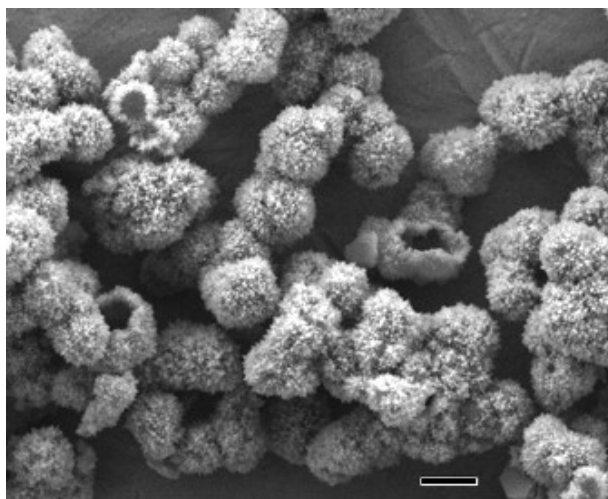


Figure 1.5 Panoramic SEM images of the as-synthesized TiO_2 hollow spheres after ultrasonic treatment for 15 min, the scale bars is 1 μm .

Not only for the preparation of zero-dimensional nano-structural TiO_2 materials as discussed above, chemical methods are also selected to prepare one-dimensional nano-structural TiO_2 materials, especially nanotubes. Miao et al. prepared TiO_2 nanotube arrays through combination of sol-gel and electro-deposition method.²¹ By hydrothermal reaction of TiO_2 with NaOH aqueous solution, TiO_2 nanotubes were formed.²² Notably, one simple method for the preparation of TiO_2 nanotubes is electrochemical anodization of titanium metal. The first anodization of self-organized TiO_2 nanotube structures was reported in 1999.²³ Thereafter, this method was widely investigated and got great improvement. Anodic TiO_2 nanotubes exhibited a better photocatalytic activity than that of P25 nanoparticulate film of almost the same

thickness.²⁴

For the two-dimensional nano-structural TiO_2 , TiO_2 nano-sheets with (001) facets can be prepared and exhibited a higher photocatalytic activity than that of P25 TiO_2 particles.²⁵ Alkaline hydrothermal method was widely adopted to prepare TiO_2 nano-sheets using TiO_2 powder as a precursor or from protonic titanate hydrates. Sol-gel method is important for the preparation of three-dimensional interconnected TiO_2 materials. For example, by using poly-(ethylene oxide) as a phase separator and N-methylformamide as a proton scavenger, a macro-porous TiO_2 monolith was prepared for use in chromatographic applications.²⁶ TiO_2 photonic crystal structures is also available by sol-gel technique using colloidal templates, it holds a higher photocatalytic activity than the commercial P25 TiO_2 nanoparticles.²⁷

1.2.3 Applications of TiO_2 nanomaterials

Due to the high physico-chemical stability, no-toxicity and low-cost, nanostructural TiO_2 have been demonstrated for wide applications in many fields such as water splitting, degradation of pollutants, dye-sensitized solar cells (DSSCs), self-cleaning, super-hydrophilicity and so on.

(a) Water splitting

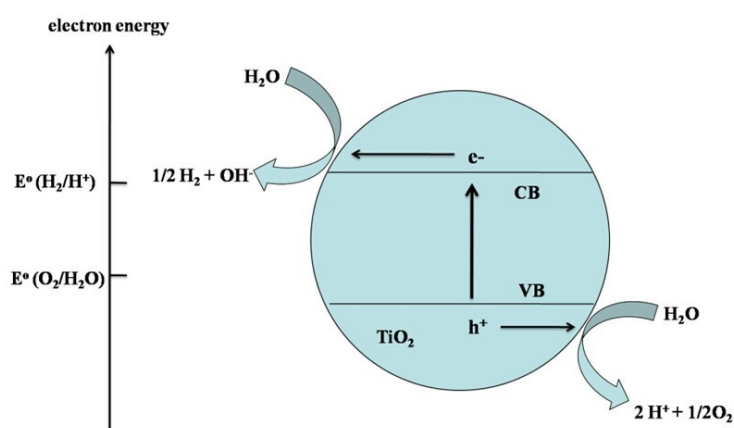
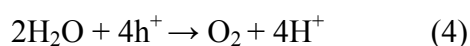
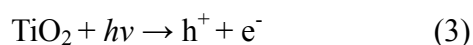


Figure 1.6 Mechanism of TiO_2 photocatalytic water splitting for hydrogen generation.

In 1972, Fujishima et al. firstly reported the photo-electrochemical decomposition of water into H_2 and O_2 by TiO_2 .²⁸ The water splitting by TiO_2 provides a new route

to utilize solar energy, it then attracted wide interest and got greatly improved. The mechanism of water splitting is shown in Figure 1.6. Due to the over potential for the evolution of H₂ and O₂ on the TiO₂ surface, H₂O can hardly be photo-decomposed on clean TiO₂ surfaces.²⁹ So an external voltage is necessary to effectively separate the photo-generated electrons and holes. When the TiO₂ electrode is irradiated by UV light, the electrons will flow through the external circuit to the Pt electrode, water molecules are reduced to hydrogen gas, while the holes left in the TiO₂ electrode will oxidize the water to oxygen. Electrochemical reactions can be shown below:



TiO₂ nanotube arrays were reported to show high water splitting efficiencies. For well-defined TiO₂ nanotube geometry, various catalysts and dopants can also be easily incorporated inside. By decorating the nanotube arrays with TiO₂ nanoparticles, the O₂ evolution reaction can be accelerated for an enlarged surface area. Doping nanotube arrays with appropriate elements (such as Ru and Nb) is also suitable to further increase the efficiency of water splitting.

(b) Degradation of pollutant

TiO₂ shows many advantages for pollutant degradation. One advantage is its low cost, only TiO₂ photocatalysts and UV light are involved in the process of pollutant degradation. Another advantage is non-toxicity. This makes TiO₂ photocatalysts very environment-friendly and attractive in water purification. For water purification, both organic and inorganic pollutants in contaminated water can be removed by TiO₂ photocatalysts. Water disinfection by TiO₂ photocatalysts is also available to produce drinking water, this is very helpful to improve the public health. Besides water purification, air purification is also one of the most important applications of TiO₂. Many kinds of organic compounds, such as formaldehyde and toluene, can be removed from the indoor air. The bacteria floating in indoor air can also be killed. Because the photocatalytic air cleaning of TiO₂ results in decomposing the organic

compounds instead of accumulating them, TiO_2 photocatalyst does not lose its function after a certain period of use. Air-cleaning devices based on TiO_2 photocatalysts are widely used in air cleaners, air-conditioners and refrigerators. Recently, some companies in Japan are also using TiO_2 photocatalysts to remove the NO_x exhausted from automobiles.

(c) Dye-sensitized solar cells (DSSCs)

In 1991, Grätzel et al. invented the dye-sensitized solar cells. The important part of the dye-sensitized solar cells comprises porous titania, which are coated with absorbed dye.³⁰ Under visible light, the absorbed dye can be excited, excited electrons are transferred to the conductive band of TiO_2 , transport through the TiO_2 to the back side of the anode and finally through the electric circuit to the cathode. After flowing through the external circuit, the electrons will be re-introduced into the electrolyte and the electrolyte transports the electrons back to the dye molecules. Many factors can affect the power conversion efficiency of dye-sensitized solar cells (DSSCs), they include morphologies and crystal structures of titania, amount of absorbed dye, and geometry of photoanode, etc.

Recently, the work on dye-sensitized solar cells based on the anodic TiO_2 nanotube arrays was also reported in many papers. To date, the power conversion efficiency of DSSCs based on nanotubular titania can reach *ca.* 5.2% for back side illumination or *ca.* 7% for front side illumination.^{31,32} Even so, considerable work still exists for further improving the overall efficiency of DSSCs. By adjusting the anodization parameters, various TiO_2 nanostructure were produced and investigated. For instance, titania mesoporous structures were obtained by anodizing method and show a higher solar cell conversion efficiency compared with nanotube arrays. The better performance can be attributed to higher specific dye loading, and possibly to the crystallite orientation.³³

(d) Super-hydrophilicity

In 1995, Fujishima has found the remarkable change of the water wettability of

TiO₂ surface before and after UV irradiation,³⁴ this effect is based on the electronic property of TiO₂ and its high photocatalytic activity. By UV light irradiation, photo-generated holes can lead to an increase in the number of -OH groups on the TiO₂ surface and cause the highly super-hydrophilic conversion. The new -OH groups produced by UV light irradiation are thermodynamically less stable than the initial -OH groups. For the water droplets, it is substantially larger than the hydrophilic domains, so it will instantaneously spread completely on the surface of TiO₂ film. This is the so-called photo-induced hydrophilicity.

The super-hydrophilicity of TiO₂ film can be used in the anti-fogging. The fogging surface of mirror or glass usually occurs in moist air condition, many water droplets on the surface tend either to scatter, reflect or refract light randomly. If the glass or mirror is treated with TiO₂ photocatalysts, the surface will become high hydrophilic, a uniform thin film of water will be formed on the surface. So the anti-fogging function of TiO₂ is achieved.

(e) Other applications

Many papers are also emerging to investigate other applications of TiO₂ materials. TiO₂ film, which is coated on 304 type stainless steel, can inject electrons into the steel and improve the anti-corrosion property of 304 type stainless steel.³⁵ For the anodic TiO₂ nanotube arrays, it can be used for the electrode of super-capacitors, higher energy and power density were achieved than those of dielectric capacitors and batteries.^{36,37} After modified with silane and phosphonate, TiO₂ nanotube layers can exhibit a super-hydrophobic surface, the wettability of nanotube layer can be highly defined alternative upon UV light illumination.³⁸

In summary, for nano-TiO₂ materials, the above mentioned applications enable them to be deeply investigated until now. Preparation and basic scientific research of nano-TiO₂ materials can still be further carried out and motivate other new applications.

1.3 Self-organization by electrochemical method

High ordered nano-materials, which have many unique catalytic, electronic, magnetic, opto-electronic and mechanic properties, have been applied in various fields of nano-phonic, photocatalytic, micro-fluidic and sensing devices, as well as functional electrodes and magnetic recording media.³⁹ Many methods have been chosen to produce high ordered nanoparticles, nanowires and nanotubes, these mainly include: lithography patterning,⁴⁰ molecular beam epitaxy,⁴¹ laser focused atomic deposition, chemical deposition,⁴² sol-gel,⁴³ wet impregnation⁴⁴ and electrochemical technique.⁴⁵ Among these methods, electrochemical anodization can be applied to produce highly ordered arrays of nanopore and nanotubes, during anodization process. Two competitive and continuous processes are necessary for the self-ordering, one is oxide dissolution at the electrolyte/oxide interface, and the other is oxidation of metal at the oxide/metal interface.

A number of metals and alloys (Si, Ti, Zr, Nb, Hf, W, Sn, TiAl, InP, TiZr) have been reported to be suitable for the anodization method.⁴⁶ Over the past decades, much attention has been given to the anodization of aluminum. In order to achieve the desired pore structures, both mild and hard anodization methods have been adopted. The anodization process is affected by many factors such as chemical composition of electrolyte, voltage, current density and temperature. For mild anodization, the current density is low. However, in hard anodization, the passing current density is much higher than that in mild anodization. The high field applied during hard anodizing will produce more heat than mild anodizing, burning or breakdown of the oxide film usually happens under excessive heat. So a suitable anodization potential should be carefully selected for hard anodization without burning. Moreover, anodic aluminum oxide (AAO) with various pore geometries can be fabricated by changing the profile of current, amplitude and period. The length and shape of periodic pore structures can be controlled by the amplitude and frequency of the cyclic signal. Several examples of AAO with uniform and asymmetrical periodicity of modulated pore structures are shown in Figure 1.7.

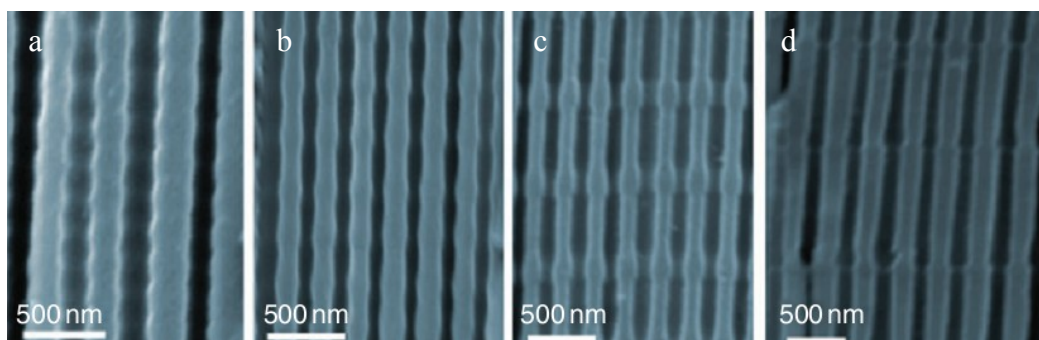


Figure 1.7 SEM images of the anodized aluminum oxide with different morphologies of pore structures using cyclic anodization in 0.1 M phosphoric acid using continuous cycle with different profiles (saw tooth, sinusoidal) and amplitudes $I_{\min} = 10$ mA to $I_{\max} = 120$ mA and periods 0.2–2 min.⁴⁷

Pre-treatment of aluminum and post-treatment of as-anodized sample also affect the geometry of anodic porous alumina. For the pre-treatment of aluminum, a two-step anodization method is commonly used to prepare high ordered arrangement of nanopores. A periodic concave pattern on the aluminum surface after the first anodizing can act as a template for the second anodizing process. The post-treatment of anodic porous alumina includes removal of aluminum substrate, removal or thinning of the barrier layer, and re-anodizing. Wet chemical immersion method is widely used to remove the aluminum base. For example, the aluminum substrate can be completely removed by immersing the anodized sample for few hours in a CuSO_4/HCl solution.⁴⁸ Removal or thinning of the barrier layer is necessary for the AAO template preparation, both opening and widening of pores can be achieved by chemical etching of the oxide. By re-anodizing method, the porosity of anodic porous alumina can be successfully determined. The self-organized anodic porous alumina was widely used as a host or template for the synthesis of nano-structured materials. These nano-materials have many forms such as particles, wires, rods, tips and tubes. Metals, semiconductors, metal oxides, carbon nanotubes, and polymers can all be prepared with the assistant of self-organized anodic porous alumina.

The material fabricated by anodization method in this research is TiO_2 nanotube arrays. In 1999, the first self-ordered TiO_2 nanostructure was obtained by anodizing Ti

in a fluoride containing electrolyte. Thereafter, investigation on the anodic TiO₂ nanotube arrays got great improvement. For the preparation of TiO₂ nanotube arrays, in the first stage, water based electrolytes were widely used, and the as-prepared TiO₂ nanotube arrays show only few hundred nanometers in length. A neutral pH value of the electrolyte can improve the length of tubes. In the second stage, non-aqueous electrolytes (such as glycerol and ethylene glycol) were investigated, TiO₂ nanotube arrays can grow to higher aspect ratios and show highly improved ordering. Similarly as anodizing of aluminum, not only nanotube arrays but also other self-organized TiO₂ morphologies can be prepared by altering the anodization voltage. Bamboo-type nanotube can be obtained by voltage pulsing between two levels. Tube branching can also be initiated if a step from higher to lower anodization voltage is applied during anodization process. With controllable dimensions of nanotube structures, tailorable surface chemistry, high surface area, chemical stability and low cost, TiO₂ nanotube arrays have been applied in many fields. It is suitable for the photocatalytic decomposition of organic pollutants. Grätzel-type solar cells can also be fabricated after dye-sensitizing of the TiO₂ nanotube arrays. Other applications such as electro-chromic, batteries, drug release materials, chemical sensors and biomedical films have also been widely investigated.

For anodization of other metals, the vertically aligned pores and nanotubular structures produced by electrochemical anodizing of Ta and W are also attractive materials for the implantable drug delivery system for coronary stents, bones and tissue engineering. ZrO₂ nanotube arrays, which prepared by anodizing, can also be applied in the field of optical, electronic, magnetic and heterogeneous catalysts.⁴⁹ On other pure metal of Hf, Ta, Nb and Fe, nanotubular oxide structures can also be formed. Nanotubes and ordered nanopores were also obtained by anodizing of alloys such as TiZr, TiNb, TiTa, TiW, TiMo, TiRu and TiAl. Compared with the anodization of pure metals, the oxide formation mechanism of anodizing of alloy is more complex due to increased number of migrating ions toward the metal-electrolyte interface. If the two different metals have similar migration rates, the distribution of elements in

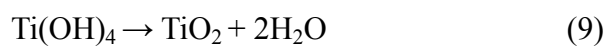
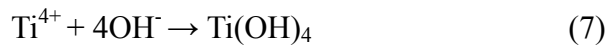
the oxide is uniform. If the migration rates of metals are considerably different, a layered structure with pure metal oxide region can be expected.

1.4 TiO₂ nanotube arrays prepared by anodization

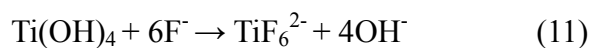
1.4.1 Development of anodic TiO₂ nanotube arrays

In general, the anodization of valve metals usually produces two different types of oxide film: a barrier-type anodic film and a porous oxide film. Taking the anodization of aluminum as an example, the nature of electrolyte used can affect the type of oxide growing on the surface. In neutral solutions, a barrier-type of anodic film can be formed without chemically affected and stays practically insoluble. If the pH value of electrolytes decreases, localized dissolution of oxide is available and causes porous alumina oxide films. Similar to the anodization of aluminum, ordered porous films can also be formed on other valve metals such as Ta and Nb. However, oxide structures with separated individual tubes are usually formed for some valve metals such as Ti, Zr and Hf.

Different from the porous aluminum oxide film, for the anodization of Ti metal, fluoride ion in the electrolyte plays an important role to produce nanotubular or porous structures, because soluble fluoro-complexes can be formed with the presence of F⁻. In the initial stage, an oxide layer is formed on the metal surface from chemical interaction between the released Ti⁴⁺ ions and O²⁻ or OH⁻ ions. The chemical reactions involved in oxide formation can be expressed below:



The latter process is the formation of the nanotube structures, which is mainly associated with the fluoride ions. The fluoride ions can form complex with Ti⁴⁺ at the surface of the oxide according to the reaction below:



Small pits due to localized chemical dissolution will be created on the surface of formed oxide film. These pits can act as pore forming centers and will continue to grow at the bottom with inward movement of the oxide layer. A typical current-time curve of TiO_2 nanotube formation during anodization process is shown in Figure 1.8, the curve contains three stages: in the first stage, the curve essentially follows the fluoride-free case, the initially high current density decays with increasing oxide thickness, a compact oxide layer can be formed. In the second stage, initial nanoscale pore formation can cause current increase. This process is determined by diffusion effects, agitation and viscosity of the electrolyte are important. Finally, progressive growth of the tubes can be realized, a relative stable current value will be achieved.

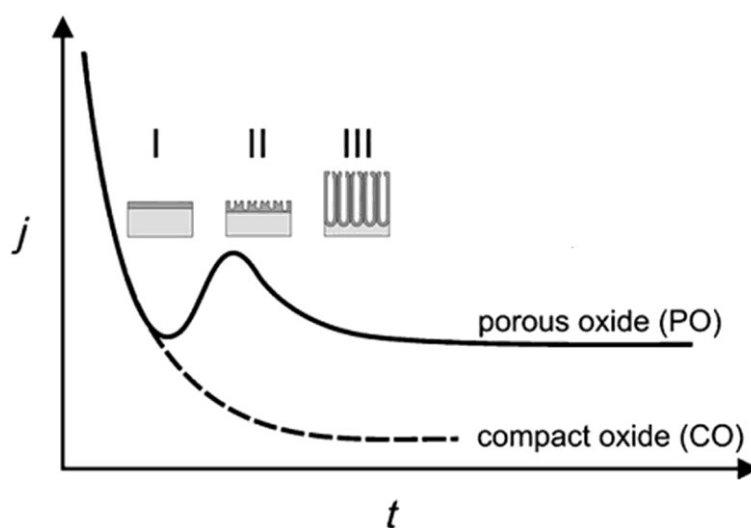


Figure 1.8 Typical current-time (j - t) characteristics after a voltage step in the absence (----) and presence (—) of fluoride ions in the electrolyte.⁵⁰

The same as the anodization of Al metal, incorporation of species in the electrolyte can also occur for the anodization of Ti metal. In the phosphoric acid electrolyte, after anodizing, phosphorous species will exist in the as-prepared TiO_2 nanotube arrays. Boron species can also be found if anodizing the Ti metal in the ammonium pentaborate electrolyte. In organic electrolytes, incorporation of carbon species into

the oxide is achievable for the anodizing of Ti metal.

For the anodization of Ti metal, other advanced geometries of nanotube arrays are also reported by changing the experimental parameters. They include tube stacks, bamboo-tube, nanolace, and branched tubes. In aqueous electrolytes, the as-anodized TiO₂ nanotube arrays usually demonstrate many ripples on the tube wall which just termed as bamboo-type. The bamboo-type nanotubes are promising in the field of dye-sensitized solar cells for a higher surface area than typical TiO₂ nanotube arrays. They can also be generated by applying alternative potential stepping. In organic electrolytes (i.e., glycerol and ethylene glycol) with very low water content, the ripples can be avoided and show smooth tube walls. The nanolace structure can be produced by selectively etching out of the TiO₂ tubes in fluoride electrolytes. Branched TiO₂ nanotube arrays can be prepared by anodizing if a step from a higher to lower anodization voltage is carried out. Recently, other structures such as bamboo leaves, squares, triangles, and flowers have also been successfully prepared. Another interesting structure is double-wall TiO₂ nanotube array, under sufficiently high voltages, a carbon rich inner wall can be formed inside the nanotubes for the decomposition of organic species in organic electrolytes.

1.4.2 Factors involved in the anodization process of TiO₂ nanotube arrays

In order to design an optimized TiO₂ nanotube arrays, many parameters should be considered during anodization process. Diameter and length of tubes, chemical composition and crystal structure can all be affected by changing the anodization parameters such as composition of electrolyte, anodization voltage, pH value of electrolyte and temperature. In the following, the influence of these factors in the anodization process on the nanotube array structure, composition and properties will be reviewed.

(a) Chemical composition of the electrolyte

Effect of composition and concentration of electrolytes on the growth and geometry of TiO₂ nanotube arrays has been widely investigated. TiO₂ nanotube arrays anodized

in organic solutions usually show different morphologies and composition compared with nanotubes grown in aqueous electrolytes. Tubes cannot grow longer than a few micrometers in aqueous electrolytes, while in ethylene glycol solution, the nanotubes can grow to more than 100 μm . TiO_2 nanotube arrays also show hydroxide rich in the inner tube layer than outer layer if the aqueous solution is used. Incorporation of carbon species occurs in the inner wall region of nanotube if organic electrolytes are used. The concentration of fluoride also strongly affects the anodizing process. If the fluoride concentration is very high, TiO_2 nanotube arrays can hardly be obtained, because releasing Ti^{4+} will react with F^- immediately and form soluble TiF_6^{2-} species. A low concentration of fluoride also causes an inefficient tube growth and result in a stable compact oxide layer. So the fluoride concentration should be carefully selected to get TiO_2 nanotube arrays. In the organic electrolytes, water content can also affect the geometry of TiO_2 nanotube arrays. For the anodizing at 20 V in the mixture of ethylene glycol and water, Rajia et al. show that minimum water content is 0.18 wt% for the anodization of highly ordered structure.⁵¹ Under higher water contents of the electrolyte (> 20 wt%), chemical etching will become serious, TiO_2 nanotube array will reach its maximum thickness quickly, and efficiency of tube growth decreases drastically. Tube diameter is also affected by the chemical composition of electrolytes. In organic electrolyte with low water content, the ratio between the outer and inner diameter is constant. However, at higher water content (> 30 wt%), the outer diameter does not change anymore.

Recently, nitrate based organic electrolyte was also reported for the preparation of self-ordered titanium oxide nanopore layers on Ti metal. In aqueous NH_4NO_3 electrolytes, the current densities are usually very high during anodization process, the self-organization of TiO_2 nanopores can hardly be established. So a water-containing organic nitrate electrolyte is suitable for ideal self-organization of nanopores. Contamination from the electrolyte is very low for the TiO_2 nanopores prepared in aqueous NH_4NO_3 electrolyte, only carbon contamination on the surface was reported until now.

(b) Anodization voltage

For anodization of TiO_2 nanotube arrays in both aqueous and non-aqueous electrolytes, the diameter especially the outer diameter of nanotubes is controlled linearly by the anodization voltage. A voltage dependence of the tube diameter for different electrolytes is shown in Figure 1.9. The growth efficiency of TiO_2 nanotube arrays also changes with the anodization voltage. At lower anodization voltage, pores structure can be obtained in the electrolyte with low water concentration. At higher anodization voltage, electro-polishing of the samples will occur for the high current density, TiO_2 nanotube arrays cannot be obtained.

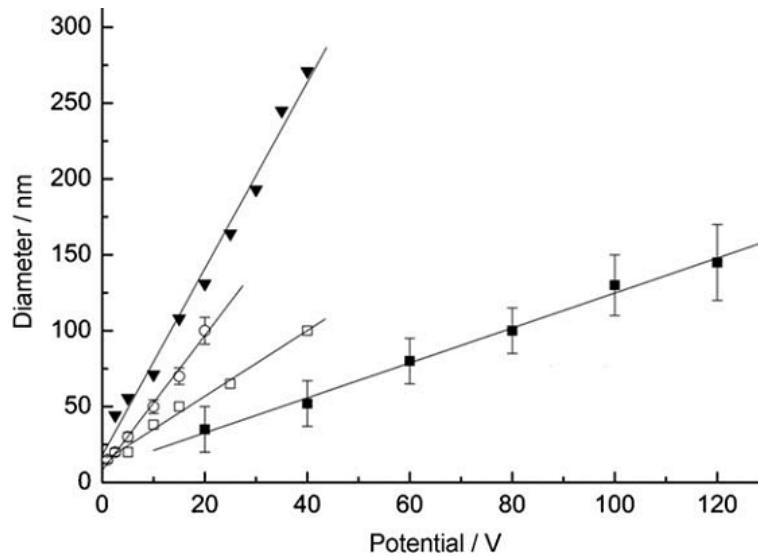


Figure 1.9 Voltage dependence of the tube diameter for different electrolytes (○ water based, ▼ glycerol/ H_2O 50:50, □ glycerol, ■ Ethylene glycol).⁴⁷

(c) pH value of electrolyte and temperature

For the pH value of electrolyte, during anodization process, the growth efficiency of TiO_2 nanotube arrays is higher in alkaline than in acidic solutions. The growth rate of TiO_2 nanotube arrays is very high in both very alkaline and very acidic solutions. However, in acidic electrolyte, a high chemical etching rate will occur, the tube tops will be etched and cause a shorter tube than that in neutral electrolyte. While in alkaline solutions, longer TiO_2 nanotube arrays free of disordered layer on the top can be obtained.

High temperature is not suitable for preparing long and highly ordered TiO_2 nanotube arrays. At high temperature, the migration of Ti^{4+} cations can be thermally accelerated, more Ti^{4+} cations will lose to the electrolyte. So an increase in current density and an avalanche effect will occur during anodization process at high temperatures. Other interesting geometries can also be prepared by anodizing at high temperatures. For example, in a hot glycerol- K_2HPO_4 electrolyte ($180 \pm 1^\circ\text{C}$) followed by chemical etching of the structure, a highly regular and robust mesoporous TiO_2 structures can be formed and show higher efficiencies in Grätzel-type DSSCs. By adjusting the applied voltage, “channel” and “fishbone” structure can also be obtained. The three distinct structures are shown in Figure 1.10.

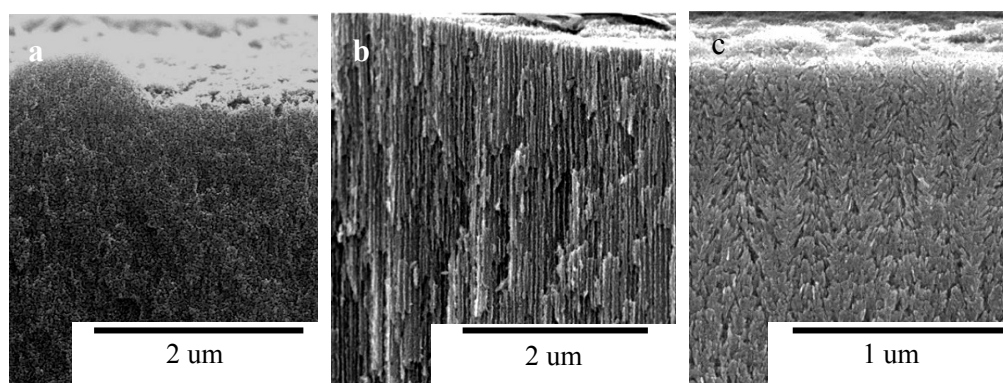


Figure 1.10 Anodic (a) mesoporous, (b) channel and (c) fishbone type TiO_2 layers.⁵²⁻⁵⁴

1.4.3 Modification of TiO_2 nanotube arrays for improved properties

Many methods were chosen to modify the TiO_2 nanotube arrays in order to enhance applications that rely on electrical, optical and chemical properties. These methods can be classified into three categories: (1) annealing, (2) doping, and (3) tube wall decoration.

Annealing is needed to convert the amorphous TiO_2 nanotube arrays to crystal structure, its effect on the morphology and chemical composition of TiO_2 nanotube arrays has been widely investigated. Under oxidizing condition (such as air or O_2), anatase and rutile phase can be obtained after annealing. However, complete

conversion of TiO₂ nanotube arrays to rutile phase is difficult to achieve, the tubes will suffer from significant morphological deterioration for the rapid grain growth. During annealing process, a thin rutile layer will also be formed underneath the tube bottoms for the thermal oxidation of titanium metal substrate. In the absence of oxidizing species or in vacuum, annealing usually will reduce the TiO₂ nanotube arrays, Ti³⁺ can be formed. This will enhance the visible light absorption and conductivity of TiO₂ nanotube arrays. Different anatase/rutile ratios of TiO₂ can also be obtained by changing gas atmospheres. Moreover, significant carbon and fluoride contamination of TiO₂ nanotube arrays can be driven out to a large content during annealing process.

Doping can introduce new energy bands or localized states in the band gap of TiO₂. The doping of TiO₂ covers many elements, such as metal and transition-metal (Cu, Co, Ni, V, Cr, Mn, Fe, Mo, Nb, Ru, Au, Ag, Pt), non-metals (N, S, C, B, P, I, F) and semiconductors with lower band gap energy. Some common methods to prepare doped TiO₂ nanotube arrays are shown below:

- (a) Treating the final or growing TiO₂ nanotube arrays in a solution or a melt of the doping species.
- (b) Thermal treating the TiO₂ nanotube arrays in gas atmospheres of the doping species.
- (c) Co-sputtering or sputtering in an atmosphere of doping species.
- (d) High-energy ion implantation.
- (e) The use of a suitable alloy substrate.

The most successful method to improve the optical properties of TiO₂ nanotube arrays is nitrogen doping. The chemical states of nitrogen in the TiO₂ changes by using various methods. For instance, sputtering in N₂ environments and proper ion implantation of N⁺ can lead to a XPS peak of N 1s at 396 eV.⁵⁵ Wet treatments in amine containing solutions typically produce XPS peaks of N 1s at around 400 or even 402 eV.⁵⁶ Because molecular N₂ adsorbed on TiO₂ also show the XPS peak of about 400 eV, the N-doping reactions that result in an XPS peak of N 1s at about 400

eV are very ambiguous. Ion implantation can successfully lead to the most effective nitrogen doping of TiO₂ nanotubes. After ion implantation, amorphization of TiO₂ nanotubes usually occurs, so re-annealing is in need to remove the defects of nanotubes. Alloy doping is a particular advantage of anodic formation of TiO₂ nanotube arrays. By using TiN containing titanium alloy substrates as anode electrode, nitrogen can be doped inside TiO₂ nanotubes after anodization experiment. Some oxides of W, Mo, Al, Ta, Zr, Nb can also be incorporated into the TiO₂ structure by anodizing of the alloy metal substrate.

The second approach to modify TiO₂ nanotube array is carbon doping. Carbon can be doped inside by treating the TiO₂ nanotube arrays under CO gas flow or acetylene at high temperatures. For the C-doping of TiO₂ nanotube arrays using acetylene, a TiOC material containing magnéli-type oxides is available, such material holds a semi-metallic conductivity as graphite and is quite promising in the use of electrochemical redox reactions. A large amount of other dopants (such as Fe, W and Cr) have also been reported. But it remains difficult to unify a true doping effect. Metal ion doping can enhance the photoactivity of TiO₂, but it can also cause thermal instability and shorter electron-hole time.

Tube wall decoration is usually related to the modification of TiO₂ nanotube arrays with nanoparticles. Nanoparticles can be metals, semiconductors and polymers. For the decoration of noble metal particles (such as Au, Ag, Pt, Pd), widely used methods contain UHV evaporation, chemical reduction and photocatalytic reduction. By photocatalytic reduction of Ag⁺ under UV illumination, silver nano-particles can be deposited on the tube wall. The silver decorated TiO₂ nanotube arrays show enhanced photocatalytic activity and performance of DSSCs. Decoration with oxide nanoparticles (e.g., WO₃, Cu₂O, Fe₂O₃, NiO, ZnO, Bi₂O₃ and TiO₂) can be obtained by slow hydrolysis of precursors electrochemically. After the decoration with TiO₂ nanoparticles, the beneficial effect is the enlarged overall surface area. However, for the decoration of TiO₂ nanotubes with WO₃ nanoparticles, electron band junction between TiO₂ and WO₃ is also responsible for the enhancement of the photocatalytic

activity. Conducting polymers are widely used to sensitize the TiO₂ nanotube arrays for sunlight absorption application, but photocatalytic degradation of polymers usually results in the failure of the structures. By chemical bath deposition or thermal treatment in the presence of precursors, some narrow band gap semiconductors (such as CdS, CdSe, PbS) quantum dots can also be deposited inside the TiO₂ nanotube arrays. Recently, zeolite was decorated in the TiO₂ nanotube arrays as molecule selective binding units, accumulation and decomposition of pollutants can occur during photocatalytic process, so photocatalytic activity can be enhanced. The morphology of TiO₂ nanotube arrays loaded ZSM-5 nanocrystals and the improved photocatalytic activity are shown in Figure 1.11.

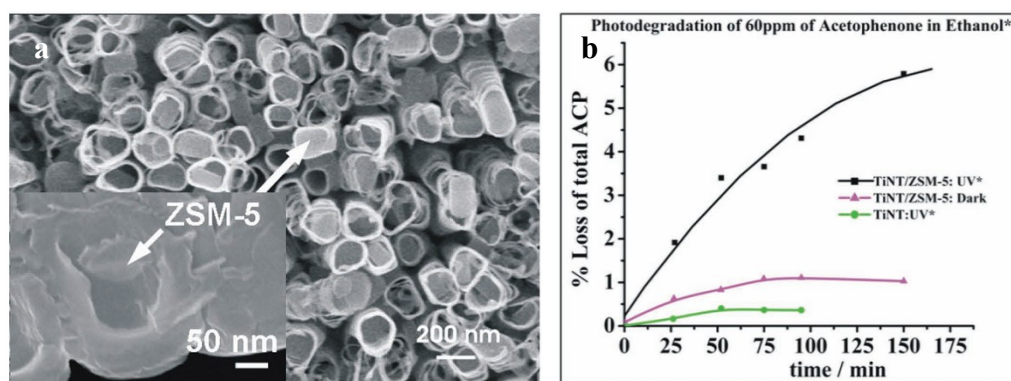


Figure 1.11 SEM image of TiO₂ nanotube arrays loaded with ZSM-15 nanocrystals (a) and improved photocatalytic property (b).⁵⁷

1.5 Purpose of the study

As described above, the use of TiO₂ as a photocatalyst for energy conversion has been widely investigated. One method to prepare more effective TiO₂ photocatalyst is the modification of structure and morphology. Among various nanostructures of TiO₂, TiO₂ nanotube arrays can be formed by a simple electrochemical oxidation of metallic titanium and attracted considerable interests over the past 10 years. In this thesis, the anodic TiO₂ nanotube arrays were studied in a glycerol-containing electrolyte. TiO₂ nanotube arrays with different morphologies (double-wall, single-wall, etc) were produced by varying a set of experimental parameters. The formation mechanism of TiO₂ nanotube arrays was discussed.

The double-wall TiO₂ nanotube array was further subjected to both *ex situ* and *in situ* annealing. For the *ex situ* annealing, the chemical composition, crystal structure and morphology of double-wall TiO₂ nanotube arrays were investigated. For the *in situ* annealing, the sintering behavior of TiO₂ nanotube was real-time monitored by a transmission electron microscope (TEM). Using a special designed TEM holder, oxygen gas was introduced and induced different sintering behaviors of TiO₂ nanotube. The function of oxygen gas molecule during *in situ* annealing of TiO₂ nanotube was discussed.

Photocatalytic activities of double- and single-wall TiO₂ nanotube arrays were also compared. In order to improve the photocatalytic properties of TiO₂ nanotube arrays. Pt nanoparticles were decorated inside both double- and single-wall TiO₂ nanotube arrays by a deposition-precipitation method. The photocatalytic activity of TiO₂ nanotube arrays after Pt decoration was evaluated.

1.6 Construction of the thesis

This thesis is organized according to the progression with the three purposes listed above. It is composed of five chapters. Chapter 1 is the introduction of this thesis.

Chapter 2 describes the preparation of TiO₂ nanotube arrays with different morphologies. Various anodization voltage, time and composition of electrolyte were selected. The mechanism of the anodizing of Ti metal was discussed to explain the formation of some special structures such as double-wall, ripples.

In chapter 3, a two-step anodization method was chosen to improve the regularity of the as-formed double-wall TiO₂ nanotube arrays. After anodization, the effect of annealing on the morphology, chemical composition and crystal structure of double-wall TiO₂ nanotube arrays was examined by both *ex situ* and *in situ* annealing method. Specially, the oxygen gas was introduced inside during *in situ* annealing process. By comparing with the high vacuum condition, TiO₂ nanotube shows a higher thermal stability in the presence of oxygen gas.

Chapter 4 demonstrates the improvement of catalytic properties of TiO₂ nanotube

arrays decorated with Pt nanoparticles. Two solutions were chosen to decorate Pt nanoparticles inside TiO₂ nanotube arrays. By comparing the results, deposition-precipitation method was found to be suitable for the uniform decoration of Pt nanoparticles. The photocatalytic activities of double- and single-wall TiO₂ nanotube arrays and those decorated with Pt nanoparticles were investigated and compared. The improvement of photocatalytic properties will be discussed. .

Chapter 5 summarizes all the findings and conclusions from chapter 2 to chapter 4.

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CHAPTER 2

Morphology Control of TiO₂ Nanotube Arrays by Anodization Under Different Experimental Conditions

2.1 Introduction

Titanium oxide (TiO₂) nanotube arrays, prepared in fluoride-containing electrolytes by anodization method, have demonstrated effective applications in hydrogen generation,^{1,2} gas sensing,³ dye-sensitized solar cells (DSSCs),⁴ photocatalysis⁵⁻⁷ and biomedical applications⁸ for their unique properties. The morphology and structure of TiO₂ nanotube arrays, including pore diameter, tube length, specific surface area and ordering of arrays, usually have a great impact on their performance. Therefore, many investigations focus on the preparation of TiO₂ nanotube arrays with different morphologies.

After an important improvement on the geometry of TiO₂ nanotubes was made by Macak et al.,⁹ TiO₂ nanotube arrays have been frequently prepared in non-aqueous solutions, the most widely used non-aqueous electrolytes are glycerol and ethylene glycol solutions. Compared with aqueous electrolytes, longer and smoother nanotube arrays can be produced in the non-aqueous condition.¹⁰ It was also observed that different pH profile within the tube is essential to prepare TiO₂ nanotube arrays with various thickness and morphologies. By a two-step anodization method,¹¹ virtually highly ordered TiO₂ nanotube arrays can be obtained. In advantage of many experimental progresses on the preparation of TiO₂ nanotubes, the formation mechanism was also discussed in order to effectively control the structure and properties of TiO₂ nanotube arrays.

The growth process of TiO₂ nanotube arrays is widely considered to be controlled by a dynamic equilibrium between the oxidation and dissolution of anodized oxide.¹²

However, recent findings have shown that the anodization process of titanium metal should be more complex. For example, the formation of inter-tube gaps leads to the separated tubes, it is much different from the porous structures of anodized Al_2O_3 nanopores.¹³ A “fluoride-rich” layer was found to explain the formation of the inter-tube gaps.¹⁴ In 2008, double-wall TiO_2 nanotube array was prepared through anodization method by Albu et al,¹⁵ it thus be expected that organic species can get decomposed and produce the inner wall of tube. Considering the complicated formation mechanism of anodic TiO_2 nanotube array, controlling the morphology of TiO_2 nanotube arrays is valuable not only to clarify more details of the formation process of TiO_2 nanotube arrays, but also to enhance the performance of TiO_2 nanotube arrays.

Until now, TiO_2 nanotube arrays with interesting morphologies discussed above were mostly prepared in the ethylene glycol-containing solution.^{16,17} Another organic solvent, glycerol, has rarely been investigated on the morphological control of TiO_2 nanotube arrays. Therefore, in this chapter, glycerol was selected to prepare electrolytes, and different morphologies of TiO_2 nanotube arrays were obtained by changing the experimental parameters.

2.2 Experimental section

2.2.1 Preparation of TiO_2 nanotube arrays

Glycerol (Wako pure chemical, Japan), H_2O (purified by Organo/ELGA Purelabo-II, > 18 M Ω), and NH_4F (Wako pure chemical, Japan) were used to prepare electrolytes for the anodization experiment. Prior to anodization, Ti foils (10 mm $\times$ 15 mm, thickness 250 μm , 99.6% purity, Nilaco, Japan) were ultra-sonicated in acetone and rinsed in purified water, then, dried under N_2 stream. As illustrated in Figure 2.1, anodization was carried out in a conventional two-electrode cell using a direct current power supply (Kikusui, Japan). A Pt foil served as the counter electrode (cathode),

and a Ti foil was used as the working electrode (anode). Distance between the two electrodes was ~ 30 mm. Ramp rate from open-circuit to final voltage was kept at 0.1 V s^{-1} . The resulting samples were washed with purified water for several times in order to remove residual solution and then dried in air. All chemicals were of analytical grade and used as received. All the experiments were conducted under room temperature.

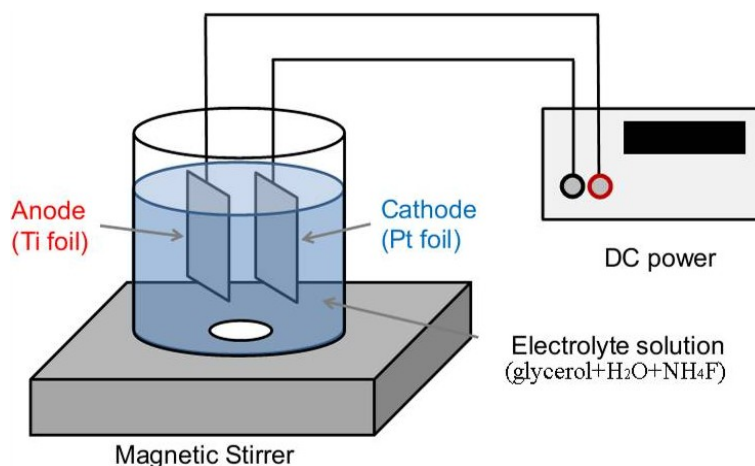


Figure 2.1 Schematic illustration of the electrochemical setup used for the preparation of TiO_2 nanotube arrays.

2.2.2 Characterization of TiO_2 nanotube arrays

A JEOL-JSM 6701F scanning electron microscope (SEM) was used to examine the surface morphology of TiO_2 nanotube arrays. Films were scraped with a steel blade previously for the observation of their side view. The scraped films were also collected for the examination using a transmission electron microscope (TEM, Hitachi HD-9500, 300 KV) and a scanning transmission electron microscope (STEM, Hitachi HD-2000, 200 KV). X-ray Photoelectron Spectroscopy (XPS) measurements were carried out on a JPS-9200 XPS system (JEOL) equipped with a monochromatic Mg Ka source operating at 100 W under ultrahigh vacuum condition ($< 1.0 \times 10^{-7}$ Pa). Binding energies were corrected by referencing to the C_{1s} peak at 284.9 eV of the adventitious carbon.¹⁸ Viscosity of solution was measured by a sine-wave vibro

viscometer (SV-1A, A&D company Ltd, Japan). After calibration by purified water at room temperature, all the solutions were measured 4 times and get the average value to eliminate the effect of temperature.

2.3 Results and discussion

2.3.1 Well-organized TiO_2 nanotube arrays prepared by anodization method

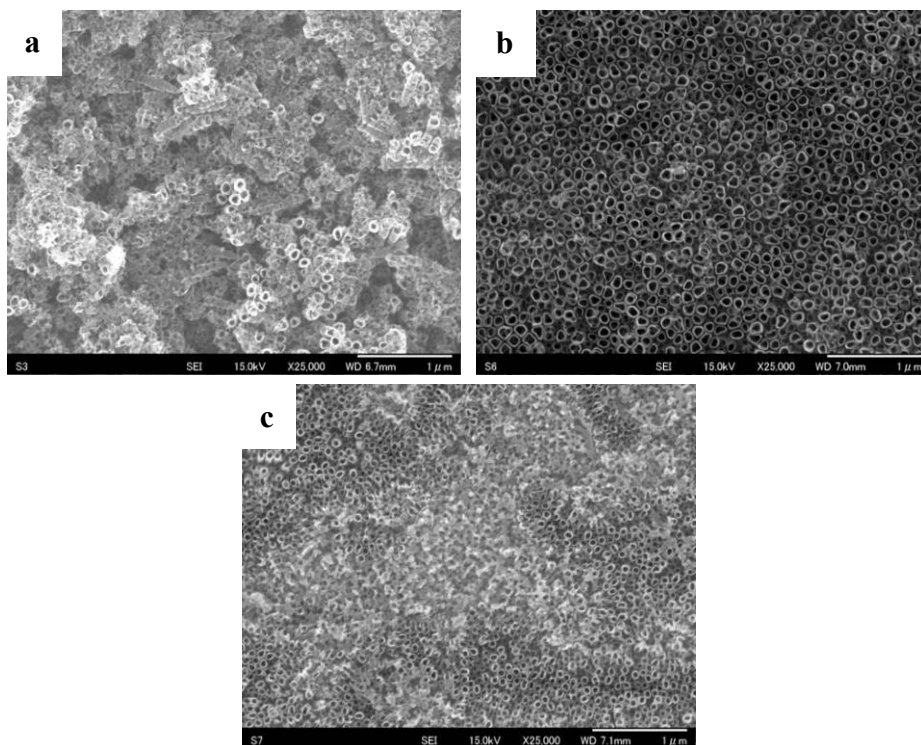


Figure 2.2 Surface images of TiO_2 nanotube arrays prepared in water-glycerol electrolytes containing (a) 70, (b) 20 and (c) 5 wt% of H_2O under 20 V for 6 h. ($w(\text{NH}_4\text{F})=0.5$ wt%).

In order to get well-organized TiO_2 nanotube arrays, firstly, TiO_2 nanotube arrays were prepared by anodization in the electrolyte with different water contents. The water content had an obvious influence on the surface morphology of TiO_2 nanotube arrays. The surface morphologies are displayed in Figure 2.2. Under water content of 70 wt%, many tubes were broken and assembled bundles on the surface, only mechanically stable nanotubes can be observed, the nanotube array was not highly

ordered. If the mass fraction of water attained to 20 wt%, a well-arranged TiO_2 nanotube array was obtained (Figure 2.2b), no break of TiO_2 nanotubes can be observed. However, after the water content was reduced to 5 wt%, in Figure 2.2c, the surface of the nanotube arrays was partially covered with a “hazy” layer, which seems to consist of some conglomerates of not well formed TiO_2 nanotubes.

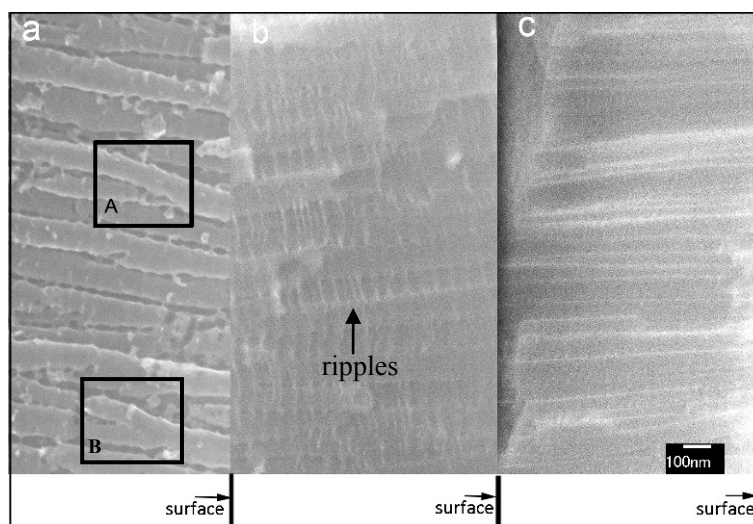


Figure 2.3 Lateral SEM images of TiO_2 nanotube arrays prepared in electrolytes containing (a) 70, (b) 20 and (c) 5 wt % of H_2O under 20 V for 6 h. ($w(\text{NH}_4\text{F})=0.5$ wt%).

Cross-sectional SEM images of the as-prepared TiO_2 nanotube arrays in Figure 2.2 were also taken and shown in Figure 2.3. As previously reported structures formed in aqueous electrolytes,¹⁹ the ripples on the sidewall of the tubes are also an evident character of our TiO_2 nanotube arrays. In Figure 2.3b, more extensive ribbing of the sidewall of nanotubes can be observed compared with Figures 2.3a and 2.3c (indicated by black arrow). In the electrolyte with 70 wt% of water, compactness of the as-formed TiO_2 nanotube arrays decreased greatly, the branched nanotubes were also formed and can be observed in the rectangular area of A and B (Figure 2.3a).

Base on previous work,²⁰ there are several factors involved in the formation of well-organized TiO_2 nanotube arrays. The unstable bundles of tubes in Figure 2.2a

could be formed due to the breakdown effects of the oxide layer. Under the water content of 70 wt%, a significantly low viscosity of the electrolyte was obtained (3.08 mPa·S shown in Figure 2.4), the anodization current may rise to a high value and leads to a rapid etching of the tubes.²¹ The breakdown effects would also cause oscillations of current during anodization process, the voltage loaded on the film will change and results in a branched nanotube. For the “hazy” layer shown in Figure 2.2c, it can be ascribed to a growth stage of “tube growth initiation”, in this stage, the initiation and growth of porous TiO₂ is mainly due to a randomly dissolution and breakdown of an initially formed compact barrier layer, in some area, it is reasonable that tubes were not well initiated and formed, the initially formed compact barrier layer still exist and form a “hazy” layer on the surface. In contrast, well-organized TiO₂ nanotube arrays were obtained under 20 wt%, the initially formed barrier layer was completely dissolved, breakdown effects did not occur probably for a relatively lower anodization current.

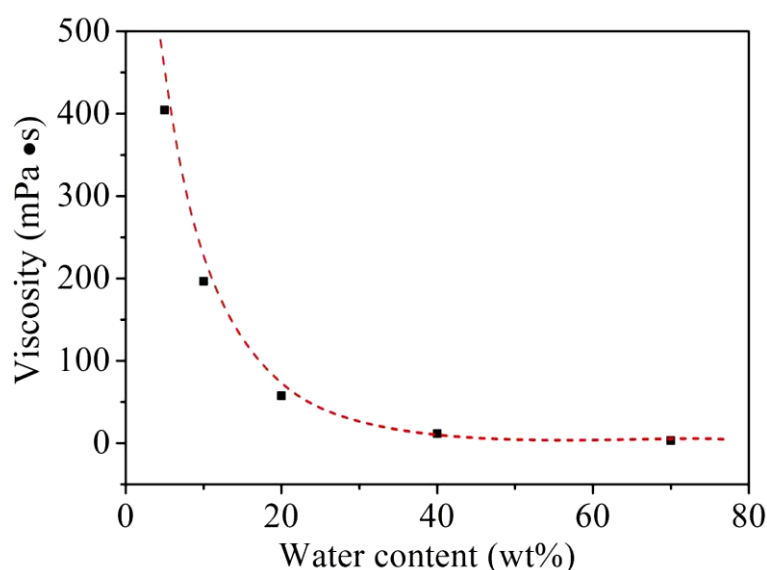


Figure 2.4 Relationship between the viscosity and water content of the aqueous glycerol electrolyte.

In the electrolyte with 20 wt% water, TiO₂ nanotube arrays were also prepared by anodization under different anodization voltages (20, 30, 40 V) for 6 h. Figure 2.5

shows the surface and lateral SEM morphologies of the as-prepared samples. All three samples show highly ordered top-tubular surface, there is a clear effect of anodization voltage on the tube diameter. As shown in Figure 2.5, with the anodization voltage increases from 20 to 40 V, after calculation, the average diameter of nanotube are around 96 nm, 142 nm and 173 nm respectively. This is consistent with previous reports about the tube diameter controlling linearly by applied voltage.²² In the lateral SEM images of Figure 2.5d, ripples are also very obvious on the sidewall of the three samples (indicated by black arrow). Under 40 V, a less extensive ribbing of the sidewall of nanotubes can be observed, the tubes showed smooth side-walls (square area). According to the report by Choi et al,²³ This is presumably due to the etching of the top of tubes, the ripples on the top of tubes were dissolved in the electrolytes.

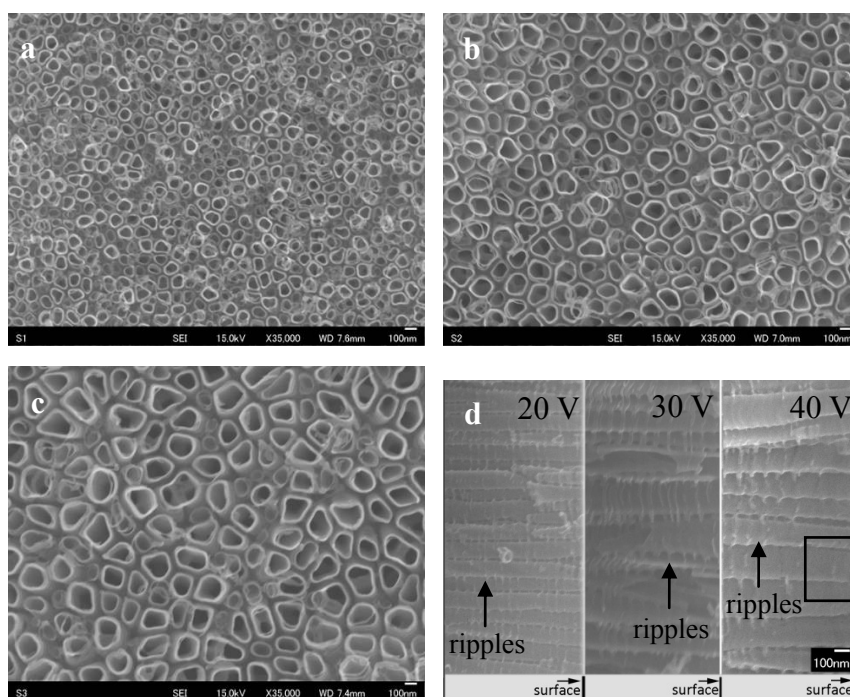


Figure 2.5 Top-view SEM images of TiO₂ nanotube arrays prepared by anodization under (a) 20 V, (b) 30 V and (c) 40 V for 6 h. (electrolyte: 79.5 wt% of glycerol; 20 wt% of H₂O; 0.5 wt% of NH₄F). (d) Lateral SEM images of TiO₂ nanotube arrays.

From the above experimental results, TiO₂ nanotube arrays were successfully prepared by anodization in water-glycerol electrolyte. For the anodization carried out

at 20 V for 6 h, a well-organized TiO₂ nanotube array was obtained by using glycerol based electrolyte with 20 wt% of water. It also showed many ripples on the side-wall of TiO₂ nanotubes. Under water content of 20 wt%, an enlarged tube diameter was observed with anodization voltage increased from 20 to 40 V, many ripples on the sidewall of TiO₂ nanotube arrays disappeared probably due to the excessive etching of the tube top. Detailed investigation and discussion on the morphological details of anodized TiO₂ nanotube arrays were given in section 2.3.2.

2.3.2 Morphological details of anodic TiO₂ nanotube arrays prepared in water-glycerol electrolytes

Figure 2.6 illustrates TEM and HRTEM images of TiO₂ nanotubes prepared in the glycerol-based electrolyte containing 20 wt% of water. In addition to a clear tubular structure of TiO₂ nanotube, the ripples on the sidewall of TiO₂ nanotube are clearly observable. As indicated by the white arrow in Figure 2.6a, the ripples bridged two nanotubes, some ripples are broken probably due to the ultrasonic treatment during sample preparation. In Figure 2.6b, the ripples are also clear (indicated by the white arrows), and the tube wall thickness is inhomogeneous. Notably, the high magnification TEM image of Figure 2.6c indicates a double layer structure of tube wall, which just termed as outer layer and inner layer. Dark area between inner layer and outer layer was observed (square area in Figure 2.6c), since no lattice fringes in the HRTEM image of the dark area can be observed (Figure 2.6d), the dark area is presumably attributed to the different thickness. So a double layer structure can be expected for the TiO₂ nanotube arrays prepared in the water-glycerol electrolyte.

For the inter-tube regions and ripples on the tube wall, they are supposed to originate from a “fluoride-rich” layer formed at the interface between the Ti substrate and the TiO₂ film. As seen in the survey XPS profile of the as-prepared TiO₂ nanotube arrays (Figure 2.7), the peaks corresponding to fluorine were observed in addition to

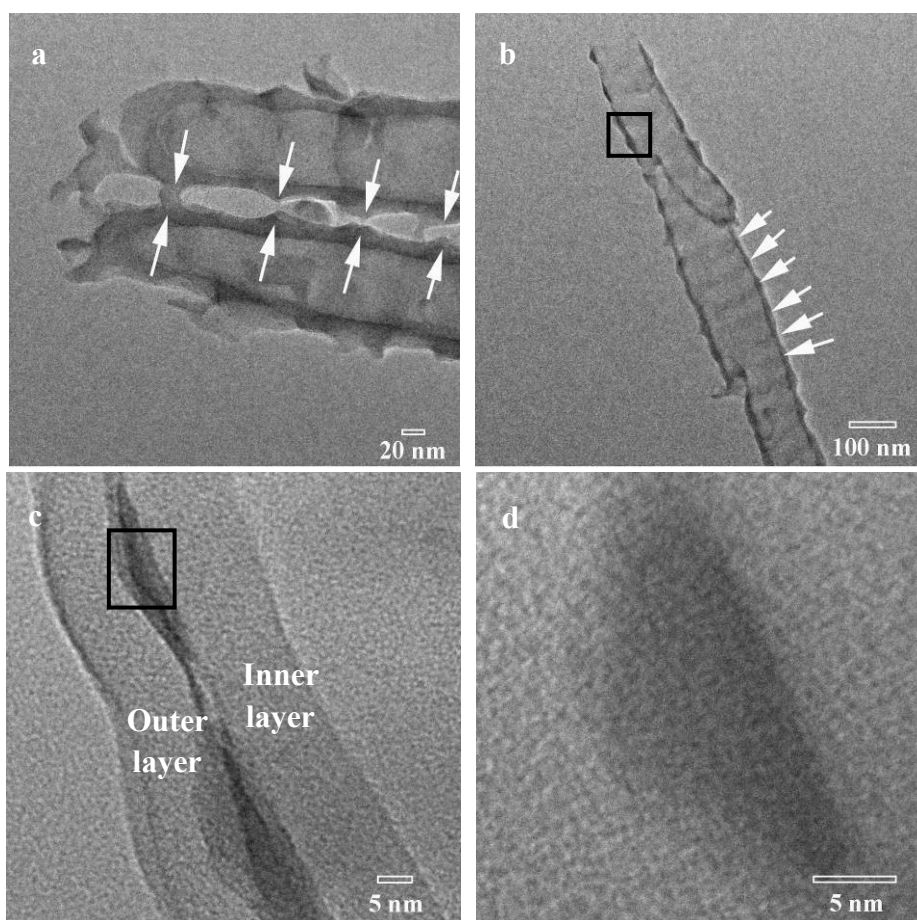


Figure 2.6 TEM and HRTEM images of TiO₂ nanotube arrays prepared in water-glycerol electrolyte (79.5 wt% of glycerol; 20 wt% of H₂O; 0.5 wt% of NH₄F) under 20 V for 6 h. (c) is the enlarge image of square area shown in (b); (d) is the enlarge image of the rectangular area shown in (c).

the peaks of titanium and oxygen. This indicates that anodization of titanium foil in the presence of NH₄F produced titanium oxide nanotube arrays containing fluoride anion (F⁻). Under the electrical field, the fluoride species migrate to the metal/oxide film interface, where they will form a “fluoride-rich” layer. In Figure 2.7b, XPS peak of F_{1s} at 685.2 eV can be found, this peak is well corresponding to that of TiOF₂ at 685.3 eV,²⁴ but not corresponding to that of TiO_{2-x}F_x at 688.6 eV.²⁵ In the inset HRTEM image of the as-prepared TiO₂ nanotubes, lattice fringes with the interval of 0.368 nm can be observed. This lattice fringe interval is also corresponding to that of TiOF₂ (100) (0.380 nm) than to that of TiO₂ (101) (0.352 nm). So the “fluoride-rich”

layer contains TiOF_2 . TiOF_2 is an intrinsic semiconductor and show poor electro-conductivity due to the Ti-F covalent bond formation,²⁶ this may cause an electrical charge of the sample during SEM observation.

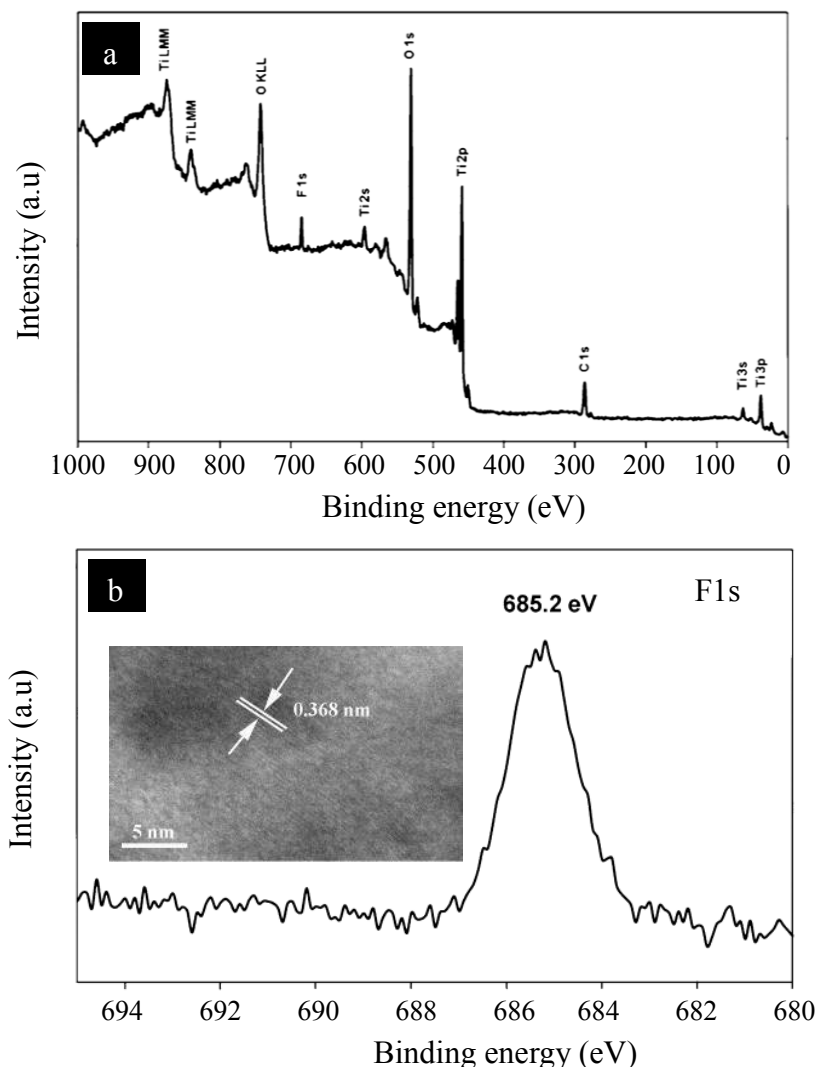


Figure 2.7 XPS profile of TiO_2 nanotube arrays prepared in the electrolyte containing 79.5 wt% of glycerol; 20 wt% of H_2O ; 0.5 wt% of NH_4F under 20 V for 6 h.

The “fluoride-rich” layer can be avoided by using NH_4NO_3 instead of NH_4F in the electrolyte. As shown in Figure 2.8, in the glycerol-based electrolyte containing NH_4NO_3 , a nano-porous TiO_2 powders was achieved on the surface after anodization (Figure 2.8a). The fast anodization on the Ti metal surface created a layer of titanium dioxide that was instantly broken down for high current values and formed powder on

the surface of the Ti metal. The powders consist of nanoporous oxide structures instead of nanotube arrays as obtained using F-containing electrolyte, the aligned pores is apparent in the top and cross-sectional SEM images of Figures 2.8b and 2.8c. The average pore diameter is around 30 nm. Without fluoride, “fluoride-rich” layer cannot be formed, the nanoporous structures are characterized by sharing tubular walls. We also conducted a series of anodization experiment in the electrolyte containing NH_4NO_3 , no nanotube was formed. This further confirms that, in fluoride-

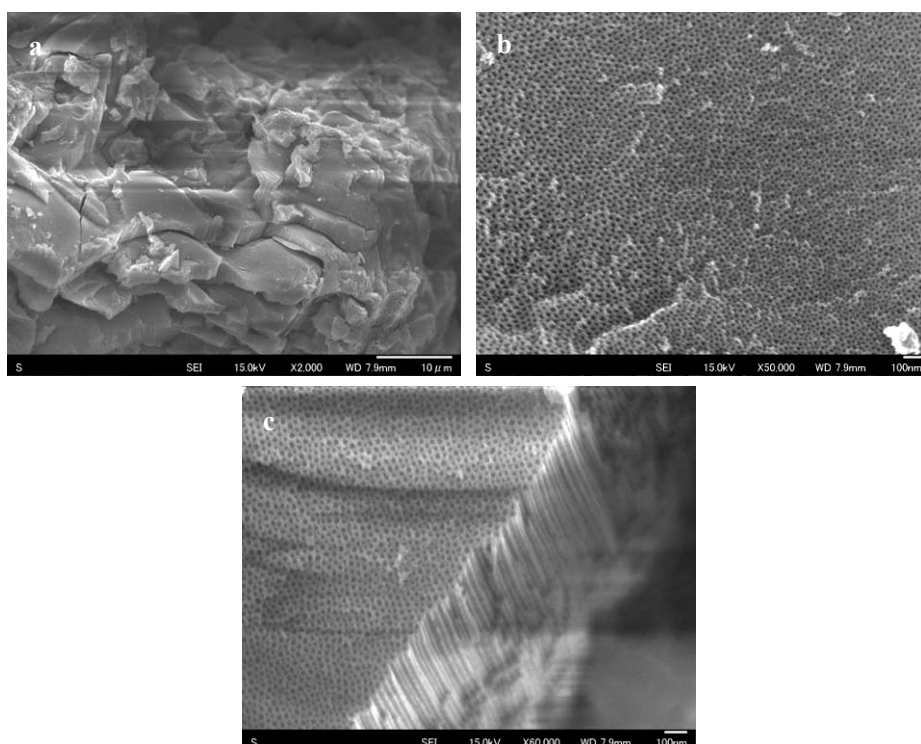


Figure 2.8 SEM images of nano-porous TiO_2 powders prepared by rapaid-breakdown anodization in the electrolyte containing 31.5 g of glycerol, 25 g of H_2O and 0.8 g of NH_4NO_3 . (anodization voltage = 30 V, time = 15 min).

containing electrolyte, the inter-tube regions and ripples of TiO_2 nanotube arrays are formed due to the “fluoride-rich” layer.

Except for the inter-tube regions and ripples on the tube wall, a double-wall structure was also observed in Figure 2.6c, so a double-wall TiO_2 nanotube array can also be expected for the anodization in water-glycerol electrolyte. As shown in Figure

2.9, SEM and TEM images show a clear double-wall structure of TiO₂ nanotubes.

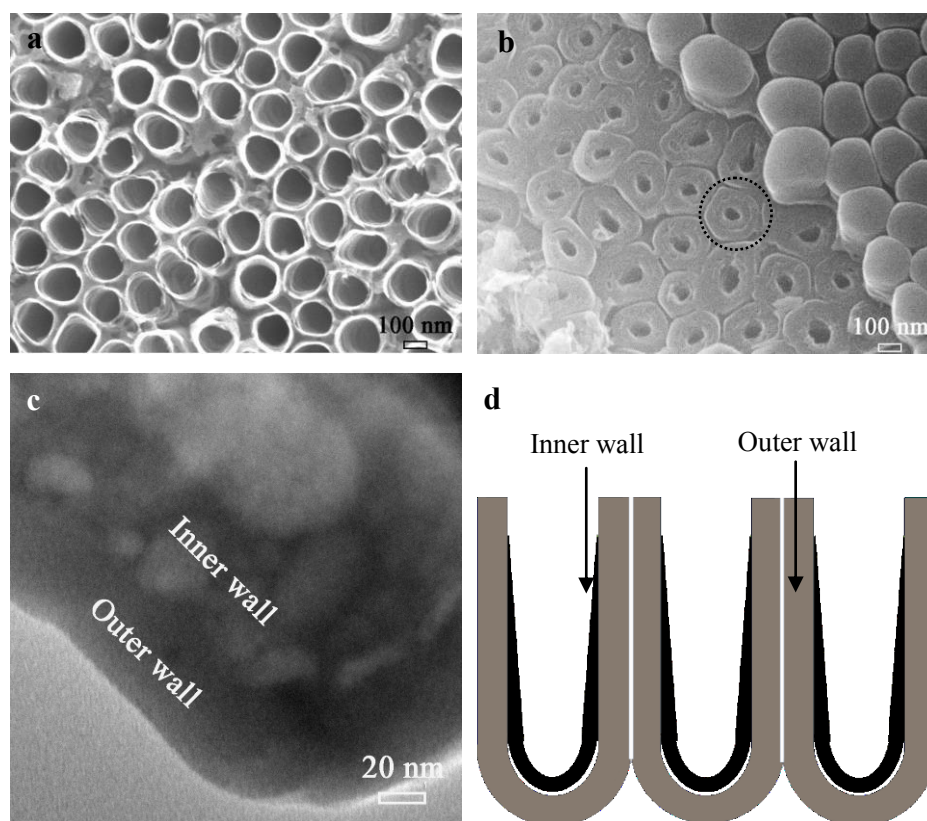


Figure 2.9 (a), (b) SEM images; (c) TEM image and (d) Schematic illustration of double-wall TiO₂ nanotube arrays prepared by anodization at 60 V for 24 h (electrolyte: 96.5 wt% of glycerol; 3 wt% of H₂O; 0.5 wt% of NH₄F).

from the top surface (Figure 2.9a), nanotubes demonstrate only single-wall structures with inner diameter of 200–250 nm. The tube walls are very thin (< 30 nm). However, from the bottom (Figure 2.9b), the tube walls became thicker (> 100 nm), and the inner diameter decreased to 90–100 nm. Judging from these SEM and TEM images, it can be concluded that the inner side of the tubes has a cone like structure as illustrated in Figure 2.9d. This unique structure is probably derived from the excessive etching of the top of tubes. In addition, tube wall also splits into a double layered structure as can be observed in the inset circle area in Figure 2.9b. The cross-sectional TEM image of the root segments of the nanotubes (Figure 2.9c) confirms their double-wall structure. The outer wall appears denser than the inner wall. Similar phenomena were

reported in the case of anodization using other polyol electrolyte.²⁷ So the double-wall TiO₂ nanotube arrays were achieved by anodization in water-glycerol electrolytes, the inner wall is loose and porous.

For the chemical composition of inner wall, it is almost stoichiometric TiO₂, as shown in Figure 2.10, The XPS spectrum of the as-prepared double-wall TiO₂ nanotubes showed that the atomic ratio of Ti:O is 1:2.07. The chemical composition of inner wall is different from that of outer wall. In Figure 2.11, EDS results reveal a high carbon content in the inner wall (Figure 2.11b), it decreased for the outer wall. This indicates a higher carbon contamination of the inner wall, while the carbon content in the outer wall is low.

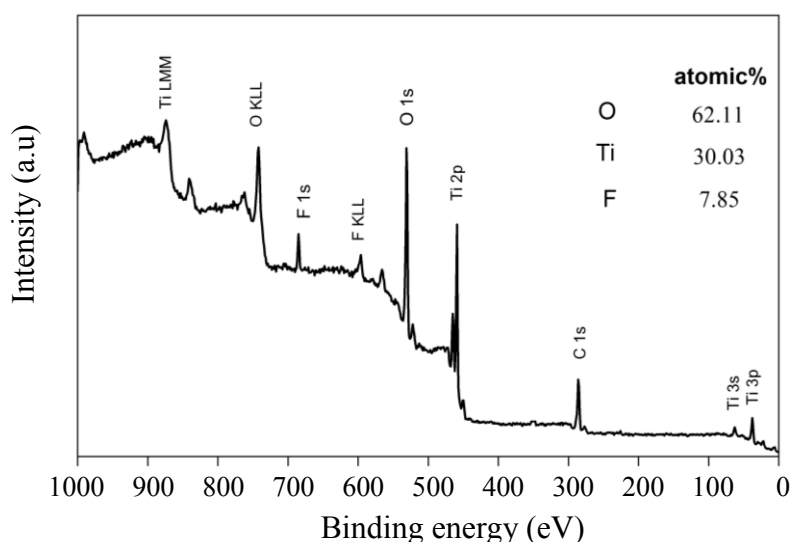


Figure 2.10 XPS profile of double-wall TiO₂ nanotube array prepared by anodization at 60 V for 24 h (electrolyte: 96.5 wt% of glycerol; 3 wt% of H₂O; 0.5 wt% of NH₄F).

Based on the above discussion on the morphological details of the anodized TiO₂ nanotube arrays, suitable experimental details should be selected to obtain TiO₂ nanotube arrays with desired morphologies and structures. It also suggested a complicated formation mechanism of anodic TiO₂ nanotube arrays in glycerol-containing solution. This complicated mechanism is related to many factors, which include anodization voltage, chemical composition of electrolyte etc. In next

section, we are intending to give a model for the formation of TiO_2 nanotube arrays, which will detailed discuss in detail the formation of various morphologies (e.g., ripples, double-wall).

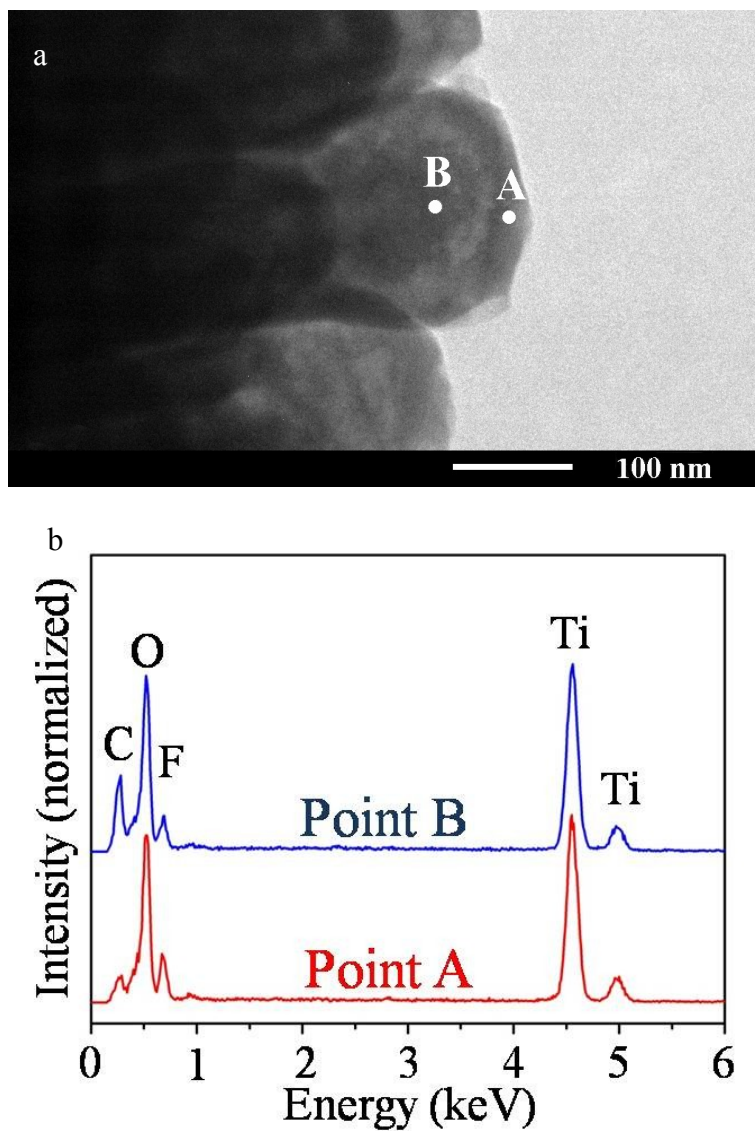


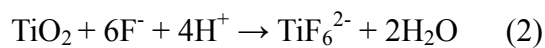
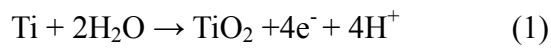
Figure 2.11 TEM/EDS results of the as-prepared TiO_2 nanotube arrays in chapter 3, (b) is the EDS results of spots A and B in (a).

2.3.3 Models for the formation of TiO_2 nanotube arrays with various morphologies

Figure 2.12 demonstrates the growth stages of TiO_2 nanotube arrays, and it is

supported by a sequence of SEM images taken from the samples anodized at different time. With the onset of anodization, an initial oxide layer is formed on titanium surface. The initial layer contains some statistically distributed “breakdown sites” due to the localized attack, round shape holes can be observed (Figure 2.12a). Because titanium oxide is soluble in F⁻-containing electrolytes, localized accelerated dissolution occurs at the breakdown sites, after 30 min, these pore nucleation events cover almost all of the surfaces (Figure 2.12b), the breakdown sites act as seeds for the growth of a disordered worm-like structure. Just after this “natural selection” stage, pronounced dissolution at the pore bottoms takes place and makes the pores deeper, a self-organized situation is established. With time increasing, the initial oxide layer was also chemically dissolved. As shown in Figure 2.12c, remnants of the initial oxide layer are visible on the surface. Underneath the remnants, a self-organized nanotube layer was fully evolved (inset in Figure 2.12c). With additional anodization time, the remnants of the barrier layer were chemically dissolved, a completely self-organized tubular morphology was obtained on the surface (Figure 2.12d).

It has been suggested that the nanotube’s growth results from the simultaneous oxidation and dissolution of the anodized oxide *via* F⁻ in the electrolytes, the reactions involved can be described below:²⁸



Results in section 2.3.2 indicate that the nanotube growth process could be more complex. Other chemical reactions can occur at the Ti/oxide and oxide/electrolytes interfaces. As shown in Figure 2.13, at the Ti/oxide interface, fluoride ions will be enriched due to its faster migration rate than oxygen,²⁹ a “fluoride-rich” layer can be formed. While at the oxide/electrolyte interface, decomposition of glycerol can occur and cause the contamination of native titanium oxide. Based on Figure 2.13, the detailed formation mechanism of ripples and double-wall structure can be discussed.

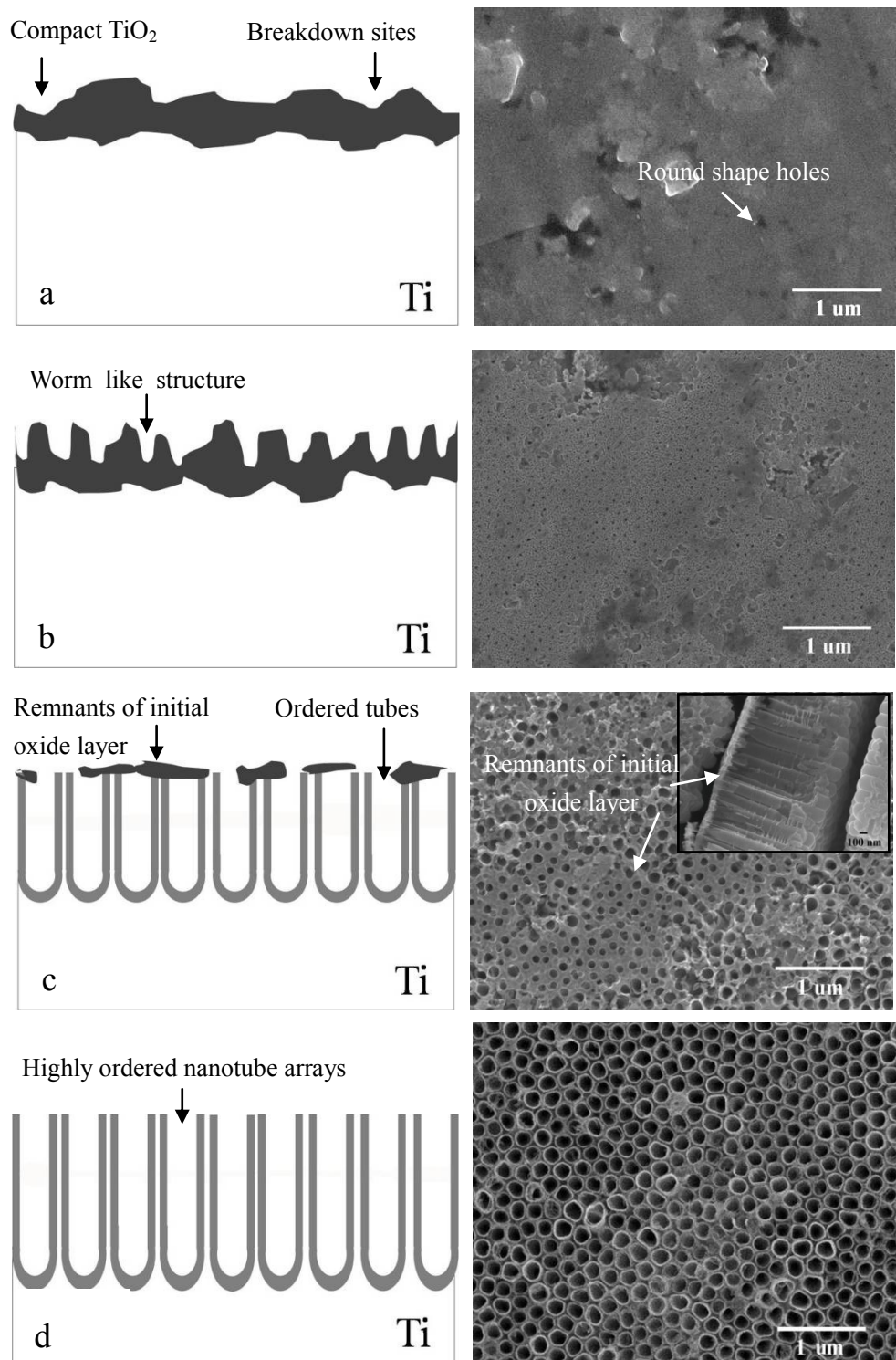


Figure 2.12 Schematic illustration (left column) and SEM sequence (right column) of the different stages of the TiO_2 layer formation. Anodization was stop after (a) 0 min, (b) 30 min, (c) 3 h, (d) 10 h after reaching 60 V in glycerol based electrolyte (96.5 wt% of glycerol; 3 wt% of H_2O ; 0.5 wt% of NH_4F)

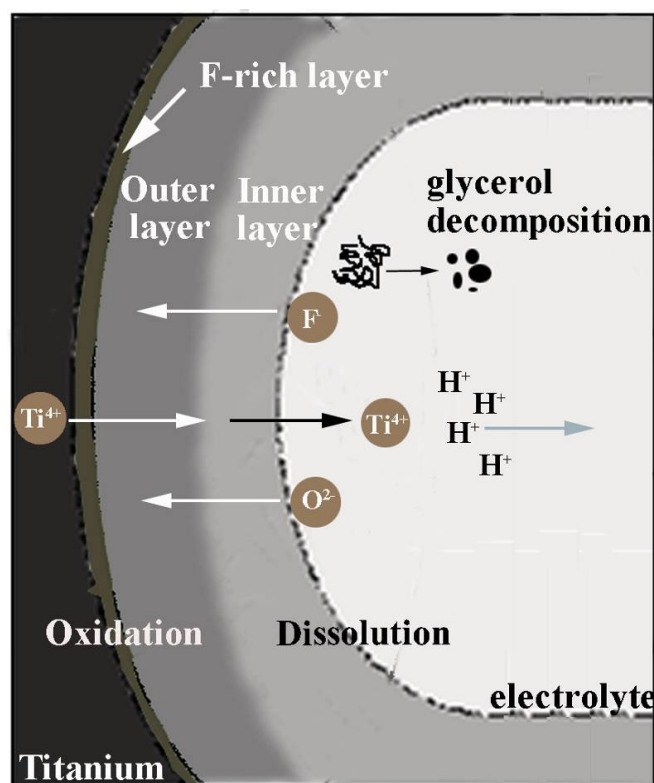


Figure 2.13 Schematic representation of the cross-sectional view of the bottom of anodic TiO_2 nanotubes in water-glycerol electrolyte.

(a) Ripples on the sidewall of nanotubes

From Figure 2.13, a “fluoride-rich” layer can be formed at the Ti/TiO_2 interface, under a plastic flow of oxide towards the regions between nanotubes,³⁰ this “fluoride-rich” layer will be displaced into the inter-tube regions. At the top of nanotubes, the “fluoride-rich” layer will be exposed to the electrolyte and be dissolved, this can create regions between nanotubes, and electrolyte will penetrate inside the gaps. However, the dissolution of the “fluoride-rich” layer at the inter-tube region is not sustainable.

As shown in Figure 2.14, if partial dissolution of the “fluoride-rich” layer occurs at the inter-tube regions, the electrical field in the residual film at inter-tube regions would exceed that in the barrier layer of the nanotubes, it will be sufficient for migration of Ti^{4+} , O^{2-} and F^- in the “fluoride-rich” layer (Figure 2.14a), this will lead

to barrier film growth at the regions between nanotubes. Similar as the formation of barrier layer, the new formed barrier film at the inter-tube regions should comprise both oxide and fluoride-rich layers (Figure 2.13), it is subsequently more stable than

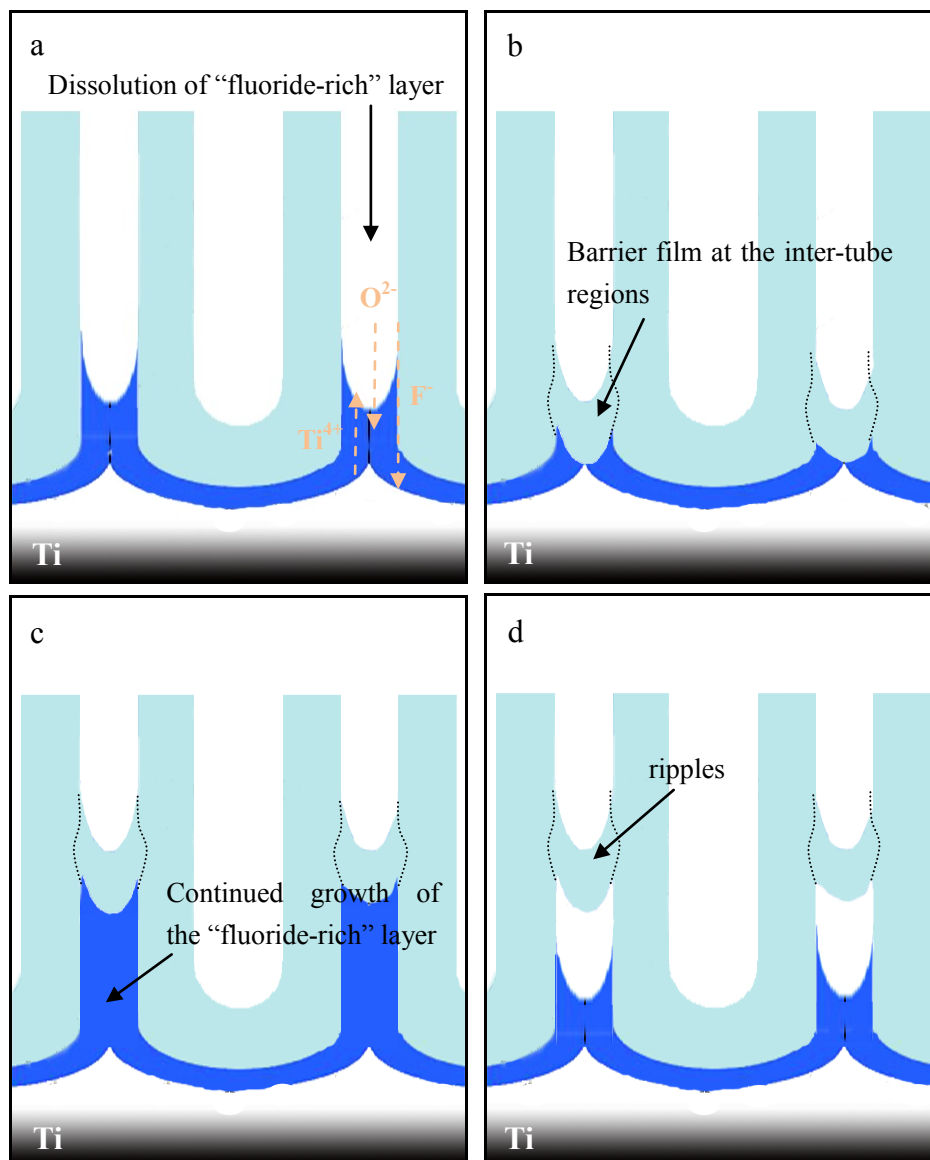


Figure 2.14 Schematic illustration of the formation of ripples on the sidewall of nanotubes. (a) dissolution of the “fluoride-rich” layer at the inter-tube regions; (b) generation of the barrier films at inter-tube regions; (c) formation of new “fluoride-rich” layers beneath the barrier layer; (d) dissolution of new formed “fluoride-rich” layer and ripples left.

the “fluoride-rich” region (Figure 2.14b). During anodization process, the continued growth of nanotubes is preferred, new “fluoride-rich” layer will be formed at inter-tube regions (Figure 2.14c). Further dissolution of the new formed “fluoride-rich” layer would be blocked by the barrier film formed above. However, the barrier film shown in Figure 2.14b may be dissolved or ruptured by film stresses, electrolyte may find paths to dissolve the “fluoride-rich” layer beneath the barrier films at the regions between nanotubes. If the new formed “fluoride-rich” layer is fully dissolved, as shown in Figure 2.14d, the barrier films at the inter-tube regions will be left on the sidewalls of nanotubes, they are just the so-called “ripples”.

(b) Double-wall structure of nanotubes

During anodization process of Al_2O_3 nanoporous structure, it is widely accepted that the anions (e.g., PO_4^{2-} , $\text{C}_2\text{O}_4^{2-}$, SO_4^{2-}) can contaminate the inner layer of the cell and cause a triple wall structure.³¹ For the formation of double-wall TiO_2 nanotube arrays which show a higher carbon content in the inner wall (Figure 2.11b), since glycerol is the only source of carbon during anodization process, glycerol is involved in the formation of double-wall structure. Glycerol could be decomposed during anodization process. This decomposition of glycerol is probably attributed to the IR-drop effects; that is, the fact that the effective voltage of the electrode $U_{\text{eff}} = U_{\text{nominal}} - IR$, where R is the resistivity of the electrolyte, and I is the current.³² During the anodization process, the viscosity of glycerol aqueous solution decreases with the adding of water.³³ Electrolytes with a low water content have a high viscosity, according to the Stokes–Einstein relationship as follows:

$$D = \frac{k_B T}{6\pi\eta a}, \quad (3)$$

where D the diffusion constant, T the absolute temperature, η the dynamic viscosity, k_B Boltzmann’s constant, and a the radius of ions. Diffusion rate of species inside the electrolyte is slow under a high viscosity, conductivity of the electrolyte should be

very low. So the IR-drop effects on the structure of the anodized TiO₂ nanotube arrays should be considered.

In this experiment, with water content decreasing of 3 wt%, fluoride ions or water molecules may be depleted by the growth of anodic film in the electrolyte adjacent to barrier layer, a significant IR-drop effect will occur and cause a thinner barrier layer.³⁴ This is confirmed in the insets of Figure 2.9c, the oxide film at the tube wall contains a barrier layer (outer wall) and a loose inner layer (inner wall). The barrier layer is less than a half of the thickness of the tube wall. At the tube bottom, such a thin

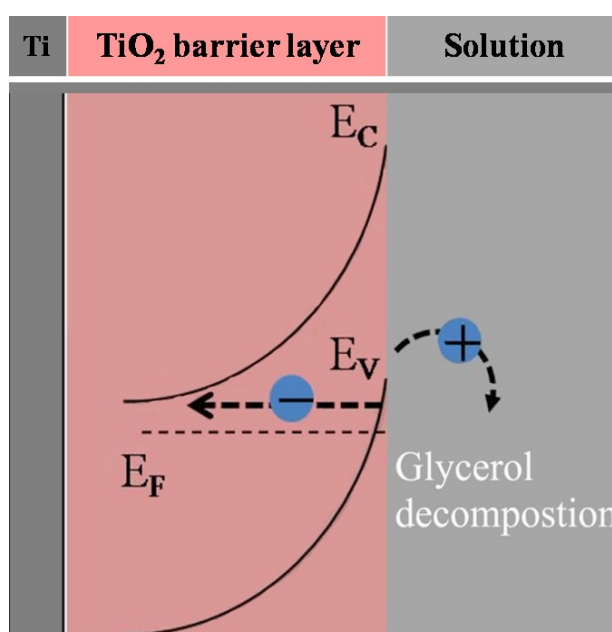
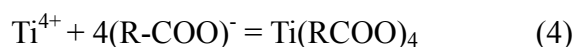


Figure 2.15 Scheme illustration of the tunneling or avalanche breakdown of the Schottky barrier which induces the glycerol decomposition under low water content (E_C : Conductive band energy; E_F : Fermi energy; E_V : Valance band energy).

barrier layer will produce a high electrical field loading under anodization voltage of 60 V during anodization process, tunneling in the Schottky barrier generates holes (Figure 2.15).³⁵ The generated holes can react with water and form hydroxyl radicals, they can decompose glycerol in the solution. The predominated decomposed products of glycerol are mainly glyceric acid, glycolaldehyde and glycolic acid.^{36,37} Ti⁴⁺,

which migrates to the electrolyte-TiO₂ interface (Figure 2.13), could react with these intermediates and form carbon condensation products according to the reaction below:



The carbon condensation products can also be oxidized by the holes according to the reaction (5), TiO₂ can be achieved.



From the reaction (4) and (5), the inner part of tube wall probably contains the carbon condensation products and TiO₂. Moreover, under the electrical field, the decomposed products of glycerol could be incorporated inside the inner part of tube wall due to the migration towards Ti/TiO₂ interface. The incorporated decomposed products (e.g., glyceric acid, glycolaldehyde and glycolic acid) can also induce a high carbon content in the inner part of tube wall. Therefore, the chemical composition of inner part of tube wall will be different with the outer part of tube wall, a high carbon contamination appeared in the inner part of tube wall, the double-wall TiO₂ nanotube array is formed.

Different from the double-wall structure prepared in ethylene glycol solution, a clear gap between outer wall and inner wall was also achieved in our experiment (Figure 2.9c). This is presumably caused by the long anodization time, the tube growth becomes very inefficient. A considerable current flow still exists when the tubes grow very slowly, gas evolution takes place at the outer wall/inner wall interface, voids can be created and lead to the separation of the tube wall.

In a word, for the tube wall of TiO₂ nanotube, its structure is strongly affected by both the organic and inorganic species inside the solution. During electrochemical anodization process, the physicochemical behavior of the species in the solution is complicated at the interfaces of Ti/TiO₂ and TiO₂/electrolyte, this will favor the research on tube wall design of TiO₂ nanotube. The physicochemical process at the

interfaces of Ti/TiO₂ and TiO₂/electrolyte needs more detailed investigation.

2.4 Conclusion

Morphological control of TiO₂ nanotube array was investigated by anodization in the glycerol-containing electrolyte. The following conclusions were achieved:

- (1) In the electrolyte containing 79.5 wt% of glycerol, 20 wt% of water and 0.5 wt% of NH₄F, by anodization at 20 V for 6 h, well-organized TiO₂ nanotube arrays can be produced. There were many ripples on the sidewall of nanotubes, tube wall also showed double layer structure.
- (2) The dissolution of “fluoride-rich” layer causes the formation of barrier oxide film at the inter-tube regions. A transient formation of the barrier oxide film at inter-tube regions is suggested to enable the generation of ripples.
- (3) In the electrolyte containing 96.5 wt% of glycerol, 3 wt% of water and 0.5 wt% of NH₄F, by anodization at 60 V for 24 h, a double-wall TiO₂ nanotube arrays was obtained. The inner wall suffered a higher carbon contamination than the outer wall. Due to the decomposition of glycerol during anodization process, carbon can be incorporated inside the inner part of tube wall, enabling the formation of inner wall.

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CHAPTER 3

Effect of Calcination on Chemical Composition and Morphology of Double-Wall TiO₂ Nanotube Arrays

3.1 Introduction

From chapter 2, since the first report on the fabrication of TiO₂ nanotubes by anodizing titanium in 1999,¹ the electrochemical anodization method has achieved many progresses in optimizing the morphology of TiO₂ nanotube array. The surface area, mechanical stability, integrity were greatly improved for the enhanced performance in gas sensing,² dye-sensitized solar cells³ and photocatalysis⁴. In addition with the morphological effect on the property of TiO₂ nanotube arrays, for higher performance applications, it is necessary to convert amorphous TiO₂ nanotube arrays to crystalline forms.⁵ Until now, although partial crystalline TiO₂ nanotube array is reported available by anodization,^{6,7} in many cases, the as-prepared TiO₂ nanotube arrays are still amorphous. Therefore, in view of the preferred application of TiO₂ in catalysis for anatase phase⁸ and dielectrics for rutile phase,⁹ annealing is in need to covert the amorphous TiO₂ nanotube array to crystalline forms.

Many efforts have been conducted to study the thermal stability of TiO₂ nanotube array. In the report by Varghese et al.,¹⁰ a “substrate-effect” showed that the supporting Ti substrate greatly affected the crystallization process of TiO₂ nanotube arrays. Another study by Yang and co-workers showed anatase phase had a (004) preferential orientation for the regular arrangement of nanotubes.¹¹ By comparing the thermal stability of TiO₂ nanotube arrays with different morphologies, Xiong et al. reported a higher thermal stability of close packed than that of loose packed TiO₂ nanotube array.¹² Through a polarized micro-Raman spectroscopy method, Schmuki et al. found preferential (101) growth of shorter TiO₂ nanotube arrays (Length ≤ 1 μm).¹³ All these work indicated that the morphology of TiO₂ nanotube array strongly

affected their thermal stability and crystallinity.

In situ TEM (transmission electron microscope) observations have been widely performed since the 1970s,¹⁴ since samples can be observed with external stresses in TEM equipment in real time. It is a good technique to the study of the 1D nanostructures of the samples.^{15,16} Recently, we have succeeded to observe the structure changes of copper and other fine particles and nanoparticles at high temperature by using this method.¹⁷⁻²⁰ With our system, as in the Kamino-Saka system,¹⁶ oxygen gas can be introduced to a TEM column during *in situ* TEM observation, and the gas pressure around the samples can be controlled. For this reason, the morphological changes of TiO₂ nanotubes at high temperature would vary with the atmosphere, that is, with oxygen gas and under high vacuum without oxygen. It may also provide valuable information about the morphological changes of TiO₂ nanotube arrays.

In this chapter, by a two-step anodization method, highly-ordered double-wall TiO₂ nanotube array were obtained in the glycerol-based solution. The as-anodized samples were subjected to annealing to examine the crystallization, chemical composition and thermal stability of double-wall TiO₂ nanotube arrays. Moreover, thermal stability of the double-wall structure was also real-time monitored and evaluated by an *in situ* annealing method with and without oxygen gas injection.

3.2 Experimental section

3.2.1 Materials and chemicals

Glycerol (C₃H₈O₃, Wako Pure Chemical, Japan), ethylene glycol (C₂H₆O₂, Wako Pure Chemical, Japan), Ammonium fluoride (NH₄F, Wako Pure Chemical, Japan), Ti foil (0.25 mm thick, 99.6% purity, Nilaco, Japan), acetone (C₃H₆O, Kanto chemical, Japan) were used as received. Water (purified by Organo/ELGA Purelabo-II system, >18 MΩ) was used throughout the experiment.

3.2.2 Preparation of double-wall TiO₂ nanotube arrays

Prior to anodization, Ti foil was cut into rectangle pieces (10 × 15 mm), then, ultra-sonicated in acetone and water, finally, dried under N₂ stream. Anodization was carried out in a two-electrode cell. Counter electrode was made of Pt. The distance between counter and working electrode was about 30 mm. The ramp rate from open-circuit to final voltage was kept at 0.1 V s⁻¹. A two-step anodization method was chosen to prepare TiO₂ nanotube array. Schematic of the experimental process is shown in Figure 3.1.

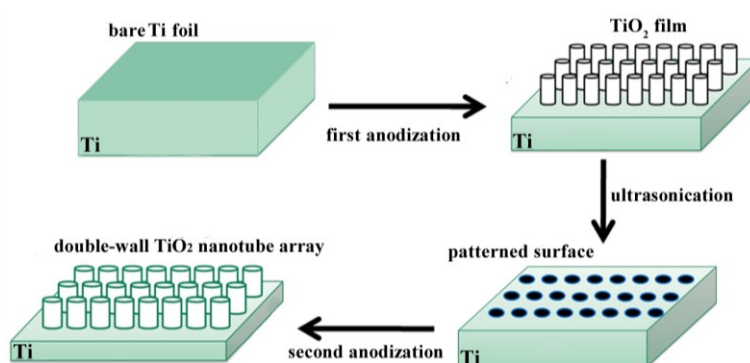


Figure 3.1 Schematic illustration of the two-step anodization of TiO₂ nanotube arrays

First anodization step: Ti foil was anodized at 60 V for 1 h. Electrolyte contains 56 g of ethylene glycol, 0.9 g of H₂O and 0.18 g of NH₄F. After anodization, the as-prepared nanotube layer was removed by using strong ultra-sonication in purified water. Finally, a Ti foil with mirror-like surface was obtained.

Second anodization step: Ti foil with mirror-like surface was anodized again in glycerol solution containing 3 wt% of H₂O and 0.5 wt% of NH₄F. Anodization voltage was 60 V, time was 1.5 h. In order to remove residual solutions, the resulted samples were all washed with pure water for several times and then dried under ambient air condition.

Thermal annealing of samples was carried out in air using an electric muffle furnace (FT-101FM, Fultech, Japan) at different temperatures for 2 h. Heating and cooling

rate was $2\text{ }^{\circ}\text{C min}^{-1}$.

3.2.3 Characterization

The surface morphology of nanotube arrays was examined by a JEOL JSM-6701F scanning electron microscope (SEM). Films were scraped with a steel blade previously for the observation of their side view. The scraped films were also collected on a carbon-coated copper grid for the examination of transmission electron microscope (JEOL JEM-2010, 200 KV). A JPS-9200 XPS system (JEOL, monochromatic Mg Ka source, 100 W) was used for the X-ray photoelectron spectroscopic (XPS) measurements, all the measurements were carried out under ultrahigh vacuum ($\sim 1.0 \times 10^{-7}$ Pa). All the XPS spectra were calibrated by using the $\text{Au}4f_{7/2}$ peak at 84.00 eV. The crystal structure of samples was investigated by X-ray diffraction (XRD) using an X'pert Philips PMD diffractometer with CuK α radiation, scanning rate (2θ) was $0.02\text{ }^{\circ}\text{s}^{-1}$.

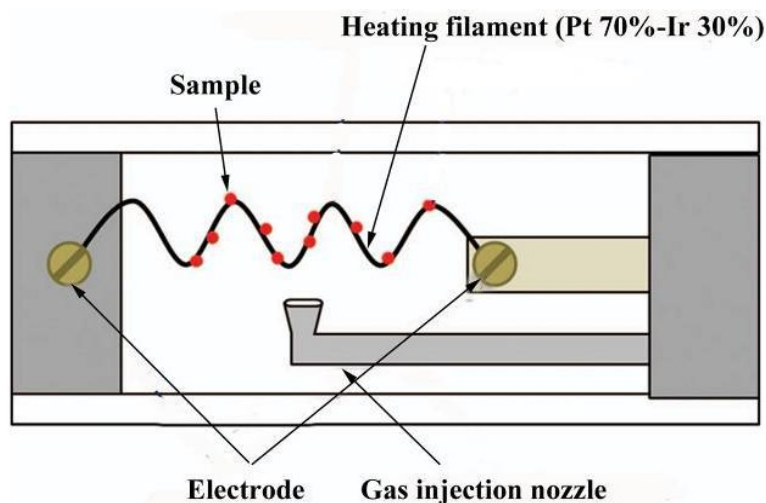


Figure 3.2 Illustration of the gas injection holder.

3.2.4 *In situ* annealing and TEM observation

Detailed nanotube structure was observed using TEM (Hitachi H-9500, 300kV). The annealing behavior of the double-wall TiO_2 nanotubes was observed in the same TEM with a filament type specimen heating holder.²⁸ The sample nanotubes were put

on a Pt (70%)-Ir (30%) filament (Figure 3.2), and a specimen behavior was recorded on an AMT CCD camera with an NTST frame rate of 29.97 fps. The filament temperature was controlled by the current value, which was calibrated by the melting points of known metals, such as Ag and Sb. The *in situ* annealing was carried out under a high vacuum ($\sim 2 \times 10^{-5}$ Pa) and an oxygen atmosphere (10^{-4} Pa oxygen). Temperature profiles of these *in situ* annealing experiments are shown in Figures 3.3a and b. Several high resolution images were also captured.

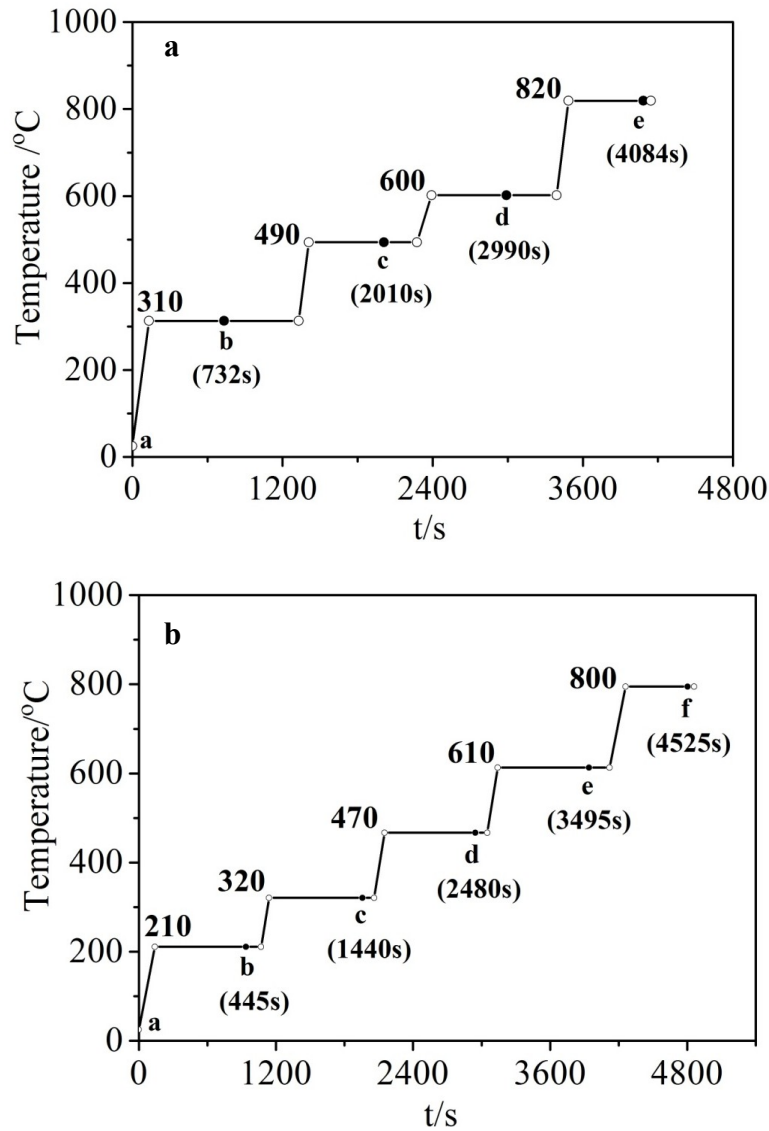


Figure 3.3 Temperature profiles of *in situ* annealing experiment ((a): with O₂ gas (10^{-4} Pa); (b): without O₂ gas under high vacuum (2×10^{-5} Pa)).

3.3 Results and discussion

3.3.1 Two-step anodization method for the preparation of highly-ordered double-wall TiO₂ nanotube arrays

In order to further improve the regularity of anodic TiO₂ nanotube arrays, a two-step anodization method was selected. A pre-treatment of Ti metal was conducted in step 1. The results showed the pre-treatment of Ti metal plays an important role for the preparation of highly-ordered TiO₂ nanotube arrays.

Without pre-treatment of Ti metal in step 1, the as-anodized TiO₂ nanotube array are irregular. As shown in Figure 3.4a, before anodization, cracks/defects in the range of several micrometers are apparent on the surface of Ti metal (indicated by black arrow). After anodization, the surface defects lead to no-uniform TiO₂ nanotube arrays, many nanotubes were not well formed (Figure 3.4b). From the lateral SEM images of TiO₂ nanotube arrays, ripples were observed on the sidewall, an irregular TiO₂ nanotube arrays are also obvious (Figure 3.4c). The region, which contains many broken TiO₂ nanotubes, can also be found in the bottom SEM image of Figure 3.4d (indicated by the white arrow). For the anodization of bare Ti metal, according to previous report,²¹ the rough surface can cause a nonuniform electrical field distribution on the surface. Pitting, which is required for the initiation of tubes, could randomly distributed on the surface. Current fluctuates and leads to the irregular TiO₂ nanotube arrays.

With pretreatment of Ti metal, well defined TiO₂ nanotube arrays were obtained. Figure 3.5 shows the SEM images of two-step anodization for preparing the highly-ordered TiO₂ nanotube arrays. In the first step, after anodization at 60 V in the ethylene glycerol solution for 1 h, TiO₂ nanotube arrays of about 8 μ m length were prepared. This nanotubular array layer can be easily removed by strong ultrasonic treatment due to the weak adhesion between TiO₂ film and the underlying Ti substrate. Clearly, a polished Ti substrate with periodical concave pattern can be reserved (Figure 3.5a). Without any other treatment, the same Ti foil was anodized again in

glycerol electrolyte at 60 V for 1.5 h. After the second step anodization, a highly self-organized TiO_2 nanotube arrays can be obtained. In Figure 3.5b, a perfect arrangement of nanotube can be observed. The imprinted Ti substrate by 1st step anodization totally works as a template to trigger the growth of tube and lead to a smooth and highly ordered porous structure on the surface. The smooth tube wall was obtained without any ripples (Figure 3.5d). In Figure 3.5c, a double-wall structure can also be observed, the bottom side image demonstrates a distinct duplex structure of the tube walls (circled area), two different regions—the inner wall and outer wall can be distinguished (inset image). This TiO_2 nanotube arrays hold double-wall structure.

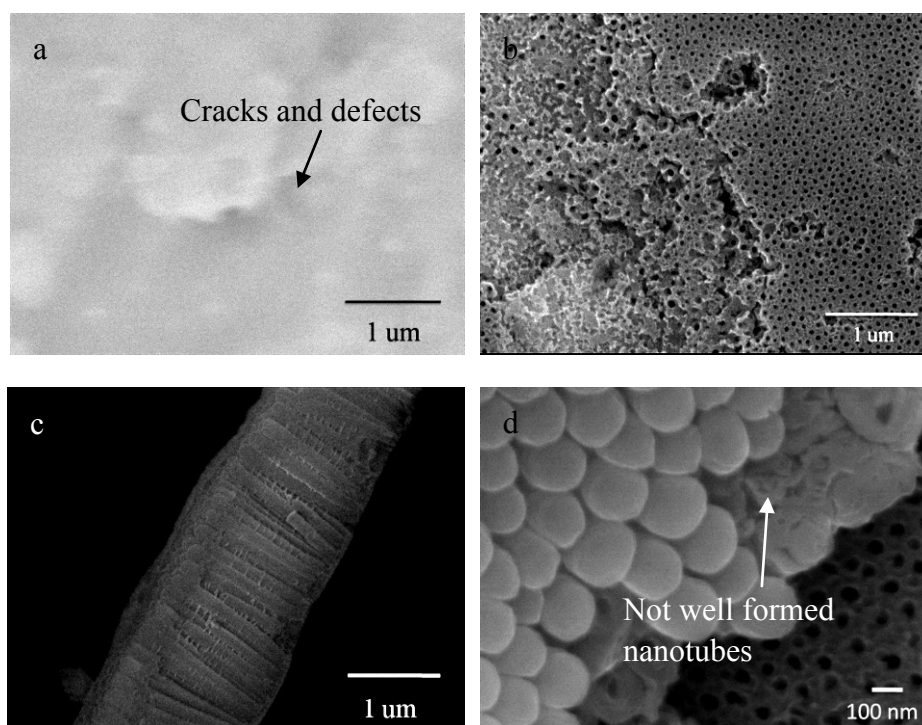


Figure 3.4 SEM images of (a) the substrate surface with no surface treatment, (b) surface, (c) bottom side and (d) lateral side of TiO_2 nanotube array prepared in glycerol-water electrolyte under 60 V for 1.5 h. (electrolyte: 57.9 g of glycerol; 1.8 g of H_2O ; 0.3 g of NH_4F).

Interestingly, SEM images of cross section of TiO_2 nanotube array (Figure 3.5d and its inset image) show ambiguous inter-tube region. As discussed in Chapter 2, the

inter-tube region is sensitized by the “fluoride-rich” layer. During anodization process, the “fluoride-rich” layer can form at the oxide-metal interface. Under a plastic flow of oxide, this “fluoride-rich” layer will be displaced into the inter-tube regions. Figures 3.6b and 3.6c are the EDX spectra of spots shown in Figure 3.6a, titanium, fluoride

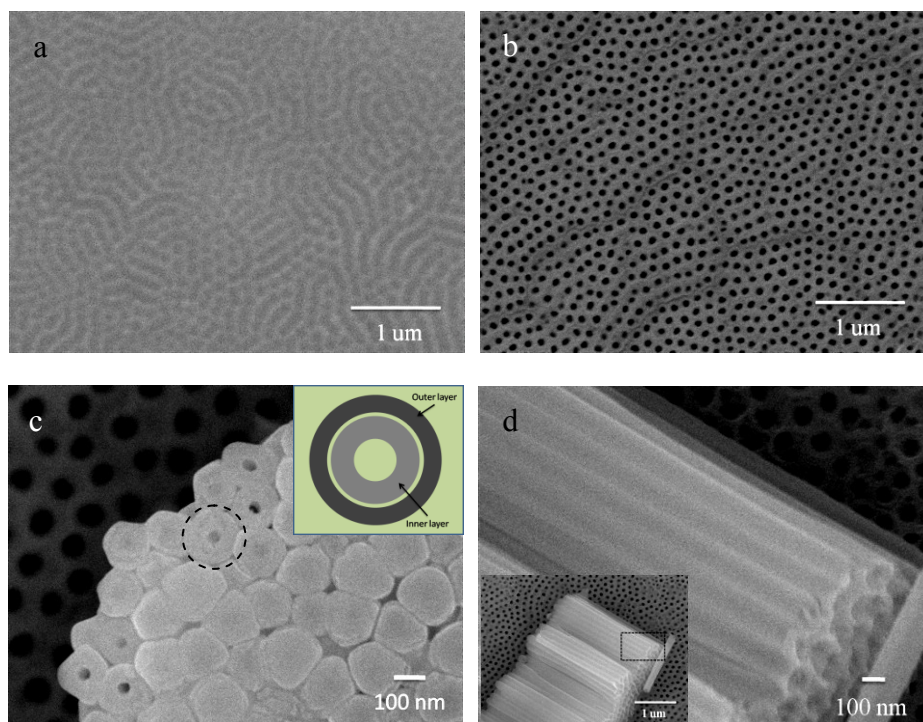


Figure 3.5 SEM images of (a) the substrate surface after removing the first anodized TiO₂ nanotube arrays, (b) surface, (c) bottom side and (d) lateral side of second anodized TiO₂ nanotube arrays prepared in water-glycerol electrolyte under 60 V for 1.5 h. (electrolyte: 57.9 g of glycerol; 1.8 g of H₂O; 0.3 g of NH₄F).

and oxygen are all evident on both the substrate and film. Table 3.1 demonstrates the calculated atomic content of EDX spectra, the three spots on the substrate show a higher atomic ratio of F:O (0.35) than that of three points on the as-formed films (0.24), so fluoride enriched at the interface between substrate and TiO₂ film, “fluoride-rich” layer was formed. At the region between nanotubes, the “fluoride-rich” layer will dissolve slowly under low water content.²² For the high viscosity of electrolyte, hydrolysis products of “fluoride-rich” layer can precipitate

easily in the region between nanotubes. Therefore, except for the double-wall structure, hydrolysis products of “fluoride-rich” layer also remain at the region between nanotubes.

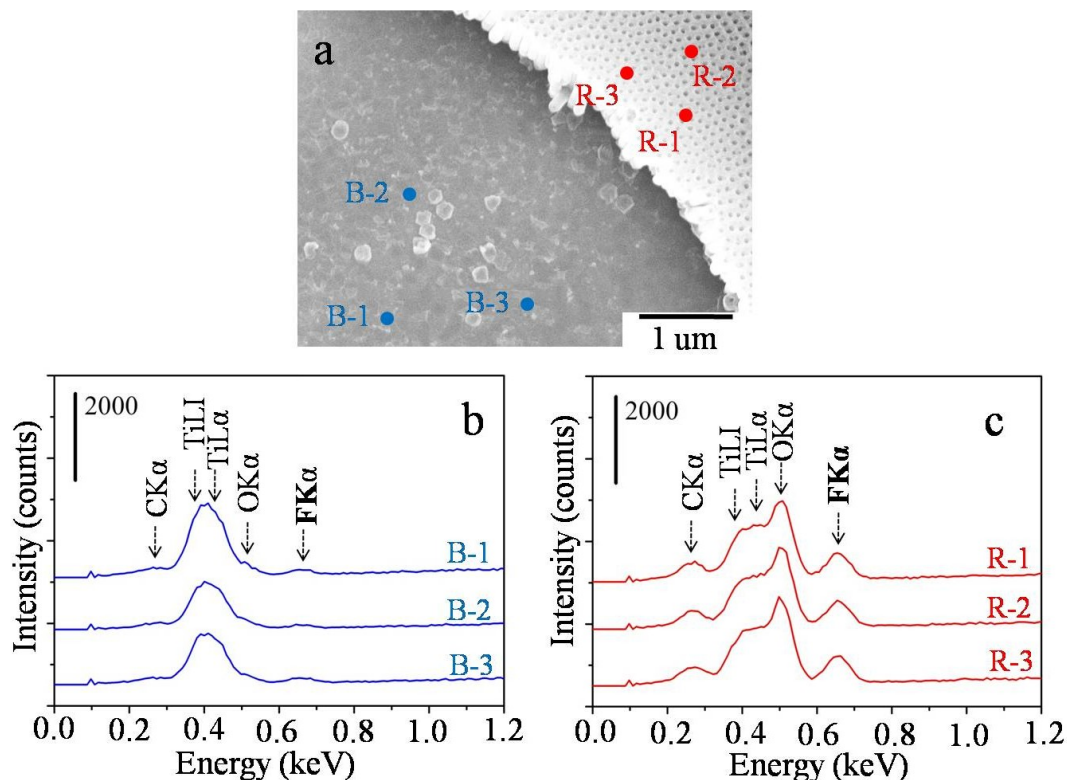


Figure 3.6 (a) SEM images of the as-prepared TiO₂ nanotube arrays by two-step anodization and Ti substrate after TiO₂ nanotube arrays removed; (b), (c) EDX spectra of positions shown in (a).

In a word, highly-ordered double-wall TiO₂ nanotube arrays were obtained by a two-step anodization method. Owing to a low water content, hydrolysis products of the “fluoride-rich” layer also remained at inter-tube regions. A simple illustration of the structure of the as-formed TiO₂ nanotube arrays is shown in Figure 3.7. The TiO₂ nanotube wall consists of three different regions: an outer wall, an inner wall and an additional “fluoride-rich” layer, the “fluoride-rich” layer also exists between the bottom of the nanotubes and the Ti substrate.

Table 3.1 Summary of atomic concentration of the chemical composition at different positions shown in Figure 3.6a. The EDX analysis was performed at 20 kV.

	Position	Atomic concentration in %					Average
		C	O	F	Ti	F/O	
TiO ₂ nanotube arrays	R-1	4.71	55.61	13.20	26.48	0.24	0.24
	R-2	4.64	55.89	12.83	26.64	0.23	
	R-3	3.99	56.50	13.58	25.93	0.24	
Ti substrate	B-1	-	13.67	4.57	81.76	0.33	0.35
	B-2	-	10.96	2.99	86.05	0.27	
	B-3	-	9.52	4.19	86.29	0.44	

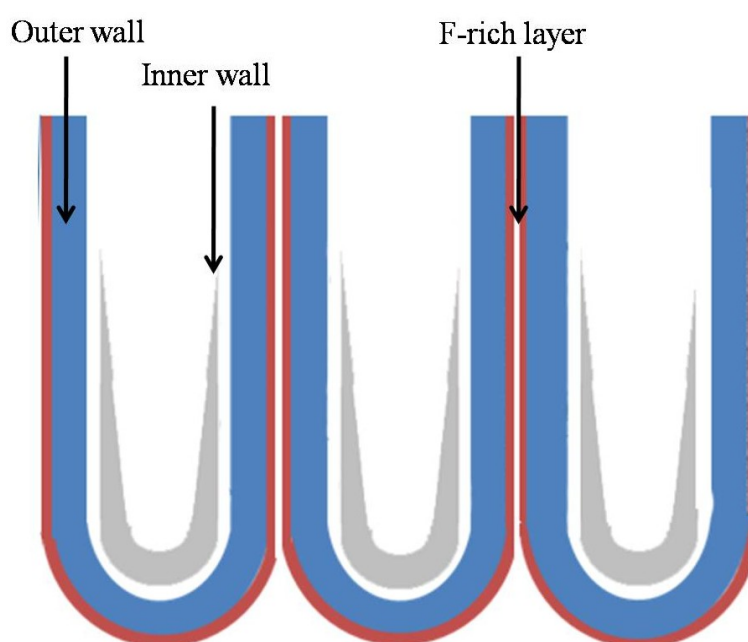


Figure 3.7 Schematic diagram of the as-formed TiO₂ nanotube array with double-wall structure and “fluoride-rich” layer remained inside.

3.3.2 *Ex situ* annealing of double-wall TiO₂ nanotube arrays with remaining “fluoride-rich” layer

Carbon and fluoride in the as-prepared TiO₂ nanotube arrays were evident in wide

scanning XPS spectra (Figure 3.8a). Peak of fluoride disappeared after calcination at 300 °C. Fluoride could be removed by evaporation as HF and F₂ gas species.²³

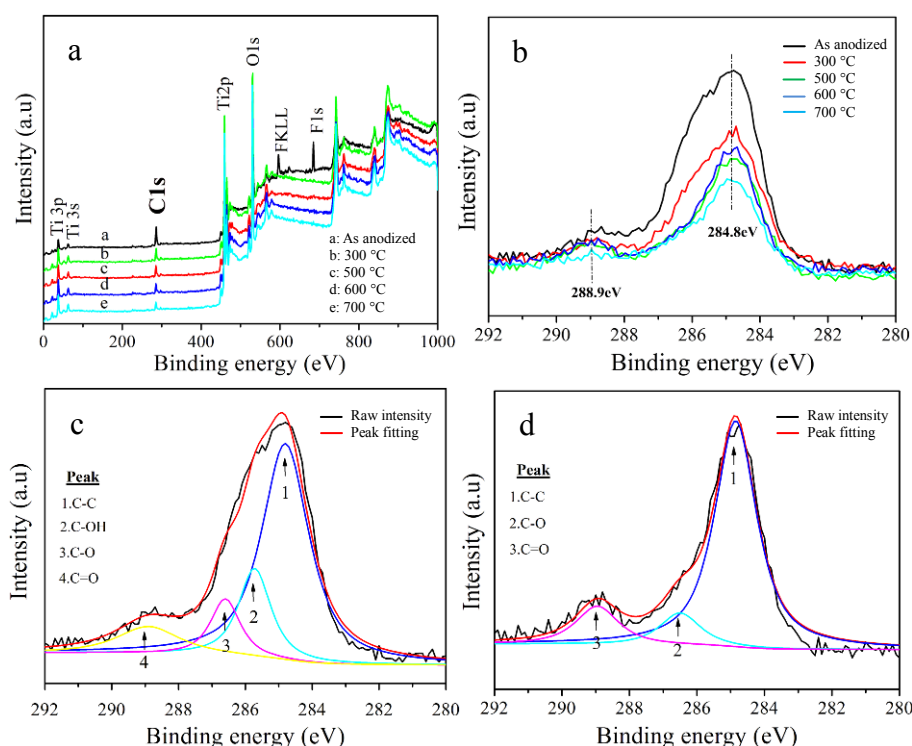


Figure 3.8 (a) Wide scanning and (b–d) high resolution XPS spectra of double-wall TiO₂ nanotube arrays before and after annealing (b: at different temperature for 2 h, c: as anodized sample, d: at 600 °C for 2 h); inset corresponds to fitting peak list and their calculated composition.

In Figure 3.8b, after annealing, the intensity of C_{1s} peak markedly decreased. It indicates the reduction of carbon content during annealing process. Notably, all C_{1s} XPS spectra show a broad asymmetric peak in the range of 283–290 eV, thus, carbon impurities was not fully removed for double-wall TiO₂ nanotube arrays. Next step, the chemical environment of carbon was further investigated by using constituent fitting of the C_{1s} peak areas. For the as-anodized sample, C_{1s} peaks were found mainly at four binding energies: 284.8, 285.6, 286.7 and 288.9 eV, corresponding to C–C, C–OH, C–O and C(O)O bonds respectively.^{24–26} The C–C bonds can be assigned to adventitious carbon, which is unavoidable contamination. Other three peaks are

associated with the inner wall which comprises mainly carbon-containing condensation products (Ti(RCOO)_4). After annealing at 600 °C for 2 h, compared with as-anodized sample, integration of the C_{1s} peak shows the absence of C-OH bonds. This could result from the thermal decomposition of Ti(RCOO)_4 species of the inner wall.²⁷ More importantly, C atoms were doped in TiO_2 , this is verified by the existence of other two peaks at 286.6 and 288.9 eV corresponding to the carbonate species.^{28,29} In Figure 3.9, the carbonate species also induced the tailing peak of O_{1s} at around 531.6 eV.³⁰ Therefore, for the carbon-rich inner wall, carbon can be not only reduced but also doped inside as carbonate species by the annealing treatment.

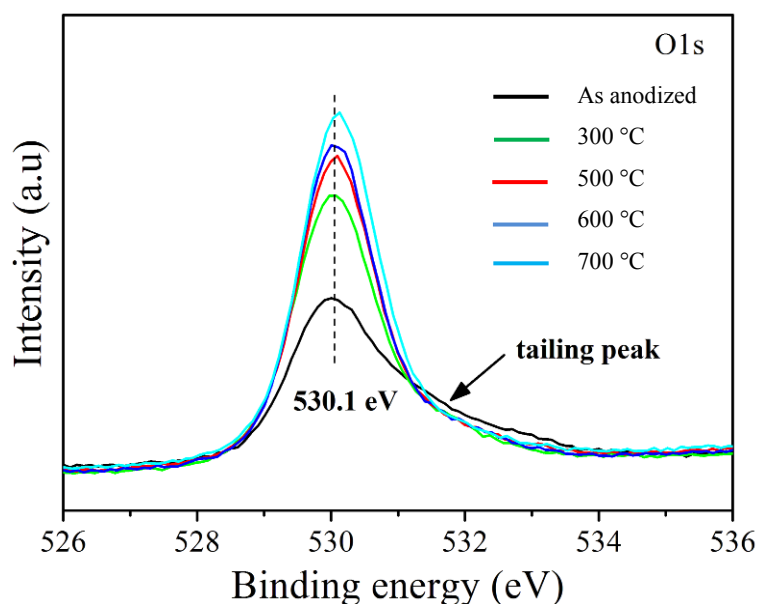


Figure 3.9 O_{1s} high resolution spectra of the as-formed double-wall TiO_2 nanotube arrays by two-step anodization after annealed at different temperatures for 2 hours.

Annealing also changed the crystalline structures and morphology of TiO_2 nanotube arrays. Figure 3.10a shows the XRD patterns of samples after annealing at different temperatures. The as-prepared TiO_2 nanotube arrays are amorphous, only the diffraction peak of titanium is observed. Anatase phase of TiO_2 occurs at 300 °C and was improved at 500 °C. After annealed at 600 °C for 2 h, rutile phase formed. At 700 °C, more anatase has transformed into rutile, and thus the nanotubes contain rutile

phase as a major constituent.

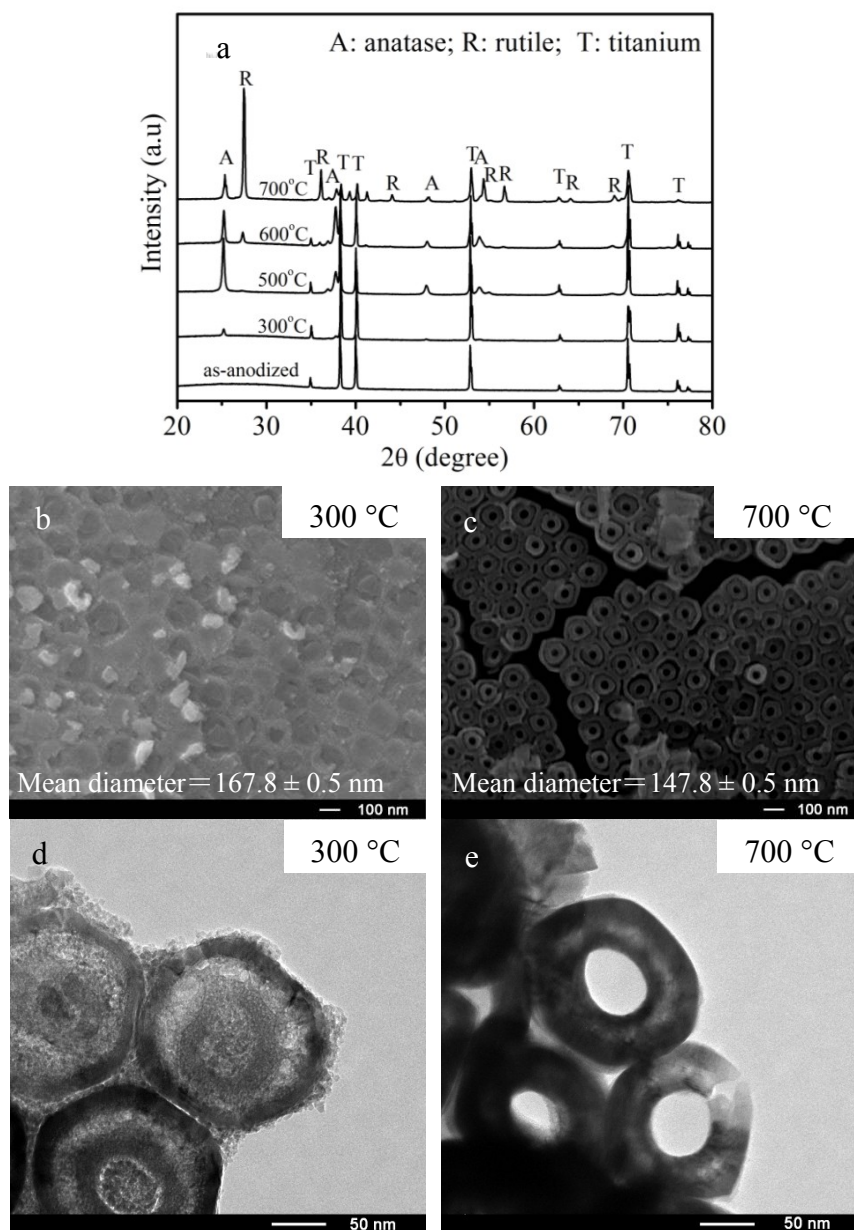


Figure 3.10 (a) X-ray diffraction patterns of double-wall TiO_2 nanotube arrays after two-step anodization after annealing at 300, 500, 600 and 700 °C for 2 h. (b–c) Bottom SEM and (d–e) TEM results of double-wall TiO_2 nanotube arrays annealed at 300 °C and 700 °C.

Figures 3.10b, 3.10c, 3.10d and 3.10e show the SEM and TEM images of double-wall TiO_2 nanotube arrays annealed at 300 and 700 °C respectively. After

annealing at 300 °C for 2 h, double-wall nanotubes were observed in both SEM and TEM images (Figures 3.10b and 3.10d). The average outer diameter is around 167.8 nm. The inner wall is not hollow. Compared with the as-anodized sample shown in Figure 3.5, particulate TiO₂ was formed at the inter-tube regions for the crystallization (Figure 3.10d). An apparent morphology change was achieved at 700 °C. First, the tube shrunk, and the outer diameter decreased to 149.8 nm. On the basis of XRD results shown in Figure 3.10a, due to the reconstructive phase transition from anatase to rutile,³¹ overall volume contraction should occurred and caused the shrinkage of tube. In Figure 3.10e, the particulate TiO₂ at the inter-tube regions disappeared, it could be crystallized to rutile phase and “swallowed” inside the sidewall of nanotube. Moreover, different from Figure 10d, a hollow structure of inner wall was obtained after annealing at 700 °C for 2 h (Figure 3.10e), the annealing optimized the double-wall structure of nanotube.

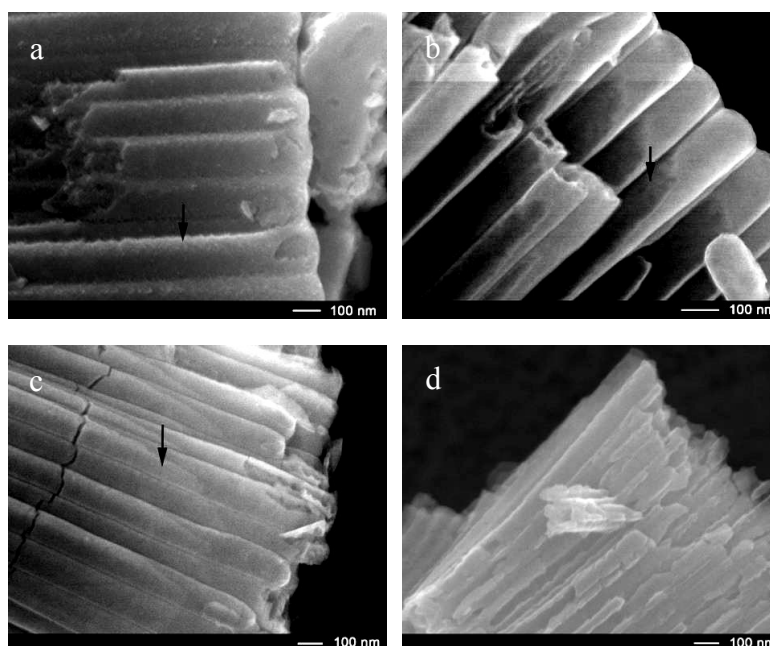


Figure 3.11 Lateral SEM images of double-wall TiO₂ nanotube arrays after annealed at different temperature (a: 300 °C; b: 500 °C; c: 600 °C; d: 700 °C) for 2 h.

After annealing, It is noted that fluoride peak observed in XPS spectrum for as-synthesized double-wall nanotube arrays at room temperature disappeared after annealing at 300 °C or higher temperature (Figure 4b), because fluoride was driven out at elevated temperature.³² However, the SEM images of annealed double-wall nanotube arrays (Figure 3.11) show that there is still a very thin layer on surface of double-wall nanotubes which could not be seen from bottom images in Figure 3.10. After annealing at 300 °C in the air, rough surface of nanotubes was clearly seen (Figure 3.11a), which is thought to be a layer of the oxidation products of the fluoride rich layer as fluoride was removed. Annealing at 300 °C for 2 h may not sufficient to smoothen this layer by sintering and crystal growth of small crystallites. At higher annealing temperatures of 500 °C and 600 °C, a smooth and dense layer can be distinguished on the surface of nanotubes and marked by arrows in Figure 3.11b and 3.11c. This is the direct capture for a layer left from the fluoride rich layer on tube walls due to annealing, which is an important evident indicates the prior existence of the fluoride rich layer surrounding as-synthesized anodic nanotubes. Hereafter, we call the layer originated from fluoride rich layer during annealing at elevated temperature “annealed fluoride rich layer”. The crystal structure of the “annealed fluoride rich layer” was investigated by using HR-TEM and results were given in Figure 3.12. The lattice spacings of 0.35 nm, which correspond to (101) planes of anatase phase,³³ were found for the “annealed fluoride rich layer” calcinated at 300 °C, 500 °C and 600 °C. The SAED pattern collected for sample annealed at 600 °C (Figure 3.12c) only showed diffraction pattern of anatase. This is consistent with XRD results (Figure 3.10a), in which rutile appeared as minor phase. Densification of the “annealed fluoride rich layer” was revealed at elevated temperature and the smoothness was improved after annealing at 500 °C and 600 °C. It is very clear in this study that thin “annealed fluoride rich layer” covering the nanotube was densified and crystalized in anatase structure with improved smoothness after annealing. These results offer a feasible approach to tailor the tube

wall structure, in which triple-wall nanotube can be obtained with maintaining fluoride rich layer and annealing.

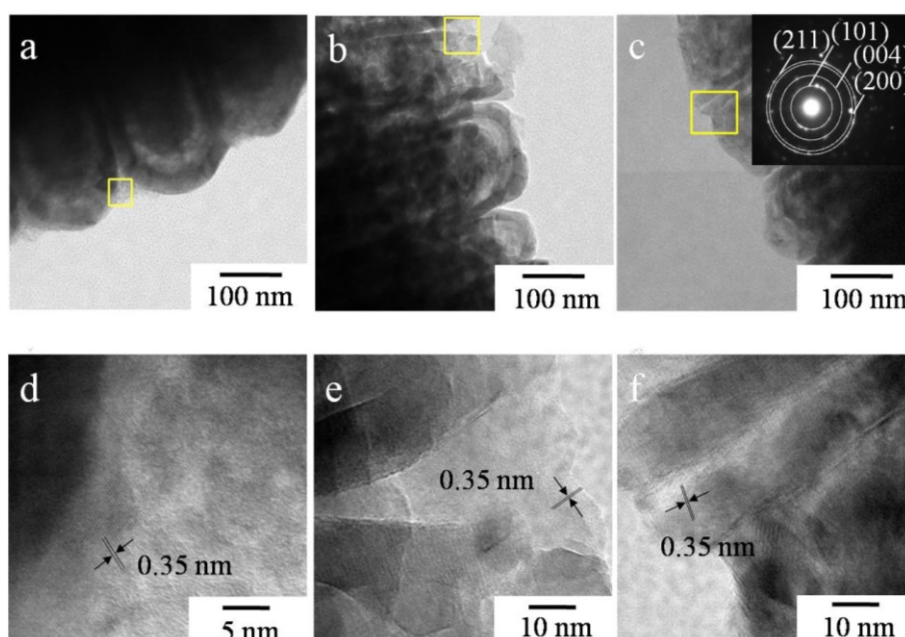


Figure 3.12 (a), (b) and (c) are TEM images of the TiO_2 nanotube arrays annealed at 300, 500 and 600 °C; (d), (e) and (f) are HRTEM images of square area in (a), (b) and (c).

3.3.3 *In situ* annealing and TEM observation of double-wall TiO_2 nanotube arrays

For the *in situ* annealing, thermal heating of TiO_2 nanotubes was performed in TEM column with and without injection of oxygen, and its morphological changes were observed. The TiO_2 nanotube arrays were also prepared by anodization in the water-glycerol electrolyte under 60 V for 24 h, the electrolyte contains 96.5 wt% of glycerol, 3 wt% of H_2O , and 0.5 wt% of NH_4F .

The double-wall TiO_2 nanotube was also *in situ* annealed at various temperatures with introduction of oxygen gas. Figure 3.13 shows the morphological changes of the nanotube and demonstrates clear structural deformation. Prior to the *in situ* annealing, a nanotube structure was observable (Figure 3.13a). In the 310 to 600 °C range, the crystallization of TiO_2 nanotubes caused the contrast change of TEM

images (Figures 3.13b, 3.13c and 3.13d).³⁴ However, there was no clear structural failure of the nanotubes. As shown in Figure 3.13d, after heating at 600 °C for 10 min, many protrude ends still exist, the nanotube did not collapse. With temperature increased to 820 °C, a structure failure of the nanotubes occurred after heating at this temperature for *ca.* 10 min. The nanotube collapsed and transformed into a coral structure which contains many inter-columnar pores (Figure 3.13e), the coalescence of crystal grains and sintering should be responsible for this transformation.

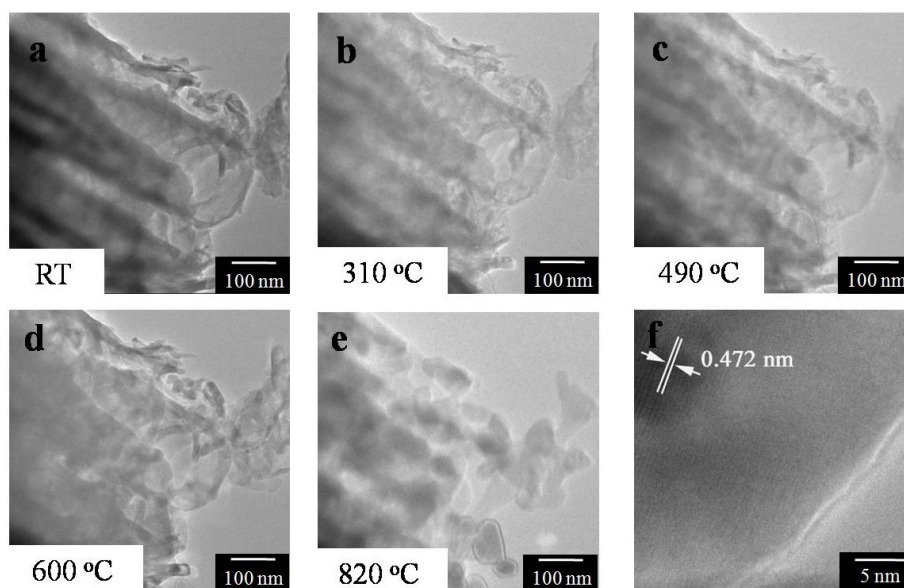


Figure 3.13 (a-e) Low magnification TEM images of double-wall TiO₂ nanotube arrays at various temperatures with the introduction of oxygen gas (all images were respectively collected at the points marked in Figure 3.3a; RT: room temperature). (f) A high magnification TEM image of a double-wall TiO₂ nanotube wall at 820 °C.

The *in situ* annealing of TiO₂ nanotubes was also conducted without the introduction of oxygen gas. Figure 3.14 shows the collected TEM images. Different from the behavior of nanotube under oxygen, where no structure failure was observable at *ca.* 600 °C, in high vacuum condition, the structural failure of nanotube already happened at 610 °C. Comparing Figure 3.14a and Figure 3.14e, the tip on the top of the tube (denoted by the black arrow) disappeared after annealing at 610 °C for *ca.* 10 min. At 800 °C, the structural failure proceeded, and a complete collapse of the

nanotube was achieved after *ca.* 10 min. The nanotube finally transformed into a stone structure (Figure 3.14f). This stone structure is also highly different from the final coral structure under oxygen gas. Therefore, during *in situ* annealing process, the nanotube show a lower structural stability in high vacuum condition than in the presence of oxygen, the sintering of TiO₂ nanotube was accelerated under high vacuum condition. Moreover, the sintering of the inner wall also optimized the double-wall structure, at 610 °C, the inner wall and outer wall are more clearly separated from each other in Figure 3.15d than in Figure 3.15a.

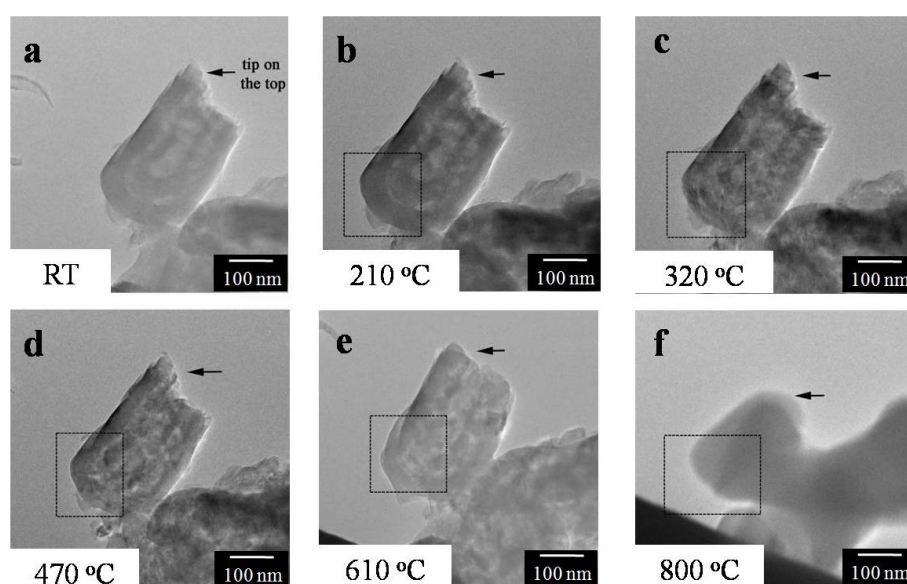


Figure 3.14 Low magnification TEM images of double-wall TiO₂ nanotubes at various temperatures without the introduction of oxygen gas (all images were respectively collected at the points marked in Figure 3.3b).

In addition to the morphological change, for nanotube subjected to *in situ* annealing in the presence of oxygen, a high-resolution TEM (HRTEM) image was also captured and is displayed in Figure 3.13f. The image shows lattice fringes (0.472 nm) similar to the lattice spacing of γ -Ti₃O₅ (002) (0.469 nm).³⁵ Under oxidizing conditions (such as air and oxygen), amorphous TiO₂ nanotube arrays usually will be converted to the anatase and rutile phase by post-annealing treatment, the titanium suboxide phase can hardly be detected.¹⁰ So the emergence of γ -Ti₃O₅ indicates that

the TiO₂ nanotubes were reduced during the *in situ* annealing process. Under “inert” atmosphere (e.g., N₂, Ar and vacuum), TiO₂ will decompose at high temperatures and low oxygen pressures.³⁶ Similarly, under the high vacuum condition, the reduction of TiO₂ nanotubes occurred reasonably during *in situ* annealing process. Under high vacuum condition, oxygen molecules adsorbed on anatase TiO₂ desorbed at about 140 °C,³⁷ so oxygen vacancy cannot be excluded due to the loss of oxygen during *in situ* annealing process.

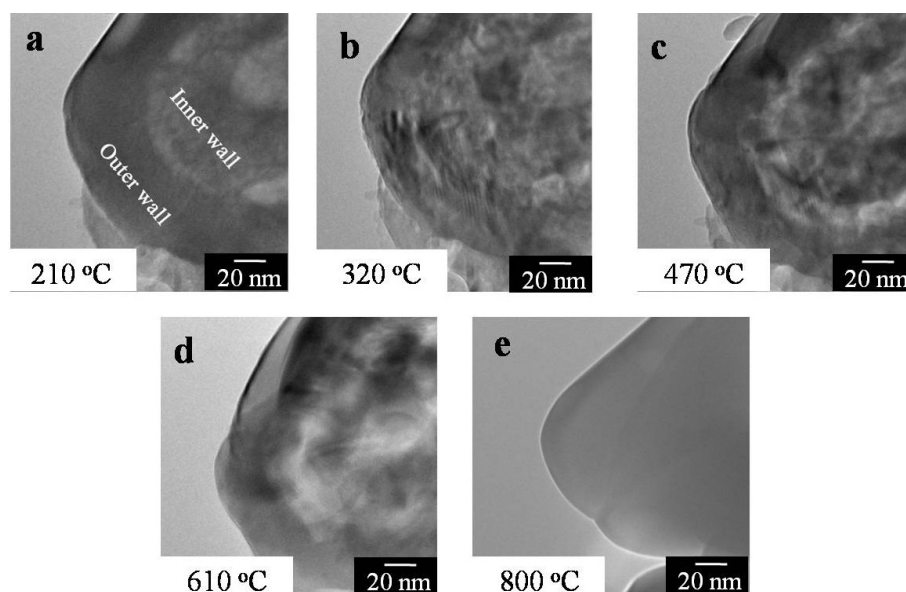


Figure 3.15 High magnification TEM images of double-wall TiO₂ nanotube arrays at high temperature without the introduction of oxygen gas (all of the images were respectively collected in the square area shown in Figure 14).

By comparing Figure 3.13 and Figure 3.14, it can be concluded that a higher morphological stability of the TiO₂ nanotubes at high temperature was obtained in the presence of oxygen gas in the TEM column. For the sintering of TiO₂ involving a transport of matter, oxygen ion diffusion is considered as the rate-determining step.³⁸ Under high vacuum condition, according to the vacancy diffusion mechanism,³⁹ oxygen vacancy tends to favor the transport of matter and accelerate the sintering of TiO₂. Inversely, under an oxygen injection condition, exposure to high doses of

oxygen leads to oxygen vacancy healing,⁴⁰ that is vacancy density decreases with O₂ exposure. This would tend to hinder the sintering of TiO₂ and stabilize the TiO₂ nanotube during *in situ* annealing process. If the reconstructive anatase-rutile phase transformation occurred during the *in situ* annealing process, according to reference 41, oxygen vacancies can also promote this phase transition and cause a faster tube failure. It could also be expected that the oxygen pressure may also affect the anatase-rutile phase transition. Sufficient selected area electron beam diffraction (SAED) pattern will be obtained to determine the crystal phase of TiO₂ nanotubes. In a word, for the *in situ* annealing of TiO₂ nanotube, a slower sintering of TiO₂ nanotube was achieved in the presence of oxygen gas. This finding indicates a dependence of the sintering of TiO₂ nanotube on oxygen gas during the *in situ* annealing process. Oxygen gas molecule can stabilize the TiO₂ nanotube. The mechanism of morphological or even crystal phase changes for the *in situ* annealing of TiO₂ nanotube needs more detailed research.

3.4 Conclusion

The following conclusion can be drawn from this chapter:

(1) The double-wall TiO₂ nanotube arrays were prepared by anodization in the water-glycerol electrolyte. Due to a low water content and faster migration rate of fluoride than oxygen. Hydrolysis of “fluoride-rich” layer is very slow and the hydrolysis products adsorb at the regions between nanotubes. So “fluoride-rich” layer can remain in the inter-tube regions after anodization.

(2) Fluoride inside the sample can be fully removed by thermal annealing. Although calcinations can greatly reduce the carbon amount, in the air condition, carbon can also be doped in TiO₂ nanotube arrays as carbonate species.

(3) After thermal annealing, the “fluoride-rich” layer was visualized in SEM images. At low temperature (below 300 °C), the outer tube wall surface became very rough

due to the crystallization of the “fluoride-rich” layer. With the temperature increasing, the outer tube wall becomes smoother due to the grain growth. “Fluoride-rich” layer was “swallowed” inside the outer tube wall due to the phase transformation from anatase to rutile.

(4) The *in situ* annealing and TEM observation method was used to real-time monitor the morphology change of TiO₂ nanotubes with temperature increasing. In the presence of oxygen gas, sintering of the TiO₂ nanotube is slow. A clear tube failure was observed at 820 °C, but the nanotubes were transformed into a coral structure. Differently, a faster sintering of the nanotube occurred under high vacuum. This indicates a dependence of morphological changes of TiO₂ nanotubes on the gas atmosphere during *in situ* annealing process, oxygen molecule can stabilize the TiO₂ nanotube.

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CHAPTER 4

Decoration of Pt Nanoparticles Inside TiO₂ Nanotube Arrays and Their Photocatalytic Properties

4.1 Introduction

Photocatalysis is one of the most important applications of the TiO₂ nanotube arrays. The catalytic behavior of TiO₂ nanotube arrays is generally related to the crystalline structure, the specific surface area and the surface -OH groups. It was reported that the ordered nanotube arrangement has higher photocatalytic performance than the standard P25 nanoparticulate film,¹ various factors (optimized reaction geometry for charge transfer, UV absorption characteristics over the tube and solution diffusion effects) can be responsible for this effect. This work triggered intense follow-up investigations on the photocatalysis of TiO₂ nanotube arrays. Many methods were examined to improve the photocatalytic activity of TiO₂ nanotube arrays. For example, compared with bare TiO₂ nanotube arrays, hetero-structured TiO₂ nanoparticle/nanotube array was reported as a more effective photocatalyst for its larger surface area. Decoration of TiO₂ nanotube arrays by noble metal nanoparticles (such as Au,² Ag,³ and Pt⁴) was also performed to enhance their photocatalytic properties, the increased band bending by junction formation is responsible for the accelerating effects. Until now, almost all of the above mentioned treatments were aimed at single-wall TiO₂ nanotube arrays, research on the double-wall TiO₂ nanotube arrays has been rarely touched on.

In order to improve the photocatalytic activity of TiO₂ nanotube arrays, the decoration of Pt nanoparticles has been chosen and widely investigated. One widely used method is reduction of Pt precursor under UV light. However, due to the short penetration depth of UV light, Pt nanoparticles can hardly be decorated very uniformly along the whole tube length. Considering this, in this chapter, Two different aqueous solutions were chosen and compared in order to improve the uniformity of

decorated Pt nanoparticles. A deposition-precipitation method was selected to decorate Pt nanoparticles inside TiO₂ nanotube arrays. Pt decoration of both double- and single-wall TiO₂ nanotube arrays was investigated. Photocatalytic degradation of methylene blue solution was used to examine the photocatalytic properties.

4.2 Experimental section

4.2.1 Sample preparation

TiO₂ nanotube arrays were fabricated at room temperature in a conventional two-electrode cell using a direct current power supply (Kikusui, Japan) as previous report. Pure Ti sheets (thickness 250 μm , 99.6 % purity, Nilaco, Japan) were used as starting materials. The sheets were cut into 10 mm $\times$ 15 mm size and degreased in acetone with ultra-sonication followed by rinsed in water (purified by Organo/ELGA Purelabo-II, $>18\text{ M}\Omega$). Then, the foils were dried under N₂ stream. The electrolyte contains glycerol (Wako, Japan), H₂O, and NH₄F (Wako, Japan). A Pt foil served as the counter electrode, and Ti foil was used as the working electrode. Distance between two electrodes was about 3 cm. At the beginning of anodization, the voltage was slowly lifted to final target voltage at a rate of 0.1 V s⁻¹. Then the voltage was kept constant for a fixed time. Resulted samples were washed with pure water for several times in order to remove residual solution and then dried in air. All chemicals were of analytical grade and used as received. Before decoration of Pt nanoparticles, the as-prepared TiO₂ nanotube arrays were annealed in air at 450 °C for 3 h at a heating rate of 2 °C min⁻¹.

For the decoration of Pt nanoparticles, two kinds of solutions were selected.

Solution 1: H₂PtCl₆ (Kojima Chemical, Japan) was used as a precursor of Pt nanoparticles. H₂PtCl₆ was dissolved in purified water and ethanol with various volume ratio for water/ethanol, the concentration of H₂PtCl₆ was fixed at different values. The as-annealed TiO₂ nanotube arrays were transferred into the solution 1 in a round bottom reaction flask. The reaction system was aged at 90 °C for 1 h. After reaction, the samples were washed with purified water for several times in order to

remove the residue solution. N_2 gas flow was used to dry the samples.

Solution 2: As the precursor of Pt nanoparticles, H_2PtCl_6 was diluted in the NaOH aqueous solution to get various $[OH^-]/[PtCl_6^{2-}]$ ratio. All the as-prepared solutions were aged for 24 h at room temperature. For the deposition of Pt nanoparticles, as-annealed TiO_2 nanotube arrays were also transferred into a round bottom reaction flash filled with solution 2. The flash was kept at 100 °C for 48 h. After chemical reaction, the samples were washed with purified water for several times and dried under nitrogen flow. In order to get metallic Pt nanoparticles on the surface of TiO_2 nanotubes, in a tube furnace (Asone, TMF-500N, Japan), the Pt loaded TiO_2 nanotube arrays were placed under H_2/N_2 (1.5 vol%) flow at 200 °C for 4 h. The typical experiment setup for the decoration of Pt nanoparticles are shown in Figure 4.1.

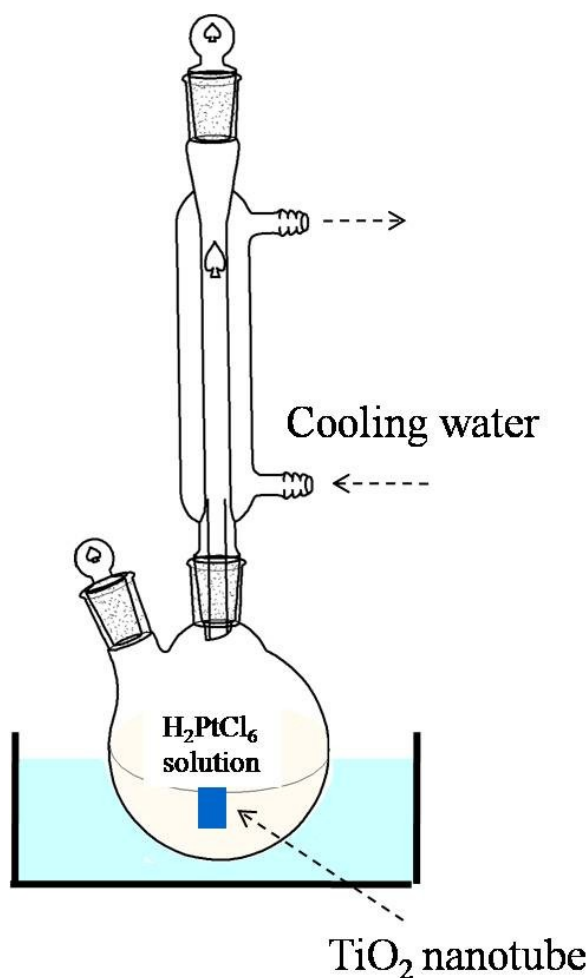


Figure 4.1 Experimental setup for the decoration of Pt nanoparticles inside TiO_2 nanotube arrays.

In order to uniformly decorate Pt nanoparticles inside TiO₂ nanotube arrays, a series of experiments were carried out and compared, their chemical composition are shown in Table 4.1.

Table 4.1 Reaction temperature, reaction time and chemical composition of different solutions for the deposition of Pt nanoparticles

Solution	Composition	T (°C)	t (h)	
No. 1	c(H ₂ PtCl ₆) = 0.25 mM volume ratio of ethanol and water: 4/1	90	1	solution 1
No. 2	c(H ₂ PtCl ₆) = 1 mM ratio of [PtCl ₆ ²⁻] and [OH ⁻] = 1/6	100	48	solution 2
No. 3	c(H ₂ PtCl ₆) = 1 mM volume ratio of ethanol and water: 4/1	90	1	solution 1
No. 4	c(H ₂ PtCl ₆) = 0.05 mM volume ratio of ethanol and water: 4/1	90	1	solution 1
No. 5	c(H ₂ PtCl ₆) = 0.1 mM (pH = 3.7) ratio of [PtCl ₆ ²⁻] and [OH ⁻] = 1/1	100	48	solution 2
No. 6	c(H ₂ PtCl ₆) = 0.1 mM (pH = 9.8) ratio of [PtCl ₆ ²⁻] and [OH ⁻] = 1/6	100	48	solution 2

4.2.2 Characterization

The microstructure of the anodized specimens was analyzed by scanning electron microscope (SEM, JEOL-JSM 6701F) and transmission electron microscope (TEM, Hitachi, H-9500, 300 KV). The cross-sectional, bottom-side SEM images and TEM images were taken from mechanically scratched films. X-ray photoelectron spectroscopy data were collected by a JPS-9200 machine (JEOL, Japan) equipped with a monochromatic MgK α source operating at 100 W under ultrahigh vacuum ($\leq 1.0 \times 10^{-7}$ Pa). Binding energies were referenced to the C_{1s} peak at 284.9 eV of the adventitious carbon. X-ray diffraction patterns were obtained on an X'pert Philips PMD diffractometer with a Panalytical X'celerator detector using CuK α radiation, and the scanning speed was 5° min⁻¹ at a step of 0.02°. The Brunauer–Emmett–Teller

(BET) specific surface area measurement of the annealed double- and single-wall TiO₂ nanotubes was carried out on a basis of N₂ adsorption by using Quadrasorb SI (Quantachrome Instruments, USA) instrument. Prior to analyses, TiO₂ nanotubes were scraped from the titanium metal surface, weighed and degassed at 150 °C for 2 h under high vacuum. The values of the specific surface areas (S_{BET}) were determined by using multi-point analysis of adsorption isotherms applying BET equation.

4.2.3 Photocatalysis measurements

For the photocatalysis measurements, all samples with 1 cm² reaction area were put into a quartz cell containing 4 mL of 1 ppm methylene blue solution. They were kept in darkness for 40 min to establish the adsorption and desorption equilibrium of methylene blue prior to the test. A UV lamp (Asone, SLUV-4, Power of 9 W, Japan) with main wavelength of 254 nm was used as a light source. The absorbance of the solutions was measured periodically in every 30 min for 3 h by a UV-vis/NIR spectrometer (Perkin Elmer Lambda 750S) at the wavelength of 664 nm which is the absorption maximum of methylene blue.

4.3 Results and discussion

4.3.1 Comparison of Pt decoration in two different solutions

For the decoration of Pt nanoparticle using solution 1 and solution 2, the as-prepared samples showed different morphologies and chemical states of Pt. In order to compare the two solutions, two samples were obtained with nearly the same loading amount of Pt. The chemical compositions of the two solutions are listed in Table 1 as No. 1 and No. 2 solutions. All the TiO₂ nanotube arrays used were anodized under 40 V for 2 h, the electrolytes contains 79.5 g of glycerol, 20 g of H₂O and 0.5 g of NH₄F. Next step, their morphologies and chemical compositions were compared.

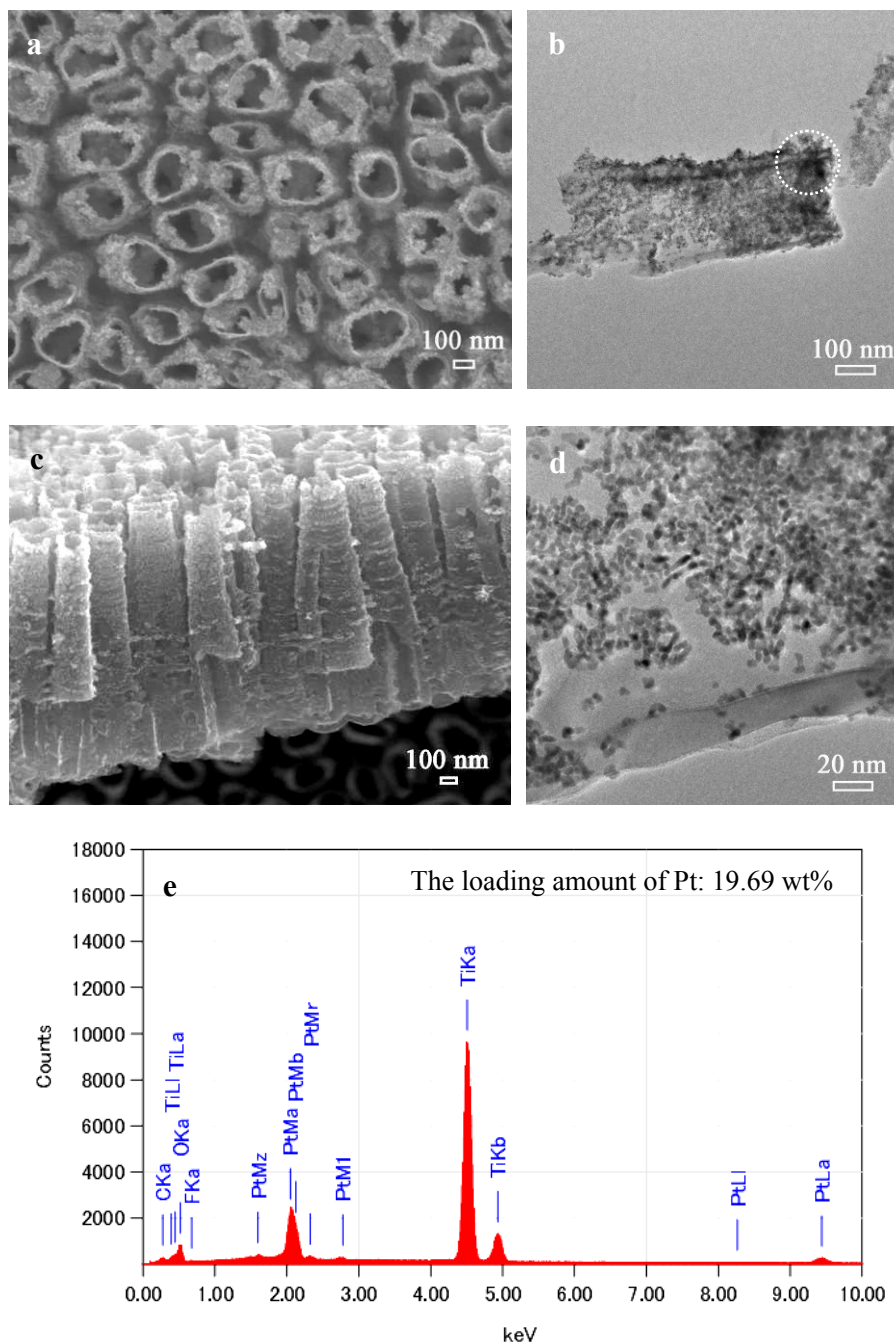


Figure 4.2 SEM (a, c) /EDS (d) and TEM (b, d) results of Pt loaded TiO₂ nanotube arrays prepared by using No. 1 solution.

For No. 1 solution, H₂PtCl₆ was diluted in the mixture of deionized water and ethanol by 0.25 mM, the water/ethanol volume ratio is 4:1. After keeping at 90 °C for 1 h, nanoparticles were successfully decorated inside the TiO₂ nanotube arrays. Figures 4.2a and 4.2c give the top and side view of the TiO₂ nanotube arrays loaded with nanoparticles. The nanotube array is observable on the top surface. However, at

the tube mouths, nanoparticles aggregated and formed many cluster-like structures. From the lateral image of Pt loaded TiO₂ nanotube arrays in Figure 4.2c, nanoparticles can also be observed on the tube wall. Therefore, by soaking TiO₂ nanotube arrays in the precursor solution at 90 °C for 1 h, the nanoparticles were successfully decorated along the whole tube length. The preferential loading of nanoparticles at the entrance of the nanotubes, which is very common for the photo-reduction method, was successfully avoided. Figures 4.2b and 4.2d are the TEM images of Pt/TiO₂ nanotube arrays which further confirm the presence of nanoparticles inside the tubes. However, the distribution of nanoparticles on the TiO₂ nanotube arrays is not uniform. As indicated by white arrow in Figure 4.2b, many nanoparticles are agglomerated and not well dispersed on the wall of TiO₂ nanotube. Energy Dispersive Spectrometer (EDS) measurement was also carried out for the Pt loaded TiO₂ nanotube arrays, the results show a high Pt loading amount of about 19.69 wt%.

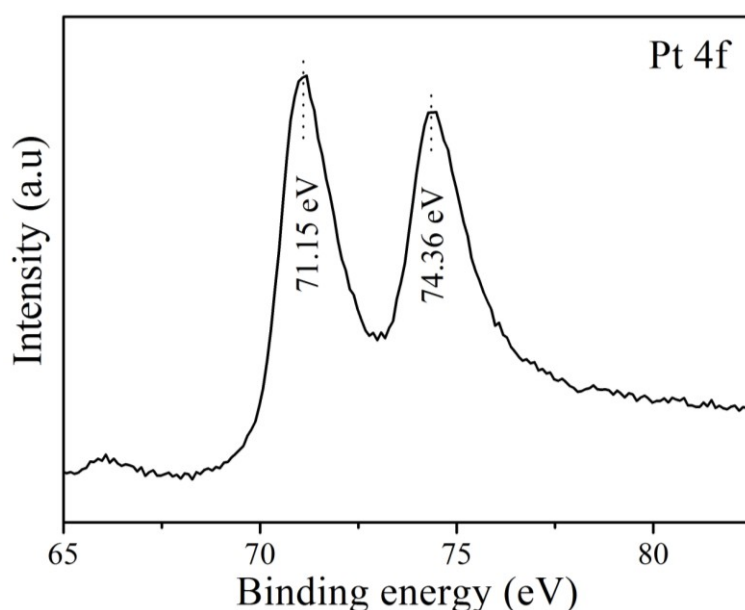


Figure 4.3 High resolution XPS spectrum of Pt for the deposited nanoparticles by chemical reduction in No.1 solution.

X-ray photoelectron spectroscopy (XPS) analysis was also conducted to determine the chemical state of deposited Pt nanoparticles. The high resolution XPS spectrum of Pt_{4f} in Figure 4.3 shows doublet peak at 71.15 eV and 74.36 eV for Pt 4f_{7/2} and Pt 4f_{5/2} respectively. The distance between Pt 4f_{7/2} and Pt 4f_{5/2} is 3.21 eV, the intensity ratio of

Pt 4f_{7/2} and Pt 4f_{5/2} is 4:3, these results confirm only metallic Pt⁰.¹⁸ Therefore, metallic Pt nanoparticles were decorated inside TiO₂ nanotube arrays in No. 1 solution.

For No. 2 solution, H₂PtCl₆ (1 mM) was diluted in sodium hydroxide aqueous solution, the ratio for [PtCl₆²⁻] and [OH⁻] is 1:6. After chemical reaction at 100 °C for 48 h, nanoparticles were also deposited inside TiO₂ nanotube arrays. Figure 4.4 shows the corresponding SEM and TEM images of Pt loaded TiO₂ nanotube arrays. Different from the sample prepared in No. 1 solution, in SEM images of Figures 4.4a and 4.4c, only TiO₂ nanotube array is observed, nanoparticles are not observable due to a small size of nanoparticles. As shown in TEM images of Figures 4.4b and 4.4d, nanoparticles with size at round 2 nm can be clearly distinguished. The distribution of nanoparticles is very uniform, aggregation of nanoparticles is not observable. Compared with the sample prepared in No. 1 solution, the small size and well distribution of nanoparticles makes the nanoparticles hardly distinguished in SEM images. In Figure 4.4e, compared with No. 1 solution, nearly the same loading amount of Pt (18.68 wt%) was obtained by using No. 2 solution.

The chemical state of deposited Pt nanoparticles by using No. 2 solution is also different from that prepared in No. 1 solution. As indicated in Figure 4.5, the emergence of two fitted peaks of Pt 4f_{7/2} at 72.80 eV and 74.85 eV can be assigned to Pt²⁺ and Pt⁴⁺,⁵ the presence of Pt²⁺ and Pt⁴⁺ implies the existence of the oxidation of Pt. No fitting peak of Pt⁰, which holds Pt 4f_{7/2} peak at 71.2 eV, can be observed. So the nanoparticles are not metallic Pt nanoparticles, they show oxidation state of 4+, 2+ for Pt.

From the above comparative discussion, compared with solution 1, solution 2 is more suitable to uniformly decorate Pt-containing nanoparticles inside TiO₂ nanotube arrays, no tube blockage. The deposited nanoparticles show mixed chemical states of Pt²⁺ and Pt⁴⁺, a further reduction process is in need to get metallic Pt nanoparticles on the surface of TiO₂. The deposition mechanism of Pt nanoparticles using solution 1 and solution 2 are also discussed in next section.

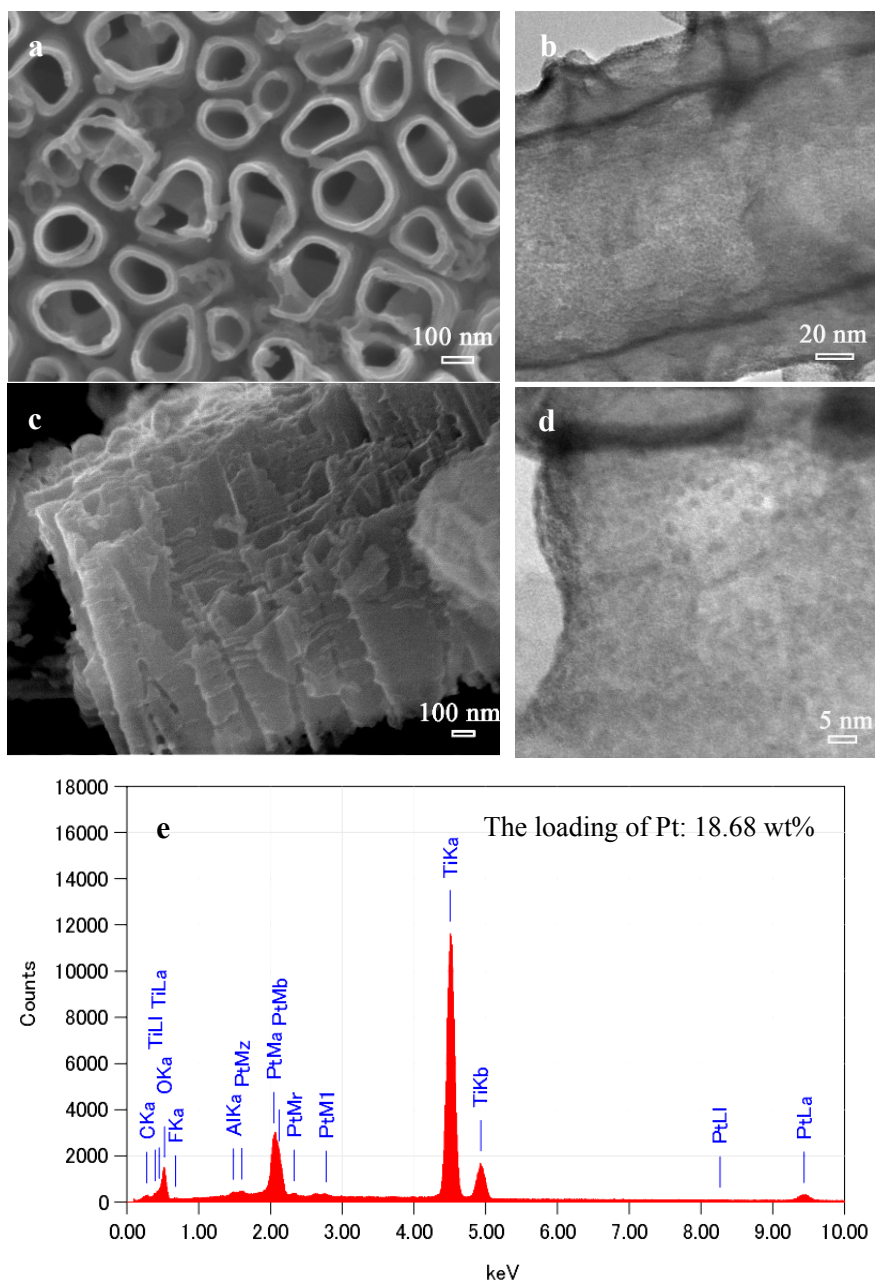


Figure 4.4 SEM (a, c)/EDS (e) and TEM (b, d) images of Pt loaded TiO₂ nanotube arrays prepared by using No. 2 solution.

4.3.2 The detailed mechanism of Pt decoration.

In light of the above different morphology of Pt loaded TiO₂ nanotube arrays in solution 1 and solution 2, experiments were also carried out to observe the changes of morphology and chemical state of decorated nanoparticles. TiO₂ nanotube arrays used were same as that in section 4.3.1. The chemical behavior of the Pt decoration was discussed for solution 1 and solution 2.

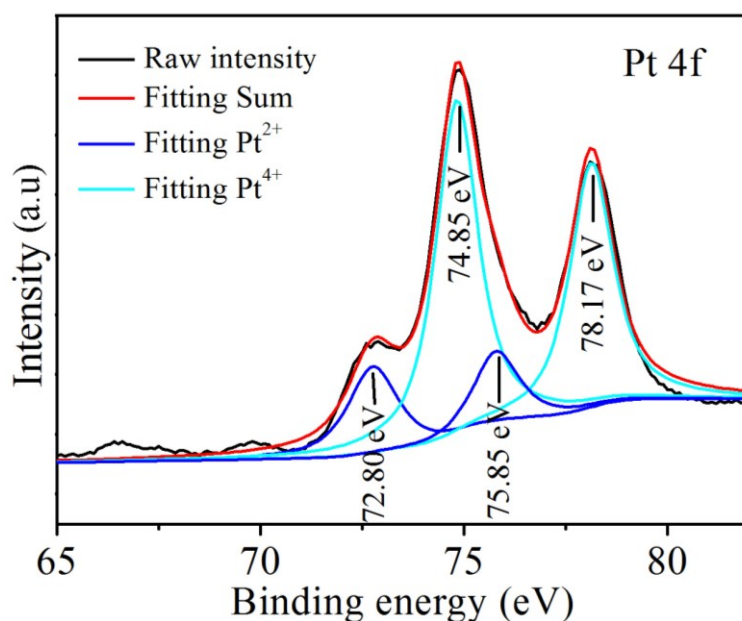


Figure 4.5 High resolution XPS spectrum of Pt for nanoparticles decorated inside TiO₂ nanotube array by using No. 2 solution.

For solution 1, the amount of Pt loading was tuned by varying the initial concentration of Pt precursors, the platinum loaded TiO₂ nanotube arrays showed different morphologies under different Pt loading amounts. As shown in Figure 4.6, when an aqueous solution of 1 mM H₂PtCl₆ (No. 3 solution in Table 1) was used for decorating the tubes, the loading amount of Pt nanoparticles is very high (65.68 wt%). Many Pt nanoparticles aggregated on the surface of TiO₂ nanotube arrays, these aggregated Pt nanoparticles also blocked the tube mouths. The inset TEM image further confirmed the high density of Pt nanoparticles decorated inside nanotubes, Aggregation of Pt nanoparticles is also clear (indicated in the circle area). By decreasing the concentration of Pt precursors to 0.05 mM (No. 4 solution in Table 1), the blockage of tube disappeared on the surface of the as-prepared sample (Figure 4.6c), porous structure on the surface of TiO₂ nanotube arrays is obvious, agglomerates of Pt nanoparticles cannot be observed. The main reason is the low loading amount of Pt nanoparticles, the loading amount of Pt nanoparticles decreased to about 3.05 wt% (Figure 4.6d). From the inset TEM image of Figure 4.6c, Pt nanoparticles are observable, but their distribution along nanotubes is still not uniform. aggregation of Pt nanoparticles is clear as indicated in the circle area.

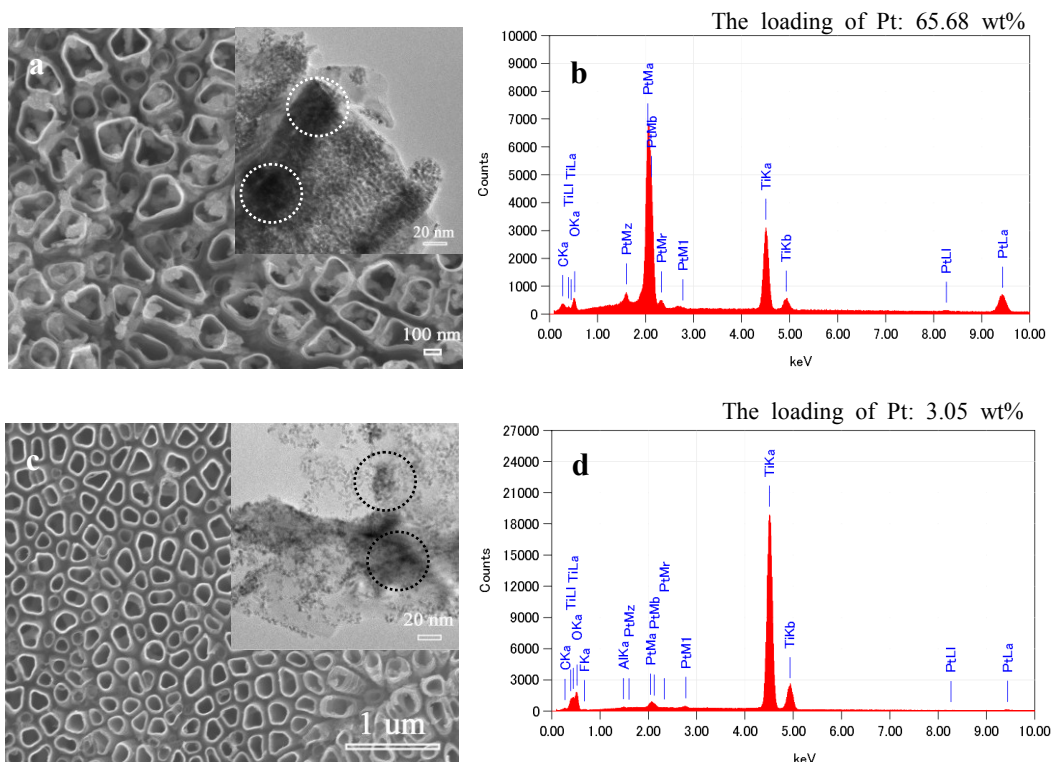
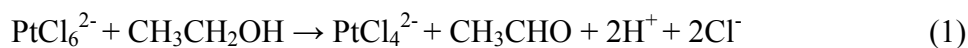


Figure 4.6 SEM (a, c)/EDS (b, d) and TEM (insets in a and c) results of Pt-TiO₂ nanotube arrays prepared by using solution 1 with concentration of Pt precursor at 1 (a, b) and 0.05 mM (c, d).

According to the above results, it can be expected that, in solution 1, the loading amount of Pt nanoparticles can be modulated by changing the initial concentration of Pt precursors. We also prepared another samples using solution 1 with different concentration of Pt precursors, the results indicate a linear relationship between Pt loading amount and the concentration of Pt precursors (Figure 4.7). However, the uniform distribution of Pt nanoparticles can hardly be obtained for all the selected concentrations of Pt precursor, as indicated in the inset TEM image, even under the lowest concentration of Pt precursor, aggregation of nanoparticles is clear (indicated in the circle area), distribution of decorated Pt nanoparticles is not uniform.

In solution 1, a two-step reduction mode proposed by Duff et al. can be used to explain the metal-ion-to-colloid reduction of PtCl_6^{2-} in ethanol:⁶



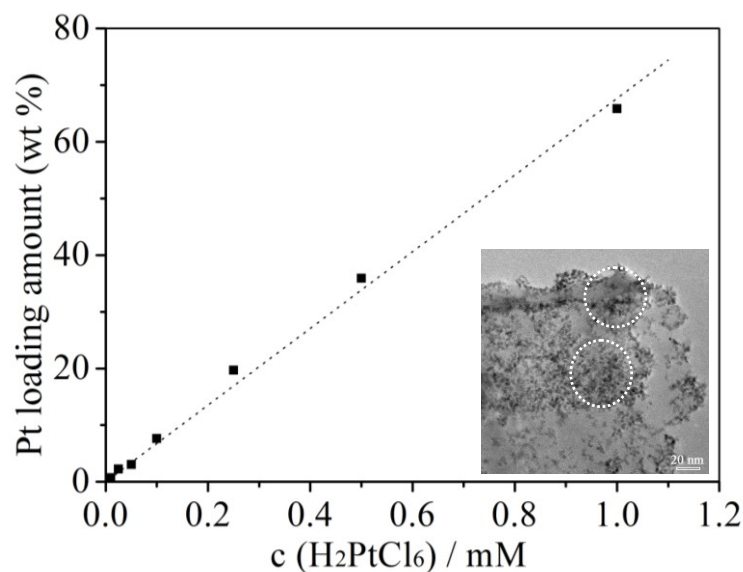


Figure 4.7 Relationship between the loading amount of Pt and the concentration of Pt precursors in solution 1 ($T = 90\text{ }^\circ\text{C}$, $t = 1\text{ h}$), inset is a TEM image of Pt loaded TiO_2 nanotube under 0.025 mM of H_2PtCl_6 .

From the above two equations, the presence of ethanol would facilitate the nucleation of Pt nuclei and increase the probability for particle collision, this will lead to an enhanced growth rate of Pt crystallites. Particulate aggregates of various morphologies will be formed when the particles are brought into close proximity by brownian motion.⁷ For the Pt decoration inside TiO_2 nanotube arrays by using solution 1, the precipitation reaction was sudden, many aggregates of nanoparticles were observed on the surface of TiO_2 , distribution of Pt nanoparticles is not uniform.

For solution 2, the decoration of nanoparticles in the solutions with pH values at *ca.* 3.7 and 9.8 was carried out, their chemical compositions are listed in Table 1 as No. 5 and No. 6 solutions. After decoration of nanoparticles, the morphology and chemical nature of deposited nanoparticles were compared and investigated. In an acid medium ($\text{pH} = 3.7$), large aggregates of nanoparticles were observed on the surface of TiO_2 nanotube arrays (Figure 4.8a), they blocked the tube mouths of the TiO_2 nanotubes. By increasing the pH value of the solution to 9.8, blockage of tube mouth for the aggregation of nanoparticles was avoided. The highly-ordered porous structure is obvious on the surface (Figure 4.8c). In Figure 4.8b and 4.8d, the Pt loading amount

prepared under pH value of 3.7 is slightly higher than that under pH value of 9.8 (9.38 wt% > 6.96 wt%). By comparing the TEM images, the size of nanoparticles prepared in the acid solution is larger than that in basic solution. However, the distribution of nanoparticles on TiO₂ is both very uniform under pH value of 3.7 and 9.8.

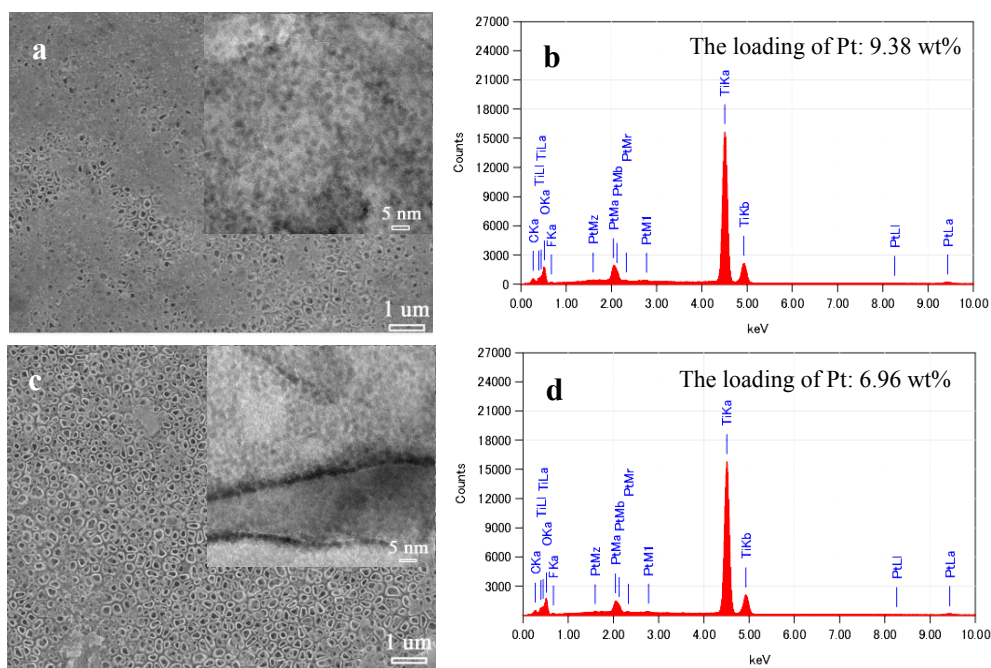
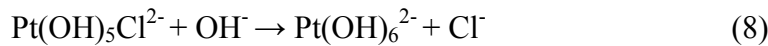
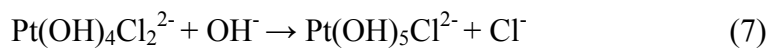
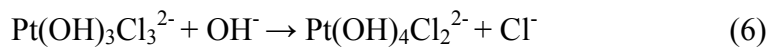
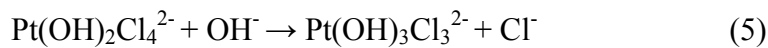
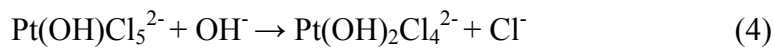
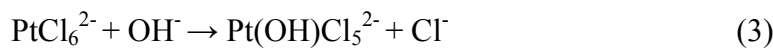


Figure 4.8 SEM (a, c)/EDS (b, d) and TEM results (insets) of Pt-TiO₂ nanotube arrays prepared in the solutions with two different pH values (a and b: pH = 3.7; c and d: pH = 9.8).

In order to determine the chemical composition of decorated nanoparticles prepared in acidic and alkaline solutions, XPS analysis was conducted and the results are shown in Figure 4.9. In Figure 4.9a, for the high loading amount of Pt nanoparticles, survey spectra of Pt-TiO₂ nanotube arrays mainly indicate the presence of chemical species Pt, O and C, signals associated with Ti were not strong. In Figure 4.9c, the emergence of two fitted peaks of Pt 4f_{7/2} at 72.80 and 74.55 eV can be assigned to Pt²⁺ and Pt⁴⁺ respectively.⁵ The O_{1s} spectra for the Pt loaded TiO₂ nanotube arrays prepared in acid solution is different from that prepared in alkaline solution. As shown in Figure 4.9c, the XPS spectra are asymmetric and could be fitted in terms of three components of oxygen species, which are associated with O²⁻ species in the lattice oxygen (530.42 eV),⁸ hydroxyl groups bonded to Pt (531.20 eV)⁹ and surface

hydroxyl groups (532.10 eV)¹⁰ respectively. In alkaline solution, the dominating peak at 530.24 eV indicates the primary contribution of titania matrix to the spectrum. While for the acid solution, the most intensive peak locates at 531.20 eV which was devoted to the Pt-OH species, the signal of lattice oxygen, which origins from the titania lattice, is not strong. This indicates that Pt loading could significantly be improved in the acid solution. From the above discussion, it could be concluded that, in solution 2, the nanoparticles are a mixture of Pt(OH)₂ and Pt(OH)₄.

Compared with solution 1, a different chemical behavior of Pt loading can be expected in solution 2 from above discussion. The deposition-precipitation process occurs during decoration of nanoparticles, a sequential hydrolysis of PtCl₆²⁻ occurs and give a series of hydrolytic products from the equation below:¹¹



Haruta et al. reported a few pieces of information concerning the possible mechanism of deposition-precipitation of Au on TiO₂ with NaOH.^{12,13} According to these work, it can be proposed that the platinum hydroxide, which is proved above, is deposited from hydrolysates on specific sites of TiO₂ which act as nucleation sites. As for the Pt²⁺ ions of platinum hydroxide, it is probably formed due to the reduction of Pt⁴⁺ ions of platinum hydroxide by electron transfer from the concentrated OH⁻ ions on the surface of TiO₂ as a catalyst of the electron transfer. The higher amount of Pt at pH value of 3.7 can be accounted by a positive charge of TiO₂ (equation 9 and 10).¹⁴



The interaction between TiO₂ and the Pt species will increase due to the positive charge in the acidic environment compared to basic environment. The increasing

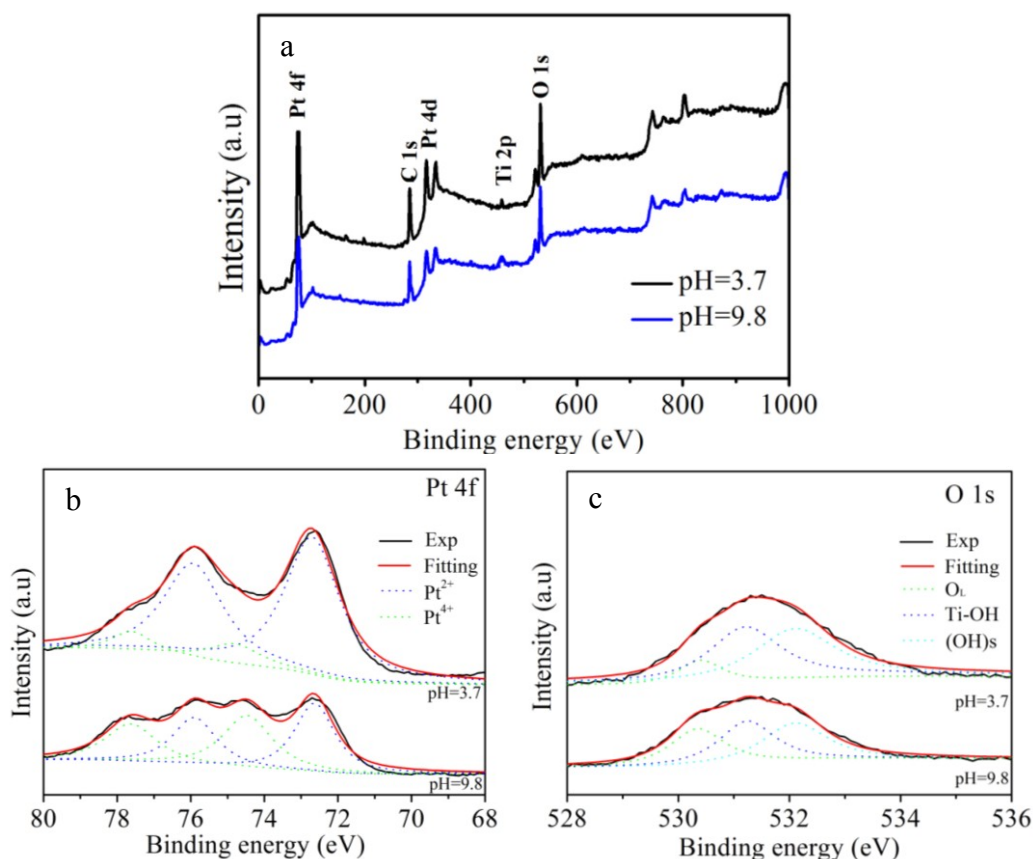


Figure 4.9 Wide and narrow scanning XPS spectra of Pt loaded TiO₂ nanotube arrays prepared in the acid (pH = 3.7) and alkaline (pH = 9.8) solutions.

solubility of Pt(OH)₄ in basic solution is also responsible for the low loading amount of Pt in the basic solution. As for the excellent dispersion of nanoparticles, the considerable adsorption amount of Pt precursor complex from solution phase could be the main reason.¹⁵

4.3.3 Pt decorated double- and single-wall TiO₂ nanotube arrays and their photocatalytic activities

Figure 4.10 shows the SEM and TEM images of two typical as-prepared TiO₂ nanotube arrays. From SEM images (Figures 4.10b and 4.10f), both films show only single-wall structure on the surface, the film thickness is about 4.3 and 4.2 μm respectively. In the TEM image of Figure 4.10g, the double-wall structure is observable at the root segment of nanotube (circle area), an inner wall was enclosed inside the outer wall (Figure 4.10h). However, this double-wall structure does not

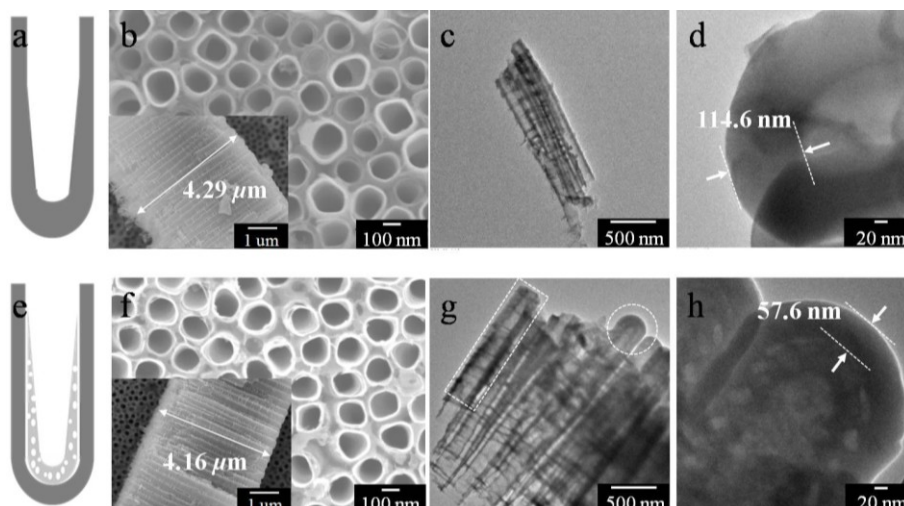


Figure 4.10 (a, e) Schematic illustrations, (b, f) SEM images, and (c, d, g, h) TEM images of ((a–d) single- and (e–h) double-wall TiO_2 nanotube arrays prepared by anodization in electrolyte (single-wall: 91.5 wt% glycerol + 8 wt% H_2O + 0.5 wt% NH_4F ; double-wall: 96.5 wt% glycerol + 3 wt% H_2O + 0.5 wt% NH_4F).

exist in Figure 4.10d, even the bottom of nanotube demonstrates only dense tube wall, which is single-wall structure (Figure 4.10d). So a transition from double- to single-wall structure was achieved by increasing the water content of the electrolyte from 3 wt% to 8 wt%. It is presumably due to the excessive etching of the tube mouth,¹⁶ TiO_2 nanotubes show a cone like structure (rectangular area in Figure 4.10g), double-wall exist only at the root segment of the tube.

Similar as the previous reports, the double-wall TiO_2 nanotubes suffer a carbon contamination in the inner wall. But as shown in XPS spectra of Figure 4.11a, the single-wall TiO_2 nanotube arrays show a lower carbon peak than the double-wall TiO_2 nanotube arrays. For both double- and single-wall structures, only their water contents of the electrolytes used are different. Thus, a single-wall structure with lower carbon contamination can be observed in the nanotube arrays prepared under higher water content.

From the reports in chapter 2, the double-wall nanotubes are formed due to a thin

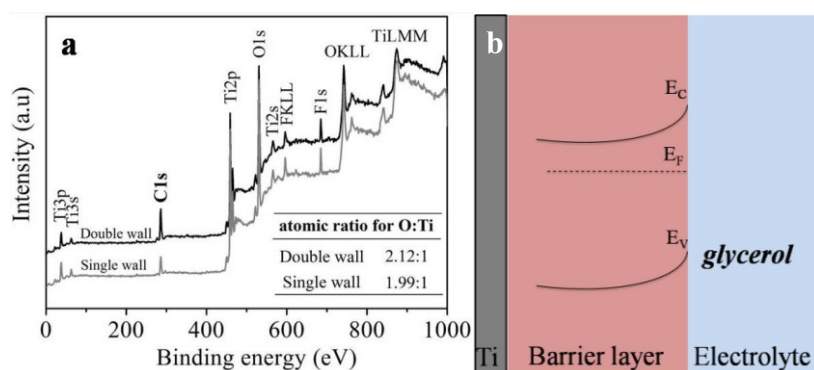


Figure 4.11 (a) Wide scanning XPS profile of double- and single-wall TiO₂ nanotube arrays prepared by anodization in electrolyte (double-wall: 96.5 wt% glycerol + 3 wt% H₂O + 0.5 wt % NH₄F; single-wall: 91.5 wt% glycerol + 8 wt% H₂O + 0.5 wt% NH₄F), Inset: atomic ratios for O : Ti of double- and single-wall TiO₂ nanotube arrays; (b) Scheme illustration of the Schottky barrier which is inefficient to induce the glycerol decomposition under high water content (E_C : Conductive band energy; E_F : Fermi energy; E_V : Valance band energy).

barrier layer under low water content, which causes the decomposition of glycerol for the tunneling of Schottky barrier layer. However, during anodization process, with water content increasing from 3 wt% to 8 wt%, the thicker barrier layer was formed. This is confirmed in the insets of Figure 4.10c and 4.10f, the thickness of barrier layer is about 114.6 nm for single-wall nanotube, which is almost two times larger than the thickness of barrier layer of double-wall structure (57.6 nm). Such a thick barrier layer will produce a low electrical field loading, thus the hole generation should be difficult due to the inefficient tunneling (Figure 4.11b). In this case, decomposition of glycerol is quite difficult, and the resulted TiO₂ nanotube contains a low carbon content and is a dense single-wall structure. Therefore, the single-wall TiO₂ nanotube array was obtained under a higher water content.

For the modification of Pt nanoparticles, the deposition-precipitation method in solution 2 (indicated as No. 6 solution in Table 1) was chosen and examined. TEM photograph of Figure 4.12c shows uniformly dispersed Pt deposits on surface of TiO₂. Diameter of Pt deposits is around 2.1 nm. Due to such a small particle size, TiO₂ nanotube array structure was well maintained (Figures 4.12a and 4.12b). Tube

blockage cannot be observed. The inset TEM images of Figures 4.12a and 4.12b also proved that both double- and single-wall structure were not destroyed after the Pt deposition.

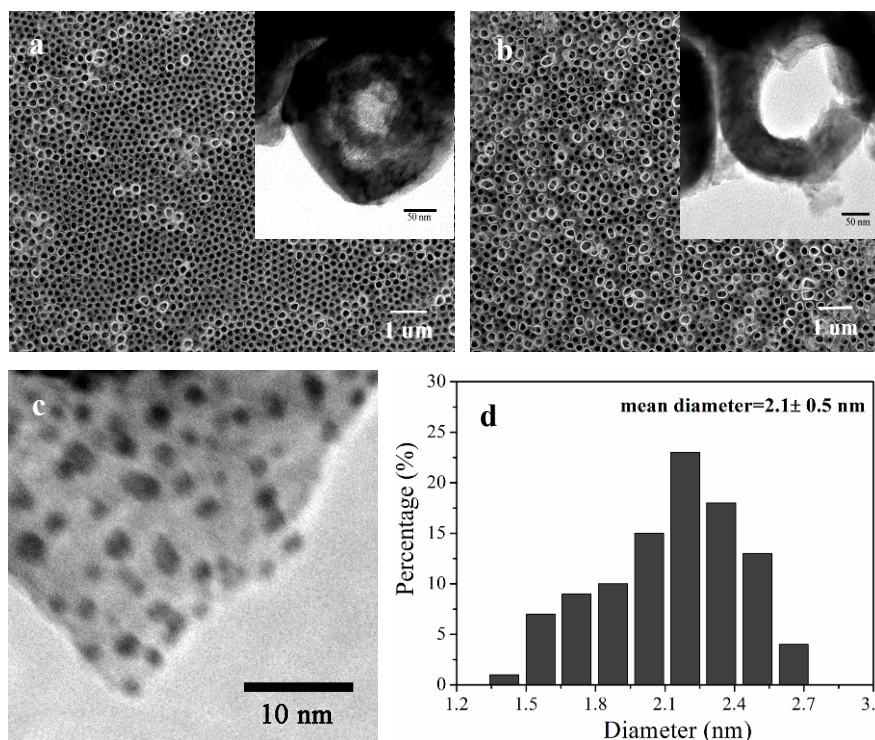


Figure 4.12 (a), (b) SEM and TEM (inset) images of nanoparticles decorating double- and single-wall TiO₂ nanotube arrays. (c) An enlarged TEM image of Pt nanoparticles decorating double-wall TiO₂ nanotube arrays. (d) Size distribution of the decorated nanoparticles on double-wall TiO₂ nanotubes, indicating that the mean diameter of nanoparticles is approximately 2.1 nm.

After thermal treating with N₂/H₂ gas at 200 °C for 2 h, the Pt deposits were reduced to metallic Pt nanoparticles. As shown in Figure 4.13a, the signals for Pt 4f_{7/2} and Pt 4f_{5/2} are located at 71.2 eV and 74.5 eV, the spin splitting matches well to the standard data of Pt⁰ (3.3 eV).¹⁷ For the double-wall structure, the tube wall splits into two layers, and the inner wall also exhibits a loose and porous structure. Both factors can contribute to the larger surface area of the double-wall TiO₂ nanotube arrays. Figure 4.13b shows that Ti 2p_{3/2} and Ti 2p_{1/2} are located at 458.8 eV and 464.7 eV, respectively, these values are very similar to that of TiO₂, suggesting that Ti is +4 oxidation state and directly bonded to oxygen.¹⁸ Judging from Figure 4.13c, the

asymmetric spectrum of O1s indicates at least two types of oxygen present. The dominant peak at 530.1 eV is from the titania lattice.¹⁹ Another tailing peak, which is indicated by the black arrow, was due to the surface hydroxyl groups.²⁰ One possible reason for this obvious amount of hydroxyl groups is the Pt nanoparticles on the surface. Pt deposition was reported in other works to significantly improve the capture ability of hydroxyl groups.^{22,21}

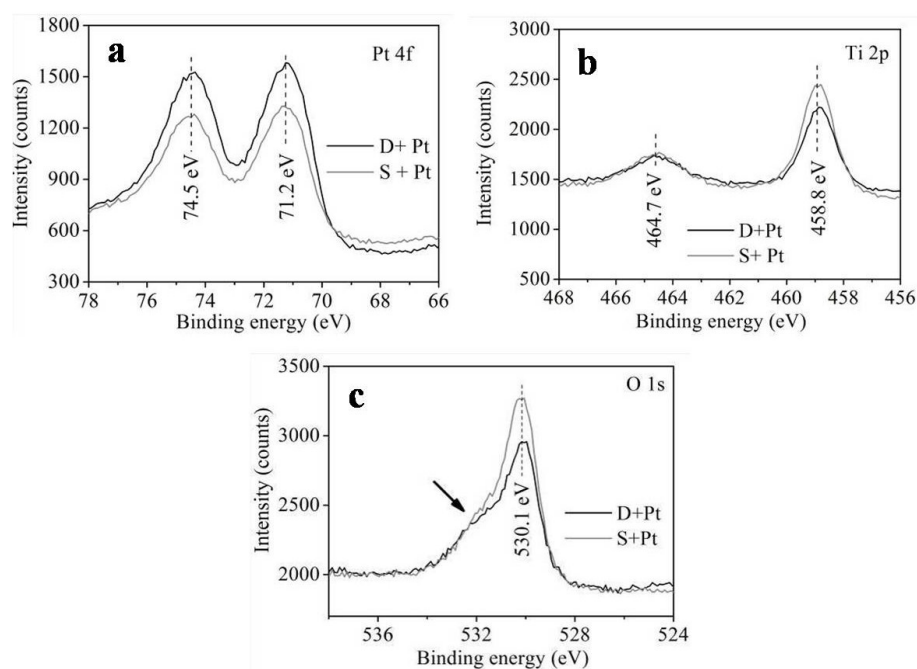


Figure 4.13 XPS spectra of double- and single-wall TiO₂ nanotube arrays decorated by Pt nanoparticles (a: Pt 4f spectra; b: Ti 2p spectra; c: O 1s spectra; D + Pt: double-wall TiO₂ nanotube arrays with Pt decoration; S + Pt: single-wall TiO₂ nanotube arrays with Pt decoration).

Figure 4.14 illustrates the photocatalytic activity of the double- and single-wall TiO₂ nanotube arrays before and after Pt decoration. Without the TiO₂ nanotube arrays almost no degradation of methylene blue was observed under the irradiation conditions. With the TiO₂ nanotube arrays, the maximum absorption peak of methylene blue at 664 nm clearly decreased with increasing UV irradiation time by the photocatalytic activity of the TiO₂ nanotubes (see Figure 4.14b). The degradation of methylene blue can be analyzed by first-order kinetics, with the classical equation

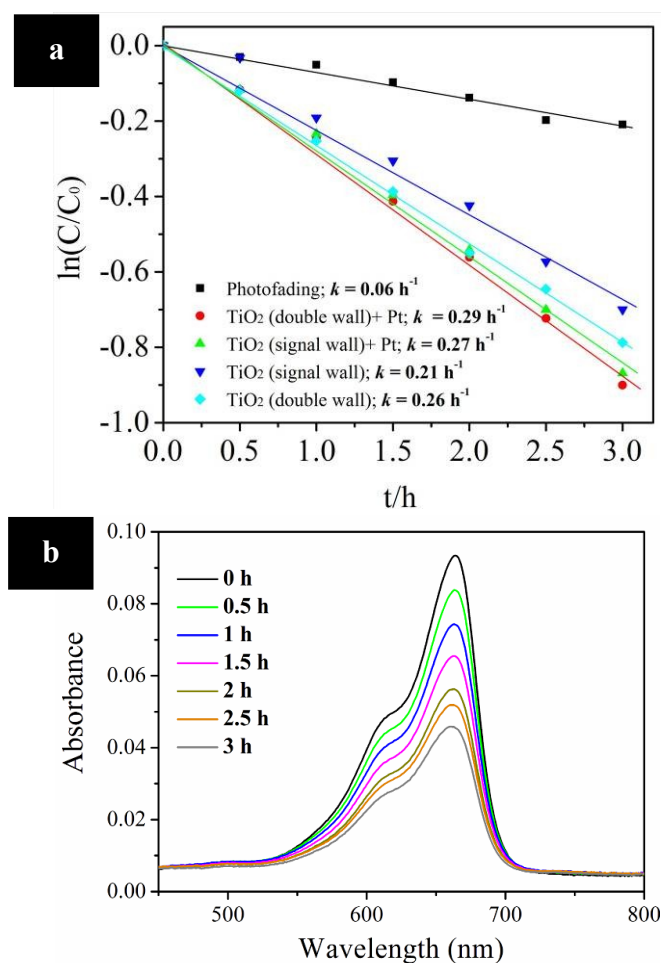


Figure 4.14 (a) Photocatalytic degradation rates of methylene blue in the presence of double- and single-wall TiO_2 nanotube arrays before and after Pt decoration; (b) UV-Vis absorption spectra of methylene blue solution photodegraded by double-wall TiO_2 nanotube arrays under UV light irradiation.

of $\ln(C/C_0) = k \times t$, where k is the rate constant and t is the time.²² By comparing the rate constants shown in Figure 4.14a, the double-wall TiO_2 nanotube arrays were observed to exhibit better photocatalytic activity than the single-wall TiO_2 nanotube arrays. With regard to this enhanced photocatalytic activity of double-wall TiO_2 nanotube arrays, XPS, XRD, SEM and specific surface area of the annealed double- and single-wall TiO_2 nanotube arrays were further characterized. After annealing, the XPS spectra (Figure 4.15a) indicates almost same chemical composition in single- and double-wall TiO_2 nanotube arrays, thus the carbon impurities in double-wall TiO_2 nanotube arrays could be released during annealing. The XRD patterns for both annealed double- and single-wall TiO_2 nanotube arrays also show identical peak

positions and the presence of anatase phase (Figure. 4.15b). However, in Figure. 4.15c and Fig. 4.15d, different from the single-wall TiO₂ nanotube, the tube wall of double-wall TiO₂ nanotube splitted into two layers, and the inner wall exhibited a loose and porous structure (Figure. 4.15c). These morphological details contribute to a larger surface area of the double-wall TiO₂ nanotube arrays. BET analysis further confirmed the enlarged surface area of the annealed double-wall TiO₂ nanotube arrays. The specific surface area of the annealed double-wall TiO₂ nanotube was 26.11 m² g⁻¹, while that of annealed single-wall TiO₂ nanotube was 17.67 m² g⁻¹. Therefore, we concluded that the enlarged surface area of double-wall TiO₂ nanotube array should be the main reason for its improved photocatalytic activity. Moreover, the specific surface area is also the most important factor in determining the amount of Pt particles on the surface.¹⁵ As shown in Figure 4.14a, a higher peak intensity of Pt was observed in the double-wall structure, indicating that this structure supports a larger amount of Pt nanoparticles than the single-wall structure.

Regarding the decoration of Pt nanoparticles, the work function of Pt ($\phi_m = 4.98\text{--}5.7$ eV) is higher than TiO₂ ($\phi_m = \sim 4.6$ eV), thus the photogenerated electrons will transfer from TiO₂ to Pt.²³ A Schottky barrier, which features a higher potential gradient, will form at the Pt-TiO₂ interface. The Schottky barrier can retard the electron-hole recombination process.²⁴ Therefore, the decoration of Pt nanoparticles could enhance the generation of photoelectron-hole pairs and achieve a higher photocatalytic activity. Moreover, an obvious amount of hydroxyl groups was confirmed in XPS profile (Figure. 4.13c). Because the photocatalytic degradation of methylene blue is mainly initiated by •OH,²⁵ this high content of surface hydroxyl groups could facilitate the photocatalytic reactions, as the -OH groups can easily capture photoinduced holes to produce •OH free radicals. Thus, as shown in Figure. 4.14a, compared with the bare samples, the photocatalytic activity was further enhanced by Pt decoration for both the double- and single-wall TiO₂ nanotube arrays.

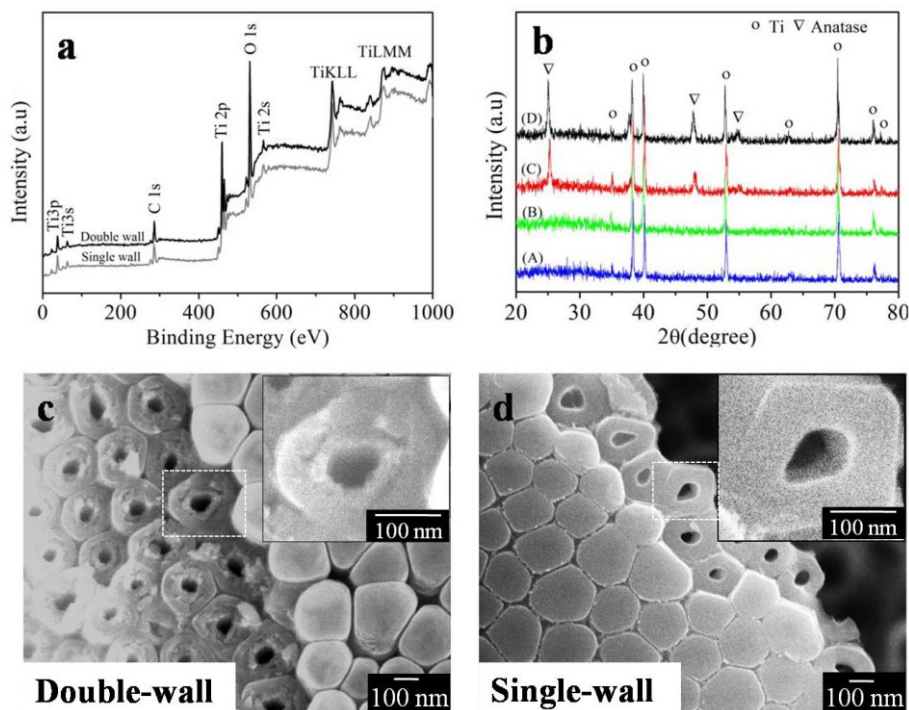


Figure 4.15 (a) XPS profiles, (b) XRD patterns, (c–d) SEM images of the bottom of double- and single-wall TiO₂ nanotube arrays after annealed at 450 °C for 3 h. (b): (A) anodized double-wall TiO₂ nanotube arrays, (B) anodized single-wall TiO₂ nanotube arrays, (C) annealed double-wall TiO₂ nanotube arrays and (D) annealed single-wall TiO₂ nanotube arrays. Inset images in (c) and (d) are the enlarged image of the rectangular area of (c) and (d). Double- and single-wall TiO₂ nanotube arrays were prepared by anodization in electrolyte (double-wall: 96.5 wt% glycerol + 3 wt% H₂O + 0.5 wt% NH₄F; single-wall: 91.5 wt% glycerol + 8 wt% H₂O + 0.5 wt% NH₄F).

4.4 Conclusion

Two kinds of methods were compared to decorated Pt nanoparticles inside TiO₂ nanotube arrays. The results showed that, in the solution mixed with water, H₂PtCl₆ and NaOH, the deposition-precipitation method is better to get uniform decoration of Pt nanoparticles inside TiO₂ nanotube arrays. The deposited Pt nanoparticles are not metallic state, it is composed of Pt⁴⁺ and Pt²⁺.

By increasing the water content in an NH₄F/glycerol-water electrolyte, a transition from double- to single-wall TiO₂ nanotube arrays was successfully achieved. The photocatalytic property of double- and single-wall TiO₂ nanotube arrays was also

compared, our double-wall TiO_2 structure exhibited better photocatalytic property than that of typical single-wall structure. The double- and single-wall TiO_2 nanotube arrays were also decorated with Pt nanoparticles, the photocatalytic property of both double- and single-wall TiO_2 nanotubes was further improved.

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CHAPTER 5

Summary

The thesis investigated the electrochemical anodized TiO₂ nanotube arrays. Since the anodization process is complicated, TiO₂ nanotube arrays with different morphologies can be obtained. For the preparation of TiO₂ nanotube arrays, the thesis mainly concentrated on the water-glycerol electrolyte. The main outcomes of the research are the morphological controlling of TiO₂ nanotube arrays, their crystal behavior and photocatalytic properties were also studied. They are presented from chapter 2 to chapter 4. In chapter 1, previous studies of photocatalysis, electrochemistry and TiO₂ nanotube arrays were generally introduced. For simplicity, the main conclusions and findings of the thesis, from chapter 2 to chapter 4, are presented in their respective chapter-wise manner as below.

In Chapter 2, TiO₂ nanotube arrays were prepared by anodizing in the water-glycerol solution. Both the chemical composition of electrolyte and anodization voltage can affect the morphologies of TiO₂ nanotube arrays. For the anodization under 20 V for 6 h, a highly ordered TiO₂ nanotube array was obtained in the electrolyte containing 79.5 wt% of glycerol, 20 wt% of water and 0.5 wt% of NH₄F, some special morphologies (such as ripples, double layer of tube wall) was observed. Considering the formation mechanism of TiO₂ nanotube arrays, the ripples on the sidewall of nanotube is formed due to the “fluoride-rich” layer at the inter-tube regions. The double layer structure was further confirmed by the production of a double-wall TiO₂ nanotube arrays. The inner wall suffers a higher carbon contamination than the outer wall, it is formed due to the decomposition of glycerol during anodizing process.

In Chapter 3, highly-ordered double-wall TiO₂ nanotube arrays with “fluoride-rich” layer survived inside were prepared by a two-step anodization method. The “fluoride-rich” layer survived at the inter-tube regions for the low water content,

hydrolysis of “fluoride-rich” layer is slow under a low water content, the hydrolyzed chemicals can easily adsorbed on the sidewall of nanotubes. During *ex situ* annealing process, the “annealed fluoride-rich layer” was clearly distinguished on the sidewall of nanotubes, it disappeared after calcinations at 700 °C for 3 h for the phase transition from anatase to rutile of tube wall. The double-wall structure was also optimized for the sintering of inner wall. A technique of *in situ* annealing and TEM observation of TiO₂ nanotubes was also investigated. A slower structural failure of the nanotubes was obtained with introduction of oxygen gas into the TEM column compared with the structural changes observed under a high vacuum condition without introduction of oxygen gas. The results showed that oxygen gas can stabilize the nanotube during *in situ* annealing process. There is a dependence of morphological changes of TiO₂ nanotubes on the gas atmosphere during *in situ* annealing process.

In Chapter 4, decoration of Pt nanoparticles inside TiO₂ nanotube arrays was investigated. A deposition-precipitation method in the aqueous solution containing NaOH and H₂PtCl₆ was found to be suitable for uniformly depositing Pt nanoparticles inside TiO₂ nanotube arrays. The photocatalytic properties of double- and single-wall TiO₂ nanotube arrays before and after Pt decoration was also compared. The transition from double- to single-wall structure of TiO₂ nanotubes was achieved by increasing the water content in the NH₄F/glycerol-water electrolyte. The double-wall TiO₂ nanotube arrays showed a higher photocatalytic activity than single-wall TiO₂ nanotube arrays. After Pt decoration, the photocatalytic properties of both structures were further improved.

In Chapter 5, the summary of the whole results was described.

List of Research Achievement

Journal Articles

- [1] Xue, C. R.; Narushima, T.; Ishida, Y.; Tokunaga, T.; Yonezawa, T. Double-Wall TiO₂ Nanotube Arrays: Enhanced Photocatalytic Activity and *In Situ* TEM Observations at High Temperature. *ACS Appl. Mater. Interfaces* (In Press, DOI: 10.1021/am505333v).
- [2] Xue, C. R.; Narushima, T.; Ishida, Y.; Tokunaga, T.; Yonezawa, T. In Situ Transmission Electron Microscopic Observation of Double-Wall TiO₂ Nanotube Arrays at High Temperature. *Chem. Lett.* **2014**, 43, 1514-1516.
- [3] Xue, C. R.; Narushima, T.; Yonezawa, T. Direct SEM Observation of Non-electroconductive TiOF₂ Nanotube Arrays Prepared by Anodization Using an Ionic Liquid as a Visualizing Reagent. *J. Inorg. Organomet. Polym. Mater.* **2013**, 23, 239-242.
- [4] Xue, C. R.; Dong, L. H.; Liu, T.; Zhang, F.; Yin, B.; Yin, Y. S. Preparation and Anticorrosion Performance of Superhydrophobic TiO₂ Nanotube Arrays on Pure Ti. *Corro. Sci. Protect. Technol.* **2012**, 24, 37-40. (Chinese)
- [5] Xue, C. R.; Zhang, F.; Chen, S. G.; Yin, Y. S.; Lin, C. Tailoring the Surface Morphology of TiO₂ Nanotube Arrays Connected with Nanowires by Anodization. *Mater. Sci. Semicon. Proc.* **2011**, 14, 157-163.
- [6] Xue, C. R.; Yonezawa, T.; Nguyen, T. M.; Lu, X. Annealed Fluoride-rich Layer and Well-defined Double-Wall TiO₂ Nanotubes (under preparation).

Presentations in Academic Conference

- [1] Xue, C. R.; Narushima, T.; Yonezawa, T. Double Walled TiO₂ Nanotube Arrays Prepared by Anodization in Fluoride/Glycerol Electrolyte, 2012 International Joint Symposium between Hokkaido University & Chungnam National University on Advanced Material Science & Technology, Sapporo, 2012/12. (Poster).
- [2] Yonezawa, T.; Xue, C. R.; Narushima, T. A Simple SEM Observation Method of TiO₂ Nanotube Arrays Using Ionic Liquid, The 68th Annual Meeting of the Japanese Society of Microscopy, Tsukuba, 2012/05. (Poster).
- [3] Xue, C. R.; Narushima, T.; Yonezawa, T. The Photocatalysis Properties of Single & Double Walled TiO₂ Nanotube Arrays Decorated with Uniform Pt Nanoparticles, Joint Summer Session of the Japan Institute of Metals and Materials & the Iron and Steel

Institute of Japan, Muroran, 2013/07. (Poster).

[4] Xue, C. R.; Yonezawa, T. Annealing Effect on Chemical Composition, Morphology and Structure of Double Walled TiO₂ Nanotube Arrays, 13th international Joint Symposium between Hokkaido University & The University of Science and Technology Beijing, Sapporo, 2014/03. (Poster).

[5] Xue, C. R.; Ishida, Y.; Yonezawa, T. Sensitive Cell Boundaries of Anodized TiO₂ Nanotube Arrays, Joint Summer Session of the Japan Institute of Metals and Materials & The Iron and Steel Institute of Japan, Sapporo, 2014/07. (Poster).

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Resume

Education Background

2004.07 Shandong, Yanggu No.3 Senior High School graduated
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2008.09 Institute of Materials Science and Engineering, Ocean University of China, Qingdao, P. R. China enrolled
2011.07 -- same as above -- graduated
2011.10 Division of Materials Science and Engineering, Graduate School of Engineering, Hokkaido University, Japan enrolled

Research Background

2007.09–2008.07 College of Materials Science and Engineering, Qingdao University of Science and Technology, P. R. China

Research title: “Optical and Morphological Properties of YVO₄: Eu”

Involved in during Bachelor’s program

2008.09–2011.07 Institute of Materials Science and Engineering, Ocean University of China, P. R. China

Research title: “Preparation and Superhydrophobic Modification of TiO₂ Nanotube Arrays and Research on Their Anticorrosion Properties”

Involved in during Master’s program

2011.10–now Division of Materials and Engineering, Graduate School of Engineering, Hokkaido University, Japan

Research title: “TiO₂ Nanotube Arrays Prepared by Anodizing in Water-Glycerol Electrolyte and Their Photocatalytic Properties”

Involved in until now